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Ensemble-Averaged QM/MM Kinetic Isotope Effects for the S_N2 Reaction of Cyanide Anion with Chloroethane in DMSO Solution

J. Javier Ruiz Pernía^[b] and Ian H. Williams^{*[a]}

Abstract: The existence of solvent fluctuations leads to populations of reactant-state (RS) and transition-state (TS) configurations and implies that property calculations must include appropriate averaging over distributions of values for individual configurations. Average kinetic isotope effects (KIE) for $\text{NC}^- + \text{EtCl} \rightarrow \text{NCEt} + \text{Cl}^-$ in DMSO solution at 30 °C are best obtained as the ratio $\langle f_{\text{RS}} \rangle / \langle f_{\text{TS}} \rangle$ of isotopic partition function ratios separately averaged over all RS and TS configurations. In this way the hybrid AM1/OPLS-AA potential yields (KIE) values for all six isotopic substitutions ($2^\circ \alpha\text{-}^2\text{H}_2$, $2^\circ \beta\text{-}^2\text{H}_3$, $\alpha\text{-}^{11}\text{C}/^{14}\text{C}$, leaving

group ^{37}Cl , and nucleophile ^{13}C and ^{15}N) for this reaction in the correct direction as measured experimentally. These thermally-averaged calculated KIEs may be compared meaningfully with experiment, and only one of them differs in magnitude from the experimental value by more than one standard deviation from the mean. This success contrasts with previous KIE calculations based upon traditional methods without averaging. The isotopic partition function ratios are best evaluated using all (internal) vibrational and (external) librational frequencies obtained from Hessians determined for subsets of atoms,

relaxed to local minima or saddle points, within frozen solvent environments of structures sampled along molecular dynamics trajectories for RS and TS. The current methodology may perfectly well be implemented with other QM or QM/MM methods, and thus provides a useful tool for investigating KIEs in relation to studies of chemical reaction mechanisms in solution or catalysed by enzymes.

Keywords: computational chemistry • isotope effects • molecular dynamics • solvent effects • transition states

Introduction

Molecules are constantly in motion. While recognized very clearly by Louis Hammett in his seminal 1940 *Physical Organic Chemistry*,¹ the implications of this fact seem not to have penetrated our understanding of chemistry as widely and deeply as they should have done by now. It is well known that kinetic isotope effects

(KIEs), as discussed in this paper, arise predominantly from subtle energetic differences in the quantized internal motions of molecules, due to isotopic substitution, that persist even at 0 K. However, a consequence of external motion of molecules, relative to each other, at non-zero is that many observable properties, including KIEs, are averages over a multitude of thermally accessible configurations of (for example) solvent molecules surrounding one or more solute molecules undergoing a chemical reaction. The purpose of this paper is to demonstrate how explicit sampling of, and averaging over, an ensemble of configurations of a thermally fluctuating molecular system allows calculated KIEs to be reconciled with experiment. In so doing, it suggests a shift away from thinking about chemical change experienced by a single molecule towards a mental picture of a distribution of chemical changes experienced by a representative collection of molecules giving rise to an average value of any property.

KIE measurements are one of the most powerful experimental techniques for probing the nature of the transition state: the magnitude and direction of a KIE contains information about the mechanistic events in a chemical reaction, reflecting differences in bonding between the reactants and the transition state.² Quantum-mechanical (QM) techniques are of value to assist interpretation of KIEs,³ but an important paper by Paneth, Matsson, Westaway (PMW) and their co-workers⁴ cast some doubt upon their ability to

[a] Prof. I. H. Williams,
Department of Chemistry, University of Bath, Bath BA2 7AY, UK
Fax: (+)44 1225 386231
E-mail: i.h.williams@bath.ac.uk

[b] Dr. J. J. Ruiz Pernía,
Department of Chemistry, University of Bath, Bath BA2 7AY, UK
and Departament de Química Física i Analítica, Universitat Jaume I,
12071 Castelló, Spain

Supporting information for this article (full details of computational procedures, plots of IPFRs and their cumulative means and standard deviations, and Tables of calculated IPFRs for all RS and TS structures) is available on the WWW under <http://www.chemeurj.org/> or from the author, from whom also the computer programs for IPFRs are freely available.

reproduce and rationalize experimental KIEs for a prototypical S_N2 reaction in solution. These authors' conclusion - that none of the many combinations of QM method and basis set they used was capable of reproducing the range of KIEs measured experimentally for isotopic substitution at six positions (Scheme 1) for reaction of cyanide anion with chloroethane in dimethylsulfoxide (DMSO) – is alarming and sets a challenge for theory. In common with most other KIE calculations,³ PMW considered only the properties of individual transition structures, but the growing ability of computational chemistry to handle larger systems with increasing intrinsic accuracy means that the reliability of a result is dictated not just by the chosen QM method but also by other factors contingent upon the increase in complexity, dimensionality and flexibility of the system. The dynamics of solvent-solvent and solvent-solute interactions introduce additional issues so that QM methods must be married with techniques of statistical mechanics in order to describe reactivity in condensed phases.

Scheme 1. Isotopic substitutions at six positions within the reactin.

We were among the first to use hybrid QM/MM methods (in which that part of a molecular system involving significant electronic reorganization is described by QM and surrounded by a molecular-mechanical (MM) environment) for KIE calculations with explicit solvation⁵ and, along with many other groups,⁶ have since used these methods in combination with molecular dynamics (MD) to compute free energy changes from potentials of mean force (PMFs).⁷ These studies have established that both reactant states and transition states of large, flexible molecular systems should be modelled by averaging over multiple configurations. In our experience the variation in KIE values calculated with a single QM method (in QM/MM) but with different solvent configurations can be as great as that between different QM methods, suggesting that comparisons of calculated and observed KIEs for reactions in explicit solution are, in general, likely to be either meaningless or fortuitous unless appropriate averaging over solvent configurations is performed. Also, for accurate calculations of secondary alpha-deuterium (2° α - ^2H) KIEs for reactions in condensed media, we have shown the need to include at least those atoms directly involved in hydrogen bonds to the substrate or, better, a complete first solvation shell within the Hessian used to compute the partition functions for isotopologues.⁸

Our purpose here is to show that theory and experiment may be reconciled for the S_N2 reaction of cyanide anion with chloroethane in DMSO (Scheme 1) provided that proper account is taken of thermal fluctuations in solvent configurations by means of appropriate averaging of the computed KIEs. We describe our procedures in detail in order to demonstrate the feasibility and promise of the method rather than as a definitive treatment of the title reaction but nonetheless, despite the known deficiencies of the QM/MM potential (AM1/OPLS-AA) used here, the overall extent of agreement between the resulting ensemble-averaged KIEs and experiment is remarkable. Not only do we succeed in correctly reproducing the direction of all six KIEs, but we gain unprecedented

Figure 1. Five steps to ensemble-averaged KIEs.

insight into the sensitivity of KIEs to fluctuations in solvent configuration, revealing surprisingly wide distributions of individual KIE values over which our average values are obtained. Moreover, the conclusion that AM1 overestimates the magnitude of the 2° α - ^2H KIE relative to experiment is validated by virtue of averaging over many solvent configurations. These findings provide a necessary corrective to the mindset that considers only a single reactant structure (RS) undergoing chemical transformation via a single transition structure (TS) and suggest that, in general, any comparison of condensed-phase experiments with results of a particular QM method may be meaningless unless the calculations include proper averaging.

Methodology

The key steps (Figure 1) of our procedure for ensemble averaging of KIEs are as follow.

- 1 Perform QM/MM MD simulations with umbrella sampling along a distinguished coordinate for the reaction at the desired temperature and compute a PMF.
- 2 At the free-energy minimum (RS) and maximum (TS) of the PMF, compute extended QM/MM MD trajectories; the TS is subject to a constraint to prevent it collapsing to the RS or product.

3 From the RS and TS trajectories, extract numerous independent configurations. For each “snapshot”, perform QM/MM geometry optimization to either a local minimum or saddle-point within a frozen environment.

4 Compute the QM/MM Hessian for a subset of selected atoms within the relaxed region and thence the isotopic partition-function ratio (IPFR) for each isotopic substitution of interest.

5 Calculate the average KIE from the IPFRs of all the RS and TS configurations.

Steps 1 – 4 are, in themselves, each quite standard but are discussed in detail below in the Methods section; they are based upon a method for computation of solvent effects on vibrational spectra of stable molecules in solution,⁹ but now applied to transition states and KIEs.¹⁰ However, it is appropriate now to describe the non-standard methods used in Stage 5, setting them in the context of other approaches to KIE calculations. Our approach bears similarities with the ensemble-averaged variational transition state theory (EA-VTST) method of Truhlar and co-workers,¹¹ but differs from it in ways that will be discussed below.

IPFRs, KIEs and averaging

IPFRs were determined from the coordinates and Hessians of the subsets in either of two ways. The first procedure ignores all coupling between the N_s subset atoms and their environment. The six librational degrees of freedom of the subset with respect to its environment are eliminated by means of a projection method which converts them into translational and rotational modes with zero eigenvalues. This leaves $3N_s - 6$ genuine vibrations which satisfy the Teller-Redlich product rule¹² for isotopologues, being entirely consistent with the masses and moments of inertia obtained from the molecular geometries of the subset atoms alone. This is the “translation/rotation” procedure. The second, simpler, procedure includes all $3N_s$ vibrational modes of the subset: it does not strictly satisfy the Teller-Redlich product rule but neither does it need to do so;¹³ this is the “all-frequencies” procedure.

A KIE is an exponential of the difference in activation free energy for an isotopologous pair of reactions. An ensemble average for this quantity could, in principle, be obtained directly by appropriate MD simulations incorporating quantum effects on nuclear motions. In practice it is usual to perform classical MD and then to replace the classical vibrational partition function by the quantum partition function for a set of harmonic oscillators, usually for only a subset of the full system. It is usually considered adequate to treat both translational and rotational motions classically. Within the Born-Oppenheimer approximation, the potential energy barrier is the same for each isotopologue and therefore does not contribute to the difference in activation free energy, which is determined solely by differences in the (natural logarithms of the) partition-functions.

Within transition-state theory, the semiclassical KIE is given by eq. 1, where Q^{RS} and Q^{TS} are molecular partition functions for RS and TS species, respectively. If translations, rotations and vibrations are considered as separable motions, each Q is the product of q_{trans} , q_{rot} and q_{vib} : the latter term is evaluated over $3N - 6$ modes for RS and but $3N - 7$ modes for TS. Re-arrangement of the partition-function factors on the middle-left-hand side of eq. 1 yields a ratio (“RS over TS”) of IPFRs (“heavy over light”), f_{RS} and f_{TS} , the values of which should each be always >1 . Note that this expression for the KIE does not explicitly include the ratio of isotopic transition frequencies $(\nu_{light}/\nu_{heavy})^\ddagger$; its effect is implicitly included within q_{trans} and q_{rot} values for the light and heavy RS and TS species.

$$KIE = \frac{(Q^{TS}/Q^{RS})_{light}}{(Q^{TS}/Q^{RS})_{heavy}} = \frac{(Q_{heavy}/Q_{light})^{RS}}{(Q_{heavy}/Q_{light})^{TS}} = \frac{f_{RS}}{f_{TS}} \quad (1)$$

It is common for the Teller-Redlich product rule to be employed in order to replace the q_{trans} and q_{rot} factors, involving masses and moments-of-inertia, by a factor involving only products of vibrational frequencies for the light and heavy species; these products are taken over all $3N - 6$ modes for both RS and TS. However, in the Bigeleisen equation (eq. 2) for the KIE,¹⁴ the vibrational products are included along with the q_{vib} factors in a representation (where $u = h\nu/k_B T$) which runs over $3N - 7$ modes for TS; this means that the ratio of the transition frequencies appears explicitly as an extra factor. The Bigeleisen equation may also be re-arranged as a ratio of IPFRs evaluated using vibrational frequencies only, but note that here the TS value involves products over only $3N - 7$ frequencies, so that $f_{TS} = (\nu_{heavy}/\nu_{light})^\ddagger \times f_{TS}^*$.

$$KIE = \left[\frac{\nu_{light}}{\nu_{heavy}} \right]^\ddagger \prod_i^{3N-6} \left[\frac{\nu_i^{RS} \sinh(u_i^{RS}/2)_{light}}{\nu_i^{RS} \sinh(u_i^{RS}/2)_{heavy}} \right] \prod_i^{3N-7} \left[\frac{\nu_i^{TS} \sinh(u_i^{TS}/2)_{light}}{\nu_i^{TS} \sinh(u_i^{TS}/2)_{heavy}} \right] \quad (2)$$

$$KIE = \left[\frac{\nu_{light}}{\nu_{heavy}} \right]^\ddagger \frac{f_{RS}}{f_{TS}^*} \quad (3)$$

We have recently pointed out¹³ that, since the Teller-Redlich product rule applies only when translational, rotational and vibrational motions are separable – which is not true for subsets of atoms within the environment of a larger system, the Bigeleisen equation in its conventional form is inappropriate for use in conjunction with subset Hessians. Instead we have shown¹³ that the product of all $3N_s$ harmonic vibrational frequency ratios for a pair of isotopologues is equal simply to the product of isotopic mass ratios, for the isotopically substituted atoms only, raised to the power of $3/2$; moreover, these terms are identical for both RS and TS and therefore disappear from the KIE (eq. 4). For reasons discussed below, it is convenient to use IPFRs in order to evaluate ensemble-averaged KIEs for systems described by subset Hessians; these are given by eqs. 5 and 6, in which the isotopic mass-ratio factors are retained solely for comparability with IPFR values obtained by means of the Bigeleisen equation.

$$KIE = \prod_i^{3N_s} \frac{\sinh(u_i^{RS}/2)_{light}}{\sinh(u_i^{RS}/2)_{heavy}} \prod_i^{3N_s-1} \frac{\sinh(u_i^{TS}/2)_{light}}{\sinh(u_i^{TS}/2)_{heavy}} \quad (4)$$

$$(f_{RS})_{subset} = \left[\prod_j^{N_{iso}} \frac{(m_j)_{light}}{(m_j)_{heavy}} \right]^{\frac{3}{2}} \prod_i^{3N_s} \frac{\sinh(u_i^{RS}/2)_{light}}{\sinh(u_i^{RS}/2)_{heavy}} \quad (5)$$

$$(f_{TS})_{subset} = \left[\prod_j^{N_{iso}} \frac{(m_j)_{light}}{(m_j)_{heavy}} \right]^{\frac{3}{2}} \prod_i^{3N_s-1} \frac{\sinh(u_i^{TS}/2)_{light}}{\sinh(u_i^{TS}/2)_{heavy}} \quad (6)$$

Two approaches are considered for obtaining average values of the KIEs from the sets of RS and TS Hessians. The first takes all possible combinations of the Ω_{RS} reactant structures (i) and Hessians with the Ω_{TS} transition structures and Hessians (j): an individual isotope effect KIE_{ij} (eq. 7) is computed for each pair, and the average $\langle KIE \rangle_{indiv}$ is found as the arithmetic mean (eq. 8) of all $\Omega_{RS} \times \Omega_{TS}$ individual values.

$$KIE_{ij} = (f_{RS})_i / (f_{TS})_j \quad (7)$$

$$\langle KIE \rangle_{\text{indiv}} = \frac{1}{\Omega_{\text{RS}} \times \Omega_{\text{TS}}} \sum_i^{\Omega_{\text{RS}}} \sum_j^{\Omega_{\text{TS}}} KIE_{ij} \quad (8)$$

The second approach considers all Ω_{RS} reactant structures as a reactant-state ensemble and all Ω_{TS} transition structures as a transition-state ensemble: the average $\langle KIE \rangle_{\text{state}}$ (eq. 11) is obtained as the quotient of the average IPFR for the transition state (eq. 9) as dividend with the average IPFR for the reactant state (eq. 10) as divisor.

$$\langle f_{\text{RS}} \rangle = \frac{1}{\Omega_{\text{RS}}} \sum_i^{\Omega_{\text{RS}}} (f_{\text{RS}})_i \quad (9)$$

$$\langle f_{\text{TS}} \rangle = \frac{1}{\Omega_{\text{TS}}} \sum_j^{\Omega_{\text{TS}}} (f_{\text{TS}})_j \quad (10)$$

$$\langle KIE \rangle_{\text{state}} = \langle f_{\text{RS}} \rangle / \langle f_{\text{TS}} \rangle \quad (11)$$

Both methods are based on the assumption that the reactant state and the transition state are entirely independent; this means that there is an equal probability of each and every individual reactant structure going to each and every individual transition structure. This assumption is entirely consistent with conventional transition-state theory but could be inappropriate if relaxation of the solvent environment were slow compared with the chemical reaction step. If KIEs were computed for pairs of RS and TS directly connected by an individual intrinsic reaction coordinate path (*cf.* ref. 11), it would not be obvious what the appropriate method for averaging should be, since there would not be an equal probability for each path. The RS and TS structures in this work are selected from MD trajectories which should already each reflect a Boltzmann distribution. In the present study the number of solvent molecules included in the Hessian for each individual RS and TS varies from 0 to 10, and therefore the molecular partition functions Q^{RS} and Q^{TS} vary very considerably in magnitude and would not be amenable to meaningful averaging over the Ω_{RS} or Ω_{TS} values. However, it is meaningful to consider the IPFRs as the basis for averaging, since variation in these quantities does not show any obvious dependence on the number of solvent molecules included in the Hessian.

Within the limits of the harmonic approximation adopted for the “all-frequencies” method for evaluating IPFRs, and thence KIEs, it is logical to include a quantum correction to the partition function not only for each separable vibrational mode with a real frequency (*i.e.* zero-point energy) but also for motion in the transition vector with its imaginary frequency (*i.e.* tunnelling). The tunnelling correction to the KIE may be obtained simply (albeit approximately) by means of Bell’s expression¹⁵ for an inverted parabola, eq. 12.

$$KIE_{\text{corr}} = \left[\frac{v_{\text{light}}}{v_{\text{heavy}}} \right]^{\ddagger} \frac{\sin(u_i^{\text{TS}/2})_{\text{heavy}}}{\sin(u_i^{\text{TS}/2})_{\text{light}}} \frac{(f_{\text{RS}})_{\text{subset}}}{(f_{\text{TS}})_{\text{subset}}} \quad (12)$$

In the event that the relaxation of the subset atoms to a local minimum or saddle point within their frozen environment yielded any residual small imaginary frequencies (not including the transition frequency for a transition structure), we treated these in either of two ways. Firstly, any small imaginary frequency was replaced by a real frequency of the same magnitude. Alternatively, any small imaginary frequency was simply omitted¹⁶ from the evaluation of the vibrational partition functions (eqs. 5 and 6) which

therefore involved products over correspondingly fewer than $3N_s$ or $3N_s - 1$ frequencies.

Results and Discussion

Stages 1 - 3. The free energy of activation ($\sim 142 \text{ kJ mol}^{-1}$ at 300 K) obtained from the AM1/OPLS-AA PMF is higher than either the experimental value³ (94.6 kJ mol^{-1}) or the *ab initio* PCM/CCSD(T)/6-311+G(2df,2p)//B3LYP/6-31G(d) estimate of $\Delta G^\ddagger = 101 \text{ kJ mol}^{-1}$ for this reaction in DMSO.¹⁷ Although AM1 gives erroneous energies, possible errors in computed KIEs are likely to be much smaller owing (in part) to their nature as exponentials of free-energy differences due to isotopic shifts.

The mean values of the making and breaking bond distances in the 100 TS structures are $C_\alpha-C_{\text{nu}} = 2.08 \pm 0.05 \text{ \AA}$ and $C_\alpha-Cl = 2.12 \pm 0.04 \text{ \AA}$ and the mean of the $C_{\text{nu}}-C_\alpha-Cl$ angle is $166^\circ \pm 2^\circ$, indicating that these key structural parameters of the transition state are well defined. The same is not true for the “reactant complex” structures determined, starting from the free-energy minimum in the PMF profile, by means of energy minimization within a frozen environment but without constraints upon the cyanide and chloroethane moieties (or on DMSO molecules in the first solvation shell): the average value of the distance $C_\alpha \cdots C_{\text{nu}}$ to the nucleophile in these 100 structures is very long ($7.733 \pm 1.713 \text{ \AA}$) with a very large standard deviation. The actual reagent used in the experimental study was tetra-*n*-butylammonium cyanide,³ and a conductometric study¹⁸ has shown that there is no ion pairing between $n\text{-Bu}_4\text{N}^+$ and NC^- in DMSO at 25°C ; this result implies that no significant amount of association between NC^- and EtCl should be expected in DMSO solution at 300 K. Inspection of each of the 100 “reactant complex” structures also reveals no evidence for any precursor ion-molecule complex ($\text{NC}^- \cdots \text{EtCl}$): the cyanide and chloroethane moieties are independently solvated and randomly oriented relative to each other. Consequently we decided to take these 100 structures together with another 100 structures for solvated NC^- by itself and 100 structures for solvated EtCl by itself as part of a single ensemble of reactant-state structures RS. Furthermore, a fraction of the locally-minimized AM1/OPLS-AA structures for solvated cyanide anion showed unrealistic bonding motifs (*e.g.* formation of a covalent adduct with DMSO); 122 RS structures remained after removal of these non-physical configurations.

Kinetic isotope effects without explicit solvation. It is helpful first to establish how the AM1 method performs for KIE calculations in a vacuum and in continuum solvent. Neither method predicts the direction (normal or inverse) of all six KIEs (Table 1, rows 1 and 2), although the PCM description of DMSO does better; neither method is correct for $k_{\text{H}}/k_{\beta\text{-}^2\text{H}_3}$, and PCM is incorrect for $k^{35}\text{Cl}/k^{37}\text{Cl}$. Whilst the inverse sense of $k_{\text{H}}/k_{\alpha\text{-}^2\text{H}_2}$ is correctly predicted by AM1, its magnitude (deviation from unity) is too large. Interestingly, not only does the M06-2X/6-31+G(d,p)/PCM method overcorrect this KIE, predicting a small normal value (Table 1, row 3), but also it incorrectly predicts inverse values for $k_{\text{H}}/k_{\beta\text{-}^2\text{H}_3}$, $k^{12}\text{C}/k^{13}\text{C}_{\text{nu}}$ and $k^{14}\text{N}/k^{15}\text{N}_{\text{nu}}$.

Average kinetic isotope effects with explicit solvation. The most striking point to notice from the AM1/OPLS-AA ensemble-averaged KIEs (Table 1) is that, regardless of which averaging method is used, there is qualitative agreement (normal or inverse) with the experimental values⁴ for all six different isotopic substitutions. PMW⁴ considered 39 different combinations of QM method and basis set available within Gaussian98, and other

Table 1. Mean values and standard deviations (1σ) of averaged kinetic isotope effects for S_N2 reaction $NC^- + EtCl$ in DMSO. ^[a]

description	reactants	T / K	$k_H/k_{\alpha-D_2}$	$k_H/k_{\beta-D_3}$	$k^{11}C_{\alpha}/k^{14}C_{\alpha}$	$k^{35}Cl/k^{37}Cl$	$k^{12}C_{nu}/k^{13}C_{nu}$	$k^{14}N/k^{15}N$
<i>Vacuum or continuum solvation:</i>								
KIE_{vacuum}	separate		0.920	0.989	1.20	1.0075	0.9870	0.9993
KIE_{PCM}	separate		0.916	0.982	1.19	0.9927	1.0018	1.0014
$KIE_{M06-2X}^{[b]}$	separate		1.043	0.964	1.19	1.0068	0.9917	0.9989
<i>Translation/rotation procedure: librational modes replaced by translations and rotations:</i>								
$\langle KIE \rangle_{indiv}$	separate	300	0.934 ± 0.023	1.012 ± 0.025	1.207 ± 0.002	1.0048 ± 0.0065	1.0022 ± 0.0083	1.0028 ± 0.0044
$\langle KIE \rangle_{state}$	separate	300	0.934 ± 0.023	1.012 ± 0.025	1.207 ± 0.002	1.0048 ± 0.0065	1.0022 ± 0.0083	1.0028 ± 0.0045
<i>All-frequencies procedure: librational modes treated as harmonic vibrations; extra imaginaries replaced by real frequencies:</i>								
$\langle KIE \rangle_{indiv}$	RS	300	0.921093 ± 0.020584	1.004112 ± 0.023234	1.191894 ± 0.005771	1.007237 ± 0.000321	1.000246 ± 0.008029	1.001740 ± 0.002079
$\langle KIE \rangle_{state}$	RS	300	0.920819 ± 0.02310	1.003877 ± 0.023605	1.191893 ± 0.005312	1.007244 ± 0.000478	1.000245 ± 0.008126	1.001742 ± 0.002068
$\langle KIE \rangle_{state}$	RS	303.15	0.921 ± 0.020	1.006 ± 0.023	1.190 ± 0.005	1.0071 ± 0.0005	1.0006 ± 0.0076	1.0014 ± 0.0016
$\langle KIE_{corr} \rangle_{state}$	RS	303.15	0.923 ± 0.020	1.014 ± 0.023	1.268 ± 0.018	1.0081 ± 0.0005	1.0032 ± 0.0079	1.0032 ± 0.0017
<i>All-frequencies procedure: librational modes treated as harmonic vibrations; extra imaginaries omitted:</i>								
$\langle KIE \rangle_{state}$	RS	303.15	0.921 ± 0.021	1.008 ± 0.031	1.190 ± 0.009	1.0077 ± 0.0047	1.0007 ± 0.0076	1.0014 ± 0.0023
<i>Experiment:</i> ^[c]								
$N^{[d]}$	separate	303.15	0.990 ± 0.004	1.014 ± 0.003	1.21 ± 0.02	1.0070 ± 0.0003	1.0009 ± 0.0007	1.0002 ± 0.0006
			4	3	12	8	18	14

[a] The number of decimal places shown for both means and standard deviations in several of the rows of this Table deliberately exceeds the number of significant figures as judged by the magnitude of those standard deviations (see text for discussion). [b] M06-2X/6-31+G(d,p)/PCM. [c] Ref. 3. [d] Number of independent experiments used to determine mean value and standard deviation of KIE.

programs for electronic structure calculations, but none of those methods predicted the direction of the isotope effect in agreement with experiment for all six substitutions. (Quantitatively, it is clear that the α - 2H_2 KIE is seriously in error: see below.) It is perhaps significant that no explicit DMSO molecules were included in that study, and certainly there was no ensemble averaging of solvent configurations. In a subsequent paper PMW and their co-workers¹⁹ studied the same reaction in THF solvent in order to test whether the discrepancy between the TS structures predicted by their calculations⁴ and by their interpretation of the experimental KIEs, and they concluded that the lack of solvation in the calculations was not responsible. The present results call this conclusion into question, and suggest that it would be of interest also to perform these simulations with ensemble averaging in THF for comparison.

The standard deviations for the calculated ensemble-averaged KIEs do not have the same significance as those reported for the experimental values. The calculated standard deviations reflect the breadth of the distribution of precisely computed IPFRs for each individual relaxed snapshot within a limited sample of RS and TS configurations spanning a range of structures determined by the model potential, whereas the experimental errors arise from uncertainties in rate-constant determinations for (effectively) complete sampling of all thermally accessible RS and TS configurations which may also span a distribution of structures. Notwithstanding this important proviso, the calculated and experimental KIEs (Table 1) agree within the degree of uncertainty of a single standard deviation (1σ) for all methods for each of the isotopic substitutions except $k_{\alpha-^1H_2}/k_{\alpha-^2H_2}$. Although in the latter case the experimental value is an average of only four determinations, it is probably safe to conclude that the calculated results for α -deuterium substitution are indeed too large in the inverse sense.

With this exception, the overall extent of agreement between ensemble-averaged AM1/OPLS-AA KIEs and experiment is remarkable, despite the acknowledged deficiencies of the method in regard to computed energies. Only one [MP2/6-31+G(d,p)] of the 39 methods considered by PMW yielded calculated KIEs that agreed within 1σ for more than three of the six experimental values.⁴ According to the ranking scheme used by PMW (based on the sum of absolute errors between calculation and experiment), the best set of results in Table 1 (row 8) is only middle-ranking as assessed by all six KIEs but is table-topping if the 2° α - 2H_2 KIE is excluded.

The mean values for $k^{12}C_{nu}/k^{13}C_{nu}$, $k^{14}N/k^{15}N$ and $k^{35}Cl/k^{37}Cl$ calculated by the “translation/rotation” method (Table 1, rows 4 and 5) each differ from experiment by more than those calculated by the “all-frequencies” method. The use of small subset Hessians involving restricted selections of atoms gives rise to errors in IPFRs and KIEs: elsewhere we have recently argued that these errors are considerably smaller for the “all-frequencies” method than for the “translation/rotation” method.¹³ The additional computational expense involved in projecting out the six librational modes of the subset and replacing them by translations and rotations is not justified by any improvements in accuracy or precision. Consequently we now only recommend use of the “all-frequencies” method.

The two averaging methods (eqs. 8 and 11) are mathematically different and indeed yield very slightly different means and standard deviations if enough decimal places are considered (Table 1, rows 6 and 7); however, they are indistinguishable if the number of significant figures is restricted to what is justified by the magnitudes of the standard deviations. (The number of decimal places shown for both means and standard deviations in several of the rows of this Table exceeds the number of significant figures. This is done

deliberately in order to allow for comparison between the methods. Once the best method has been established, the results should not be quoted with more than the correct number of significant figures.)

Figure 2. Distributions of individual KIE_{ij} values calculated by the all-frequencies method for $NC^- + EtCl$ in DMSO at 300 K; experimental means and 1σ shown in grey.

The effect of the small difference in temperature between 300 and 303.15 K is entirely as expected: the KIEs are slightly smaller in magnitude (less different from unity) at the higher temperature. The sensitivity of the IPFRs themselves (see Supporting Information) to temperature is more dramatic.

A small proportion of the locally relaxed snapshot structures produced one or more unwanted small imaginary frequencies, representing less than 0.2% of all the computed vibrational frequencies. However, the IPFRs values resulting from replacement of these extra imaginaries by real frequencies of the same magnitude are not abnormal and cannot be recognized as outliers in the distributions (see below). These structures are all included in the results presented in Table 1. Although there is little difference between the KIEs obtained either by replacing these extra imaginaries or by omitting them (*e.g.* compare rows 8 and 10 of Table 1), we recommend the former procedure for the following reason: owing to the non-separability of the internal and external modes, some of these small imaginary frequencies are isotopically sensitive to a (perhaps) surprising extent, such that their omission can cause the IPFR for that particular configuration to become <1 , which is unphysical and incorrect. Furthermore, omission leads to larger standard deviations in the IPFR values (see Supporting Information) and KIEs, whereas replacement by real frequencies appears to capture the isotopic sensitivity correctly and ensures that the vibrational product of all $3N_s$ isotopic frequency ratios is numerically equal to the isotopic mass-ratio factor (appearing in eqs. 5 and 6) as it is required to be.

Finally, inclusion of the simple quantum correction for motion in the transition vector (eq. 12) does not lead to general improvement in the agreement between the calculated average KIEs ($\langle KIE \rangle_{state}$, Table 1, row 9) and the experimental values.

Bearing in mind all of the above remarks, the “best” results are those from the state-averaged method (eq. 11) with the “all-frequencies” procedure and extra imaginaries replaced by real frequencies: $k_H/k_{\alpha-2H_2} = 0.92 \pm 0.02$, $k_H/k_{\beta-2H_3} = 1.01 \pm 0.02$, $k^{11C_a}/k^{14C_a} = 1.190 \pm 0.005$, $k^{35Cl}/k^{37Cl} = 1.0071 \pm 0.0005$, $k^{12C_{nu}}/k^{13C_{nu}} = 1.001 \pm 0.008$, and $k^{14N}/k^{15N} = 1.0014 \pm 0.0016$.

Analysis of isotope effect distributions. It is of interest to inspect the distributions of individual KIE_{ij} values that contribute to the $\langle KIE \rangle_{indiv}$ average for each of the isotopic substitutions: Figure 2 shows histograms of the number of semi-classical KIE_{ij} values (at 300 K) in small ranges of the k_{light}/k_{heavy} ratios calculated with respect to the combined reactants RS. The distributions for $k_H/k_{\alpha-2H_2}$, $k_H/k_{\beta-2H_3}$, k^{11C_a}/k^{14C_a} and k^{35Cl}/k^{37Cl} appear more or less symmetrical and bell-shaped, as would be expected for normal distributions. However, the distributions for $k^{12C_{nu}}/k^{13C_{nu}}$ and k^{14N}/k^{15N} are certainly not normal and seem to be comprised of (at least) two overlapping populations; consequently, the means and standard deviations reported in Table 1 must be treated with caution, since they do not refer to normal distributions.

The grey lines in Figure 2 indicate the means and reported standard deviations for the experimental KIEs. Clearly the calculated and experimental distributions for $k_H/k_{\alpha-2H_2}$ do not overlap, whereas the experimental values for $k_H/k_{\beta-2H_3}$ and k^{35Cl}/k^{37Cl} lie entirely within the range of the calculated distributions. Although the experimental mean for k^{11C_a}/k^{14C_a} differs from the calculated mean, most of the calculated distribution lies within the wide range of the experimental 1σ . This KIE has the largest ratio of transition frequencies (average value of $[v^{11C}/v^{14C}]^\ddagger = 1.09$) and hence the largest quantum correction (1.067 ± 0.015); although the latter may be overestimated by eq. 12, it is possible that a more complete

treatment of tunneling might bring the calculated and experimental KIEs into better agreement.

Analysis of $\ln(\text{IPFR})$ distributions. It is also very revealing to inspect the distribution of values of IPFRs f_{RS} and f_{TS} that contribute

Figure 3. Distributions of natural logarithms of isotopic partition-function ratios for isotopologous pairs of locally-relaxed RS (left) and TS (right) configurations in DMSO at 300 K.

to the averages. Simple plots of each IPFR against its number in the sequence of snapshots do not show any significant upward or downward trends away from the mean values, and therefore indicate that the equilibration is adequate. Figure 3 shows histograms of the natural logarithms $\ln(f_{\text{RS}})_{\text{subset}}$ and $\ln(f_{\text{TS}})_{\text{subset}}$ for these quantities computed for isotopologous pairs of 122 or 200 locally-relaxed RS (left) and 100 locally-relaxed TS (right) configurations in DMSO at 300 K. It is more meaningful to consider logarithms rather than the IPFRs themselves, since the former reflect differences in free energy. The envelope of each histogram is less smooth than is found, in general, for the distributions of the individual KIE_{ij} values because the population size is 100 times smaller. Even so, the distributions of $\ln(f_{\text{RS}})_{\text{subset}}$ and $\ln(f_{\text{TS}})_{\text{subset}}$ for $k_{\text{H}}/k_{\alpha\text{-}^2\text{H}_2}$, $k_{\text{H}}/k_{\beta\text{-}^2\text{H}_3}$ and $k^{35}\text{Cl}/k^{37}\text{Cl}$ also appear more or less normal. The distribution for $k^{11}\text{C}_a/k^{14}\text{C}_a$ shows one low-valued outlier for RS and a tail on the high-valued side for TS which together account for the low-valued tail in the KIE_{ij} distribution for this isotope effect. Simple consideration of the difference between the modes (as opposed, properly, to the means) of the $\ln(f_{\text{RS}})_{\text{subset}}$ and $\ln(f_{\text{TS}})_{\text{subset}}$ histograms reveals whether the average KIE is normal or inverse for these isotopic substitutions.

Relationship to other methods for KIE calculations. A virtue of the approach described in this paper is that it opens the mind as to how a fluctuating solvent environment gives rise to a whole distribution of KIE values, and therefore provides a necessary corrective to the mindset that considers only a single reactant structure undergoing chemical transformation via a single transition structure. It also makes a more general point that any comparison of condensed-phase experiments with results of a particular QM method is meaningless unless the calculations include proper averaging.

Singleton and co-workers³ have reported KIEs calculated by means of the Bigeleisen equation (eq. 2) with simple tunnelling (eq. 12) for a range of PCM-optimized TS conformations and have discussed errors associated with non-zero frequencies for external degrees of freedom, but not in the context of subset Hessians; they have also reported the use of Boltzmann-weighted IPFRs in KIE calculations involving a small number of low-energy RS conformations.²⁰ The second step of the first stage of the EA-VTST method of Truhlar and co-workers¹¹ involves averaging of vibrational frequencies over a set of configurations in order to convert a classical PMF to one with $3N - 7$ quantized nuclear motions in order to include zero-point and thermal energies: the six lowest-frequency modes are omitted on the grounds that the harmonic approximation is not applicable to these librational motions.²¹ We have argued elsewhere that treating them as harmonic vibrations incurs much less error in IPFRs and KIEs than regarding them as classical rotations and translations.¹³ The second stage of the EA-VTST method is similar to our procedure in that it involves relaxation of a mobile subset of atoms to a local saddle point within a frozen environment (primary and secondary zones in Truhlar's terminology)¹¹ to generate a TS ensemble for which the vibrational free energy is computed for $3N_s - 1$ modes. It differs from our procedure, however, in that a minimum-energy path is obtained linking each member of the TS ensemble to a particular RS structure, and the averaging is performed over the activation free energies.¹¹ The path-integral/free-energy perturbation and umbrella sampling (PI-FEP/UM) method of Major and Gao²² includes quantization in all degrees of freedom for a small number (typically four) of atoms including the site of isotopic substitution and its immediate neighbours, yielding both zero-point energy and tunnelling effects at the same time; a double averaging is performed to obtain both the

classical PMF and the quantum-mechanical correction along the classical path, and their bisection sampling method allows the Boltzmann-weighted free-energy difference between light and heavy isotopologues to be obtained from the same simulation by FEP in mass from the light to the heavy isotope. By avoiding separate simulations for each isotopologue, this method is capable of yielding both primary and secondary KIEs with acceptably small errors; presumably, however, in view of the small number of quantized atoms, determination of KIEs for multiple isotopic substitutions requires multiple (expensive) PI-FEP/UM simulations. In a sense, our use of the same Hessian for both isotopologues may also be considered as a one-step FEP in mass, albeit within the limitations of the harmonic approximation, and which requires only diagonalization of the subset Hessian for each additional isotopologue.

Methods

Full details of the computational procedures employed in each step of our procedure are provided in the Supporting Information, but key points are highlighted here.

Hessians for subsets of selected atoms relaxed to a local stationary point within a frozen environment were computed using full QM/MM gradient vectors for the entire system. KIEs were obtained as ratios of IPFRs for RS and TS, which were calculated in two different ways. On the one hand, our CAMVIB and CAMVIB programs were employed, first to remove translational and rotational contributions from computed subset Hessians by a projection method,²³ and second to evaluate partition functions for translation, rotation and vibration of the subset atoms, and thence KIEs, within the harmonic-oscillator, rigid-rotor, ideal-gas approximations and the standard transition-state theory of isotope effects.² On the other hand, IPFRs for the subset atoms were determined treating both the internal and external degrees of freedom as harmonic vibrational modes, by means of a new program UISO and KIEs were evaluated at both 300 K and 303.15 K (the temperature at which the experimental KIEs were determined).

In step 3, a representative number (Ω) of “snapshot” structures from each of the step 2 MD trajectories were taken in order to re-optimize each to a local stationary point, either an energy minimum or a saddle point. The time separation of these snapshots along each trajectory should be sufficient to ensure statistical independence of the solvent configurations. We chose to select snapshots at 10 ps intervals, thereby obtaining 100 structures for each species. The first solvation shell of DMSO molecules surrounding each solute species was included with the solute in the flexible region for these local relaxations, but the remainder of the solvent was kept frozen in the geometry as found in each individual snapshot from the respective MD trajectory. The reason for this was to generate a set of local stationary points with different solvent configurations representative of the thermal fluctuations occurring at 300 K. Some tests were performed in which the first solvation shell was treated by MM, and the solute by QM, but more generally it was found necessary to treat the first solvation shell and the solute by QM in order to obtain a better description of solute-solvent interactions affecting the KIEs.

The advantage of allowing each snapshot structure to optimize only to a local minimum within a frozen configuration of the environment is that each different structure is more likely to be representative of the whole system at the temperature of the simulation. In contrast, if for each snapshot the whole system is minimised,²⁴ then the configuration of the environment changes to something corresponding to a much lower temperature and which is

unrepresentative of the real system. The method should capture the effects of specific interactions between a substrate and its environment that a continuum model is incapable of doing (for solutes in solution). The sizes of the flexible and frozen regions are a matter of choice, as are the extents of the QM and MM regions and the number of atoms included in the Hessian.

In step 4 a QM/MM Hessian was computed for a subset of atoms from each locally relaxed structure. Usually this subset contained the same atoms as were in the QM region, but sometimes it also included some atoms from the MM region. Any subset of N_s atoms within the environment of a larger N -atomic system possesses $3N_s$ vibrational modes, of which $3N_s - 6$ correspond to internal motions within the subset and 6 correspond to motions (librations) of the subset relative to its environment. Although the subset has been relaxed to a local stationary point within a frozen environment, this is not a stationary point within the full system, and the 6 librations are not strictly separable from the $3N_s - 6$ vibrations.

Conclusion

Ensemble-averaged KIEs take account of multiple configurations in solution at finite temperature, and the methodologies proposed in this study are appropriate for use in situations where specific solute-solvent interactions may be important, which traditional approaches to KIE calculations would neglect. Solvent molecules in the first solvation shell must be included in the Hessian. Provided this is done, then the methods described here and implemented with the hybrid AM1/OPLS-AA potential yield results in (at least) qualitative agreement with experiment, correctly predicting the directions (normal or inverse) of KIEs for six isotopic substitutions.

Although the $\langle KIE \rangle_{\text{indiv}}$ or $\langle KIE \rangle_{\text{state}}$ averaging methods give essentially the same average KIEs, unless one requires to see the distribution of the individual KIE values, for practical purposes we recommend the latter method since it involves less work. We also recommend use of the “all-frequencies” method for evaluation of IPFRs from subset Hessians. The logarithms of the IPFRs for RS and TS do not always show single normal distributions, but appear to reflect different families of solvation configurations. It is not clear whether this is a consequence of the choice of QM method or of inadequate sampling: a more reliable QM method would not necessarily improve either the means or the standard deviations of the average KIEs if the sample of independent solvent configurations is insufficiently representative. How many configurations should be sampled to obtain reliable KIEs? An heuristic approach to answering that important question would be to construct the $\ln(\text{IPFR})$ histogram and to update it with each new configuration sampled until the resulting distribution is satisfactory.

Since average KIEs are apparently not very sensitive to the presence of unwanted extra imaginary frequencies, an effective practical procedure might be to sample more snapshot configurations at the expense of less relaxation of the subset atoms to a local stationary point.

The thermally-averaged KIEs may be compared meaningfully with experimental values and the current methodology may perfectly well be implemented with other QM or QM/MM methods, and thus provides a useful tool for investigating KIEs in relation to studies of chemical reaction mechanisms in solution or catalysed by enzymes.

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-
- [1] L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1940: 'any approach to the effect of structure upon equilibrium or heat of reaction that treats a molecule as a rigid lifeless structure can be no more than the crudest approximation. The liveliness, the flexibility that is characteristic of a complicated organic molecule, is not lost even at the absolute zero...' (p.76).
- [2] *Isotope Effects in Chemical Reactions*, eds. C. J. Collins and N. S. Bowman, Van Nostrand Reinhold, New York, 1970; L. Melander and W. H. Saunders, *Reaction Rates of Isotopic Molecules*, Wiley, New York, 1980.
- [3] J. S. Hirschi, T. Takeya, C. Hang and D. A. Singleton, *J. Am. Chem. Soc.* **2009**, *131*, 2397-2403 and references cited therein.
- [4] Y. Fang, Y. Gao, P. Ryberg, J. Eriksson, M. Kołodziejska-Huben, A. Dybala-Defratyka, S. Madhavan, R. Danielsson, P. Paneth, O. Matsson and K. C. Westaway, *Chem. Eur. J.* **2003**, *9*, 2696.
- [5] (a) J. A. Barnes and I. H. Williams, *Chem. Commun.* **1996**, 193. (b) J. A. Barnes and I. H. Williams, *Biochem. Soc. Trans.* **1996**, *24*, 263-268. (c) A. J. Turner, V. Moliner and I. H. Williams, *Phys. Chem. Chem. Phys.* **1999**, *1*, 1323-1331. (d) S. Martí, V. Moliner, I. Tuñón and I. H. Williams, *Org. Biomol. Chem.* **2003**, *1*, 483-487.
- [6] e.g. K. E. Ranaghan and A. J. Mulholland, *Int. Rev. Phys. Chem.* **2010**, *29*, 65-133.
- [7] M. Roca, S. Martí, J. Andres, V. Moliner, I. Tuñón, J. Bertran and I. H. Williams, *J. Am. Chem. Soc.* **2003**, *125*, 7726 – 7737.
- [8] G. D. Ruggiero, S. J. Guy, S. Martí, V. Moliner and I. H. Williams, *J. Phys. Org. Chem.* **2004**, *17*, 592 – 601.
- [9] M. Klähn, G. Mathias, C. Kötting, M. Nonella, J. Schlitter, K. Gerwert and P. Tavan, *J. Phys. Chem. A* **2004**, *108*, 6186-6194.
- [10] N. Kanaan, J. J. Ruiz Pernía and I. H. Williams, *Chem. Commun.* **2008**, 6114–6116.
-
- [11] D. G. Truhlar, J. Gao, M. Garcia-Viloca, C. Alhambra, J. Corchado, M. L. Sanchez and T. D. Poulsen, *Int. J. Quantum Chem.* **2004**, *100*, 1136-1152.
- [12] O. Redlich, *Z. physik. Chem.* **1935**, *B28*, 371; E. Teller, quoted by W. R. Angus, C. R. Bailey, J. B. Hale; C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson and C. L. Wilson, *J. Chem. Soc.* **1936**, 971-987.
- [13] I. H. Williams, *J. Chem. Theor. Comput.* DOI: 10.1021/ct200771t.
- [14] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.* **1947**, *15*, 261-267; J. Bigeleisen and M. Wolfsberg, *Adv. Chem. Phys.* **1958**, *1*, 15-76.
- [15] R. P. Bell, *Trans. Faraday Soc.* **1959**, *55*, 1-4.
- [16] M. Saunders, K. E. Laidig and M. Wolfsberg, *J. Am. Chem. Soc.* **1989**, *111*, 8989 – 8994.
- [17] G. I. Almerindo and J. R. Pliego, *Org. Letters* **2005**, *7*, 1821-1823.
- [18] S. MacMillar, Y. Fang, K. C. Westaway, O. Matsson and P. Beronius, *J. Phys. Org. Chem.* **2008**, *21*, 237 – 241.
- [19] Y. Fang, S. MacMillar, J. Eriksson, M. Kołodziejska-Huben, A. Dybala-Defratyka, S. Madhavan, R. Danielsson, P. Paneth, O. Matsson and K. C. Westaway, *J. Org. Chem.* **2006**, *71*, 4742 – 4747.
- [20] O. M. Gonzalez-James and D. A. Singleton, *J. Am. Chem. Soc.* **2010**, *132*, 6896 – 6897.
- [21] M. Garcia-Viloca, C. Alhambra, D. G. Truhlar and J. Gao, *J. Chem. Phys.* **2001**, *114*, 9953-9958.
- [22] D. T. Major and J. Gao, *J. Chem. Theory Comput.* **2007**, *3*, 949-960.
- [23] (a) I. H. Williams, *Chem. Phys. Lett.* **1982**, *88*, 462-466. (b) I. H. Williams, *J. Molec. Struct., Theochem* **1983**, *94*, 275-284. (c) I. H. Williams, *J. Am. Chem. Soc.* **1984**, *106*, 7206-7212. (d) I. H. Williams, *J. Chem. Soc., Chem. Commun.* **1985**, 510-511.
- [24] Q. Cui and M. Karplus, *J. Chem. Phys.* **2000**, *112*, 1133-1149.
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Entry for the Table of Contents

Better on average

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Ensemble-Averaged QM/MM Kinetic Isotope Effects for the S_N2 Reaction of Cyanide Anion with Chloroethane in DMSO Solution

In contrast to calculations using traditional methods, average AM1/OPLS-AA KIEs computed for $\text{NC}^- + \text{EtCl}$ in DMSO agree with experiment for isotopic substitutions in six positions, and their distributions for individual

configurations provide insight into solvent fluctuation effects. A single-molecule view of chemical change should be replaced by a picture involving averages over representative collections of molecules.

Ensemble-Average QM/MM Kinetic Isotope Effects for the S_N2 Reaction of Cyanide Anion with Chloroethane in DMSO Solution

J. Javier Ruiz Pernía^{a,b} and Ian H. Williams^{a*}

^a *Department of Chemistry, University of Bath, Bath, BA2 7AY, UK*

^b *Departament de Química Física i Analítica, Universitat Jaume I, 12071 Castelló, Spain*

email: i.h.williams@bath.ac.uk

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Computational Methods

QM calculations for species in vacuum or in a polarized continuum model^{S1} for solution were carried out by means of the Gaussian03^{S2} and Gaussian09 programs^{S3} with AM1. QM/MM energy minimizations, saddle-point searches and MD calculations, were performed by means of the fDYNAMO library^{S4} along with the GRACEFULL interface^{S5} to GRACE.^{S6} (N.B. the program library GRACE, developed at the University of Bath by Alex J. Turner from 1994 – 1997 and described in his Ph.D. thesis,^{S7} should not be confused with the completely separate commercial program of the same name, developed by Marcus A. Neumann of Avant-garde Materials Simulations from 2002 onwards and apparently first reported^{S8} in the open literature in 2008.) At each Newton-Raphson step of a QM/MM energy minimization in a control space (the QM subsystem) all geometrical coordinates belonging to the complementary space are minimized. In all cases, the Baker algorithm was employed to localize and characterize the stationary points. All QM/MM minimizations and MD simulations were carried out at 300 K using periodic boundary conditions and Langevin-Verlet NVT conditions, corresponding to the canonical ensemble, in order to keep the number of molecules (and density) constant. A switched cut-off radius of 16.0 Å was employed for all kind of interactions. All atoms of the system were allowed to move, and the time step was 1 fs.

Preliminaries. An initial S_N2 transition structure was introduced into the center of a pre-equilibrated cubic box (side length 42.5 Å) of explicit DMSO molecules, from which were removed any with a sulfur, oxygen or carbon atom closer than 2.5 Å to any solute atom. The 10 QM atoms of the solute $^{\ddagger}(\text{NC.Et.Cl})^-$ were treated by AM1 and the 5390 MM atoms of 539 DMSO molecules were described by OPLS-AA force field potentials.^{S9} A similar procedure was followed for both NC⁻ and EtCl individually. Full QM/MM optimization was performed for each of the three species NC⁻, EtCl and $^{\ddagger}(\text{NC.Et.Cl})^-$ using the LBFGS method^{S10} until the gradient of the energy was converged to < 0.1 kJ mol⁻¹. Each solute species in DMSO was then subjected to 500 ps of QM/MM MD at 300 K in order to stabilize and equilibrate the solution; for this purpose the PCM/MP2/6-31+G(d,p) optimized C_α-Cl and C_α-C_{nu} distances of $^{\ddagger}(\text{NC.Et.Cl})^-$ were subjected to harmonic constraints. Finally, an optimized saddle-point structure for $^{\ddagger}(\text{NC.Et.Cl})^-$ was obtained.

Stage 1. A QM/MM PMF was computed starting from the optimized saddle-point structure for $^{\ddagger}(\text{NC.Et.Cl})^-$ and tracing towards both reactants and products using the difference of distances $d(\text{C}_{\alpha}\text{-Cl}) - d(\text{C}_{\alpha}\text{-C}_{\text{nu}})$ as the distinguished coordinate. The initial structure of each window was the final structure of the previous one, and a total of 151 windows were run to

cover the range of interest; in each window a total of 12 ps of QM/MM MD were run: 2 ps relaxation and 10 ps production.

Stage 2. A 1 ns QM/MM MD trajectory was computed for the TS, $^{\ddagger}(\text{NC}^-\text{EtCl})^-$, within the window corresponding to the free energy maximum in the PMF. The distances $\text{C}_{\alpha}\text{--Cl}$ and $\text{C}_{\alpha}\text{--C}_{\text{nu}}$ were subjected to an umbrella potential with a force constant of $10^4 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$. In addition, the angle $\text{Cl--C}_{\alpha}\text{--C}_{\text{nu}}$ was kept at 180° by means of a harmonic constraint with a very low force constant ($5 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$): this led to structures being sampled having reasonable orientations of the nucleophile and leaving group, but running the simulation without the angle constraint did not significantly affect the energies and forces. A similar 1 ns QM/MM MD simulation was run without constraints for the apparent “reactant complex” corresponding to the free energy minimum in the PMF, and also for each of the individual reactants NC^- and EtCl in its own DMSO box; note the comments above regarding the non-existence of a well-defined precursor ion-molecule complex ($\text{NC}^-\cdots\text{EtCl}$).

- S1 S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117-129.
- S2 Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- S3 Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R.

- Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- S4 M. J. Field, M. Albe, C. Bret, F. Proust-De Martin, A. Thomas, *J. Comput. Chem.* **2000**, *21*, 1088-1100.
- S5 S. Martí, V. Moliner, I. Tuñón, *J. Chem. Theory Comput.* **2005**, *1*, 1008-1016.
- S6 (a) V. Moliner, A. J. Turner, I. H. Williams, *J. Chem. Soc., Chem. Commun.* **1997**, 1271 – 1272. (b) A. J. Turner, V. Moliner, I. H. Williams, *Phys. Chem. Chem. Phys.* **1999**, *1*, 1323-1331.
- S7 A. J. Turner, Ph.D. thesis, University of Bath, **1997**.
- S8 M. A. Neumann, F. J. J. Leusen, J. Kendrick, *Angew. Chem. Int. Ed.* **2008**, *47*, 2427 – 2430.
- S9 W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives, *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236; Y.-J. Zheng, R. L. Ornstein, *J. Am. Chem. Soc.* **1996**, *118*, 4175-4180.
- S10 R. H. Byrd, P. Lu, J. Nocedal, C. Zhu, *SIAM J. Sci. Comp. (USA)* **1995**, *16*, 1190-1208.

Figure 4S. Plots of isotopic partition-function ratios (black dots) against sequence number in the series of locally-relaxed snapshot TS structures for six isotopic substitutions: all IPFRs are computed at 303.15 K by the all-frequencies method, with the left-hand panel showing values obtained by omission of extra imaginary frequencies and the right-hand panel showing values obtained by replacing extra imaginaries by real frequencies of the same magnitude. The red dots show the cumulative mean value of the IPFR up to and including each point in the sequence.

Figure 5S. Plots of standard deviation (1σ) corresponding to the cumulative means shown in Fig. S5 isotopic partition-function ratios value of the IPFR up to and including each point in the sequence of locally-relaxed snapshot TS structures for six isotopic substitutions; the left-hand panel is for IPFRs obtained by omission of extra imaginary frequencies and the right-hand panel is for those obtained by replacing extra imaginaries by real frequencies of the same magnitude

α -D₂/ α -H₂ isotopic partition-function ratios for [NC $\cdots$ Et $\cdots$ Cl]⁻.nDMSO transition structures

structure sequence number	number extra <i>n</i>	imaginaries	extra imaginaries treated as reals				extra imaginaries omitted			
			300 K		303.15K		300 K		303.15K	
			f_{TS}	$(f_{TS})_{corr}$	f_{TS}	$(f_{TS})_{corr}$	f_{TS}	$(f_{TS})_{corr}$	f_{TS}	$(f_{TS})_{corr}$
1	8	2	170.976379	170.566264	159.410385	159.037143	170.314285	169.905758	158.793091	158.421294
2	8		175.125015	174.768423	163.222122	162.897784	175.125015	174.768423	163.222122	162.897784
3	4	1	175.230103	174.823466	163.323746	162.953734	175.209732	174.803143	163.304749	162.934780
4	5	1	172.626404	172.189622	160.926086	160.528625	172.206863	171.771143	160.534988	160.138493
5	4		172.645538	172.272632	160.950134	160.610807	172.645538	172.272632	160.950134	160.610807
6	4	1	174.354279	174.031223	162.523483	162.229691	174.178680	173.855950	162.359818	162.066321
7	4		172.614044	172.081115	160.912445	160.427681	172.614044	172.081115	160.912445	160.427681
8	5		174.083710	173.670893	162.272141	161.896609	174.083710	173.670893	162.272141	161.896609
9	3		176.882858	176.468401	164.838501	164.461658	176.882858	176.468401	164.838501	164.461658
10	4		174.377823	173.986967	162.544144	162.188677	174.377823	173.986967	162.544144	162.188677
11	7		177.457306	177.030608	165.375534	164.987557	177.457306	177.030608	165.375534	164.987557
12	8		176.150238	175.836412	164.172531	163.887051	176.150238	175.836412	164.172531	163.887051
13	8		172.800537	172.441293	161.087265	160.760255	172.800537	172.441293	161.087265	160.760255
14	8	1	174.408630	173.964896	162.564819	162.161150	174.352448	173.908856	162.512436	162.108896
15	6		174.648392	174.221473	162.787445	162.399213	174.648392	174.221473	162.787445	162.399213
16	6		170.780975	170.514205	159.224899	158.981951	170.780975	170.514205	159.224899	158.981951
17	5	1	173.589691	173.074340	161.811569	161.342759	173.583405	173.068072	161.805710	161.336916
18	5		171.606888	170.890612	159.980713	159.330128	171.606888	170.890612	159.980713	159.330128
19	5	1	176.707413	176.218574	164.664063	164.219582	176.290909	175.803223	164.275940	163.832507
20	6		178.215515	177.705998	166.065887	165.602954	178.215515	177.705998	166.065887	165.602954
21	6		170.741730	169.691565	159.176559	158.224624	170.741730	169.691565	159.176559	158.224624
22	8		165.693008	164.693194	154.524139	153.616744	165.693008	164.693194	154.524139	153.616744
23	5		168.995422	167.903760	157.577606	156.585604	168.995422	167.903760	157.577606	156.585604
24	7	1	172.798340	172.379507	161.081421	160.700148	172.793198	172.374378	161.076630	160.695368
25	3		171.102921	170.777740	159.522964	159.226695	171.102921	170.777740	159.522964	159.226695
26	8		172.454620	172.218838	160.773453	160.558855	172.454620	172.218838	160.773453	160.558855
27	7		170.201004	169.806819	158.688461	158.329499	170.201004	169.806819	158.688461	158.329499

28	5	1	172.750534	172.197167	161.043808	160.540775	171.899246	171.348606	160.250229	159.749674
29	6		176.928070	176.440172	164.876221	164.432632	176.928070	176.440172	164.876221	164.432632
30	7		164.736008	163.730804	153.643143	152.730911	164.736008	163.730804	153.643143	152.730911
31	4		174.940460	174.709851	163.064926	162.854938	174.940460	174.709851	163.064926	162.854938
32	5		174.914932	174.656801	163.031494	162.796478	174.914932	174.656801	163.031494	162.796478
33	5	1	163.063339	162.453500	152.107483	151.553713	161.796280	161.191179	150.925552	150.376085
34	7	1	175.271011	174.972343	163.362061	163.090287	173.888855	173.592542	162.073837	161.804207
35	3		167.959305	167.727206	156.636551	156.424944	167.959305	167.727206	156.636551	156.424944
36	5		168.317368	167.236145	156.959732	155.978421	168.317368	167.236145	156.959732	155.978421
37	5	1	171.931580	171.589750	160.283569	159.972302	171.878906	171.537181	160.234451	159.923279
38	7	1	175.197067	174.912497	163.289841	163.030811	175.191010	174.906449	163.284195	163.025174
39	9		175.067749	174.795118	163.172226	162.924023	175.067749	174.795118	163.172226	162.924023
40	8	1	173.648987	173.193046	161.863113	161.448210	172.652435	172.199111	160.934189	160.521667
41	6	2	170.366165	170.172476	158.849304	158.672875	168.751587	168.559733	157.343872	157.169114
42	5		173.404327	173.155671	161.650772	161.424443	173.404327	173.155671	161.650772	161.424443
43	7		177.737335	177.314403	165.621124	165.236579	177.737335	177.314403	165.621124	165.236579
44	7		172.477768	172.153553	160.799332	160.504228	172.477768	172.153553	160.799332	160.504228
45	4		176.907104	176.590907	164.868027	164.580364	176.907104	176.590907	164.868027	164.580364
46	4		176.325287	176.007029	164.331528	164.042000	176.325287	176.007029	164.331528	164.042000
47	6	2	176.009735	175.610647	164.028976	163.665941	175.902420	175.503575	163.928955	163.566141
48	6		171.346481	171.112337	159.753448	159.540250	171.346481	171.112337	159.753448	159.540250
49	6		172.565109	172.371882	160.872467	160.696456	172.565109	172.371882	160.872467	160.696456
50	7		172.013916	171.681950	160.369720	160.067472	172.013916	171.681950	160.369720	160.067472
51	6		169.889084	169.566606	158.410629	158.116973	169.889084	169.566606	158.410629	158.116973
52	6		172.898209	172.522108	161.185806	160.843734	172.898209	172.522108	161.185806	160.843734
53	4		174.120697	173.817461	162.307953	162.031984	174.120697	173.817461	162.307953	162.031984
54	6	1	175.083450	174.654696	163.183273	162.793475	174.263962	173.837214	162.419495	162.031521
55	6		175.870377	175.507550	163.905991	163.575897	175.870377	175.507550	163.905991	163.575897
56	6		175.697662	175.356178	163.754471	163.443813	175.697662	175.356178	163.754471	163.443813
57	7		175.108688	174.729794	163.202972	162.858331	175.108688	174.729794	163.202972	162.858331
58	4		172.459396	171.777318	160.762177	160.142066	172.459396	171.777318	160.762177	160.142066
59	6		179.343567	178.941623	167.094101	166.728644	179.343567	178.941623	167.094101	166.728644
60	7		174.554611	174.287908	162.690002	162.447149	174.554611	174.287908	162.690002	162.447149
61	5		176.193390	175.821443	164.205627	163.867384	176.193390	175.821443	164.205627	163.867384
62	6	1	173.953964	173.514445	162.148544	161.748895	173.745407	173.306415	161.954132	161.554962
63	6		164.413116	163.861036	153.351501	152.849891	164.413116	163.861036	153.351501	152.849891
64	7		167.818466	166.747541	156.476791	155.504814	167.818466	166.747541	156.476791	155.504814
65	6		176.088699	175.767688	164.108994	163.816894	176.088699	175.767688	164.108994	163.816894
66	4		178.468506	177.835795	166.292114	165.717033	178.468506	177.835795	166.292114	165.717033
67	5		172.277603	171.828734	160.599655	160.191446	172.277603	171.828734	160.599655	160.191446

68	7	2	170.749985	170.555798	159.196732	159.019840	168.759201	168.567279	157.340668	157.165839
69	5		172.169525	171.983350	160.512604	160.343004	172.169525	171.983350	160.512604	160.343004
70	6	1	177.020630	176.631510	164.969040	164.615192	174.416550	174.033154	162.542267	162.193625
71	7		173.328201	172.978440	161.571625	161.253166	173.328201	172.978440	161.571625	161.253166
72	7		171.708298	171.334673	160.073517	159.733643	171.708298	171.334673	160.073517	159.733643
73	5		176.452377	176.130840	164.442322	164.149727	176.452377	176.130840	164.442322	164.149727
74	3		173.362747	173.104561	161.602768	161.367721	173.362747	173.104561	161.602768	161.367721
75	4		171.085510	170.733350	159.510452	159.189914	171.085510	170.733350	159.510452	159.189914
76	9	1	173.119751	172.617301	161.379211	160.922350	173.047867	172.545625	161.312195	160.855523
77	7		174.638275	174.271078	162.779068	162.445131	174.638275	174.271078	162.779068	162.445131
78	7		174.422928	174.033790	162.582520	162.228703	174.422928	174.033790	162.582520	162.228703
79	9		168.542419	168.275841	157.156845	156.913998	168.542419	168.275841	157.156845	156.913998
80	7		174.098602	173.544518	162.276871	161.773168	174.098602	173.544518	162.276871	161.773168
81	8	1	173.243668	172.837985	161.496964	161.127846	172.204453	171.801203	160.528259	160.161356
82	6	1	172.376465	172.135385	160.704544	160.485114	172.359573	172.118518	160.688812	160.469404
83	10		172.524277	172.249015	160.837158	160.586602	172.524277	172.249015	160.837158	160.586602
84	6		173.448669	172.985387	161.678055	161.256678	173.448669	172.985387	161.678055	161.256678
85	6		173.475204	173.179369	161.710129	161.440959	173.475204	173.179369	161.710129	161.440959
86	6	1	176.181778	175.585412	164.191742	163.649604	176.014160	175.418361	164.035522	163.493900
87	8		173.689194	173.399319	161.907104	161.643214	173.689194	173.399319	161.907104	161.643214
88	7		171.953644	171.791286	160.310959	160.163014	171.953644	171.791286	160.310959	160.163014
89	8		176.379501	175.939089	164.376846	163.976153	176.379501	175.939089	164.376846	163.976153
90	7	1	174.066742	173.718042	162.253021	161.935724	173.969101	173.620597	162.162003	161.844884
91	8		177.180359	176.837261	165.119308	164.807134	177.180359	176.837261	165.119308	164.807134
92	7	1	171.197342	170.919115	159.606354	159.352996	171.196884	170.918658	159.605942	159.352585
93	6	2	177.526825	177.139503	165.428223	165.076013	177.270920	176.884156	165.189758	164.838056
94	7		173.703018	173.215358	161.912750	161.469105	173.703018	173.215358	161.912750	161.469105
95	7		177.137070	176.645924	165.071518	164.625023	177.137070	176.645924	165.071518	164.625023
96	7		172.118973	171.721577	160.463623	160.101898	172.118973	171.721577	160.463623	160.101898
97	9	4	174.973175	174.555725	163.083862	162.703983	173.637192	173.222929	161.838684	161.461705
98	7	1	172.534637	172.288401	160.839203	160.614930	171.531693	171.286887	159.904236	159.681267
99	5	1	174.603210	174.329211	162.739029	162.489622	173.182571	172.910801	161.414948	161.167570
100	7		173.451782	173.075408	161.685989	161.343578	173.451782	173.075408	161.685989	161.343578

β -D₃/ β -H₃ isotopic partition-function ratios for [NC $\cdots$ Et $\cdots$ Cl]⁻.*n*DMSO transition structures

structure sequence number	number extra <i>n</i>	imaginaries	extra imaginaries treated as reals				extra imaginaries omitted			
			300 K		303.15K		300 K		303.15K	
			f_{TS}	$(f_{TS})_{corr}$	f_{TS}	$(f_{TS})_{corr}$	f_{TS}	$(f_{TS})_{corr}$	f_{TS}	$(f_{TS})_{corr}$
1	8	2	1853.868652	1839.330275	1675.373047	1662.547026	1822.517608	1808.225092	1660.059204	1647.350421
2	8		1825.052124	1809.766027	1649.608521	1636.123535	1809.766027	1794.607962	1649.608521	1636.123535
3	4	1	1858.934326	1844.431124	1679.807739	1667.011948	1840.383726	1826.025254	1676.121582	1663.353870
4	5	1	1853.907715	1839.555337	1675.387451	1662.725492	1797.475687	1783.560188	1637.063354	1624.691035
5	4		1834.571045	1820.629490	1657.977539	1645.678206	1820.629490	1806.793883	1657.977539	1645.678206
6	4	1	1836.002197	1819.642104	1659.392944	1644.965205	1806.361120	1790.265150	1647.281738	1632.959300
7	4		1880.895752	1865.503817	1699.412476	1685.841357	1865.503817	1850.237838	1699.412476	1685.841357
8	5		1762.019897	1747.938938	1593.240845	1580.814068	1747.938938	1733.970505	1593.240845	1580.814068
9	3		1824.000732	1808.507417	1648.757813	1635.092079	1808.507417	1793.145704	1648.757813	1635.092079
10	4		1869.625977	1853.621083	1689.295654	1675.184876	1853.621083	1837.753199	1689.295654	1675.184876
11	7		1821.012451	1805.638081	1646.105713	1632.544771	1805.638081	1790.393513	1646.105713	1632.544771
12	8		1860.274170	1845.189034	1681.098022	1667.791296	1845.189034	1830.226225	1681.098022	1667.791296
13	8		1836.559570	1822.048123	1660.008423	1647.199303	1822.048123	1807.651337	1660.008423	1647.199303
14	8	1	1853.515625	1838.326427	1675.108276	1661.709280	1837.690447	1822.630933	1674.528687	1661.134326
15	6		1803.705811	1788.278987	1630.600708	1616.992749	1788.278987	1772.984106	1630.600708	1616.992749
16	6		1808.643311	1796.528995	1635.058716	1624.360071	1796.528995	1784.495822	1635.058716	1624.360071
17	5	1	1862.759644	1847.301613	1683.354370	1669.720148	1846.921130	1831.594535	1683.007690	1669.376276
18	5		1859.707520	1841.487343	1680.381592	1664.339598	1841.487343	1823.445675	1680.381592	1664.339598
19	5	1	1826.318237	1811.438894	1650.865112	1637.739738	1800.005344	1785.340377	1640.445190	1627.402660
20	6		1838.177246	1821.175777	1661.404053	1646.419326	1821.175777	1804.331557	1661.404053	1646.419326
21	6		1803.267578	1782.991209	1630.271484	1612.445715	1782.991209	1762.942833	1630.271484	1612.445715
22	8		1770.656250	1752.671186	1601.185425	1585.356827	1752.671186	1734.868802	1601.185425	1585.356827
23	5		1791.895264	1776.380088	1620.162109	1606.490134	1776.380088	1760.999251	1620.162109	1606.490134
24	7	1	1848.780518	1834.917652	1670.841675	1658.605957	1834.356099	1820.601393	1670.330322	1658.098349
25	3		1821.526367	1809.237601	1646.566162	1635.709879	1809.237601	1797.031740	1646.566162	1635.709879
26	8		1827.344604	1812.803477	1651.599976	1638.767828	1812.803477	1798.378060	1651.599976	1638.767828

27	7		1828.554565	1815.415888	1652.708618	1641.108875	1815.415888	1802.371616	1652.708618	1641.108875
28	5	1	1841.737793	1825.410351	1664.501831	1650.111224	1727.048574	1711.737878	1574.811768	1561.196584
29	6		1817.357056	1801.602137	1642.696899	1628.801372	1801.602137	1785.983799	1642.696899	1628.801372
30	7		1793.787842	1775.259793	1621.763916	1605.463064	1775.259793	1756.923120	1621.763916	1605.463064
31	4		1838.546021	1825.992958	1661.661865	1650.577593	1825.992958	1813.525603	1661.661865	1650.577593
32	5		1825.256226	1812.823820	1649.862793	1638.884370	1812.823820	1800.476095	1649.862793	1638.884370
33	5	1	1798.429810	1777.612800	1625.807861	1607.485319	1759.604451	1739.236849	1609.337402	1591.200479
34	7	1	1847.291016	1832.882287	1669.563843	1656.848870	1815.327904	1801.168485	1653.573730	1640.980534
35	3		1847.403931	1837.326861	1669.570068	1660.666440	1837.326861	1827.304759	1669.570068	1660.666440
36	5		1784.420166	1766.677023	1613.259521	1597.645809	1766.677023	1749.110307	1613.259521	1597.645809
37	5	1	1859.815674	1846.229118	1680.655884	1668.662444	1846.109393	1832.622966	1680.546997	1668.554335
38	7	1	1811.705078	1798.664792	1637.736328	1626.222537	1797.906132	1784.965168	1637.045654	1625.536719
39	9		1836.901611	1823.922700	1660.158447	1648.699969	1823.922700	1811.035494	1660.158447	1648.699969
40	8	1	1870.512573	1856.429446	1689.917114	1677.494565	1846.038546	1832.139685	1680.458374	1668.105356
41	6	2	1819.924438	1807.840435	1645.167236	1634.494429	1784.972416	1773.120487	1624.357056	1613.819251
42	5		1823.442993	1809.356678	1648.307007	1635.872800	1809.356678	1795.379181	1648.307007	1635.872800
43	7		1814.677246	1799.369018	1640.479858	1626.975041	1799.369018	1784.189926	1640.479858	1626.975041
44	7		1885.237427	1870.583735	1703.374268	1690.446273	1870.583735	1856.043944	1703.374268	1690.446273
45	4		1824.626221	1810.652354	1649.220581	1636.889284	1810.652354	1796.785507	1649.220581	1636.889284
46	4		1857.172974	1842.304711	1678.388550	1665.270937	1842.304711	1827.555482	1678.388550	1665.270937
47	6	2	1856.364136	1841.067945	1677.685425	1664.190616	1840.394706	1825.230101	1677.072021	1663.582147
48	6		1825.644287	1812.473636	1650.212036	1638.583881	1812.473636	1799.398001	1650.212036	1638.583881
49	6		1822.324585	1810.844642	1647.309570	1637.168688	1810.844642	1799.437018	1647.309570	1637.168688
50	7		1860.754761	1847.008622	1681.486572	1669.354107	1847.008622	1833.364031	1681.486572	1669.354107
51	6		1873.565308	1859.451603	1692.929810	1680.473914	1859.451603	1845.444217	1692.929810	1680.473914
52	6		1826.689819	1811.641625	1650.825439	1637.556327	1811.641625	1796.717398	1650.825439	1637.556327
53	4		1857.562988	1843.712437	1678.694824	1666.473039	1843.712437	1829.965159	1678.694824	1666.473039
54	6	1	1825.743408	1809.695094	1650.235718	1636.084516	1797.947344	1782.143358	1639.523193	1625.463855
55	6		1807.817383	1794.116530	1634.389160	1622.296375	1794.116530	1780.519511	1634.389160	1622.296375
56	6		1806.513306	1792.414672	1633.203369	1620.760831	1792.414672	1778.426069	1633.203369	1620.760831
57	7		1802.959106	1788.724757	1629.903931	1617.343816	1788.724757	1774.602788	1629.903931	1617.343816
58	4		1860.542603	1844.248065	1681.302246	1666.939959	1844.248065	1828.096235	1681.302246	1666.939959
59	6		1811.786011	1796.866641	1637.916992	1624.753491	1796.866641	1782.070127	1637.916992	1624.753491
60	7		1792.515381	1781.238610	1620.707031	1610.745081	1781.238610	1770.032781	1620.707031	1610.745081
61	5		1823.040039	1807.712552	1647.937866	1634.416640	1807.712552	1792.513933	1647.937866	1634.416640
62	6	1	1866.385742	1850.693486	1686.472290	1672.638711	1845.946263	1830.425858	1682.146240	1668.348146
63	6		1811.379517	1792.788634	1637.454712	1621.081742	1792.788634	1774.388557	1637.454712	1621.081742
64	7		1764.297363	1746.875453	1595.574707	1580.237149	1746.875453	1729.625580	1595.574707	1580.237149
65	6		1831.330200	1817.594364	1655.191528	1643.069234	1817.594364	1803.961552	1655.191528	1643.069234
66	4		1873.240356	1857.580684	1692.517456	1678.714290	1857.580684	1842.051921	1692.517456	1678.714290

67	5		1828.127930	1812.675833	1652.420532	1638.793877	1812.675833	1797.354344	1652.420532	1638.793877
68	7	2	1801.812012	1790.752227	1628.946899	1619.176839	1616.401051	1606.479345	1470.351685	1461.532843
69	5		1918.717041	1907.262527	1733.101807	1722.991229	1907.262527	1895.876394	1733.101807	1722.991229
70	6	1	1799.353027	1784.075723	1626.775635	1613.296658	1632.170818	1618.312965	1488.264893	1475.933574
71	7		1858.578003	1845.006138	1679.595947	1667.615177	1845.006138	1831.533379	1679.595947	1667.615177
72	7		1846.841187	1831.376554	1669.026367	1655.387821	1831.376554	1816.041415	1669.026367	1655.387821
73	5		1857.603516	1844.156243	1678.547363	1666.681126	1844.156243	1830.806315	1678.547363	1666.681126
74	3		1812.998047	1799.895395	1638.994751	1627.425611	1799.895395	1786.887438	1638.994751	1627.425611
75	4		1892.354980	1877.505086	1709.625244	1696.526404	1877.505086	1862.771723	1709.625244	1696.526404
76	9	1	1898.959351	1882.744776	1715.455933	1701.166922	1882.456366	1866.382705	1715.193237	1700.906415
77	7		1832.332520	1816.949403	1656.131104	1642.564073	1816.949403	1801.695434	1656.131104	1642.564073
78	7		1818.299072	1802.418937	1643.678711	1629.674165	1802.418937	1786.677492	1643.678711	1629.674165
79	9		1824.514404	1811.949701	1648.956665	1637.861316	1811.949701	1799.471525	1648.956665	1637.861316
80	7		1840.589478	1825.412846	1663.223267	1649.846671	1825.412846	1810.361354	1663.223267	1649.846671
81	8	1	1861.950806	1847.056390	1682.558716	1669.420245	1829.299554	1814.666327	1666.383789	1653.371622
82	6	1	1819.456177	1805.737717	1644.638794	1632.530656	1805.614023	1791.999930	1644.526123	1632.418814
83	10		1824.613892	1810.962145	1649.189575	1637.140531	1810.962145	1797.412540	1649.189575	1637.140531
84	6		1864.977417	1849.092687	1685.279175	1671.271257	1849.092687	1833.343254	1685.279175	1671.271257
85	6		1827.629272	1813.132286	1651.829346	1639.039229	1813.132286	1798.750291	1651.829346	1639.039229
86	6	1	1851.513428	1835.748783	1673.172485	1659.274671	1831.423379	1815.829791	1669.230103	1655.365035
87	8		1805.885498	1793.302587	1632.536743	1621.427034	1793.302587	1780.807351	1632.536743	1621.427034
88	7		1816.932495	1806.703677	1642.396851	1633.359134	1806.703677	1796.532444	1642.396851	1633.359134
89	8		1843.844971	1829.246725	1666.447266	1653.565616	1829.246725	1814.764057	1666.447266	1653.565616
90	7	1	1859.041016	1845.133790	1679.840210	1667.571637	1842.197669	1828.416446	1677.167236	1664.918185
91	8		1834.617554	1820.865152	1658.278076	1646.140590	1820.865152	1807.215840	1658.278076	1646.140590
92	7	1	1801.847290	1789.316144	1628.952759	1617.886761	1789.302568	1776.858665	1628.940430	1617.874516
93	6	2	1845.433472	1829.911109	1667.642944	1653.953280	1826.230658	1810.869815	1664.288940	1650.626809
94	7		1834.956543	1820.603008	1658.564209	1645.900680	1820.603008	1806.361750	1658.564209	1645.900680
95	7		1831.290283	1815.513031	1655.152100	1641.239806	1815.513031	1799.871707	1655.152100	1641.239806
96	7		1856.586670	1842.393487	1677.690186	1665.166620	1842.393487	1828.308808	1677.690186	1665.166620
97	9	4	1844.624512	1829.887056	1667.017822	1654.013224	1798.885636	1784.513607	1638.775879	1625.991599
98	7	1	1844.124878	1832.547612	1666.604614	1656.381408	1803.933341	1792.608394	1640.581543	1630.517966
99	5	1	1823.596924	1811.079517	1648.326782	1637.275953	1745.103144	1733.124528	1588.279541	1577.631285
100	7		1840.478394	1825.479187	1663.388916	1650.157525	1825.479187	1810.602218	1663.388916	1650.157525

α -¹⁴C/ α -¹¹C isotopic partition-function ratios for [NC⋯Et⋯Cl][−].*n*DMSO transition structures

structure sequence number	number extra <i>n</i>	imaginaries	extra imaginaries treated as reals				extra imaginaries omitted			
			300 K		303.15K		300 K		303.15K	
			<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}
1	8	2	1.251411	1.175983	1.245848	1.172492	1.247621	1.172421	1.242075	1.168941
2	8		1.247473	1.165087	1.241926	1.161815	1.247473	1.165087	1.241926	1.161815
3	4	1	1.249057	1.175234	1.243493	1.171689	1.248776	1.174969	1.243213	1.171425
4	5	1	1.250206	1.174806	1.244664	1.171333	1.249062	1.173731	1.243525	1.170261
5	4		1.247968	1.170468	1.242441	1.167069	1.247968	1.170468	1.242441	1.167069
6	4	1	1.248983	1.161574	1.243420	1.158442	1.247495	1.160190	1.241938	1.157061
7	4		1.249643	1.166068	1.244098	1.162840	1.249643	1.166068	1.244098	1.162840
8	5		1.247972	1.166789	1.242435	1.163491	1.247972	1.166789	1.242435	1.163491
9	3		1.246808	1.159597	1.241258	1.156468	1.246808	1.159597	1.241258	1.156468
10	4		1.247070	1.159982	1.241538	1.156868	1.247070	1.159982	1.241538	1.156868
11	7		1.249913	1.163629	1.244342	1.160457	1.249913	1.163629	1.244342	1.160457
12	8		1.250162	1.171912	1.244596	1.168501	1.250162	1.171912	1.244596	1.168501
13	8		1.255299	1.188679	1.249702	1.184896	1.255299	1.188679	1.249702	1.184896
14	8	1	1.250172	1.171211	1.244612	1.167828	1.249684	1.170754	1.244127	1.167372
15	6		1.248381	1.161157	1.242835	1.158037	1.248381	1.161157	1.242835	1.158037
16	6		1.248705	1.187464	1.243174	1.183581	1.248705	1.187464	1.243174	1.183581
17	5	1	1.251257	1.171399	1.245692	1.168040	1.251238	1.171381	1.245673	1.168022
18	5		1.261466	1.156054	1.255807	1.153447	1.261466	1.156054	1.255807	1.153447
19	5	1	1.249245	1.165089	1.243686	1.161863	1.244971	1.161104	1.239431	1.157888
20	6		1.247903	1.148239	1.242344	1.145495	1.247903	1.148239	1.242344	1.145495
21	6		1.260334	1.122619	1.254692	1.121172	1.260334	1.122619	1.254692	1.121172
22	8		1.264832	1.144383	1.259162	1.142313	1.264832	1.144383	1.259162	1.142313
23	5		1.273493	1.182393	1.267786	1.179320	1.273493	1.182393	1.267786	1.179320
24	7	1	1.251180	1.183872	1.245593	1.180113	1.251166	1.183859	1.245578	1.180100
25	3		1.260697	1.211687	1.255045	1.207344	1.260697	1.211687	1.255045	1.207344
26	8		1.248610	1.175194	1.243072	1.171662	1.248610	1.175194	1.243072	1.171662

27	7		1.253300	1.191661	1.247737	1.187763	1.253300	1.191661	1.247737	1.187763
28	5	1	1.249796	1.153957	1.244255	1.151119	1.244544	1.149108	1.239027	1.146282
29	6		1.248988	1.162333	1.243426	1.159181	1.248988	1.162333	1.243426	1.159181
30	7		1.266845	1.145662	1.261152	1.143608	1.266845	1.145662	1.261152	1.143608
31	4		1.249392	1.189925	1.243848	1.185978	1.249392	1.189925	1.243848	1.185978
32	5		1.248379	1.187381	1.242845	1.183488	1.248379	1.187381	1.242845	1.183488
33	5	1	1.262194	1.144193	1.256524	1.142015	1.257573	1.140004	1.251924	1.137834
34	7	1	1.248456	1.175145	1.242911	1.171602	1.245411	1.172279	1.239879	1.168745
35	3		1.261466	1.221306	1.255834	1.216734	1.261466	1.221306	1.255834	1.216734
36	5		1.269416	1.153560	1.263707	1.151311	1.269416	1.153560	1.263707	1.151311
37	5	1	1.252769	1.191210	1.247186	1.187290	1.252472	1.190927	1.246890	1.187007
38	7	1	1.248515	1.182687	1.242967	1.178920	1.248449	1.182625	1.242901	1.178858
39	9		1.249615	1.187036	1.244054	1.183164	1.249615	1.187036	1.244054	1.183164
40	8	1	1.251817	1.179393	1.246246	1.175803	1.242514	1.170628	1.236984	1.167065
41	6	2	1.248453	1.189918	1.242919	1.185954	1.231533	1.173791	1.226074	1.169881
42	5		1.248475	1.177343	1.242917	1.173722	1.248475	1.177343	1.242917	1.173722
43	7		1.248185	1.163240	1.242632	1.160041	1.248185	1.163240	1.242632	1.160041
44	7		1.252037	1.181049	1.246466	1.177416	1.252037	1.181049	1.246466	1.177416
45	4		1.248096	1.172660	1.242535	1.169164	1.248096	1.172660	1.242535	1.169164
46	4		1.249525	1.173181	1.243966	1.169717	1.249525	1.173181	1.243966	1.169717
47	6	2	1.251119	1.174376	1.245535	1.170903	1.250534	1.173827	1.244953	1.170356
48	6		1.248034	1.182909	1.242509	1.179144	1.248034	1.182909	1.242509	1.179144
49	6		1.247830	1.193131	1.242302	1.189062	1.247830	1.193131	1.242302	1.189062
50	7		1.250690	1.185205	1.245133	1.181421	1.250690	1.185205	1.245133	1.181421
51	6		1.252356	1.188191	1.246793	1.184366	1.252356	1.188191	1.246793	1.184366
52	6		1.249741	1.162763	1.244185	1.159628	1.249741	1.162763	1.244185	1.159628
53	4		1.247899	1.175580	1.242366	1.172020	1.247899	1.175580	1.242366	1.172020
54	6	1	1.247155	1.155601	1.241609	1.152613	1.239996	1.148968	1.234482	1.145997
55	6		1.249677	1.174984	1.244124	1.171478	1.249677	1.174984	1.244124	1.171478
56	6		1.248876	1.171553	1.243334	1.168134	1.248876	1.171553	1.243334	1.168134
57	7		1.247214	1.167381	1.241693	1.164060	1.247214	1.167381	1.241693	1.164060
58	4		1.250603	1.157271	1.245037	1.154327	1.250603	1.157271	1.245037	1.154327
59	6		1.248023	1.164925	1.242461	1.161660	1.248023	1.164925	1.242461	1.161660
60	7		1.252591	1.196293	1.247024	1.192236	1.252591	1.196293	1.247024	1.192236
61	5		1.248041	1.163652	1.242487	1.160436	1.248041	1.163652	1.242487	1.160436
62	6	1	1.249702	1.160058	1.244135	1.156995	1.247579	1.158087	1.242021	1.155028
63	6		1.255303	1.145493	1.249723	1.143101	1.255303	1.145493	1.249723	1.143101
64	7		1.268133	1.152982	1.262422	1.150699	1.268133	1.152982	1.262422	1.150699
65	6		1.246910	1.174496	1.241372	1.170932	1.246910	1.174496	1.241372	1.170932
66	4		1.250988	1.161300	1.245411	1.158231	1.250988	1.161300	1.245411	1.158231

67	5		1.247251	1.157641	1.241713	1.154601	1.247251	1.157641	1.241713	1.154601
68	7	2	1.249451	1.194203	1.243920	1.190150	1.244341	1.189319	1.238833	1.185282
69	5		1.247454	1.193186	1.241934	1.189114	1.247454	1.193186	1.241934	1.189114
70	6	1	1.248084	1.163371	1.242532	1.160166	1.244924	1.160426	1.239387	1.157229
71	7		1.251368	1.188874	1.245795	1.184987	1.251368	1.188874	1.245795	1.184987
72	7		1.247497	1.162710	1.241948	1.159510	1.247497	1.162710	1.241948	1.159510
73	5		1.246658	1.176782	1.241129	1.173152	1.246658	1.176782	1.241129	1.173152
74	3		1.249203	1.183122	1.243654	1.179363	1.249203	1.183122	1.243654	1.179363
75	4		1.249114	1.176136	1.243577	1.172594	1.249114	1.176136	1.243577	1.172594
76	9	1	1.250558	1.160351	1.244997	1.157315	1.250057	1.159886	1.244498	1.156851
77	7		1.247133	1.160406	1.241601	1.157282	1.247133	1.160406	1.241601	1.157282
78	7		1.247490	1.156877	1.241958	1.153876	1.247490	1.156877	1.241958	1.153876
79	9		1.254703	1.199084	1.249116	1.194990	1.254703	1.199084	1.249116	1.194990
80	7		1.248943	1.155536	1.243391	1.152607	1.248943	1.155536	1.243391	1.152607
81	8	1	1.250539	1.173391	1.244981	1.169956	1.248317	1.171306	1.242769	1.167877
82	6	1	1.248789	1.177284	1.243260	1.173704	1.248735	1.177233	1.243206	1.173654
83	10		1.248971	1.178689	1.243438	1.175071	1.248971	1.178689	1.243438	1.175071
84	6		1.250703	1.167244	1.245132	1.163987	1.250703	1.167244	1.245132	1.163987
85	6		1.246696	1.167894	1.241169	1.164531	1.246696	1.167894	1.241169	1.164531
86	6	1	1.250971	1.160851	1.245399	1.157800	1.249277	1.159279	1.243712	1.156233
87	8		1.249358	1.183313	1.243820	1.179564	1.249358	1.183313	1.243820	1.179564
88	7		1.249123	1.200640	1.243582	1.196383	1.249123	1.200640	1.243582	1.196383
89	8		1.252853	1.179689	1.247248	1.176088	1.252853	1.179689	1.247248	1.176088
90	7	1	1.249519	1.174987	1.243972	1.171482	1.248775	1.174287	1.243232	1.170785
91	8		1.249416	1.177152	1.243856	1.173565	1.249416	1.177152	1.243856	1.173565
92	7	1	1.250559	1.188080	1.245011	1.184219	1.250554	1.188075	1.245005	1.184214
93	6	2	1.249864	1.167244	1.244280	1.163947	1.247499	1.165036	1.241926	1.161745
94	7		1.253894	1.176946	1.248308	1.173482	1.253894	1.176946	1.248308	1.173482
95	7		1.248857	1.159158	1.243287	1.156090	1.248857	1.159158	1.243287	1.156090
96	7		1.252166	1.182452	1.246606	1.178795	1.252166	1.182452	1.246606	1.178795
97	9	4	1.250733	1.179159	1.245161	1.175543	1.237777	1.166945	1.232264	1.163366
98	7	1	1.248732	1.191644	1.243186	1.187626	1.237810	1.181221	1.232312	1.177238
99	5	1	1.248301	1.182554	1.242760	1.178792	1.233814	1.168830	1.228337	1.165111
100	7		1.247979	1.167933	1.242446	1.164606	1.247979	1.167933	1.242446	1.164606

Ig-³⁷Cl/³⁵Cl isotopic partition-function ratios for [NC···Et···Cl]⁻.*n*DMSO transition structures

structure sequence number	number extra <i>n</i>	imaginaries	extra imaginaries treated as reals				extra imaginaries omitted			
			300 K		303.15K		300 K		303.15K	
			<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}
1	8	2	1.003197	1.002305	1.002242	1.002220	1.001004	1.000114	1.000919	1.000050
2	8		1.003243	1.002342	1.002279	1.002257	1.003243	1.002342	1.003159	1.002279
3	4	1	1.003179	1.002362	1.002299	1.002279	1.002701	1.001885	1.002617	1.001821
4	5	1	1.003112	1.002191	1.002129	1.002107	1.003057	1.002136	1.002973	1.002074
5	4		1.003205	1.002345	1.002282	1.002261	1.003205	1.002345	1.003121	1.002282
6	4	1	1.003052	1.002179	1.002121	1.002100	1.002255	1.001383	1.002176	1.001325
7	4		1.003273	1.002362	1.002300	1.002278	1.003273	1.002362	1.003188	1.002300
8	5		1.003166	1.002287	1.002225	1.002204	1.003166	1.002287	1.003083	1.002225
9	3		1.003231	1.002397	1.002336	1.002315	1.003231	1.002397	1.003149	1.002336
10	4		1.002863	1.001987	1.001933	1.001912	1.002863	1.001987	1.002787	1.001933
11	7		1.002825	1.001858	1.001805	1.001781	1.002825	1.001858	1.002749	1.001805
12	8		1.002996	1.002044	1.001985	1.001962	1.002996	1.002044	1.002914	1.001985
13	8		1.002597	1.001510	1.001453	1.001428	1.002597	1.001510	1.002515	1.001453
14	8	1	1.003019	1.002095	1.002036	1.002014	1.002501	1.001578	1.002420	1.001519
15	6		1.003101	1.002214	1.002156	1.002135	1.003101	1.002214	1.003021	1.002156
16	6		1.003183	1.002216	1.002146	1.002123	1.003183	1.002216	1.003090	1.002146
17	5	1	1.003343	1.002401	1.002335	1.002313	1.003337	1.002394	1.003249	1.002329
18	5		1.002959	1.001783	1.001736	1.001705	1.002959	1.001783	1.002881	1.001736
19	5	1	1.003167	1.002251	1.002191	1.002169	1.001602	1.000687	1.001520	1.000627
20	6		1.003385	1.002512	1.002452	1.002430	1.003385	1.002512	1.003303	1.002452
21	6		1.002880	1.001662	1.001625	1.001591	1.002880	1.001662	1.002808	1.001625
22	8		1.002666	1.001414	1.001377	1.001344	1.002666	1.001414	1.002596	1.001377
23	5		1.002941	1.001390	1.001344	1.001304	1.002941	1.001390	1.002856	1.001344
24	7	1	1.003420	1.002502	1.002430	1.002409	1.003407	1.002489	1.003314	1.002417
25	3		1.002156	1.001037	1.000978	1.000952	1.002156	1.001037	1.002071	1.000978
26	8		1.002589	1.001550	1.001496	1.001472	1.002589	1.001550	1.002511	1.001496

27	7		1.002786	1.001583	1.001519	1.001491	1.002786	1.001583	1.002693	1.001519
28	5	1	1.002921	1.001927	1.001876	1.001851	0.997157	0.996169	0.997081	0.996118
29	6		1.003453	1.002653	1.002587	1.002568	1.003453	1.002653	1.003368	1.002587
30	7		1.002755	1.001548	1.001510	1.001478	1.002755	1.001548	1.002684	1.001510
31	4		1.003006	1.002101	1.002034	1.002013	1.003006	1.002101	1.002918	1.002034
32	5		1.002941	1.002026	1.001961	1.001940	1.002941	1.002026	1.002855	1.001961
33	5	1	1.002519	1.001325	1.001290	1.001258	0.987442	0.986267	0.987376	0.986232
34	7	1	1.003058	1.002133	1.002071	1.002049	0.993611	0.992694	0.993527	0.992633
35	3		1.001963	1.000830	1.000764	1.000739	1.001963	1.000830	1.001872	1.000764
36	5		1.002907	1.001574	1.001533	1.001497	1.002907	1.001574	1.002830	1.001533
37	5	1	1.003019	1.002150	1.002085	1.002065	1.001974	1.001106	1.001888	1.001041
38	7	1	1.003057	1.002132	1.002067	1.002045	1.003002	1.002077	1.002915	1.002011
39	9		1.002995	1.001946	1.001879	1.001855	1.002995	1.001946	1.002904	1.001879
40	8	1	1.002809	1.001709	1.001651	1.001625	0.993104	0.992016	0.993021	0.991958
41	6	2	1.002962	1.002088	1.002021	1.002001	0.993858	0.992992	0.993772	0.992926
42	5		1.002904	1.002012	1.001952	1.001931	1.002904	1.002012	1.002823	1.001952
43	7		1.003041	1.002163	1.002105	1.002084	1.003041	1.002163	1.002962	1.002105
44	7		1.002859	1.001904	1.001845	1.001822	1.002859	1.001904	1.002777	1.001845
45	4		1.003172	1.002287	1.002223	1.002202	1.003172	1.002287	1.003087	1.002223
46	4		1.002931	1.001949	1.001890	1.001867	1.002931	1.001949	1.002849	1.001890
47	6	2	1.003197	1.002363	1.002300	1.002280	1.001134	1.000301	1.001051	1.000238
48	6		1.002975	1.002028	1.001963	1.001941	1.002975	1.002028	1.002888	1.001963
49	6		1.003216	1.002449	1.002376	1.002359	1.003216	1.002449	1.003126	1.002376
50	7		1.002862	1.001987	1.001926	1.001906	1.002862	1.001987	1.002780	1.001926
51	6		1.003032	1.001908	1.001841	1.001815	1.003032	1.001908	1.002939	1.001841
52	6		1.002676	1.001679	1.001630	1.001605	1.002676	1.001679	1.002602	1.001630
53	4		1.003079	1.002206	1.002144	1.002123	1.003079	1.002206	1.002995	1.002144
54	6	1	1.003159	1.002280	1.002222	1.002200	0.989327	0.988460	0.989248	0.988402
55	6		1.003199	1.002282	1.002217	1.002195	1.003199	1.002282	1.003113	1.002217
56	6		1.003339	1.002449	1.002383	1.002362	1.003339	1.002449	1.003252	1.002383
57	7		1.003230	1.002295	1.002232	1.002209	1.003230	1.002295	1.003145	1.002232
58	4		1.003428	1.002550	1.002488	1.002466	1.003428	1.002550	1.003343	1.002488
59	6		1.003128	1.002257	1.002197	1.002176	1.003128	1.002257	1.003047	1.002197
60	7		1.002786	1.001674	1.001607	1.001582	1.002786	1.001674	1.002694	1.001607
61	5		1.003216	1.002361	1.002300	1.002279	1.003216	1.002361	1.003134	1.002300
62	6	1	1.003065	1.002125	1.002068	1.002045	1.002161	1.001222	1.002081	1.001166
63	6		1.002763	1.001281	1.001241	1.001202	1.002763	1.001281	1.002684	1.001241
64	7		1.002861	1.001605	1.001564	1.001530	1.002861	1.001605	1.002787	1.001564
65	6		1.003364	1.002543	1.002475	1.002456	1.003364	1.002543	1.003276	1.002475
66	4		1.003425	1.002583	1.002520	1.002499	1.003425	1.002583	1.003341	1.002520

67	5		1.003245	1.002343	1.002283	1.002261	1.003245	1.002343	1.003163	1.002283
68	7	2	1.002786	1.001749	1.001682	1.001658	1.002288	1.001252	1.002197	1.001185
69	5		1.003441	1.002629	1.002551	1.002533	1.003441	1.002629	1.003344	1.002551
70	6	1	1.002919	1.001971	1.001916	1.001893	1.000751	0.999806	1.000673	0.999750
71	7		1.003129	1.002288	1.002221	1.002201	1.003129	1.002288	1.003042	1.002221
72	7		1.003210	1.002342	1.002280	1.002259	1.003210	1.002342	1.003127	1.002280
73	5		1.003374	1.002597	1.002528	1.002510	1.003374	1.002597	1.003287	1.002528
74	3		1.002745	1.001792	1.001733	1.001711	1.002745	1.001792	1.002663	1.001733
75	4		1.003376	1.002489	1.002421	1.002400	1.003376	1.002489	1.003286	1.002421
76	9	1	1.003150	1.002213	1.002155	1.002132	1.002551	1.001615	1.002470	1.001557
77	7		1.003023	1.002114	1.002057	1.002035	1.003023	1.002114	1.002944	1.002057
78	7		1.003033	1.002113	1.002058	1.002035	1.003033	1.002113	1.002955	1.002058
79	9		1.003080	1.001958	1.001885	1.001859	1.003080	1.001958	1.002981	1.001885
80	7		1.003397	1.002535	1.002473	1.002451	1.003397	1.002535	1.003313	1.002473
81	8	1	1.002868	1.001912	1.001856	1.001833	0.996787	0.995837	0.996708	0.995780
82	6	1	1.002749	1.001807	1.001750	1.001728	1.002743	1.001802	1.002664	1.001745
83	10		1.002794	1.001790	1.001732	1.001708	1.002794	1.001790	1.002712	1.001732
84	6		1.003101	1.002164	1.002105	1.002082	1.003101	1.002164	1.003018	1.002105
85	6		1.002865	1.001908	1.001852	1.001829	1.002865	1.001908	1.002785	1.001852
86	6	1	1.003039	1.002101	1.002046	1.002022	1.000712	0.999777	1.000633	0.999721
87	8		1.002643	1.001623	1.001566	1.001542	1.002643	1.001623	1.002561	1.001566
88	7		1.003108	1.002345	1.002270	1.002253	1.003108	1.002345	1.003016	1.002270
89	8		1.002954	1.002017	1.001957	1.001935	1.002954	1.002017	1.002872	1.001957
90	7	1	1.002852	1.001876	1.001818	1.001795	1.002700	1.001725	1.002620	1.001667
91	8		1.002858	1.001904	1.001846	1.001823	1.002858	1.001904	1.002776	1.001846
92	7	1	1.002868	1.001697	1.001631	1.001604	1.002867	1.001696	1.002774	1.001630
93	6	2	1.003056	1.002129	1.002070	1.002048	1.000971	1.000046	1.000890	0.999987
94	7		1.003647	1.002704	1.002632	1.002610	1.003647	1.002704	1.003553	1.002632
95	7		1.003081	1.002161	1.002103	1.002081	1.003081	1.002161	1.003001	1.002103
96	7		1.002913	1.001941	1.001880	1.001857	1.002913	1.001941	1.002830	1.001880
97	9	4	1.003164	1.002288	1.002224	1.002203	0.983896	0.983037	0.983813	0.982974
98	7	1	1.002981	1.002166	1.002099	1.002080	0.999177	0.998366	0.999092	0.998299
99	5	1	1.003123	1.002232	1.002165	1.002145	0.990506	0.989626	0.990420	0.989561
100	7		1.003235	1.002253	1.002190	1.002166	1.003235	1.002253	1.003148	1.002190

nu-¹³C/¹²C isotopic partition-function ratios for [NC...Et...Cl]⁻.*n*DMSO transition structures

structure sequence number	number		extra imaginaries treated as reals				extra imaginaries omitted			
	extra <i>n</i>	imaginaries	300 K		303.15K		300 K		303.15K	
			<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}
1	8	2	1.118786	1.116306	1.117074	1.114658	1.111847	1.109383	1.110146	1.107744
2	8		1.119737	1.117451	1.118014	1.115787	1.119737	1.117451	1.118014	1.115787
3	4	1	1.120021	1.117794	1.118289	1.116120	1.120011	1.117794	1.118280	1.116110
4	5	1	1.118931	1.116439	1.117215	1.114787	1.118592	1.116439	1.116876	1.114448
5	4		1.118627	1.116256	1.116920	1.114610	1.118627	1.116256	1.116920	1.114610
6	4	1	1.120214	1.117500	1.118471	1.115827	1.119830	1.117500	1.118088	1.115444
7	4		1.119722	1.117029	1.117993	1.115368	1.119722	1.117029	1.117993	1.115368
8	5		1.119378	1.116737	1.117654	1.115081	1.119378	1.116737	1.117654	1.115081
9	3		1.120119	1.117659	1.118388	1.115991	1.120119	1.117659	1.118388	1.115991
10	4		1.119806	1.117209	1.118078	1.115548	1.119806	1.117209	1.118078	1.115548
11	7		1.119479	1.116869	1.117755	1.115213	1.119479	1.116869	1.117755	1.115213
12	8		1.119664	1.117201	1.117935	1.115535	1.119664	1.117201	1.117935	1.115535
13	8		1.118349	1.115886	1.116639	1.114237	1.118349	1.115886	1.116639	1.114237
14	8	1	1.120258	1.117882	1.118521	1.116205	1.120151	1.117882	1.118414	1.116098
15	6		1.119124	1.116458	1.117407	1.114810	1.119124	1.116458	1.117407	1.114810
16	6		1.118444	1.116660	1.116748	1.115008	1.118444	1.116660	1.116748	1.115008
17	5	1	1.119162	1.116601	1.117443	1.114947	1.119155	1.116601	1.117435	1.114940
18	5		1.116048	1.108274	1.114301	1.106738	1.116048	1.108274	1.114301	1.106738
19	5	1	1.119136	1.116505	1.117419	1.114855	1.116667	1.116505	1.114953	1.112395
20	6		1.119762	1.116699	1.118032	1.115049	1.119762	1.116699	1.118032	1.115049
21	6		1.116075	1.104397	1.114306	1.102969	1.116075	1.104397	1.114306	1.102969
22	8		1.114274	1.102303	1.112515	1.100883	1.114274	1.102303	1.112515	1.100883
23	5		1.111467	1.100773	1.109752	1.099346	1.111467	1.100773	1.109752	1.099346
24	7	1	1.118497	1.116667	1.116803	1.115019	1.118492	1.116667	1.116799	1.115015
25	3		1.117907	1.116003	1.116204	1.114347	1.117907	1.116003	1.116204	1.114347
26	8		1.120106	1.117960	1.118371	1.116279	1.120106	1.117960	1.118371	1.116279

27	7		1.118564	1.116762	1.116865	1.115107	1.118564	1.116762	1.116865	1.115107
28	5	1	1.119388	1.115883	1.117652	1.114240	1.118723	1.115883	1.116988	1.113577
29	6		1.119643	1.116794	1.117913	1.115138	1.119643	1.116794	1.117913	1.115138
30	7		1.113608	1.100702	1.111851	1.099312	1.113608	1.100702	1.111851	1.099312
31	4		1.118787	1.116973	1.117081	1.115313	1.118787	1.116973	1.117081	1.115313
32	5		1.119566	1.117862	1.117849	1.116187	1.119566	1.117862	1.117849	1.116187
33	5	1	1.115838	1.105817	1.114073	1.104333	1.115378	1.105817	1.113614	1.103878
34	7	1	1.119602	1.117398	1.117878	1.115730	1.119546	1.117398	1.117823	1.115674
35	3		1.116219	1.114917	1.114563	1.113291	1.116219	1.114917	1.114563	1.113291
36	5		1.114159	1.101251	1.112387	1.099843	1.114159	1.101251	1.112387	1.099843
37	5	1	1.119909	1.117797	1.118172	1.116112	1.119905	1.117797	1.118168	1.116108
38	7	1	1.118905	1.117129	1.117204	1.115472	1.118845	1.117129	1.117145	1.115413
39	9		1.118757	1.117040	1.117058	1.115384	1.118757	1.117040	1.117058	1.115384
40	8	1	1.119153	1.117003	1.117440	1.115344	1.117653	1.117003	1.115942	1.113849
41	6	2	1.118541	1.117007	1.116848	1.115352	1.113266	1.117007	1.111580	1.110092
42	5		1.119411	1.117461	1.117695	1.115794	1.119411	1.117461	1.117695	1.115794
43	7		1.119121	1.116693	1.117410	1.115045	1.119121	1.116693	1.117410	1.115045
44	7		1.119209	1.116948	1.117488	1.115284	1.119209	1.116948	1.117488	1.115284
45	4		1.119627	1.117525	1.117906	1.115858	1.119627	1.117525	1.117906	1.115858
46	4		1.119756	1.117385	1.118025	1.115714	1.119756	1.117385	1.118025	1.115714
47	6	2	1.118951	1.116458	1.117234	1.114805	1.118844	1.116458	1.117128	1.114698
48	6		1.119246	1.117432	1.117534	1.115764	1.119246	1.117432	1.117534	1.115764
49	6		1.118252	1.116797	1.116565	1.115146	1.118252	1.116797	1.116565	1.115146
50	7		1.118692	1.116789	1.116990	1.115135	1.118692	1.116789	1.116990	1.115135
51	6		1.118497	1.116552	1.116796	1.114899	1.118497	1.116552	1.116796	1.114899
52	6		1.119923	1.117065	1.118183	1.115400	1.119923	1.117065	1.118183	1.115400
53	4		1.119828	1.117621	1.118099	1.115947	1.119828	1.117621	1.118099	1.115947
54	6	1	1.120257	1.117521	1.118518	1.115853	1.120105	1.117521	1.118366	1.115701
55	6		1.118369	1.115963	1.116665	1.114321	1.118369	1.115963	1.116665	1.114321
56	6		1.118580	1.116334	1.116877	1.114689	1.118580	1.116334	1.116877	1.114689
57	7		1.119458	1.117091	1.117737	1.115430	1.119458	1.117091	1.117737	1.115430
58	4		1.119282	1.115832	1.117548	1.114188	1.119282	1.115832	1.117548	1.114188
59	6		1.119967	1.117620	1.118238	1.115952	1.119967	1.117620	1.118238	1.115952
60	7		1.117642	1.116084	1.115966	1.114446	1.117642	1.116084	1.115966	1.114446
61	5		1.119497	1.116993	1.117774	1.115334	1.119497	1.116993	1.117774	1.115334
62	6	1	1.119941	1.117140	1.118204	1.115476	1.119442	1.117140	1.117706	1.114979
63	6		1.117741	1.110953	1.115980	1.109378	1.117741	1.110953	1.115980	1.109378
64	7		1.113528	1.101310	1.111774	1.099899	1.113528	1.101310	1.111774	1.099899
65	6		1.119859	1.117880	1.118134	1.116205	1.119859	1.117880	1.118134	1.116205
66	4		1.118943	1.115557	1.117217	1.113919	1.118943	1.115557	1.117217	1.113919

67	5		1.119751	1.116853	1.118019	1.115196	1.119751	1.116853	1.118019	1.115196
68	7	2	1.118508	1.117035	1.116815	1.115379	1.116308	1.117035	1.114619	1.113185
69	5		1.118811	1.117342	1.117110	1.115678	1.118811	1.117342	1.117110	1.115678
70	6	1	1.119918	1.117512	1.118189	1.115845	1.119611	1.117512	1.117882	1.115539
71	7		1.118216	1.116461	1.116527	1.114816	1.118216	1.116461	1.116527	1.114816
72	7		1.119903	1.117418	1.118174	1.115753	1.119903	1.117418	1.118174	1.115753
73	5		1.118739	1.116689	1.117037	1.115039	1.118739	1.116689	1.117037	1.115039
74	3		1.119353	1.117570	1.117640	1.115901	1.119353	1.117570	1.117640	1.115901
75	4		1.119459	1.117177	1.117735	1.115510	1.119459	1.117177	1.117735	1.115510
76	9	1	1.119955	1.116858	1.118213	1.115197	1.119815	1.116858	1.118074	1.115058
77	7		1.120538	1.117941	1.118793	1.116262	1.120538	1.117941	1.118793	1.116262
78	7		1.120013	1.117222	1.118275	1.115557	1.120013	1.117222	1.118275	1.115557
79	9		1.117653	1.115987	1.115972	1.114346	1.117653	1.115987	1.115972	1.114346
80	7		1.119718	1.116579	1.117983	1.114927	1.119718	1.116579	1.117983	1.114927
81	8	1	1.119143	1.116716	1.117425	1.115060	1.118938	1.116716	1.117221	1.114856
82	6	1	1.119110	1.116959	1.117393	1.115296	1.119042	1.116959	1.117325	1.115229
83	10		1.119247	1.117015	1.117526	1.115350	1.119247	1.117015	1.117526	1.115350
84	6		1.119268	1.116575	1.117546	1.114923	1.119268	1.116575	1.117546	1.114923
85	6		1.120209	1.118068	1.118476	1.116390	1.120209	1.118068	1.118476	1.116390
86	6	1	1.119023	1.116051	1.117304	1.114410	1.118939	1.116051	1.117219	1.114326
87	8		1.118648	1.116727	1.116946	1.115073	1.118648	1.116727	1.116946	1.115073
88	7		1.118108	1.116862	1.116425	1.115209	1.118108	1.116862	1.116425	1.115209
89	8		1.118716	1.116488	1.117011	1.114839	1.118716	1.116488	1.117011	1.114839
90	7	1	1.119143	1.116761	1.117425	1.115103	1.118170	1.116761	1.116454	1.114134
91	8		1.119123	1.117130	1.117414	1.115471	1.119123	1.117130	1.117414	1.115471
92	7	1	1.118465	1.116827	1.116774	1.115176	1.118462	1.116827	1.116771	1.115173
93	6	2	1.119943	1.117361	1.118208	1.115692	1.119599	1.117361	1.117864	1.115349
94	7		1.118328	1.115640	1.116621	1.114001	1.118328	1.115640	1.116621	1.114001
95	7		1.120194	1.117548	1.118456	1.115879	1.120194	1.117548	1.118456	1.115879
96	7		1.119208	1.116594	1.117478	1.114930	1.119208	1.116594	1.117478	1.114930
97	9	4	1.119550	1.117364	1.117826	1.115695	1.117692	1.117364	1.115971	1.113843
98	7	1	1.118566	1.117035	1.116872	1.115379	1.113940	1.117035	1.112254	1.110767
99	5	1	1.118942	1.117133	1.117237	1.115474	1.117254	1.117133	1.115552	1.113791
100	7		1.119781	1.117231	1.118049	1.115564	1.119781	1.117231	1.118049	1.115564

nu-¹⁵N/¹⁴N isotopic partition-function ratios for [NC...Et...Cl]⁻.*n*DMSO transition structures

structure sequence number	number extra <i>n</i>	imaginaries	extra imaginaries treated as reals				extra imaginaries omitted			
			300 K		303.15K		300 K		303.15K	
			<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}	<i>f</i> _{TS}	(<i>f</i> _{TS}) _{corr}
1	8	2	1.078337	1.076049	1.077239	1.075007	1.070751	1.068479	1.069661	1.067445
2	8		1.079101	1.076963	1.077993	1.075909	1.079101	1.076963	1.077993	1.075909
3	4	1	1.078967	1.076990	1.077863	1.075934	1.078961	1.076984	1.077856	1.075928
4	5	1	1.077990	1.075818	1.076900	1.074782	1.077687	1.075515	1.076597	1.074479
5	4		1.077185	1.075075	1.076113	1.074055	1.077185	1.075075	1.076113	1.074055
6	4	1	1.077642	1.075215	1.076560	1.074195	1.077235	1.074809	1.076154	1.073790
7	4		1.080012	1.077626	1.078883	1.076557	1.080012	1.077626	1.078883	1.076557
8	5		1.079865	1.077773	1.078744	1.076704	1.079865	1.077773	1.078744	1.076704
9	3		1.078449	1.076185	1.077356	1.075149	1.078449	1.076185	1.077356	1.075149
10	4		1.077979	1.075639	1.076893	1.074613	1.077979	1.075639	1.076893	1.074613
11	7		1.077866	1.075462	1.076780	1.074437	1.077866	1.075462	1.076780	1.074437
12	8		1.079097	1.076915	1.077985	1.075858	1.079097	1.076915	1.077985	1.075858
13	8		1.077737	1.075970	1.076657	1.074934	1.077737	1.075970	1.076657	1.074934
14	8	1	1.078033	1.075781	1.076942	1.074746	1.077931	1.075679	1.076841	1.074645
15	6		1.078462	1.076029	1.077363	1.074992	1.078462	1.076029	1.077363	1.074992
16	6		1.077848	1.076416	1.076770	1.075373	1.077848	1.076416	1.076770	1.075373
17	5	1	1.077770	1.075421	1.076682	1.074393	1.077764	1.075416	1.076677	1.074387
18	5		1.079657	1.077501	1.078550	1.076451	1.079657	1.077501	1.078550	1.076451
19	5	1	1.079015	1.076764	1.077907	1.075712	1.076500	1.074254	1.075395	1.073205
20	6		1.079691	1.076907	1.078572	1.075860	1.079691	1.076907	1.078572	1.075860
21	6		1.080037	1.077556	1.078931	1.076521	1.080037	1.077556	1.078931	1.076521
22	8		1.080075	1.078207	1.078969	1.077154	1.080075	1.078207	1.078969	1.077154
23	5		1.080712	1.079287	1.079595	1.078207	1.080712	1.079287	1.079595	1.078207
24	7	1	1.078335	1.076582	1.077243	1.075533	1.078331	1.076578	1.077240	1.075530
25	3		1.077609	1.076436	1.076536	1.075392	1.077609	1.076436	1.076536	1.075392
26	8		1.078013	1.076191	1.076929	1.075152	1.078013	1.076191	1.076929	1.075152

27	7		1.077835	1.076217	1.076753	1.075174	1.077835	1.076217	1.076753	1.075174
28	5	1	1.078187	1.075367	1.077092	1.074345	1.077917	1.075099	1.076823	1.074077
29	6		1.077781	1.075388	1.076700	1.074368	1.077781	1.075388	1.076700	1.074368
30	7		1.080691	1.078760	1.079572	1.077695	1.080691	1.078760	1.079572	1.077695
31	4		1.077296	1.075916	1.076230	1.074883	1.077296	1.075916	1.076230	1.074883
32	5		1.077989	1.076519	1.076907	1.075472	1.077989	1.076519	1.076907	1.075472
33	5	1	1.080017	1.077871	1.078908	1.076821	1.079272	1.077127	1.078164	1.076078
34	7	1	1.077982	1.076134	1.076898	1.075095	1.077948	1.076099	1.076863	1.075060
35	3		1.077301	1.076143	1.076221	1.075091	1.077301	1.076143	1.076221	1.075091
36	5		1.081054	1.079373	1.079931	1.078297	1.081054	1.079373	1.079931	1.078297
37	5	1	1.078995	1.077372	1.077888	1.076305	1.078985	1.077363	1.077879	1.076296
38	7	1	1.077762	1.076142	1.076683	1.075103	1.077650	1.076030	1.076571	1.074990
39	9		1.077620	1.076157	1.076546	1.075118	1.077620	1.076157	1.076546	1.075118
40	8	1	1.077530	1.075538	1.076451	1.074509	1.076121	1.074132	1.075044	1.073105
41	6	2	1.077354	1.075878	1.076280	1.074839	1.072006	1.070537	1.070937	1.069503
42	5		1.077787	1.075984	1.076705	1.074947	1.077787	1.075984	1.076705	1.074947
43	7		1.077654	1.075376	1.076574	1.074353	1.077654	1.075376	1.076574	1.074353
44	7		1.077855	1.075755	1.076764	1.074716	1.077855	1.075755	1.076764	1.074716
45	4		1.077831	1.075909	1.076748	1.074874	1.077831	1.075909	1.076748	1.074874
46	4		1.077991	1.076038	1.076907	1.075002	1.077991	1.076038	1.076907	1.075002
47	6	2	1.077930	1.075743	1.076843	1.074710	1.077743	1.075556	1.076657	1.074524
48	6		1.077648	1.076020	1.076571	1.074982	1.077648	1.076020	1.076571	1.074982
49	6		1.077173	1.075812	1.076103	1.074775	1.077173	1.075812	1.076103	1.074775
50	7		1.077832	1.076009	1.076745	1.074967	1.077832	1.076009	1.076745	1.074967
51	6		1.077754	1.076009	1.076669	1.074966	1.077754	1.076009	1.076669	1.074966
52	6		1.078601	1.076189	1.077502	1.075150	1.078601	1.076189	1.077502	1.075150
53	4		1.078521	1.076682	1.077427	1.075633	1.078521	1.076682	1.077427	1.075633
54	6	1	1.077845	1.075390	1.076762	1.074371	1.077801	1.075347	1.076719	1.074327
55	6		1.077270	1.075327	1.076199	1.074304	1.077270	1.075327	1.076199	1.074304
56	6		1.077579	1.075405	1.076495	1.074375	1.077579	1.075405	1.076495	1.074375
57	7		1.078203	1.076050	1.077114	1.075015	1.078203	1.076050	1.077114	1.075015
58	4		1.079378	1.076875	1.078266	1.075827	1.079378	1.076875	1.078266	1.075827
59	6		1.078716	1.076609	1.077618	1.075565	1.078716	1.076609	1.077618	1.075565
60	7		1.076800	1.075384	1.075739	1.074357	1.076800	1.075384	1.075739	1.074357
61	5		1.078673	1.076328	1.077569	1.075284	1.078673	1.076328	1.077569	1.075284
62	6	1	1.077899	1.075302	1.076808	1.074277	1.077594	1.074998	1.076504	1.073973
63	6		1.079758	1.077431	1.078648	1.076383	1.079758	1.077431	1.078648	1.076383
64	7		1.080386	1.078609	1.079275	1.077546	1.080386	1.078609	1.079275	1.077546
65	6		1.077907	1.076084	1.076824	1.075045	1.077907	1.076084	1.076824	1.075045
66	4		1.078290	1.075909	1.077201	1.074881	1.078290	1.075909	1.077201	1.074881

67	5		1.078177	1.075911	1.077092	1.074883	1.078177	1.075911	1.077092	1.074883
68	7	2	1.077405	1.076047	1.076333	1.075007	1.075054	1.073698	1.073984	1.072661
69	5		1.077225	1.075876	1.076155	1.074839	1.077225	1.075876	1.076155	1.074839
70	6	1	1.078501	1.076305	1.077407	1.075266	1.078289	1.076093	1.077195	1.075054
71	7		1.076876	1.075151	1.075809	1.074126	1.076876	1.075151	1.075809	1.074126
72	7		1.078921	1.076674	1.077818	1.075627	1.078921	1.076674	1.077818	1.075627
73	5		1.078223	1.076468	1.077135	1.075423	1.078223	1.076468	1.077135	1.075423
74	3		1.077908	1.076204	1.076823	1.075161	1.077908	1.076204	1.076823	1.075161
75	4		1.078361	1.076302	1.077261	1.075254	1.078361	1.076302	1.077261	1.075254
76	9	1	1.078517	1.075749	1.077416	1.074719	1.078344	1.075577	1.077244	1.074547
77	7		1.078009	1.075705	1.076922	1.074677	1.078009	1.075705	1.076922	1.074677
78	7		1.079515	1.076988	1.078394	1.075932	1.079515	1.076988	1.078394	1.075932
79	9		1.076883	1.075459	1.075821	1.074431	1.076883	1.075459	1.075821	1.074431
80	7		1.078797	1.076019	1.077691	1.074984	1.078797	1.076019	1.077691	1.074984
81	8	1	1.077304	1.075087	1.076229	1.074067	1.077028	1.074811	1.075953	1.073791
82	6	1	1.077192	1.075190	1.076115	1.074163	1.077072	1.075071	1.075995	1.074043
83	10		1.078213	1.076387	1.077122	1.075341	1.078213	1.076387	1.077122	1.075341
84	6		1.077551	1.075217	1.076473	1.074198	1.077551	1.075217	1.076473	1.074198
85	6		1.077806	1.075759	1.076724	1.074728	1.077806	1.075759	1.076724	1.074728
86	6	1	1.078056	1.075456	1.076966	1.074432	1.078023	1.075424	1.076933	1.074400
87	8		1.077381	1.075691	1.076308	1.074659	1.077381	1.075691	1.076308	1.074659
88	7		1.077248	1.075999	1.076175	1.074955	1.077248	1.075999	1.076175	1.074955
89	8		1.077639	1.075577	1.076557	1.074546	1.077639	1.075577	1.076557	1.074546
90	7	1	1.077927	1.075882	1.076839	1.074845	1.076171	1.074130	1.075085	1.073094
91	8		1.077873	1.075975	1.076787	1.074937	1.077873	1.075975	1.076787	1.074937
92	7	1	1.077720	1.076180	1.076643	1.075140	1.077717	1.076177	1.076640	1.075137
93	6	2	1.078492	1.076355	1.077395	1.075312	1.078302	1.076166	1.077205	1.075123
94	7		1.078747	1.076266	1.077635	1.075216	1.078747	1.076266	1.077635	1.075216
95	7		1.079006	1.076577	1.077899	1.075532	1.079006	1.076577	1.077899	1.075532
96	7		1.078076	1.076263	1.076990	1.075222	1.078076	1.076263	1.076990	1.075222
97	9	4	1.077695	1.075719	1.076612	1.074684	1.075030	1.073059	1.073949	1.072026
98	7	1	1.077758	1.076353	1.076679	1.075307	1.072607	1.071208	1.071533	1.070167
99	5	1	1.077859	1.076105	1.076771	1.075060	1.076936	1.075184	1.075849	1.074140
100	7		1.078713	1.076642	1.077615	1.075596	1.078713	1.076642	1.077615	1.075596

α -D₂/ α -H₂ isotopic partition-function ratios for (NC⁻...EtCl).*n*DMSO reactant structures:

structure sequence number	number extra <i>n</i>	imaginaries	extra imaginaries treated as reals		extra imaginaries omitted	
			300 K	303.15K	300 K	303.15K
			f_{RS}	f_{RS}	f_{RS}	f_{RS}
1	4		1.485658	1.487392	1.496313	1.487392
2	5	1	1.489546	1.480933	1.466005	1.457355
3	4		1.489312	1.485943	1.494842	1.485943
4	4		1.494034	1.485614	1.494518	1.485614
5	4		1.492251	1.484102	1.492956	1.484102
6	7		1.492662	1.484928	1.493801	1.484928
7	3		1.495041	1.483348	1.492183	1.483348
8	6	1	1.489251	1.480280	1.489054	1.480280
9	5		1.491427	1.484418	1.493281	1.484418
10	1	10	1.490087	1.457695	1.389013	1.381033
11	4	1	1.490570	1.483660	1.492465	1.483616
12	3		1.490085	1.478033	1.486766	1.478033
13	4		1.486591	1.483775	1.492627	1.483775
14	5		1.489969	1.487842	1.496775	1.487842
15	5		1.487888	1.483187	1.492029	1.483187
16	4	2	1.488601	1.481520	1.453649	1.445061
17	7	1	1.488431	1.485199	1.493392	1.484520
18	5		1.490577	1.480582	1.489362	1.480583
19	3		1.494932	1.483431	1.492273	1.483431
20	2		1.490487	1.478435	1.487171	1.478435
21	3		1.492495	1.485187	1.494071	1.485187
22	5		1.487931	1.481461	1.490257	1.481461
23	2		1.493347	1.481878	1.490685	1.481878
24	4		1.490277	1.479312	1.488069	1.479312
25	3		1.495011	1.486655	1.495560	1.486655
26	5		1.490232	1.480524	1.489303	1.480524

27	6		1.488479	1.479836	1.488606	1.479836
28	5		1.489360	1.480901	1.489692	1.480901
29	6		1.491543	1.485622	1.494538	1.485623
30	5	1	1.492838	1.484653	1.471887	1.463152
31	4		1.487960	1.487058	1.495970	1.487058
32	3		1.481694	1.482000	1.490813	1.482000
33	2		1.490343	1.483105	1.491939	1.483105
34	5		1.492925	1.480974	1.489765	1.480974
35	6		1.490406	1.484410	1.493281	1.484410
36	6		1.491229	1.484540	1.493418	1.484541
37	5		1.493200	1.484620	1.493492	1.484620
38	5		1.490195	1.480829	1.489625	1.480829
39	4		1.491176	1.482250	1.491064	1.482250
40	5	1	1.488048	1.482946	1.489022	1.480194
41	5		1.488002	1.481975	1.490785	1.481975
42	4		1.489745	1.478909	1.487659	1.478909
43	2		1.487639	1.482276	1.491096	1.482276
44	6		1.490662	1.484164	1.493029	1.484164
45	5	1	1.490754	1.480592	1.485975	1.477208
46	4		1.489568	1.484434	1.493292	1.484434
47	4	1	1.490479	1.484164	1.492985	1.484124
48	3		1.491059	1.484271	1.493128	1.484271
49	4		1.492961	1.483226	1.492060	1.483226
50	4		1.488396	1.483608	1.492458	1.483608
51	4		1.485992	1.483110	1.491943	1.483110
52	3		1.486688	1.483062	1.491892	1.483062
53	4		1.485513	1.482974	1.491808	1.482974
54	4	1	1.486939	1.481321	1.490078	1.481279
55	2		1.487088	1.485237	1.494134	1.485237
56	3		1.492096	1.486999	1.495917	1.486999
57	2		1.494206	1.484773	1.493647	1.484773
58	6		1.487099	1.484089	1.492941	1.484089
59	2		1.491593	1.481931	1.490737	1.481931
60	2		1.491013	1.481462	1.490263	1.481462
61	4		1.487842	1.484769	1.493646	1.484769
62	6		1.491998	1.486881	1.495802	1.486881
63	4	1	1.489714	1.486381	1.454426	1.445767
64	4		1.498233	1.484538	1.493410	1.484538
65	2		1.487541	1.484280	1.493151	1.484280
66	4		1.491876	1.485023	1.493895	1.485023

67	3		1.494723	1.484632	1.493500	1.484632
68	6		1.490505	1.486368	1.495272	1.486368
69	5		1.487017	1.484143	1.493002	1.484143
70	7	1	1.491892	1.485502	1.494382	1.485499
71	3		1.490005	1.484087	1.492940	1.484087
72	5		1.489044	1.484518	1.493382	1.484518
73	5		1.481098	1.485576	1.494473	1.485576
74	3		1.485907	1.485036	1.493911	1.485036
75	4		1.486212	1.487415	1.496340	1.487415
76	4	1	1.485839	1.487504	1.496427	1.487504
77	6		1.493681	1.479580	1.488344	1.479580
78	2		1.492457	1.485866	1.494756	1.485866
79	5		1.496172	1.480756	1.489547	1.480756
80	5		1.491701	1.486661	1.495582	1.486661
81	3	1	1.494453	1.483869	1.449552	1.440955
82	4		1.495608	1.486197	1.495098	1.486197
83	0		1.496437	1.482670	1.491496	1.482670
84	4		1.493455	1.484390	1.493250	1.484390
85	5		1.492077	1.484060	1.492920	1.484060
86	7	2	1.495684	1.481434	1.483299	1.474542
87	6		1.491491	1.485241	1.494128	1.485241
88	2		1.490886	1.486408	1.495308	1.486408
89	5		1.488840	1.491135	1.500157	1.491135
90	2		1.490806	1.487562	1.496487	1.487562
91	4		1.486625	1.483561	1.492405	1.483561
92	3		1.489903	1.483930	1.492786	1.483930
93	6		1.489295	1.481279	1.490073	1.481279
94	1		1.487901	1.486953	1.495864	1.486953
95	2		1.492588	1.482943	1.491782	1.482943
96	4		1.491244	1.487363	1.496284	1.487363
97	3		1.484455	1.484213	1.493084	1.484213
98	4		1.487070	1.482765	1.491601	1.482765
99	4		1.487673	1.482491	1.491311	1.482492
100	4		1.485230	1.482251	1.491066	1.482251
101	3		1.496313	1.476950	1.484323	1.475622
102	5		1.489723	1.480754	1.489546	1.480754
103	5		1.494842	1.480530	1.489312	1.480530
104	4		1.494518	1.485157	1.494034	1.485157
105	5		1.492956	1.483393	1.492251	1.483393
106	4		1.493801	1.483806	1.492662	1.483806

107	5	3	1.492183	1.486141	1.495041	1.486141
108	4	2	1.489054	1.480472	1.489251	1.480472
109	3	1	1.493281	1.482596	1.491427	1.482596
110	4		1.466119	1.481285	1.460314	1.451688
111	3		1.492510	1.481746	1.490570	1.481746
112	4		1.486766	1.481283	1.490085	1.481283
113	3		1.492626	1.477860	1.486591	1.477860
114	3		1.496775	1.481169	1.489969	1.481169
115	4		1.492029	1.479133	1.487888	1.479133
116	4		1.490324	1.479830	1.488601	1.479830
117	4		1.494075	1.479665	1.488431	1.479665
118	4		1.489362	1.481758	1.490577	1.481758
119	3	19	1.492273	1.486041	1.494932	1.486041
120	4		1.487171	1.481686	1.490488	1.481686
121	4		1.494071	1.483647	1.492495	1.483647
122	3	1	1.490257	1.479170	1.487931	1.479170
123	5	1	1.490685	1.484487	1.493347	1.484487
124	5	1	1.488069	1.481466	1.490192	1.481382
125	4		1.495560	1.486113	1.495011	1.486113
126	4		1.489303	1.481424	1.490232	1.481424
127	5	1	1.488606	1.479715	1.488479	1.479716
128	4		1.489692	1.480578	1.489360	1.480578
129	4		1.494537	1.482709	1.491543	1.482709
130	4	1	1.493517	1.483985	1.492838	1.483985
131	5		1.495970	1.479197	1.487960	1.479197
132	5	1	1.490813	1.473060	1.481694	1.473060
133	4	2	1.491939	1.481517	1.490343	1.481517
134	4		1.489765	1.484061	1.492925	1.484061
135	3		1.493281	1.481590	1.490406	1.481590
136	4	1	1.493418	1.482391	1.491229	1.482391
137	2		1.493492	1.484327	1.479866	1.471073
138	4	2	1.489625	1.481384	1.490195	1.481384
139	3		1.491064	1.482341	1.491176	1.482341
140	3		1.491790	1.479283	1.488048	1.479283
141	5		1.490785	1.479229	1.488002	1.479229
142	4		1.487659	1.480936	1.489745	1.480936
143	5		1.491096	1.478885	1.487639	1.478885
144	4		1.493029	1.481845	1.490662	1.481845
145	5		1.489378	1.481928	1.490754	1.481928
146	5		1.493292	1.480773	1.489568	1.480773

147	5	1	1.493024	1.481661	1.487639	1.478839
148	5		1.493128	1.482229	1.491059	1.482228
149	4		1.492060	1.484109	1.492961	1.484109
150	4		1.492458	1.479626	1.484683	1.475935
151	4		1.491943	1.477271	1.452740	1.444214
152	5		1.491892	1.477952	1.486688	1.477952
153	3		1.491808	1.476801	1.485513	1.476801
154	4		1.490120	1.478195	1.486939	1.478195
155	5		1.494134	1.478340	1.487088	1.478340
156	6	1	1.495917	1.483243	1.492096	1.483243
157	5		1.493647	1.485315	1.494206	1.485315
158	5		1.492941	1.478347	1.487099	1.478347
159	5		1.490737	1.482753	1.491593	1.482753
160	4		1.490263	1.482190	1.491013	1.482190
161	4		1.493646	1.479083	1.487842	1.479083
162	6	1	1.495802	1.483155	1.489466	1.480638
163	5		1.495283	1.480911	1.489714	1.480911
164	6		1.493410	1.489267	1.498233	1.489267
165	5		1.493151	1.478785	1.487541	1.478785
166	6		1.493894	1.483036	1.491876	1.483036
167	5	3	1.493500	1.485819	1.483702	1.474864
168	6	1	1.495272	1.481693	1.490505	1.481693
169	5		1.493002	1.478274	1.487017	1.478273
170	6	1	1.494384	1.483056	1.479295	1.470534
171	6		1.492940	1.481199	1.490005	1.481199
172	5		1.493382	1.480257	1.489044	1.480257
173	5	2	1.494473	1.472474	1.481098	1.472474
174	4		1.493911	1.477187	1.485907	1.477187
175	4		1.496340	1.477490	1.486158	1.477436
176	4	1	1.496427	1.477120	1.485839	1.477120
177	5		1.488345	1.484797	1.493680	1.484796
178	5		1.494756	1.483607	1.492457	1.483607
179	3		1.489547	1.487243	1.496172	1.487243
180	4		1.495582	1.482864	1.491688	1.482851
181	3		1.492722	1.485568	1.494453	1.485568
182	3		1.495098	1.486703	1.495608	1.486703
183	4		1.491496	1.487506	1.496424	1.487493
184	3		1.493250	1.484575	1.493455	1.484575
185	6		1.492920	1.483225	1.492077	1.483225
186	6		1.490232	1.486766	1.495684	1.486766

187	4	1.494128	1.482665	1.491491	1.482665
188	5	1.495308	1.482067	1.490886	1.482067
189	5	1.500157	1.480061	1.488840	1.480061
190	4	1.496487	1.481981	1.490806	1.481981
191	4	1.492405	1.477892	1.455883	1.447331
192	4	1.492786	1.481102	1.489904	1.481102
193	5	1.490073	1.480501	1.489294	1.480501
194	3	1.495864	1.479148	1.487901	1.479148
195	3	1.491782	1.483725	1.492588	1.483725
196	3	1.496284	1.482415	1.491244	1.482415
197	4	1.493084	1.475771	1.484455	1.475771
198	5	1.491601	1.478331	1.487070	1.478331
199	5	1.491311	1.478918	1.469607	1.460958
200	4	1.491066	1.476528	1.485230	1.476528

β -D₃/ β -H₃ isotopic partition-function ratios for (NC⁻...EtCl).*n*DMSO reactant structures:

structure sequence number	number extra <i>n</i>	imaginaries	extra imaginaries treated as reals		extra imaginaries omitted	
			300 K	303.15K	300 K	303.15K
			f_{RS}	f_{RS}	f_{RS}	f_{RS}
1	4		1816.146484	1632.392700	1805.446777	1632.392944
2	5	1	1829.145752	1643.610474	1766.000000	1596.779663
3	4		1849.433838	1673.411377	1851.555664	1673.411377
4	4		1898.890137	1688.045532	1867.604004	1688.045532
5	4		1837.795898	1666.448975	1843.587769	1666.448975
6	7		1864.273682	1635.368652	1808.987671	1635.368530
7	3		1860.055054	1687.562012	1867.167236	1687.562012
8	6	1	1853.967407	1643.359741	1818.014404	1643.354492
9	5		1861.541870	1665.907837	1843.073486	1665.907837
10	1	10	1828.223755	1485.596313	1512.629150	1368.797607
11	4	1	1833.292114	1701.884521	1883.257690	1701.838501
12	3		1847.828979	1650.487061	1826.038574	1650.487183
13	4		1834.366821	1667.444458	1844.636719	1667.444946
14	5		1834.269043	1671.647339	1849.437134	1671.647339
15	5		1861.102783	1670.680908	1848.115112	1670.680908
16	4	2	1813.257935	1682.442139	1814.354004	1639.927124
17	7	1	1848.263672	1654.454468	1828.895630	1653.390259
18	5		1854.676758	1673.359985	1851.300781	1673.359863
19	3		1864.107422	1698.096313	1878.989014	1698.096313
20	2		1829.285278	1673.126465	1850.847778	1673.126465
21	3		1810.458862	1682.432007	1861.446777	1682.432007
22	5		1829.140259	1708.909424	1891.178223	1708.909424
23	2		1878.046021	1715.537476	1898.615723	1715.537476
24	4		1823.902588	1661.129639	1837.796509	1661.129639
25	3		1924.818848	1694.475098	1874.857422	1694.475098
26	5		1838.996216	1655.973022	1832.069458	1655.972900

27	6		1836.555176	1642.178711	1816.537720	1642.177734
28	5		1829.402832	1649.294678	1824.475708	1649.294678
29	6		1827.894287	1656.967896	1832.790527	1656.967407
30	5	1	1862.466187	1636.222900	1782.047241	1611.164185
31	4		1842.494873	1688.743042	1868.450684	1688.743286
32	3		1819.875488	1640.556152	1814.613647	1640.556152
33	2		1825.720459	1642.536743	1816.739258	1642.536743
34	5		1829.656494	1672.090942	1849.715088	1672.090942
35	6		1831.388672	1662.140991	1838.714844	1662.140991
36	6		1803.693115	1678.568481	1857.085571	1678.568481
37	5		1828.456055	1668.716431	1846.045654	1668.716431
38	5		1837.378296	1675.380005	1853.497681	1675.380005
39	4		1841.353638	1671.145142	1848.719849	1671.145142
40	5	1	1817.239624	1664.989990	1837.284058	1660.850830
41	5		1819.646606	1651.404419	1826.591187	1651.404541
42	4		1864.914795	1709.855835	1892.260742	1709.855713
43	2		1836.147583	1733.708130	1918.814575	1733.708130
44	6		1808.925293	1696.546387	1877.201904	1696.546387
45	5	1	1824.726685	1721.254761	1902.193726	1718.650269
46	4		1808.703369	1697.338257	1878.004639	1697.338257
47	4	1	1838.550537	1634.991699	1807.932739	1634.720581
48	3		1846.363403	1666.102295	1843.027100	1666.102417
49	4		1851.685669	1688.957153	1868.585449	1688.957031
50	4		1836.891724	1681.664429	1860.482422	1681.664429
51	4		1775.258179	1629.641968	1802.481079	1629.641968
52	3		1827.602173	1630.962891	1803.854980	1630.962891
53	4		1802.556152	1658.449585	1834.440430	1658.449585
54	4	1	1821.580688	1668.204102	1845.534912	1668.130615
55	2		1819.047241	1690.671875	1870.591919	1690.671875
56	3		1807.854736	1700.827637	1882.072144	1700.827759
57	2		1818.426514	1681.773071	1860.601685	1681.773193
58	6		1828.040161	1680.793457	1859.688843	1680.793457
59	2		1842.206299	1695.293823	1875.719604	1695.293823
60	2		1816.738037	1659.898315	1836.066528	1659.898315
61	4		1820.907471	1668.812744	1846.248413	1668.812866
62	6		1808.409058	1672.082520	1849.682373	1672.082642
63	4	1	1807.900513	1641.195923	1785.979858	1614.731567
64	4		1809.078247	1648.097412	1823.041260	1648.097412
65	2		1820.642456	1713.547485	1896.306396	1713.547485
66	4		1874.463745	1675.516113	1853.565674	1675.516235

67	3		1824.188232	1710.936768	1893.348999	1710.936768
68	6		1850.995117	1695.206787	1875.749634	1695.206787
69	5		1802.957031	1677.201904	1855.463257	1677.202026
70	7	1	1847.588379	1660.190308	1836.517700	1660.185913
71	3		1814.329468	1656.012451	1831.806396	1656.012451
72	5		1803.203857	1679.094482	1857.634277	1679.094482
73	5		1824.457886	1660.074585	1836.284302	1660.074585
74	3		1799.848999	1693.653809	1873.909790	1693.653809
75	4		1831.188110	1665.465210	1842.268799	1665.465210
76	4	1	1804.912231	1660.172607	1836.484253	1660.171021
77	6		1822.101685	1641.742554	1815.827759	1641.742554
78	2		1823.282471	1655.427002	1831.290649	1655.427002
79	5		1873.289673	1663.803223	1840.645630	1663.803101
80	5		1851.673218	1672.321289	1850.031372	1672.321289
81	3	1	1843.345947	1694.665283	1752.516968	1583.917603
82	4		1836.276611	1642.056030	1816.245239	1642.056030
83	0		1847.901978	1694.452026	1874.807983	1694.452026
84	4		1816.201294	1650.622437	1825.832520	1650.622437
85	5		1822.429688	1678.234619	1856.838013	1678.234619
86	7	2	1819.656006	1627.751709	1789.091187	1617.562866
87	6		1819.678955	1668.930420	1846.365234	1668.930420
88	2		1845.404175	1688.522217	1868.109985	1688.522217
89	5		1822.349243	1703.162354	1884.673462	1703.162354
90	2		1852.906982	1748.890381	1935.978760	1748.890015
91	4		1788.806030	1682.121338	1861.029663	1682.121338
92	3		1816.816528	1731.649048	1916.644897	1731.649048
93	6		1807.261353	1680.214233	1858.827515	1680.214233
94	1		1833.010986	1675.353638	1853.317505	1675.353638
95	2		1862.527100	1689.256348	1869.029175	1689.256348
96	4		1816.293701	1691.312378	1871.539673	1691.312378
97	3		1838.750000	1721.769165	1905.523071	1721.769165
98	4		1816.983276	1753.301147	1941.224243	1753.301025
99	4		1823.266357	1690.015381	1869.983887	1690.015381
100	4		1888.466309	1698.734619	1879.671997	1698.734619
101	3		1805.446533	1641.908203	1815.715942	1641.519165
102	5		1817.793945	1653.711792	1829.145752	1653.711792
103	5		1851.555664	1671.786987	1849.433838	1671.786987
104	4		1867.604004	1715.626099	1898.890137	1715.626099
105	5		1843.587769	1661.454102	1837.796021	1661.454102
106	4		1808.987793	1685.007324	1864.273682	1685.007324

107	5	3	1867.167236	1681.197632	1860.054932	1681.197510
108	4	2	1818.020142	1675.693115	1853.967407	1675.693115
109	3	1	1843.073608	1682.584229	1861.541870	1682.584229
110	4		1641.702759	1652.904541	1701.913696	1538.707520
111	3		1883.308716	1657.441895	1833.292114	1657.441895
112	4		1826.038574	1670.371704	1847.828979	1670.371704
113	3		1844.636108	1658.269165	1834.366821	1658.269165
114	3		1849.437134	1658.182129	1834.269043	1658.182129
115	4		1848.115234	1682.137695	1861.102783	1682.137695
116	4		1861.391235	1639.476807	1813.257935	1639.476807
117	4		1830.072876	1670.787842	1848.263672	1670.787842
118	4		1851.300903	1676.485352	1854.676758	1676.485352
119	3	19	1878.989014	1684.936279	1864.107422	1684.936279
120	4		1850.847778	1653.615112	1829.285400	1653.615234
121	4		1861.446777	1636.805176	1810.458862	1636.805176
122	3	1	1891.178223	1653.754761	1829.140259	1653.754761
123	5	1	1898.615723	1697.140869	1878.046021	1697.140869
124	5	1	1837.796509	1648.926392	1823.676758	1648.722290
125	4		1874.857422	1738.880615	1924.818848	1738.880615
126	4		1832.069580	1662.576538	1838.996216	1662.576538
127	5	1	1816.538818	1660.224731	1836.555176	1660.224731
128	4		1824.475708	1653.853638	1829.402832	1653.853638
129	4		1832.791016	1652.574585	1827.894287	1652.574585
130	4	1	1809.763794	1683.448120	1862.466187	1683.448120
131	5		1868.450439	1665.675171	1842.494873	1665.675171
132	5	1	1814.613647	1645.421265	1819.875732	1645.421509
133	4	2	1816.739258	1650.641113	1825.720459	1650.640991
134	4		1849.715088	1653.974976	1829.656494	1653.974976
135	3		1838.714844	1655.744995	1831.388672	1655.744995
136	4	1	1857.085571	1630.958008	1803.693115	1630.958008
137	2		1846.045654	1652.929810	1803.155518	1630.058228
138	4	2	1853.497681	1661.092773	1837.378296	1661.092773
139	3		1848.719849	1664.600342	1841.353638	1664.600342
140	3		1841.863037	1642.888550	1817.239624	1642.888550
141	5		1826.591187	1645.169800	1819.646606	1645.169800
142	4		1892.260742	1685.463989	1864.914795	1685.463989
143	5		1918.814697	1659.783447	1836.147583	1659.783447
144	4		1877.201904	1635.467896	1808.925293	1635.467896
145	5		1905.076416	1649.535889	1824.726685	1649.535767
146	5		1878.004639	1635.335693	1808.703369	1635.335693

147	5	1	1808.232788	1661.761475	1835.201172	1658.734131
148	5		1843.027100	1668.991333	1846.363403	1668.991333
149	4		1868.585571	1673.741821	1851.685669	1673.741821
150	4		1860.482422	1660.500122	1834.271118	1658.131226
151	4		1802.481079	1605.485718	1670.665771	1510.896362
152	5		1803.855103	1652.348633	1827.602173	1652.348633
153	3		1834.440430	1629.808472	1802.556152	1629.808472
154	4		1845.616211	1646.694092	1821.580688	1646.694092
155	5		1870.591919	1644.585449	1819.047241	1644.585449
156	6	1	1882.072144	1634.556030	1807.854736	1634.556030
157	5		1860.601685	1643.801636	1818.426636	1643.801636
158	5		1859.688843	1652.553955	1828.040161	1652.553955
159	5		1875.719604	1665.218872	1842.206299	1665.218872
160	4		1836.066528	1642.613281	1816.738037	1642.613281
161	4		1846.248291	1646.252930	1820.907471	1646.252930
162	6	1	1849.682251	1634.879028	1805.306396	1632.073975
163	5		1815.250977	1634.426636	1807.900513	1634.426636
164	6		1823.041260	1635.587158	1809.078247	1635.587158
165	5		1896.306396	1646.073120	1820.642456	1646.073120
166	6		1853.565552	1694.080322	1874.463745	1694.080322
167	5	3	1893.348999	1648.953979	1756.271118	1587.561279
168	6	1	1875.749634	1673.114868	1850.995117	1673.114868
169	5		1855.463135	1630.102173	1802.957031	1630.102173
170	6	1	1836.522583	1669.823486	1844.083008	1666.655396
171	6		1831.806396	1640.365601	1814.329468	1640.365601
172	5		1857.634277	1630.244385	1803.203857	1630.244385
173	5	2	1836.284180	1649.338867	1824.457886	1649.338867
174	4		1873.909790	1627.305420	1799.849121	1627.305420
175	4		1842.268799	1655.575439	1830.909058	1655.323120
176	4	1	1836.485962	1631.930176	1804.912231	1631.930176
177	5		1815.827759	1647.354248	1822.101563	1647.354126
178	5		1831.290649	1648.266968	1823.282471	1648.266968
179	3		1840.645752	1692.964478	1873.289673	1692.964478
180	4		1850.031372	1673.813721	1851.452759	1673.614502
181	3		1875.053345	1666.383545	1843.345947	1666.383545
182	3		1816.245239	1659.999634	1836.276733	1659.999878
183	4		1874.807983	1670.167603	1847.887085	1670.154175
184	3		1825.832520	1642.065063	1816.201538	1642.065308
185	6		1856.838013	1647.323364	1822.429688	1647.323242
186	6		1800.360718	1644.985962	1819.656006	1644.985962

187	4	1846.365234	1645.067993	1819.679077	1645.067993
188	5	1868.109985	1668.205444	1845.404175	1668.205322
189	5	1884.673462	1647.653198	1822.349243	1647.653198
190	4	1935.979126	1674.962891	1852.906982	1674.962891
191	4	1861.029663	1617.401001	1719.564819	1554.794678
192	4	1916.644897	1642.538940	1816.816650	1642.539063
193	5	1858.827515	1634.001343	1807.261353	1634.001343
194	3	1853.317505	1656.979980	1833.010986	1656.979980
195	3	1869.029175	1683.320313	1862.526978	1683.320313
196	3	1871.539673	1642.019775	1816.293701	1642.019775
197	4	1905.523071	1662.090210	1838.749878	1662.090088
198	5	1941.224365	1642.681030	1816.983276	1642.681030
199	5	1869.983887	1648.409668	1772.750732	1602.738892
200	4	1879.671875	1706.346802	1888.466309	1706.346802

α -¹⁴C/ α -¹¹C isotopic partition-function ratios for (NC⁻...EtCl).*n*DMSO reactant structures:

structure sequence number	number extra <i>n</i>	imaginaries	extra imaginaries treated as reals		extra imaginaries omitted	
			300 K	303.15K	300 K	303.15K
			f_{RS}	f_{RS}	f_{RS}	f_{RS}
1	4		1.485658	1.487392	1.496313	1.487392
2	5	1	1.489546	1.480933	1.466005	1.457355
3	4		1.489312	1.485943	1.494842	1.485943
4	4		1.494034	1.485614	1.494518	1.485614
5	4		1.492251	1.484102	1.492956	1.484102
6	7		1.492662	1.484928	1.493801	1.484928
7	3		1.495041	1.483348	1.492183	1.483348
8	6	1	1.489251	1.480280	1.489054	1.480280
9	5		1.491427	1.484418	1.493281	1.484418
10	1	10	1.490087	1.457695	1.389013	1.381033
11	4	1	1.490570	1.483660	1.492465	1.483616
12	3		1.490085	1.478033	1.486766	1.478033
13	4		1.486591	1.483775	1.492627	1.483775
14	5		1.489969	1.487842	1.496775	1.487842
15	5		1.487888	1.483187	1.492029	1.483187
16	4	2	1.488601	1.481520	1.453649	1.445061
17	7	1	1.488431	1.485199	1.493392	1.484520
18	5		1.490577	1.480582	1.489362	1.480583
19	3		1.494932	1.483431	1.492273	1.483431
20	2		1.490487	1.478435	1.487171	1.478435
21	3		1.492495	1.485187	1.494071	1.485187
22	5		1.487931	1.481461	1.490257	1.481461
23	2		1.493347	1.481878	1.490685	1.481878
24	4		1.490277	1.479312	1.488069	1.479312
25	3		1.495011	1.486655	1.495560	1.486655
26	5		1.490232	1.480524	1.489303	1.480524

27	6		1.488479	1.479836	1.488606	1.479836
28	5		1.489360	1.480901	1.489692	1.480901
29	6		1.491543	1.485622	1.494538	1.485623
30	5	1	1.492838	1.484653	1.471887	1.463152
31	4		1.487960	1.487058	1.495970	1.487058
32	3		1.481694	1.482000	1.490813	1.482000
33	2		1.490343	1.483105	1.491939	1.483105
34	5		1.492925	1.480974	1.489765	1.480974
35	6		1.490406	1.484410	1.493281	1.484410
36	6		1.491229	1.484540	1.493418	1.484541
37	5		1.493200	1.484620	1.493492	1.484620
38	5		1.490195	1.480829	1.489625	1.480829
39	4		1.491176	1.482250	1.491064	1.482250
40	5	1	1.488048	1.482946	1.489022	1.480194
41	5		1.488002	1.481975	1.490785	1.481975
42	4		1.489745	1.478909	1.487659	1.478909
43	2		1.487639	1.482276	1.491096	1.482276
44	6		1.490662	1.484164	1.493029	1.484164
45	5	1	1.490754	1.480592	1.485975	1.477208
46	4		1.489568	1.484434	1.493292	1.484434
47	4	1	1.490479	1.484164	1.492985	1.484124
48	3		1.491059	1.484271	1.493128	1.484271
49	4		1.492961	1.483226	1.492060	1.483226
50	4		1.488396	1.483608	1.492458	1.483608
51	4		1.485992	1.483110	1.491943	1.483110
52	3		1.486688	1.483062	1.491892	1.483062
53	4		1.485513	1.482974	1.491808	1.482974
54	4	1	1.486939	1.481321	1.490078	1.481279
55	2		1.487088	1.485237	1.494134	1.485237
56	3		1.492096	1.486999	1.495917	1.486999
57	2		1.494206	1.484773	1.493647	1.484773
58	6		1.487099	1.484089	1.492941	1.484089
59	2		1.491593	1.481931	1.490737	1.481931
60	2		1.491013	1.481462	1.490263	1.481462
61	4		1.487842	1.484769	1.493646	1.484769
62	6		1.491998	1.486881	1.495802	1.486881
63	4	1	1.489714	1.486381	1.454426	1.445767
64	4		1.498233	1.484538	1.493410	1.484538
65	2		1.487541	1.484280	1.493151	1.484280
66	4		1.491876	1.485023	1.493895	1.485023

67	3		1.494723	1.484632	1.493500	1.484632
68	6		1.490505	1.486368	1.495272	1.486368
69	5		1.487017	1.484143	1.493002	1.484143
70	7	1	1.491892	1.485502	1.494382	1.485499
71	3		1.490005	1.484087	1.492940	1.484087
72	5		1.489044	1.484518	1.493382	1.484518
73	5		1.481098	1.485576	1.494473	1.485576
74	3		1.485907	1.485036	1.493911	1.485036
75	4		1.486212	1.487415	1.496340	1.487415
76	4	1	1.485839	1.487504	1.496427	1.487504
77	6		1.493681	1.479580	1.488344	1.479580
78	2		1.492457	1.485866	1.494756	1.485866
79	5		1.496172	1.480756	1.489547	1.480756
80	5		1.491701	1.486661	1.495582	1.486661
81	3	1	1.494453	1.483869	1.449552	1.440955
82	4		1.495608	1.486197	1.495098	1.486197
83	0		1.496437	1.482670	1.491496	1.482670
84	4		1.493455	1.484390	1.493250	1.484390
85	5		1.492077	1.484060	1.492920	1.484060
86	7	2	1.495684	1.481434	1.483299	1.474542
87	6		1.491491	1.485241	1.494128	1.485241
88	2		1.490886	1.486408	1.495308	1.486408
89	5		1.488840	1.491135	1.500157	1.491135
90	2		1.490806	1.487562	1.496487	1.487562
91	4		1.486625	1.483561	1.492405	1.483561
92	3		1.489903	1.483930	1.492786	1.483930
93	6		1.489295	1.481279	1.490073	1.481279
94	1		1.487901	1.486953	1.495864	1.486953
95	2		1.492588	1.482943	1.491782	1.482943
96	4		1.491244	1.487363	1.496284	1.487363
97	3		1.484455	1.484213	1.493084	1.484213
98	4		1.487070	1.482765	1.491601	1.482765
99	4		1.487673	1.482491	1.491311	1.482492
100	4		1.485230	1.482251	1.491066	1.482251
101	3		1.496313	1.476950	1.484323	1.475622
102	5		1.489723	1.480754	1.489546	1.480754
103	5		1.494842	1.480530	1.489312	1.480530
104	4		1.494518	1.485157	1.494034	1.485157
105	5		1.492956	1.483393	1.492251	1.483393
106	4		1.493801	1.483806	1.492662	1.483806

107	5	3	1.492183	1.486141	1.495041	1.486141
108	4	2	1.489054	1.480472	1.489251	1.480472
109	3	1	1.493281	1.482596	1.491427	1.482596
110	4		1.466119	1.481285	1.460314	1.451688
111	3		1.492510	1.481746	1.490570	1.481746
112	4		1.486766	1.481283	1.490085	1.481283
113	3		1.492626	1.477860	1.486591	1.477860
114	3		1.496775	1.481169	1.489969	1.481169
115	4		1.492029	1.479133	1.487888	1.479133
116	4		1.490324	1.479830	1.488601	1.479830
117	4		1.494075	1.479665	1.488431	1.479665
118	4		1.489362	1.481758	1.490577	1.481758
119	3	19	1.492273	1.486041	1.494932	1.486041
120	4		1.487171	1.481686	1.490488	1.481686
121	4		1.494071	1.483647	1.492495	1.483647
122	3	1	1.490257	1.479170	1.487931	1.479170
123	5	1	1.490685	1.484487	1.493347	1.484487
124	5	1	1.488069	1.481466	1.490192	1.481382
125	4		1.495560	1.486113	1.495011	1.486113
126	4		1.489303	1.481424	1.490232	1.481424
127	5	1	1.488606	1.479715	1.488479	1.479716
128	4		1.489692	1.480578	1.489360	1.480578
129	4		1.494537	1.482709	1.491543	1.482709
130	4	1	1.493517	1.483985	1.492838	1.483985
131	5		1.495970	1.479197	1.487960	1.479197
132	5	1	1.490813	1.473060	1.481694	1.473060
133	4	2	1.491939	1.481517	1.490343	1.481517
134	4		1.489765	1.484061	1.492925	1.484061
135	3		1.493281	1.481590	1.490406	1.481590
136	4	1	1.493418	1.482391	1.491229	1.482391
137	2		1.493492	1.484327	1.479866	1.471073
138	4	2	1.489625	1.481384	1.490195	1.481384
139	3		1.491064	1.482341	1.491176	1.482341
140	3		1.491790	1.479283	1.488048	1.479283
141	5		1.490785	1.479229	1.488002	1.479229
142	4		1.487659	1.480936	1.489745	1.480936
143	5		1.491096	1.478885	1.487639	1.478885
144	4		1.493029	1.481845	1.490662	1.481845
145	5		1.489378	1.481928	1.490754	1.481928
146	5		1.493292	1.480773	1.489568	1.480773

147	5	1	1.493024	1.481661	1.487639	1.478839
148	5		1.493128	1.482229	1.491059	1.482228
149	4		1.492060	1.484109	1.492961	1.484109
150	4		1.492458	1.479626	1.484683	1.475935
151	4		1.491943	1.477271	1.452740	1.444214
152	5		1.491892	1.477952	1.486688	1.477952
153	3		1.491808	1.476801	1.485513	1.476801
154	4		1.490120	1.478195	1.486939	1.478195
155	5		1.494134	1.478340	1.487088	1.478340
156	6	1	1.495917	1.483243	1.492096	1.483243
157	5		1.493647	1.485315	1.494206	1.485315
158	5		1.492941	1.478347	1.487099	1.478347
159	5		1.490737	1.482753	1.491593	1.482753
160	4		1.490263	1.482190	1.491013	1.482190
161	4		1.493646	1.479083	1.487842	1.479083
162	6	1	1.495802	1.483155	1.489466	1.480638
163	5		1.495283	1.480911	1.489714	1.480911
164	6		1.493410	1.489267	1.498233	1.489267
165	5		1.493151	1.478785	1.487541	1.478785
166	6		1.493894	1.483036	1.491876	1.483036
167	5	3	1.493500	1.485819	1.483702	1.474864
168	6	1	1.495272	1.481693	1.490505	1.481693
169	5		1.493002	1.478274	1.487017	1.478273
170	6	1	1.494384	1.483056	1.479295	1.470534
171	6		1.492940	1.481199	1.490005	1.481199
172	5		1.493382	1.480257	1.489044	1.480257
173	5	2	1.494473	1.472474	1.481098	1.472474
174	4		1.493911	1.477187	1.485907	1.477187
175	4		1.496340	1.477490	1.486158	1.477436
176	4	1	1.496427	1.477120	1.485839	1.477120
177	5		1.488345	1.484797	1.493680	1.484796
178	5		1.494756	1.483607	1.492457	1.483607
179	3		1.489547	1.487243	1.496172	1.487243
180	4		1.495582	1.482864	1.491688	1.482851
181	3		1.492722	1.485568	1.494453	1.485568
182	3		1.495098	1.486703	1.495608	1.486703
183	4		1.491496	1.487506	1.496424	1.487493
184	3		1.493250	1.484575	1.493455	1.484575
185	6		1.492920	1.483225	1.492077	1.483225
186	6		1.490232	1.486766	1.495684	1.486766

187	4	1.494128	1.482665	1.491491	1.482665
188	5	1.495308	1.482067	1.490886	1.482067
189	5	1.500157	1.480061	1.488840	1.480061
190	4	1.496487	1.481981	1.490806	1.481981
191	4	1.492405	1.477892	1.455883	1.447331
192	4	1.492786	1.481102	1.489904	1.481102
193	5	1.490073	1.480501	1.489294	1.480501
194	3	1.495864	1.479148	1.487901	1.479148
195	3	1.491782	1.483725	1.492588	1.483725
196	3	1.496284	1.482415	1.491244	1.482415
197	4	1.493084	1.475771	1.484455	1.475771
198	5	1.491601	1.478331	1.487070	1.478331
199	5	1.491311	1.478918	1.469607	1.460958
200	4	1.491066	1.476528	1.485230	1.476528

Ig-³⁷Cl/³⁵Cl isotopic partition-function ratios for (NC⁻...EtCl).*n*DMSO reactant structures:

structure sequence number	number extra <i>n</i>	imaginaries	extra imaginaries treated as reals		extra imaginaries omitted	
			300 K	303.15K	300 K	303.15K
			f_{RS}	f_{RS}	f_{RS}	f_{RS}
1	4		1.009940	1.010489	1.010679	1.010489
2	5	1	1.010239	1.009905	0.993815	0.993638
3	4		1.010248	1.010177	1.010362	1.010177
4	4		1.010497	1.010219	1.010405	1.010219
5	4		1.010332	1.010175	1.010359	1.010175
6	7		1.010430	1.010212	1.010397	1.010212
7	3		1.010372	1.010134	1.010317	1.010134
8	6	1	1.010054	1.009993	1.010173	1.009991
9	5		1.010359	1.010092	1.010274	1.010092
10	1	10	1.010354	1.010576	0.992161	0.991974
11	4	1	1.010167	1.010156	1.010239	1.010055
12	3		1.010440	1.009743	1.009921	1.009743
13	4		1.010005	1.010138	1.010322	1.010138
14	5		1.010484	1.010459	1.010648	1.010459
15	5		1.010207	1.010270	1.010456	1.010270
16	4	2	1.010135	1.010026	0.995741	0.995561
17	7	1	1.010043	1.010205	1.010278	1.010093
18	5		1.010338	1.009927	1.010107	1.009927
19	3		1.010548	1.010084	1.010267	1.010084
20	2		1.010256	1.009763	1.009941	1.009763
21	3		1.010300	1.010126	1.010309	1.010126
22	5		1.010179	1.010066	1.010249	1.010067
23	2		1.010521	1.010058	1.010241	1.010058
24	4		1.010285	1.009882	1.010062	1.009882
25	3		1.010491	1.010422	1.010611	1.010422
26	5		1.010267	1.009951	1.010132	1.009951

27	6		1.010131	1.009789	1.009967	1.009789
28	5		1.010178	1.010026	1.010208	1.010026
29	6		1.010263	1.010122	1.010306	1.010122
30	5	1	1.010583	1.010121	0.992470	0.992290
31	4		1.010065	1.010353	1.010540	1.010353
32	3		1.009796	1.010108	1.010292	1.010108
33	2		1.010225	1.010071	1.010253	1.010071
34	5		1.010355	1.010158	1.010343	1.010158
35	6		1.010245	1.010110	1.010293	1.010110
36	6		1.010311	1.010128	1.010311	1.010128
37	5		1.010338	1.010251	1.010437	1.010251
38	5		1.010104	1.010073	1.010257	1.010073
39	4		1.010151	1.010077	1.010260	1.010077
40	5	1	1.010223	1.010087	1.009333	1.009150
41	5		1.009962	1.009891	1.010070	1.009891
42	4		1.010173	1.009942	1.010124	1.009942
43	2		1.010244	1.010061	1.010244	1.010061
44	6		1.010284	1.010156	1.010340	1.010156
45	5	1	1.010183	1.009960	1.008875	1.008695
46	4		1.010247	1.010144	1.010328	1.010144
47	4	1	1.010346	1.010090	1.010264	1.010081
48	3		1.010323	1.010206	1.010391	1.010206
49	4		1.010293	1.010114	1.010298	1.010114
50	4		1.010075	1.010102	1.010286	1.010102
51	4		1.009961	1.010162	1.010347	1.010162
52	3		1.010049	1.010118	1.010302	1.010118
53	4		1.009961	1.010131	1.010315	1.010131
54	4	1	1.010149	1.009925	1.010023	1.009843
55	2		1.010122	1.010105	1.010288	1.010105
56	3		1.010287	1.010291	1.010477	1.010291
57	2		1.010448	1.010160	1.010344	1.010160
58	6		1.010396	1.010136	1.010320	1.010136
59	2		1.010332	1.010031	1.010213	1.010031
60	2		1.010398	1.009953	1.010134	1.009953
61	4		1.010122	1.010185	1.010370	1.010185
62	6		1.010270	1.010432	1.010620	1.010432
63	4	1	1.010128	1.010303	0.996683	0.996499
64	4		1.010678	1.010206	1.010391	1.010206
65	2		1.010118	1.010044	1.010226	1.010044
66	4		1.010308	1.010252	1.010438	1.010252

67	3		1.010373	1.010174	1.010359	1.010174
68	6		1.010159	1.010272	1.010458	1.010272
69	5		1.010050	1.010223	1.010409	1.010223
70	7	1	1.010250	1.010239	1.010424	1.010239
71	3		1.010232	1.010138	1.010322	1.010138
72	5		1.010247	1.010162	1.010346	1.010162
73	5		1.009801	1.010209	1.010394	1.010209
74	3		1.009923	1.010149	1.010333	1.010149
75	4		1.010064	1.010474	1.010664	1.010474
76	4	1	1.010043	1.010398	1.010585	1.010397
77	6		1.010510	1.009955	1.010136	1.009955
78	2		1.010295	1.010218	1.010403	1.010218
79	5		1.010583	1.010039	1.010221	1.010038
80	5		1.010274	1.010290	1.010476	1.010290
81	3	1	1.010832	1.010288	1.007120	1.006934
82	4		1.010631	1.010451	1.010641	1.010451
83	0		1.010646	1.010112	1.010296	1.010112
84	4		1.010376	1.010239	1.010425	1.010239
85	5		1.010265	1.010205	1.010390	1.010205
86	7	2	1.010467	1.009980	1.007946	1.007765
87	6		1.010276	1.010218	1.010403	1.010218
88	2		1.010200	1.010445	1.010634	1.010445
89	5		1.010162	1.010561	1.010752	1.010561
90	2		1.010224	1.010403	1.010591	1.010403
91	4		1.010018	1.010140	1.010324	1.010140
92	3		1.010119	1.010053	1.010235	1.010053
93	6		1.010178	1.010141	1.010325	1.010141
94	1		1.010175	1.010374	1.010562	1.010374
95	2		1.010377	1.010091	1.010275	1.010091
96	4		1.010325	1.010445	1.010633	1.010445
97	3		1.009832	1.010265	1.010451	1.010265
98	4		1.010180	1.010121	1.010305	1.010121
99	4		1.010148	1.010028	1.010210	1.010028
100	4		1.010144	1.010175	1.010361	1.010175
101	3		1.010679	1.009761	1.009677	1.009499
102	5		1.010085	1.010055	1.010239	1.010055
103	5		1.010362	1.010065	1.010248	1.010065
104	4		1.010405	1.010310	1.010497	1.010310
105	5		1.010359	1.010147	1.010332	1.010147
106	4		1.010397	1.010244	1.010430	1.010244

107	5	3	1.010317	1.010188	1.010372	1.010188
108	4	2	1.010175	1.009875	1.010055	1.009875
109	3	1	1.010274	1.010174	1.010359	1.010174
110	4		1.010766	1.010169	1.009195	1.009010
111	3		1.010340	1.009985	1.010167	1.009985
112	4		1.009921	1.010253	1.010440	1.010253
113	3		1.010322	1.009825	1.010005	1.009825
114	3		1.010648	1.010296	1.010484	1.010296
115	4		1.010456	1.010024	1.010207	1.010024
116	4		1.010208	1.009953	1.010135	1.009953
117	4		1.010390	1.009863	1.010043	1.009863
118	4		1.010107	1.010153	1.010338	1.010153
119	3	19	1.010267	1.010360	1.010548	1.010360
120	4		1.009941	1.010073	1.010256	1.010073
121	4		1.010309	1.010116	1.010300	1.010116
122	3	1	1.010249	1.009997	1.010179	1.009997
123	5	1	1.010241	1.010334	1.010521	1.010334
124	5	1	1.010062	1.010101	1.010210	1.010026
125	4		1.010611	1.010304	1.010491	1.010304
126	4		1.010132	1.010083	1.010267	1.010083
127	5	1	1.009967	1.009949	1.010131	1.009949
128	4		1.010208	1.009996	1.010178	1.009996
129	4		1.010306	1.010080	1.010263	1.010080
130	4	1	1.010305	1.010393	1.010583	1.010393
131	5		1.010540	1.009884	1.010064	1.009884
132	5	1	1.010292	1.009619	1.009796	1.009620
133	4	2	1.010253	1.010042	1.010225	1.010042
134	4		1.010343	1.010170	1.010355	1.010170
135	3		1.010293	1.010062	1.010245	1.010062
136	4	1	1.010311	1.010127	1.010311	1.010127
137	2		1.010437	1.010154	0.990331	0.990150
138	4	2	1.010257	1.009923	1.010104	1.009923
139	3		1.010260	1.009969	1.010151	1.009969
140	3		1.010270	1.010039	1.010223	1.010039
141	5		1.010070	1.009783	1.009962	1.009783
142	4		1.010124	1.009991	1.010173	1.009991
143	5		1.010244	1.010060	1.010244	1.010060
144	4		1.010340	1.010100	1.010284	1.010100
145	5		1.010141	1.010001	1.010183	1.010001
146	5		1.010328	1.010063	1.010247	1.010063

147	5	1	1.010273	1.010160	1.008681	1.008496
148	5		1.010391	1.010138	1.010323	1.010138
149	4		1.010298	1.010110	1.010293	1.010110
150	4		1.010286	1.009894	1.007132	1.006952
151	4		1.010347	1.009782	1.005347	1.005169
152	5		1.010302	1.009869	1.010049	1.009869
153	3		1.010315	1.009782	1.009961	1.009782
154	4		1.010106	1.009967	1.010149	1.009967
155	5		1.010288	1.009940	1.010122	1.009940
156	6	1	1.010477	1.010103	1.010287	1.010103
157	5		1.010344	1.010262	1.010448	1.010262
158	5		1.010320	1.010209	1.010396	1.010209
159	5		1.010213	1.010148	1.010332	1.010148
160	4		1.010134	1.010212	1.010398	1.010212
161	4		1.010370	1.009941	1.010122	1.009941
162	6	1	1.010620	1.010086	1.009265	1.009082
163	5		1.010490	1.009947	1.010128	1.009947
164	6		1.010391	1.010489	1.010678	1.010489
165	5		1.010226	1.009936	1.010118	1.009936
166	6		1.010438	1.010124	1.010308	1.010124
167	5	3	1.010359	1.010189	1.002584	1.002401
168	6	1	1.010458	1.009978	1.010159	1.009978
169	5		1.010409	1.009870	1.010050	1.009870
170	6	1	1.010424	1.010067	0.989550	0.989371
171	6		1.010322	1.010049	1.010232	1.010049
172	5		1.010346	1.010063	1.010247	1.010063
173	5	2	1.010394	1.009624	1.009801	1.009624
174	4		1.010333	1.009745	1.009923	1.009745
175	4		1.010664	1.009884	1.010027	1.009846
176	4	1	1.010585	1.009863	1.010043	1.009863
177	5		1.010136	1.010323	1.010510	1.010322
178	5		1.010403	1.010111	1.010295	1.010111
179	3		1.010221	1.010395	1.010583	1.010395
180	4		1.010476	1.010090	1.010254	1.010071
181	3		1.010475	1.010639	1.010832	1.010639
182	3		1.010641	1.010442	1.010632	1.010443
183	4		1.010296	1.010457	1.010638	1.010449
184	3		1.010425	1.010191	1.010377	1.010192
185	6		1.010390	1.010082	1.010265	1.010082
186	6		1.010161	1.010281	1.010467	1.010281

187	4	1.010403	1.010093	1.010276	1.010093
188	5	1.010634	1.010018	1.010200	1.010018
189	5	1.010752	1.009980	1.010162	1.009980
190	4	1.010591	1.010041	1.010224	1.010041
191	4	1.010324	1.009839	1.004395	1.004216
192	4	1.010235	1.009938	1.010119	1.009938
193	5	1.010325	1.009996	1.010178	1.009996
194	3	1.010562	1.009993	1.010175	1.009993
195	3	1.010275	1.010192	1.010377	1.010192
196	3	1.010633	1.010140	1.010325	1.010140
197	4	1.010451	1.009656	1.009832	1.009656
198	5	1.010305	1.009997	1.010180	1.009997
199	5	1.010210	1.009966	0.992390	0.992211
200	4	1.010361	1.009962	1.010144	1.009962

nu-¹³C/¹²C isotopic partition-function ratios for (NC⁻...EtCl).*n*DMSO reactant structures:

structure sequence number	number <i>n</i>	extra imaginaries	abnormal*	extra imaginaries treated as reals		extra imaginaries omitted	
				300 K	303.15K	300 K	303.15K
				<i>f</i> _{RS}	<i>f</i> _{RS}	<i>f</i> _{RS}	<i>f</i> _{RS}
1	4		*	1.116211	1.108452	1.109943	1.108452
2	5	1		1.113856	1.111586	1.113122	1.111580
3	4			1.108669	1.124971	1.126748	1.124971
4	4			1.115215	1.111433	1.112969	1.111433
5	4			1.130445	1.120358	1.122059	1.120358
6	7		*	1.113486	1.128289	1.130154	1.128289
7	3		*	1.129724	1.125587	1.127400	1.125587
8	6	1	*	1.129036	1.128212	1.129884	1.128023
9	5			1.130447	1.129439	1.131281	1.129439
10	1	10	*	1.133034	1.106147	1.063134	1.061776
11	4	1	*	1.115967	1.127141	1.128935	1.127093
12	3			1.130821	1.140291	1.142282	1.140291
13	4			1.109380	1.131190	1.133060	1.131191
14	5			1.131310	1.123103	1.124842	1.123103
15	5			1.108749	1.114023	1.115605	1.114023
16	4	2		1.129358	1.120514	1.121269	1.119575
17	7	1		1.107933	1.113304	1.114679	1.113110
18	5			1.110336	1.112904	1.114470	1.112904
19	3			1.119492	1.111840	1.113390	1.111840
20	2		*	1.114799	1.127867	1.129722	1.127867
21	3		*	1.112945	1.127829	1.129681	1.127829
22	5			1.130361	1.113769	1.115350	1.113769
23	2			1.111475	1.119567	1.121247	1.119567
24	4			1.112133	1.111045	1.112576	1.111045
25	3			1.116282	1.135570	1.137505	1.135570
26	5			1.113837	1.122398	1.124126	1.122398

27	6		*	1.130093	1.125155	1.126959	1.125154
28	5			1.128861	1.123103	1.124848	1.123103
29	6		*	1.114196	1.106218	1.107669	1.106218
30	5	1	*	1.134180	1.130240	1.132139	1.130240
31	4			1.121428	1.121272	1.122980	1.121272
32	3			1.122678	1.146538	1.148624	1.146538
33	2			1.129805	1.146066	1.148143	1.146066
34	5			1.128835	1.126437	1.128238	1.126437
35	6			1.130105	1.145140	1.147199	1.145140
36	6			1.119553	1.125163	1.126939	1.125163
37	5			1.121577	1.120499	1.122196	1.120499
38	5			1.119493	1.113662	1.115241	1.113662
39	4			1.114622	1.112634	1.114191	1.112634
40	5	1		1.122978	1.115505	1.117108	1.115500
41	5		*	1.127337	1.106442	1.107895	1.106442
42	4			1.108894	1.119982	1.121672	1.119982
43	2			1.115849	1.114401	1.115994	1.114401
44	6			1.111275	1.116282	1.117907	1.116282
45	5	1		1.108727	1.114172	1.115627	1.114037
46	4			1.112629	1.138309	1.140300	1.138309
47	4	1	*	1.128361	1.128455	1.130317	1.128455
48	3			1.117815	1.119833	1.121524	1.119833
49	4			1.111833	1.119121	1.120792	1.119121
50	4			1.117132	1.110396	1.111914	1.110396
51	4			1.117761	1.110258	1.111780	1.110258
52	3			1.117571	1.119878	1.121566	1.119878
53	4		*	1.120411	1.106481	1.107938	1.106481
54	4	1	*	1.116650	1.108324	1.086050	1.084588
55	2			1.111874	1.125448	1.127228	1.125448
56	3		*	1.117613	1.129762	1.131659	1.129762
57	2			1.111412	1.105165	1.106596	1.105165
58	6		*	1.113813	1.107031	1.108495	1.107031
59	2			1.118639	1.108561	1.110055	1.108561
60	2			1.115963	1.120985	1.122692	1.120985
61	4		*	1.131041	1.126689	1.128521	1.126689
62	6		*	1.111877	1.126296	1.128120	1.126296
63	4	1	*	1.129380	1.114788	1.116386	1.114787
64	4			1.114724	1.113188	1.114762	1.113188
65	2			1.107363	1.114809	1.116412	1.114809
66	4			1.108915	1.114628	1.116223	1.114628

67	3			1.126427	1.120010	1.121704	1.120010
68	6			1.114340	1.117774	1.119425	1.117774
69	5			1.107839	1.117841	1.119495	1.117841
70	7	1		1.128108	1.113457	1.114355	1.112782
71	3			1.128425	1.104806	1.106223	1.104806
72	5		*	1.107890	1.106462	1.107910	1.106462
73	5			1.128030	1.109874	1.111386	1.109874
74	3			1.108983	1.113837	1.115417	1.113837
75	4			1.119640	1.115200	1.116807	1.115200
76	4	1		1.118810	1.113399	1.113906	1.112335
77	6			1.108753	1.116049	1.117670	1.116049
78	2		*	1.112837	1.105645	1.107109	1.105645
79	5			1.129730	1.118896	1.120564	1.118896
80	5		*	1.109561	1.128203	1.130065	1.128203
81	3	1	*	1.109306	1.126439	1.128274	1.126439
82	4			1.108374	1.135178	1.137108	1.135178
83	0			1.128713	1.107028	1.108495	1.107028
84	4			1.107575	1.120465	1.122160	1.120465
85	5		*	1.107195	1.127320	1.129168	1.127320
86	7	2	*	1.130546	1.127245	1.128276	1.126435
87	6			1.137668	1.126181	1.127980	1.126181
88	2			1.115768	1.119641	1.121325	1.119641
89	5		*	1.117107	1.107095	1.108562	1.107095
90	2			1.108323	1.113213	1.114784	1.113213
91	4		*	1.116061	1.127110	1.128951	1.127110
92	3		*	1.111087	1.125285	1.127090	1.125285
93	6		*	1.128311	1.125474	1.127284	1.125474
94	1			1.120032	1.106207	1.107654	1.106207
95	2			1.120853	1.115628	1.117244	1.115628
96	4		*	1.129214	1.107922	1.109430	1.107922
97	3			1.130960	1.110787	1.112314	1.110787
98	4			1.129313	1.121171	1.122882	1.121171
99	4			1.114873	1.112832	1.114402	1.112832
100	4			1.126861	1.115869	1.117487	1.115869
101	3			1.109944	1.114619	1.116211	1.114619
102	5			1.113128	1.112300	1.113856	1.112300
103	5		*	1.126748	1.107201	1.108669	1.107201
104	4			1.112969	1.113635	1.115215	1.113635
105	5		*	1.122059	1.128577	1.130445	1.128577
106	4			1.130154	1.111937	1.113486	1.111937

107	5	3	*	1.127400	1.127869	1.129397	1.127542
108	4	2	*	1.130074	1.127192	1.128191	1.126348
109	3	1	*	1.131281	1.128578	1.128075	1.126210
110	4			1.107586	1.131163	1.133034	1.131163
111	3			1.128983	1.114373	1.115967	1.114373
112	4		*	1.142282	1.128945	1.130821	1.128945
113	3		*	1.133060	1.107899	1.109380	1.107899
114	3		*	1.124842	1.129428	1.131310	1.129428
115	4		*	1.115605	1.107283	1.108749	1.107283
116	4		*	1.122209	1.127511	1.129358	1.127511
117	4		*	1.114873	1.106484	1.107933	1.106485
118	4		*	1.114470	1.108847	1.110336	1.108847
119	3	19	*	1.113390	1.117847	1.054456	1.053068
120	4			1.129722	1.113230	1.114799	1.113230
121	4			1.129681	1.111409	1.112945	1.111409
122	3	1	*	1.115350	1.128496	1.130003	1.128138
123	5	1	*	1.121247	1.109960	1.109625	1.108113
124	5	1		1.112576	1.110597	1.107405	1.105875
125	4			1.137505	1.114686	1.116282	1.114686
126	4			1.124126	1.112283	1.113837	1.112283
127	5	1	*	1.126961	1.128233	1.127778	1.125921
128	4		*	1.124848	1.127021	1.128861	1.127021
129	4			1.107669	1.112635	1.114196	1.112635
130	4	1		1.132139	1.132283	1.131413	1.129521
131	5			1.122980	1.119748	1.121429	1.119749
132	5	1		1.148624	1.120969	1.120048	1.118343
133	4	2	*	1.148143	1.127948	1.124944	1.123095
134	4		*	1.128238	1.126995	1.128835	1.126995
135	3		*	1.147199	1.128243	1.130105	1.128243
136	4	1		1.126939	1.117898	1.117328	1.115676
137	2			1.122196	1.119889	1.121577	1.119889
138	4	2		1.115241	1.117841	1.119177	1.117526
139	3			1.114191	1.113055	1.114622	1.113055
140	3			1.117113	1.121265	1.122978	1.121265
141	5			1.107895	1.125550	1.127337	1.125550
142	4		*	1.121672	1.107422	1.108894	1.107422
143	5			1.115994	1.114262	1.115849	1.114262
144	4			1.117907	1.109765	1.111275	1.109765
145	5		*	1.115761	1.107262	1.108727	1.107262
146	5			1.140300	1.111096	1.112629	1.111097

147	5	1	*	1.130317	1.126532	1.127444	1.125617
148	5			1.121524	1.116191	1.117815	1.116191
149	4			1.120792	1.110314	1.111833	1.110314
150	4			1.111914	1.115522	1.117132	1.115522
151	4			1.111780	1.116144	1.117761	1.116144
152	5			1.121566	1.115951	1.117571	1.115951
153	3			1.107938	1.118746	1.120411	1.118746
154	4			1.109820	1.115043	1.116650	1.115043
155	5			1.127229	1.110356	1.111874	1.110356
156	6	1		1.131659	1.115994	1.117607	1.115988
157	5			1.106596	1.109899	1.111412	1.109899
158	5			1.108495	1.112257	1.113813	1.112257
159	5			1.110055	1.117003	1.118639	1.117003
160	4			1.122692	1.114369	1.115963	1.114369
161	4		*	1.128521	1.129164	1.131041	1.129164
162	6	1		1.128120	1.110355	1.107448	1.105933
163	5		*	1.116388	1.127532	1.129380	1.127532
164	6			1.114762	1.113156	1.114724	1.113156
165	5			1.116412	1.105921	1.107363	1.105921
166	6		*	1.116223	1.107445	1.108915	1.107445
167	5	3	*	1.121704	1.124631	1.124045	1.122253
168	6	1	*	1.119425	1.112772	1.111742	1.110178
169	5		*	1.119495	1.106379	1.107839	1.106379
170	6	1	*	1.115031	1.126283	1.127729	1.125905
171	6		*	1.106223	1.126592	1.128425	1.126592
172	5		*	1.107910	1.106439	1.107890	1.106439
173	5	2	*	1.111386	1.126203	1.123822	1.122002
174	4		*	1.115417	1.107513	1.108983	1.107513
175	4			1.116807	1.117985	1.119640	1.117985
176	4	1		1.114972	1.117171	1.114401	1.112768
177	5		*	1.117670	1.107284	1.108753	1.107284
178	5			1.107109	1.111298	1.112837	1.111298
179	3		*	1.120564	1.127873	1.129730	1.127873
180	4		*	1.130065	1.108054	1.109561	1.108054
181	3		*	1.128274	1.107799	1.109306	1.107799
182	3		*	1.137108	1.106912	1.108374	1.106912
183	4		*	1.108495	1.126874	1.128713	1.126874
184	3		*	1.122160	1.106129	1.107575	1.106129
185	6			1.129168	1.105756	1.107195	1.105756
186	6			1.129087	1.128712	1.130546	1.128712

187	4		1.127980	1.135736	1.137668	1.135736
188	5		1.121325	1.114184	1.115768	1.114184
189	5		1.108562	1.115500	1.117107	1.115500
190	4	*	1.114784	1.106854	1.108323	1.106854
191	4		1.128951	1.114468	1.116061	1.114468
192	4		1.127090	1.109579	1.111087	1.109579
193	5	*	1.127284	1.126482	1.128311	1.126482
194	3		1.107654	1.118375	1.120032	1.118375
195	3		1.117244	1.119180	1.120853	1.119180
196	3	*	1.109430	1.127368	1.129214	1.127368
197	4	*	1.112314	1.129082	1.130960	1.129082
198	5	*	1.122882	1.127466	1.129313	1.127466
199	5		1.114402	1.113300	1.114873	1.113300
200	4		1.117487	1.125088	1.126862	1.125089

* structure omitted from ensemble of 122 RS configurations for isotopic substitution in cyanide anion

nu-¹⁵N/¹⁴N isotopic partition-function ratios for (NC⁻...EtCl).*n*DMSO reactant structures:

structure sequence number	number <i>n</i>	extra imaginaries	abnormal*	extra imaginaries treated as reals		extra imaginaries omitted	
				300 K	303.15K	300 K	303.15K
				<i>f</i> _{RS}	<i>f</i> _{RS}	<i>f</i> _{RS}	<i>f</i> _{RS}
1	4		*	1.078916	1.076604	1.077630	1.076604
2	5	1		1.078968	1.078029	1.079080	1.078025
3	4			1.078605	1.079064	1.080143	1.079064
4	4			1.079173	1.076945	1.077978	1.076945
5	4			1.083022	1.080407	1.081513	1.080407
6	7		*	1.078717	1.081513	1.082640	1.081513
7	3		*	1.082732	1.080556	1.081664	1.080556
8	6	1	*	1.082689	1.081216	1.080725	1.079606
9	5			1.083151	1.080580	1.081688	1.080580
10	1	10	*	1.082310	1.077139	1.039249	1.038273
11	4	1	*	1.078953	1.081388	1.082497	1.081371
12	3			1.082455	1.082171	1.083292	1.082171
13	4			1.078682	1.081163	1.082283	1.081164
14	5			1.082916	1.079418	1.080503	1.079418
15	5			1.078497	1.077309	1.078350	1.077309
16	4	2		1.082900	1.078705	1.079311	1.078241
17	7	1		1.078455	1.077605	1.078424	1.077376
18	5			1.077795	1.078025	1.079084	1.078025
19	3			1.086346	1.077676	1.078724	1.077676
20	2		*	1.078386	1.081647	1.082778	1.081647
21	3		*	1.078306	1.082123	1.083262	1.082123
22	5			1.082686	1.079027	1.080102	1.079027
23	2			1.078566	1.079052	1.080131	1.079052
24	4			1.078552	1.077057	1.078094	1.077057
25	3			1.078846	1.081710	1.082833	1.081710
26	5			1.078878	1.079729	1.080821	1.079729

27	6		*	1.082883	1.080318	1.081421	1.080317
28	5			1.082558	1.080074	1.081174	1.080074
29	6		*	1.078761	1.076345	1.077371	1.076344
30	5	1	*	1.081919	1.081982	1.083118	1.081981
31	4			1.080174	1.079078	1.080156	1.079078
32	3			1.079941	1.083850	1.084994	1.083850
33	2			1.082265	1.083196	1.084326	1.083196
34	5			1.082276	1.080735	1.081849	1.080735
35	6			1.082965	1.083496	1.084632	1.083496
36	6			1.079877	1.079723	1.080815	1.079723
37	5			1.079345	1.078963	1.080038	1.078963
38	5			1.079628	1.077547	1.078593	1.077547
39	4			1.079944	1.078651	1.079721	1.078651
40	5	1		1.080354	1.078434	1.079483	1.078419
41	5		*	1.081081	1.077026	1.078062	1.077026
42	4			1.077840	1.078827	1.079899	1.078827
43	2			1.078757	1.078292	1.079351	1.078292
44	6			1.078233	1.078008	1.079062	1.078008
45	5	1		1.077536	1.077825	1.078406	1.077355
46	4			1.078913	1.082783	1.083927	1.082783
47	4	1	*	1.082169	1.082901	1.084055	1.082901
48	3			1.079121	1.077900	1.078953	1.077900
49	4			1.078569	1.079637	1.080729	1.079637
50	4			1.079304	1.077224	1.078262	1.077224
51	4			1.079421	1.077484	1.078528	1.077484
52	3			1.080193	1.079057	1.080134	1.079057
53	4		*	1.079334	1.077190	1.078231	1.077190
54	4	1	*	1.078151	1.077662	1.076424	1.075370
55	2			1.077803	1.080367	1.081472	1.080367
56	3		*	1.078780	1.082377	1.083524	1.082377
57	2			1.077935	1.077329	1.078373	1.077329
58	6		*	1.078393	1.076933	1.077970	1.076933
59	2			1.078965	1.077468	1.078514	1.077468
60	2			1.078772	1.079179	1.080260	1.079179
61	4		*	1.083053	1.081217	1.082338	1.081217
62	6		*	1.078518	1.081005	1.082122	1.081005
63	4	1	*	1.082441	1.078668	1.079733	1.078661
64	4			1.078863	1.077704	1.078753	1.077704
65	2			1.078813	1.078464	1.079529	1.078464
66	4			1.077995	1.078267	1.079327	1.078267

67	3			1.082142	1.078923	1.079999	1.078923
68	6			1.078992	1.078932	1.080008	1.078932
69	5			1.078494	1.078809	1.079879	1.078809
70	7	1		1.082392	1.078127	1.078241	1.077182
71	3			1.082071	1.077036	1.078073	1.077036
72	5		*	1.077754	1.077141	1.078180	1.077141
73	5			1.082265	1.077823	1.078873	1.077823
74	3			1.077839	1.078174	1.079233	1.078174
75	4			1.080175	1.078806	1.079880	1.078806
76	4	1		1.078930	1.078183	1.077440	1.076381
77	6			1.077284	1.077813	1.078865	1.077813
78	2		*	1.078194	1.084571	1.085763	1.084571
79	5			1.082461	1.078625	1.079694	1.078625
80	5		*	1.087466	1.082574	1.083723	1.082574
81	3	1	*	1.087516	1.080770	1.081882	1.080769
82	4			1.078959	1.081575	1.082697	1.081575
83	0			1.082559	1.075715	1.076724	1.075715
84	4			1.076912	1.079057	1.080135	1.079057
85	5		*	1.077580	1.081825	1.082957	1.081825
86	7	2	*	1.081262	1.081597	1.080911	1.079783
87	6			1.083027	1.079756	1.080848	1.079756
88	2			1.078397	1.079149	1.080229	1.079149
89	5		*	1.079351	1.076985	1.078021	1.076985
90	2			1.078624	1.078063	1.079121	1.078062
91	4		*	1.078874	1.082102	1.083239	1.082102
92	3		*	1.078489	1.081387	1.082512	1.081387
93	6		*	1.082627	1.081307	1.082432	1.081307
94	1			1.080301	1.076993	1.078029	1.076993
95	2			1.080130	1.077863	1.078916	1.077863
96	4		*	1.082969	1.085721	1.086936	1.085721
97	3			1.083676	1.076895	1.077927	1.076895
98	4			1.082684	1.080131	1.081230	1.080131
99	4			1.079258	1.076934	1.077964	1.076934
100	4			1.080809	1.078171	1.079230	1.078171
101	3			1.077630	1.077863	1.078916	1.077863
102	5			1.079084	1.077914	1.078968	1.077914
103	5		*	1.080143	1.077556	1.078605	1.077556
104	4			1.077978	1.078115	1.079173	1.078115
105	5		*	1.081513	1.081887	1.083022	1.081887
106	4			1.082640	1.077668	1.078717	1.077668

107	5	3	*	1.081664	1.081603	1.082363	1.081234
108	4	2	*	1.082336	1.081561	1.082067	1.080940
109	3	1	*	1.081688	1.082014	1.078638	1.077507
110	4			1.078171	1.081189	1.082310	1.081189
111	3			1.082514	1.077899	1.078953	1.077899
112	4		*	1.083292	1.081331	1.082455	1.081331
113	3		*	1.082283	1.077634	1.078682	1.077634
114	3		*	1.080503	1.081784	1.082916	1.081784
115	4		*	1.078350	1.077453	1.078497	1.077453
116	4		*	1.079776	1.081768	1.082900	1.081768
117	4		*	1.078653	1.077409	1.078455	1.077409
118	4		*	1.079084	1.076764	1.077795	1.076764
119	3	19	*	1.078724	1.085176	1.038021	1.037016
120	4			1.082778	1.077344	1.078386	1.077344
121	4			1.083262	1.077265	1.078306	1.077265
122	3	1	*	1.080102	1.081558	1.082488	1.081360
123	5	1	*	1.080131	1.077521	1.076945	1.075901
124	5	1		1.078094	1.077499	1.069673	1.068629
125	4			1.082833	1.077794	1.078846	1.077794
126	4			1.080821	1.117970	1.078878	1.077824
127	5	1	*	1.081423	1.081750	1.077785	1.076657
128	4		*	1.081174	1.081433	1.082558	1.081433
129	4			1.077372	1.077713	1.078761	1.077713
130	4	1		1.083118	1.080808	1.078727	1.077619
131	5			1.080156	1.079096	1.080175	1.079096
132	5	1		1.084994	1.078868	1.073107	1.072041
133	4	2	*	1.084326	1.081145	1.075363	1.074250
134	4		*	1.081849	1.081156	1.082276	1.081156
135	3		*	1.084632	1.081832	1.082965	1.081832
136	4	1		1.080815	1.078806	1.078250	1.077181
137	2			1.080038	1.078284	1.079345	1.078284
138	4	2		1.078593	1.078560	1.079404	1.078337
139	3			1.079721	1.078868	1.079944	1.078868
140	3			1.079498	1.079272	1.080354	1.079272
141	5			1.078062	1.079983	1.081081	1.079983
142	4		*	1.079899	1.076807	1.077840	1.076807
143	5			1.079350	1.077708	1.078757	1.077708
144	4			1.079062	1.077192	1.078233	1.077192
145	5		*	1.078876	1.076511	1.077536	1.076511
146	5			1.083927	1.077860	1.078913	1.077860

147	5	1	*	1.084055	1.081051	1.081420	1.080303
148	5			1.078953	1.078064	1.079121	1.078064
149	4			1.080729	1.077524	1.078569	1.077524
150	4			1.078262	1.078244	1.079304	1.078244
151	4			1.078528	1.078358	1.079421	1.078358
152	5			1.080134	1.079113	1.080193	1.079113
153	3			1.078231	1.078273	1.079334	1.078273
154	4			1.078718	1.077116	1.078151	1.077116
155	5			1.081472	1.076771	1.077803	1.076771
156	6	1		1.083524	1.077730	1.078770	1.077720
157	5			1.078373	1.076902	1.077935	1.076902
158	5			1.077970	1.077352	1.078393	1.077352
159	5			1.078514	1.077912	1.078965	1.077912
160	4			1.080260	1.077722	1.078772	1.077722
161	4		*	1.082338	1.081917	1.083053	1.081917
162	6	1		1.082122	1.077470	1.074838	1.073795
163	5		*	1.079741	1.081317	1.082441	1.081316
164	6			1.078753	1.077812	1.078863	1.077812
165	5			1.079529	1.077760	1.078813	1.077760
166	6		*	1.079327	1.076960	1.077995	1.076960
167	5	3	*	1.079999	1.081022	1.077919	1.076805
168	6	1	*	1.080008	1.077932	1.076262	1.075204
169	5		*	1.079879	1.077444	1.078494	1.077444
170	6	1	*	1.079186	1.081268	1.081857	1.080734
171	6		*	1.078073	1.080954	1.082071	1.080954
172	5		*	1.078180	1.076722	1.077754	1.076722
173	5	2	*	1.078873	1.081144	1.074379	1.073267
174	4		*	1.079233	1.076806	1.077839	1.076806
175	4			1.079880	1.079096	1.080175	1.079096
176	4	1		1.079245	1.077876	1.074633	1.073583
177	5		*	1.078865	1.076262	1.077284	1.076262
178	5			1.085763	1.077158	1.078194	1.077158
179	3		*	1.079694	1.081337	1.082461	1.081337
180	4		*	1.083723	1.086243	1.087466	1.086243
181	3		*	1.081882	1.086291	1.087516	1.086291
182	3		*	1.082697	1.077903	1.078959	1.077903
183	4		*	1.076724	1.081432	1.082559	1.081432
184	3		*	1.080135	1.075897	1.076912	1.075897
185	6			1.082957	1.076549	1.077580	1.076549
186	6			1.082727	1.080162	1.081262	1.080162

187	4		1.080848	1.081901	1.083027	1.081901
188	5		1.080229	1.077355	1.078397	1.077355
189	5		1.078021	1.078289	1.079351	1.078289
190	4	*	1.079121	1.077569	1.078624	1.077569
191	4		1.083239	1.077822	1.078874	1.077822
192	4		1.082512	1.077443	1.078489	1.077443
193	5	*	1.082432	1.081500	1.082627	1.081500
194	3		1.078029	1.079222	1.080301	1.079222
195	3		1.078916	1.079052	1.080130	1.079052
196	3	*	1.086936	1.081835	1.082969	1.081835
197	4	*	1.077927	1.082527	1.083676	1.082527
198	5	*	1.081230	1.081556	1.082684	1.081556
199	5		1.077964	1.078199	1.079258	1.078199
200	4		1.079229	1.079717	1.080810	1.079718

* structure omitted from ensemble of 122 RS configurations for isotopic substitution in cyanide anion