Dynamic NMR Study of 1,3,5,7-Tetraoxacyclooctane in Liquid and Liquid Crystalline Solutions and in the Solid State

L. Calucci,^{†,‡} H. Zimmermann,[§] R. Poupko,[‡] and Z. Luz*,[‡]

The Weizmann Intitute of Science, 76100 Rehovot, Israel, and Max-Planck-Institut für Medizinische Forschung, AG Molekülkristalle, Heidelberg, Germany

Received: May 30, 1995[®]

Deuterium, proton, and carbon-13 NMR spectra of 1,3,5,7-tetraoxacyclooctane (tetroxocane) were recorded in liquid crystalline and isotropic solutions as well as in the solid state. In solution, tetroxocane exists as a mixture of the boat—chair (BC) and crown (Cr) conformers. Pseudorotation and inversion is extremely fast in the BC form, while inversion in the crown conformer is relatively slow (on the NMR time scale). Analysis of the NMR line shape and 2D exchange experiments shows that the ring inversion in the Cr form occurs via the BC form. Interconversion rate constants and equilibrium constants between the two forms over a wide temperature range were determined in several normal and liquid crystalline solvents. In the solid state tetroxocane crystallizes in a (slightly distorted) crown form. Deuterium NMR in a powder sample of solid tetroxocane- d_8 exhibits dynamic spectra consistent with molecular 4-fold jumps about their pseudo- C_4 axes. Quantitative analysis of the dynamic line shape is consistent with a small C_2 deformation of the molecule, as found previously by X-ray analysis, and yields the following kinetic equation for the jump rate, k_J (s⁻¹) = 5.9 $\times 10^{16}$ exp (-15.9/RT), where R is in kcal mol⁻¹ K⁻¹.

Introduction

The structure of the eight-member cyclic ether, 1,3,5,7tetraoxacyclooctane (tetroxocane), was the subject of numerous experimental investigations in the gas¹, liquid,²⁻⁵ and solid states,⁶⁻⁸ as well as of theoretical studies of its various conformations in the free state.⁹ These studies show that in the gas phase and in solution tetroxocane exists predominantly as a mixture of two conformers (Figure 1): boat-chair (BC) (or a family of distorted BCs) and crown (Cr) (or a family of distorted Cr's, particularly chair-chair), with relative concentrations depending on the temperature and the nature of the solvent.¹⁰⁻¹² Dynamic NMR studies in solution provided estimates for the thermodynamic and kinetic parameters relating the two major conformers. The results show^{2,3} that pseudorotation and inversion of the BC conformations is extremely fast even at very low temperatures, while inversion of the crown form is very slow. In fact, on the basis of energy considerations, Anet has proposed¹⁰ that the crown conformer undergoes inversion only via the BC form a direct inversion being energetically unfavorable. In the first part of the present work we prove this supposition and determine accurate kinetic parameters for the interconversion of the tetroxocane conformers and their equilibria in solutions, by various NMR techniques. These include deuterium 2D-exchange experiments in liquid crystalline solutions,^{13,14} as well as detailed line shape analysis of ¹H and ¹³C NMR spectra in normal (isotropic) liquids.

The solid state properties of tetroxocane, in particular with regard to its polymerization to poly(oxymethylene) have been extensively investigated by Wegner et al.¹⁵ So far, however, no dynamic NMR studies of neat tetroxocane in the solid state were reported. Crystallographic measurements⁶ indicate that tetroxocane crystallizes in the monoclinic space group C2/c, with four symmetry-related molecules per unit cell. The



Figure 1. Schematic representation of the boat—chair (BC) and crown (Cr) forms of tetroxocane, a projection of the molecular structure in the solid state down the C_2 axis and the coordinate system used to describe the C–D bond orientation.

molecules have a slightly distorted crown shape with approximately $C_{4\nu}$ (exact C_2) symmetry. We have used deuterium NMR analysis of a tetroxocane- d_8 sample to study its dynamic properties in the solid state. The results confirm the distorted crown structure of tetroxocane in the crystalline state and also show that the molecules undergo 4-fold jumps about their pseudo- C_4 axes.

Experimental Section

A. Materials. Tetroxocane was first prepared by Staudiger,¹⁶ 70 years ago, via thermal decomposition of a high molecular weight poly(oxymethylene diacetate) in vacuum. For the present work we scaled down an industrial process based on a Belgian patent¹⁷ involving acid-catalyzed condensation of formaldehyde (or deuterated formaldehyde for tetroxocane- d_8). To 500 mL of 1,1,2,2-tetrachloroethane was added a suspension of 9 g of (CH₂O) in 10 mL of H₂O (or (CD₂O) in D₂O), and

[†] Permanent address: Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa, 56126 Pisa Italy.

[‡] The Weizmann Institute of Science.

[§] Max-Planck-Institut für Medizinische.

[®] Abstract published in Advance ACS Abstracts, September 1, 1995.



Figure 2. (left) Deuterium quadrupole echo spectra ($\tau = 20 \ \mu$ s) of tetroxocane- d_8 in two nematic solvents as function of temperature. The concentrations were 1.96 wt % in Phase V and 1.35 wt % in ZLI2452. Each spectrum is the sum of 10 000-60 000 scans, depending on the line width. The recycle time was 0.8 s. (right) Simulated dynamic spectra with the indicated rate constants. The exchange-independent line widths, $1/T_2$, used in the calculations were 630 s⁻¹ for Phase V and 1250 s⁻¹ for ZLI2452.

the resulting mixture was vigorously stirred at 100 °C. The acid catalyst 5-amino-2-naphthalenesulfonic acid (0.4 g) was then added while the color changed to red and the paraformaldehyde slowly dissolved. After heating and stirring for 2 h the mixture was allowed to cool, and the clear solvent phase was separated and dried over K_2SO_4 . The first 400 mL was distilled off at atmospheric pressure. This was followed by a reduced pressure (10 mmHg) distillation, while the last 20 mL was carefully removed at room temperature using a closed vacuum system and a liquid nitrogen trap. The crystalline residue was recrystallized from ethanol/petroleum ether (40 °C), and vacuum sublimation at 80 °C in a sealed vial followed resulting in 380 mg of tetroxocane (mp 110–112 °C, bp 170 °C).

B. NMR Measurements. High-resolution proton and carbon-13 NMR measurements were performed on a Bruker AM500 spectrometer at 500 and 125.75 MHz, respectively. The deuterium NMR measurements of the liquid crystalline solutions and of the solid powder sample were performed on a Bruker CXP300 spectrometer at 47.06 MHz. These spectra were



Figure 3. Equilibrium ratios, [Cr]/[BC], for tetroxocane in different liquid crystalline and isotropic solvents, as a function of reciprocal absolute temperature.

recorded by the quadrupole echo sequence and, unless otherwise stated, with a time interval between the two $\pi/2$ pulses of $\pi = 20 \ \mu s$.

Results and Discussion

Deuterium NMR in Liquid Crystalline Solutions. Deuterium NMR spectra of tetroxocane- d_8 were recorded in two nematic solvents, viz., ZL12452 (Merck, Darmstadt) and Phase V (Merck, Darmstadt) (see Figure 2). Below room temperature the spectra, in both solvents, consist of three pairs of doublets: two outer pairs of equal integrated intensity, which are assigned to the Cr form, and an inner more intense pair, due to the BC conformer. The assignment is based on previous observations which indicated that only these conformers are present in solution with the BC undergoing fast pseudorotation-inversion.²⁻⁵ This process averages out the quadrupolar interactions of all methylene deuterons in the molecule, resulting in a single sharp doublet. The two crown doublets correspond to the axial (outer pair) and equatorial deuterons as indicated in the low-temperature spectra in Figure 2. This assignment is based on the fact that in the crown form with average C_{4v} symmetry, the C-D^{ax} bonds are nearly parallel to the C_4 axis, while the C-D^{eq} are more nearly perpendicular to this axis. The ratio of the two doublet splittings is 2.03, especially independent of temperature (below room temperature) and of the nematic solvent. For exact C_{4v} symmetry this ratio should be

$$R = \frac{\langle \nu_q^{ax} \rangle}{\langle \nu_q^{eq} \rangle} = \frac{\nu_q^{ax} S^1 /_2 (3 \cos^2 \beta^{ax} - 1)}{\nu_q^{eq} S^1 /_2 (3 \cos^2 \beta^{eq} - 1)}$$
(1)

where $\langle v_q^i \rangle$ is half of the observed doublet splitting of the *i*th deuteron, v_q^i is its static quadrupole interaction constant, S is the orientational order parameter of the molecular C_4 axis, β^i is the angle between the C-D^{*i*} bond and C_4 (see Figure 1), and we assumed that the quadrupole interaction is axially symmetric along the corresponding C-D bond. Using the PC Model molecular mechanics program,¹⁸ we obtained for the crown form of tetroxocane, $\beta^{ax} = 9.0^{\circ}$ and $\beta^{eq} = 96.9^{\circ}$. Substituting in eq 1 with $v_q^{ax} = v_q^{eq}$ yields R = -2.01 in excellent agreement with the experimental (absolute) value of 2.03.

As the nematic solutions are heated to above room temperature (Figure 2) all lines broaden and eventually coalesce to a



Figure 4. Arrhenius plots of the Cr-BC interconversion rate constant, k_1 , in the different solvents studied, as obtained from the various NMR active nuclei.

single average doublet. Complete coalescence could only be observed in ZLI2452, where the clearing temperature is 110 °C, not in Phase V where the clearing point is 75 °C. To simulate these spectra we need to consider the following interconversion scheme

$$\begin{array}{c}
\text{BC} & \xrightarrow{k_{-1}} & \text{Cr} \\
\xrightarrow{k_p} & & \downarrow \\
\text{BC} & \xrightarrow{k_1} & \downarrow \\
\text{Cr} & & \downarrow \\$$

where k_p is the rate constant for combined pseudorotationinversion of the BC form, k_i the rate constant for the direct ring inversion of the Cr form, and k_1 , k_{-1} are the Cr-BC interconversion rate constants, with $k_{-1}/k_1 = [Cr]/[BC] = K$. This ratio can be determined from the relative intensities of the various peaks in the low-temperature spectra. It is plotted, together with results for the isotropic solutions, to be discussed later, in Figure 3.

For the simulation of the dynamic spectra we apply methods described earlier^{19,20} for deuterium NMR in ordered systems. Since the pseudorotation—inversion of the BC form completely averages the quadrupole interactions of all its deuterons, k_p drops out of the calculation and the problem reduces to that of jumps between three sites having the relative equilibrium populations, P_i : [Cr]/2, [Cr]/2, [BC], for respectively, the axial Cr, equatorial Cr, and BC forms with the following exchange matrix,

$$\mathbf{R}^{\mathrm{D}} = \begin{pmatrix} -k_{1} - k_{i} & k_{i} & k_{1}K \\ k_{i} & -k_{1} - k_{i} & k_{1}K \\ k_{1} & k_{1} & -2k_{1}K \end{pmatrix}$$
(3)

In practice it turned out that the spectra could be well simulated with just the Cr-BC interconversion rate constants, k_1 and $k_{-1} = k_1 K$, without including k_i . This confirms Anet's supposition¹⁰ that the crown interconversion does not occur directly but rather via the BC form. The rate constant, k_1 , obtained by fitting the experimental spectra with simulated spectra are plotted in Figure 4 (together with other results, to be discussed shortly). Examples of simulated spectra are shown in the right column of Figure 2. For these simulations it was necessary to know the variation of the $\langle v_q^i \rangle$'s with temperature and their relative signs. The latter were determined by the two-dimensional experiments described in the next paragraph, while the magnitude of the $\langle v_q^i \rangle$'s was determined by extrapolation of the low-temperature values and by best fitting to the experimental results. The observed splittings (experimental points) and extrapolated values (full curves) of the $\langle v_q^i \rangle$'s are plotted for the two solvents in Figure 5. For the ZLI2452 solvent the splitting of the coalesced doublet, $\langle \bar{v}_q \rangle$ (see triangles in Figure 5b) provided an additional check for the extrapolation procedure.

Further support for the negligibility of the direct interconversion of the crown form comes from 2D-exchange experiments performed on the Phase V solution.^{14,21} We have measured such 2D-exchange spectra at -3 °C, with mixing times ranging up to 10 ms. Examples for three τ_m values are shown in Figure 6. It may be seen that for intermediate $\tau_{\rm m}$'s $(\leq 2 \text{ ms})$ no cross peaks between the axial and equatorial signals of the crown form appear, while well-developed cross peaks with the BC forms are observed. At longer $\tau_{\rm m}$'s, axialequatorial cross peaks begin to appear, but they are formed via the Cr-BC interconversion process. This can readily be seen from the plots of the 2D-exchange peak intensities against $\tau_{\rm m}$, shown in Figure 7. While the diagonal peaks and the Cr-BC cross peaks decrease or increase linearly with τ_m (first order), the initial growth of the axial-equatorial cross peaks is quadratic (second order). This is in accord with the exchange matrix, eq 3, only if $k_i = 0$. In fact, the whole evolution of the 2D-exchange spectra is consistent with this exchange mechanism as demonstrated by the full lines in Figure 7 which were computed from the expression,

$$I_{ii}(\tau_{\rm m}) = \left[\exp(R^{\rm D}\tau_{\rm m})\right]_{ii}P_i \tag{4}$$

with $k_i = 0$, $k = 200 \text{ s}^{-1}$, and K = 1.44.

An important piece of additional information included in the 2D-exchange spectra of Figure 6 concerns the relative signs of the various quadrupole interactions. From the cross peak positions it may be seen that while the quadrupole interaction of the BC deuterons has the same sign as the axial crown deuterons, it is opposite to that of the equatorial ones. We have used this information in simulating the 1D spectra of Figure 2.

Proton and Carbon-13 NMR in Isotropic Solvents. We have extended the dynamic studies described above to two (deuterated) isotropic solvents, chloroform (CDCl₃) and acetonitrile (CD₃CN), using both proton and carbon-13 NMR. Examples of spectra are shown in Figures 8 and 9. The peak assignment is as determined by earlier work.²⁻⁴ The carbon-13 spectrum of tetroxocane at low temperatures consists of two unequal peaks due to the Cr (101.20 ppm in CDCl₃; 101.50 ppm in CD₃CN) and BC (92.34 ppm in CDCl₃; 92.87 in CD₃CN) conformers. The exchange matrix

$$\mathbf{R}^{\mathrm{C}} = \begin{bmatrix} -k_1 & k_1 K \\ k_1 & -k_1 K \end{bmatrix}$$
(5)

depends only on the Cr-BC interconversion, since all carbons in the crown form are equivalent, as they also are in the BC conformer, due to its fast pseudorotation-inversion.

The proton spectrum of tetroxocane at low temperatures consists of an AB quartet due to the crown protons (with J =8.70 Hz for CDCl₃ and 8.96 Hz for CD₃CN, and chemical shifts, δ , depending on the temperature and solvent) and a sharp singlet due to the BC form. The relative peak intensities in this



Figure 5. Observed quadrupole splittings, $\langle v_q^i \rangle$ (half the doublet separation), of the various tetroxocane- d_8 deuterons in the nematic solvents: Phase V (a) and ZLI2452 (b). The relative signs of the splittings were determined by the 2D-exchange experiments shown in Figure 6. The points are experimental while the full lines are the best fit values used to simulate the dynamic spectra in Figure 2. The triangles and associated line in (b) are the weight averaged splittings, $\langle \bar{v}_q \rangle$, of all doublets. The triangles at high temperatures are experimental, while at low temperatures they are calculated from the experimental points for the other doublets.



Figure 6. Deuterium 2D-exchange spectra of the Phase V solution described in the legend of Figure 2, at -3 °C and three mixing times as indicated. The dashed lines in the $\tau_m = 2$ ms spectrum link the first-order cross peaks of the BC with the axial and equatorial crown peaks. Those in the $\tau_m = 4$ ms spectrum link the second-order cross peaks of the axial and equatorial crown signals. Note the relative signs of the various quadrupole interactions.

spectrum are $[Cr](1 - \epsilon)/4$, $[Cr](1 + \epsilon)/4$, $[Cr](1 + \epsilon)/4$, $[Cr](1 - \epsilon)/4$, [BC], where $\epsilon = J/(J^2 + \delta^2)^{1/2}$, and the exchange matrix, \mathbf{R}^{H} is given in Chart 1.

CHART 1

The relative concentrations of the Cr and BC forms were measured from the peak intensities in both the carbon-13 and proton spectra at low temperature, and the results for the two solvents are plotted in Figure 3. These plots were extrapolated to higher temperature in order to obtain the relative concentrations in the dynamic region for the kinetic analysis. As for the liquid crystalline solutions the analysis of the NMR spectra showed that k_i is too slow to affect the line shape. The results for k_1 derived from the ¹H and ¹³C spectra in both isotropic solvents are included in Figure 4. It may be seen that k_1 values in the various isotropic and nematic solvents are quite similar, the deviations being within the range of the experimental uncertainty. An overall kinetic analysis yields the rate equation, $k_1 = \exp(\Delta S^{\dagger}/R) \exp(-\Delta H^{\dagger}/RT)$ with $\Delta S^{\dagger} = 0.7$ eu and $\Delta H^{\dagger} = 12.9$ kcal/mol. These results may be compared with the earlier values of ΔG^{\dagger} (258 K) = 12.0 kcal/mol in CHFCl₂ and ΔG^{\ddagger} (300 K) = 13.33 kcal/mol in chloroform.^{3,4}

The Cr-BC equilibrium constant, K, depends on the solvent and temperature as shown in Figure 3. Analysis of these results in terms of the equilibrium equation, $K = [Cr]/[BC] = \exp(\Delta S/$ R) $\exp(-\Delta H/RT)$ yields the enthalpy and entropy differences as summarized in Table 1. It may be noted that ΔS in all solvents is negative at approximately -7 eu. This suggests that the entropy difference between the Cr and BC forms is mainly due to internal degrees of freedom rather than due to interaction with the solvent. The higher entropy associated with the BC form most likely reflects its fluxional nature through which it undergoes fast pseudorotation-inversion. On the other hand the Cr form has a lower enthalpy than that of the BC form. The combined effects of ΔH and ΔS result in a dramatic inversion of the [Cr]/[BC] ratio: while at low temperature [Cr] > [BC], at high temperatures [BC] > [Cr] in all solvents. The most important effect of the solvent on K appears to be the



Figure 7. Plots of the relative peak intensities in the 2D-exchange spectra, of the type shown in Figure 6, as a function of the mixing time, τ_m . The filled symbols refer to the experimental diagonal peaks, the open triangles are sums over all the Cr-BC (Cr^{ax}-BC + Cr^{eq}-BC) cross peaks, and the open diamonds correspond to the pair of axial-equatorial cross peaks. The full lines are calculated using parameters given in the text.

stabilization of the Cr form, which has a larger electric dipole moment compared to BC, by the solvent polarity as reflected in the higher values determined in acetonitrile. Another point to notice is the fact that k_1 is nearly the same in all solvents. Since K is solvent dependent this means that k_{-1} , which corresponds to the BC \rightarrow Cr interconversion, is different in the different solvent. Apparently the transition state is more similar to the crown form than it is to the BC.

Deuterium NMR in the Solid State. To learn about the dynamics of tetroxocane in the solid state we have recorded the deuterium quadrupole echo spectra of a powder crystalline sample of tetroxocane- d_8 over the temperature range -35-100°C. Examples of such spectra are shown in Figure 10. The low-temperature spectrum at -20 °C is typical of a rigid system and corresponds to a superposition of a number of Pake doublets with slightly different quadrupolar interactions. This may reflect differences in the static v_q^i values for the axial and equatorial deuterons and perhaps also between different methylenes in the crystal; since the exact symmetry of the molecule is C_2 (rather than $C_{4\nu}$) the quadrupolar interactions of the various deuterons could be pairwise different. A fit to the observed spectrum could in fact be obtained with four equally intense axially symmetric Pake doublets, corresponding to two pairs of axial and two pairs of equatorial deuterons, with quadrupole interaction constants as summarized in Table 2A. The assignment to axial and equatorial splittings is based on the fitting of the dynamic spectra discussed below.

On heating to room temperature and above the spectra gradually broaden and exhibit clear dynamic features resulting at high temperatures (100 °C) in an averaged spectrum, consisting of a 1:1 superposition of two Pake doublets. One subspectrum is very nearly axially symmetric with $\langle \nu_q \rangle = 105.0$ kHz, while the second subspectrum is biaxial with $\langle \nu_q \rangle = 53.7$



Figure 8. (left) Proton and carbon-13 high-resolution spectra of a 2.5 wt % solution of tetroxocane in CD_3CN at different temperatures. (right) Simulated spectra using the indicated rate constants and the [Cr]/[BC] ratios in Figure 3.

kHz and an asymmetry parameter of $\eta = 0.14$. This evolution of the spectrum can readily be understood in terms of molecular 4-fold jumps about their pseudo- C_4 axes, with the axially symmetric subspectrum corresponding to the axial deuterons and the inner subspectrum to the equatorial deuterons. To simulate the spectra in the intermediate dynamic regime we used the following exchange matrix to represent the 4-fold jump process for, respectively, the four axial and four equatorial deuterons,

$$\mathbf{R}^{\mathrm{S}} = \begin{pmatrix} -k_{\mathrm{J}} & \frac{1}{2}k_{\mathrm{J}} & 0 & \frac{1}{2}k_{\mathrm{J}} \\ \frac{1}{2}k_{\mathrm{J}} & -k_{\mathrm{J}} & \frac{1}{2}k_{\mathrm{J}} & 0 \\ 0 & \frac{1}{2}k_{\mathrm{J}} & -k_{\mathrm{J}} & \frac{1}{2}k_{\mathrm{J}} \\ \frac{1}{2}k_{\mathrm{J}} & 0 & \frac{1}{2}k_{\mathrm{J}} & -k_{\mathrm{J}} \end{pmatrix}$$
(7)

The calculated line shapes turned out to be quite sensitive to the assumed orientations of the principal axes of the deuterium quadrupole interactions. For the initial calculations the orientations of the principal quadrupole axes were taken along the corresponding C-D bonds, as calculated from the crystal structure. According to Chatani et al.⁶ the deformation of the molecule from ideal $C_{4\nu}$ symmetry corresponds to a small elongation of the O³-O⁷ and a concomitant shortening of the O¹-O⁵ distances (see the molecular projection in Figure 1). The



Figure 9. Same as in Figure 8 but for a 3.5 wt % solution of tetroxocane in CDCl₃.

 TABLE 1: Equilibrium Constants ([Cr]/[BC]) and

 Thermodynamic Parameters for Tetroxoane in Various

 Solutions

solvent	K (298 K)	ΔH (kcal/mol)	ΔS (eu)	ref
Phase V	1.19	-2.30	-7.4	present work
ZLI2452	0.81	-2.88	-10.1	present work
CD ₃ CN	2.50	-2.74	-7.4	present work
CDCl ₃	0.74	-2.13	-7.7	present work
CDCl ₃	0.67	-2.30	-8.5	2
CHCl ₂ F	0.99	-1.78	-6.0	3

four carbons, however, still form a nearly perfect square. We define an orthogonal coordinate system with x along C^8-C^2 , y along $C^8 - C^6$, and z perpendicular to both, forming a righthanded system. In this coordinate system the planes of the CD₂ groups are twisted relative to the planes of the main diagonals, i.e., the azimuthal angles of the C-D bonds deviate from $\pm \pi/4$ or $\pm 3\pi/4$. It is this distortion that is responsible for the biaxiality of the average quadrupole tensor of the equatorial deuterons. The polar (β^i) and azimuthal (ϕ^i) angles of the various $C-D^i$ bonds in the x,y,z coordinate system, as calculated from the crystal structure, are summarized in the first line of Table 2B. When these values are used to simulate the dynamic line shapes, the general features of the experimental spectra, in particular the growth of the inner part of the spectrum due to the equatorial deuterons, clearly show up. However, in detail the fit is not perfect, notably the frequencies of the singularities due to these deuterons deviated from their exact experimental positions. We found that the fit could be improved considerably



Figure 10. (left) deuterium NMR spectra of a powder sample of deuterated tetroxocane- d_8 as function of temperature using the quadrupole echo sequence with $\tau = 20 \ \mu$ s. Each spectrum is a sum of about 240 scans, and the recycle time ranged from 2 s at high temperatures to 10 min at low temperatures. (right) simulated dynamic spectra for the indicated k_1 values, using the parameters of Table 2 and $1/T_2 = 2200 \ s^{-1}$ (except for the $-20 \ ^{\circ}$ C spectrum for which $1/T_2 = 5500 \ s^{-1}$ was taken).

TABLE 2: Magnetic and Geometric Parameters forTetroxocane Used To Simulate the Solid State DeuteriumNMR Spectra in Figure 10. The Atomic Labeling Is as inFigure 1

A. Quadrupole Interactions					
methylene groups	v ^{ax} (kHz)	$\nu^{eq} \left(kHz \right)$			
2, 6	117.5	124.0			
4, 8	112.5	126.0			

B. Geometrical F	Parameters
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	C-D ² bond			C-D ⁸ bond ^c				
	β^{ax}	$eta^{ ext{eq}}$	ϕ^{ax}	$\phi^{ m eq}$	β^{ax}	$eta^{ ext{eq}}$	ϕ^{ax}	$\phi^{ m eq}$
cryst ^a NMR ^b	12.7 12.7	100.8 100.8	124.9 124.9	135.5 136.4	4.4 4.4	103.5 103.5	24.5 24.5	44.8 43.9

^{*a*} Values calculated from the crystal structure (ref 6). ^{*b*} Values actually used for the line shape simulations. ^{*c*} The corresponding values for the C–D⁶ and C–D⁸ bonds are $\beta(6) = \beta(2)$; $\beta(4) = \beta(8)$; $\phi(6) = \phi(2) + \pi$; $\phi(4) = \phi(8) + \pi$.

by slightly adjusting the aximuthal angles of the equatorial deuterons as shown in the second line of Table 2B. The spectra calculated with these modified angles are shown in the right column of Figure 10. The derived Arrhenius plot for the jump rate constant, k_J , is given in Figure 11. It corresponds to the rate equation

$$k_{\rm r}({\rm s}^{-1}) = 5.9 \times 10^{16} \exp(-15.9/RT)$$

The deviation of the adjusted ϕ^{i} 's from those calculated from the crystallographic data is quite small (<1°) and may indicate that the unique quadrupole axis is not exactly along the C–D bond. The fitting could probably be further improved by adjusting other parameters such as the β^{ax} 's and the ν_q 's and by introducing a small biaxiality to the static quadrupole interaction. In view of the good fit of the simulated and experimental spectra, obtained with minimal adjustable parameters, this was not deemed necessary. At any rate, it would



Figure 11. An Arrhenius plot of the rate constants for the 4-fold jumps, k_J , in solid tetroxocane, as derived from simulations of the type shown in Figure 10.

not have changed to any significant extent the kinetic parameters derived for the jump process. It should be emphasized that this process interchanges all axial and likewise all equatorial deuterons but does not involve ring inversion that interchanges the two types of deuterons, as it does e.g. in "merry go round" types of motions.²² The situation is more similar to that observed in the lower homologue of the cyclic polyether family, trioxane,²³ where at around room temperature an almost identical rate constant of ~10⁵ s⁻¹ was also observed for the corresponding 3-fold jump process.

Acknowledgment. This research was partly supported by the Israel Science Foundation administered by the Israel Academy of Sciences and Humanities and by the MINERVA Foundation, Münich Germany. L.C. thanks Pisa University for an Exchange Fellowship to the Weizmann Institute.

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JP9514842