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Cope Rearrangement in Bullvalene by Dynamic Deuterium NMR Spectroscopy in Liquid Crystalline Solvents

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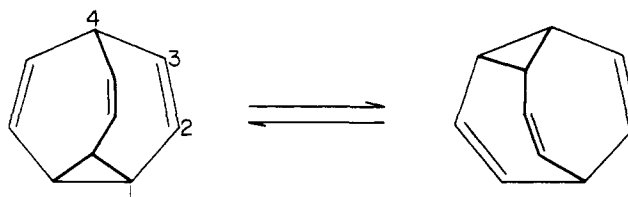
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Abstract: Deuterium NMR of deuterated bullvalene dissolved in liquid crystalline solvents was studied as function of temperature, in the range -35 to $+115$ °C. In this region the spectral line shape is strongly temperature dependent due to the Cope rearrangement process. At the low end of the temperature range four distinct quadrupole doublets with relative intensities 3:3:3:1, due to the four inequivalent groups of deuterons, are observed. As the temperature is raised above about -15 °C, line broadening sets in followed by coalescence of the spectrum into a single doublet. Comparison of the experimental results with theoretically simulated spectra gave the following kinetic parameters for the Cope rearrangement reaction: $1/\tau$ (300 °C) = 4.6×10^3 s⁻¹, E_a = 13.9 kcal/mol, ΔH^\ddagger = 13.3 kcal/mol, ΔS^\ddagger = +2.5 eu.

Line-shape analysis of NMR spectra in normal liquids has been extensively used to study rates and mechanisms of dynamic processes in liquids.^{1,2} The range of reaction rates accessible by this method depends on the magnitude of the interactions that are modulated by the dynamic process. For ¹H and ¹³C NMR these interactions are the spin-spin coupling and the chemical shift which for the latter nucleus may reach several kHz, thus making it possible to study processes as fast as 10⁶ s⁻¹ and higher.

In recent years we have shown that in certain cases the dynamic range accessible by the NMR method may be extended even further by using liquid crystals rather than normal liquids as solvents.³ In such solvents the spectrum is affected by additional interactions, i.e., dipole-dipole, and for nuclei with spins $I \geq 1$ also by quadrupolar interactions. These interactions may be considerably larger than the chemical shifts or the spin-spin couplings and thus may allow the determination of much faster rates. Also, for ¹H NMR results taken in liquid crystals the spectrum which is dominated by dipolar interactions is generally of the strong interaction type, and therefore the dynamic spectrum may provide mechanistic details that cannot always be obtained in normal fluids. On the other hand the complexity of the ¹H NMR spectra, in particular of medium and large molecules, often renders their interpretation extremely difficult.⁴⁻⁶

Deuterium NMR spectroscopy of deuterated compounds dissolved in liquid crystals may be more useful and is relatively easy to interpret: In this case, the dominant effect is usually due to the quadrupolar interaction while dipolar couplings are small and may be neglected. Thus, any reaction that modulates the quadrupolar interaction will in principle affect the spectral line shape and may be studied by this method.^{7,8} In the present paper we have used this approach to study the kinetics of the Cope rearrangement in bullvalene using partially deuterated bullvalene. This reaction was studied over the years by several research



groups⁹⁻¹⁶ using ¹H and ¹³C NMR spectroscopy, including more recently a new type of 2D spectroscopy.¹⁶ The present results substantiate the earlier findings and demonstrate the possibilities and advantages of using deuterium NMR spectroscopy in liquid crystalline solvents for dynamic studies.

Experimental Section

Materials. Partially deuterated bullvalene was obtained from the normal compound by exchange with tri-*n*-butylcarbinol-*d* under strongly

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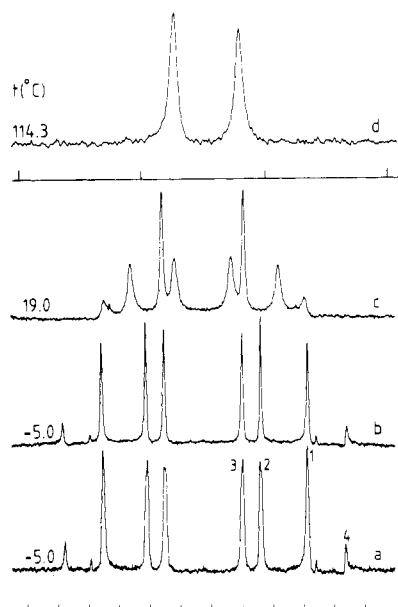


Figure 1. Deuterium NMR spectra of partially deuterated bullvalene dissolved in nematic liquid crystals. Traces a and b correspond to a 3.8 wt % solution in ZLI2452 and were recorded respectively without and with proton decoupling. Trace c is of the same solution (without proton decoupling) but at a somewhat higher temperature as indicated. Trace d is of a 4.7 wt % solution in DHAB. The assignment of the deuteron peaks in the bottom trace is made according to the numbering system of Figure 2. (The weak peaks between lines 1 and 4 are due to impurities.) The frequency markers are 5 kHz apart.

basic (*n*-Bu₃COK) conditions.¹⁷ For the success of the exchange reaction it is crucial to work under absolutely anhydrous conditions. The reaction was therefore carried out in a vacuum manifold in the following way: Potassium metal and subsequently carbinol-*d* (kept over LiAlD₄) were distilled from different side arms in several steps into the reaction cell containing about 200 mg of bullvalene. The reaction cell was then sealed off and placed in an oven at 180 °C for 10 days. Subsequently, the bullvalene was sublimed out from the reaction mixture in a high vacuum system onto a "cold finger" and further purified by repeated sublimations. The degree of deuteration was estimated from mass spectrometry to be about 25–30 atom %.

Three different liquid crystals were used: (i) Phase V Licristal (Merck, Darmstadt), which is a nematic mixture that can readily be supercooled down to -40 °C (its clearing point is 75 °C but is considerably reduced when solute is added); (ii) ZLI2452 (Merck, Darmstadt) which is also a nematic mixture (clearing point 110 °C) (it is quite fluid down to -35 °C and becomes smectic at around -40 °C); and (iii) DHAB (dihexyloxyazoxybenzene, Eastman Kodak Inc.), which has a nematic phase in the range 80–128 °C. The anisotropic magnetic susceptibility of all three solvents is positive, i.e., in all cases the director aligns parallel to the magnetic field direction.

Solutions were prepared by dissolving approximately 25 mg of the deuterated bullvalene in 500 mg of solvent and sealing the solution in 10-mm sample tubes for the NMR measurements.

NMR Measurements. The deuterium NMR spectra of the bullvalene solutions were recorded on a Bruker CXP300 spectrometer at 46.07 MHz, using the quadrupole echo method. This method consists of a series of [90°_x-*t*-90°_y-*t*-acquisition]_{*n*} pulse cycles, in which the acquisition corresponds to the second half of the echo signal starting at time *t* after the second pulse. Fourier transformation of this signal gives the desired spectrum. The rf power used was such that the 90° pulses had durations of about 14 μs. The number of accumulations, *n*, ranged between 400 and 4000 depending on the width of the spectral lines and the desired signal-to-noise ratio. The time interval between pulses, *t*, was usually 30 μs, but it could be varied over wide ranges. The quadrupole echo method was used in order to eliminate line-shape distortion of broad spectra that might occur due to dead-time problems in single pulse experiments. It should be noted however that the dynamic line shape might depend on the time interval, *t*, between the two 90° pulses, in particular when *t* is of the order of the correlation time of the reaction.¹⁸ To check

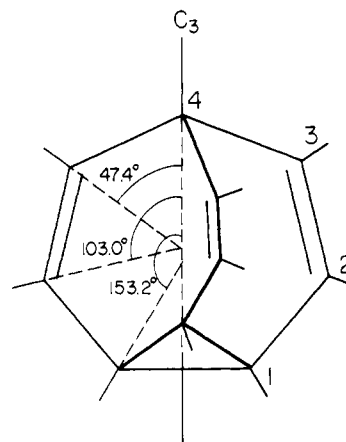


Figure 2. Numbering system and a molecular model of bullvalene with the average γ^i values used in the analysis of the NMR spectra.

Table I. NMR Parameters Used in the Interpretation of the Bullvalene Results and the Simulation of the Dynamic Spectra

	deuteron no.			
	1	2	3	4
relative population	3/10	3/10	3/10	1/10
γ^i , deg ^a	153.2	103.0	47.4	0
R^i ^b	0.695	-0.478	0.211	1
ZLI2452				
δ^i (Hz, -14 °C) ^c	+12	+219	+219	0
ν_Q^i (kHz, -14 °C) ^d	32.380	-17.850	12.085	44.525
ν_Q^i/ν_Q^4 (-14 °C) ^d	0.727	-0.401	0.271	1
phase V				
δ^i (Hz, -10 °C) ^c	-9	+177	+171	0
ν_Q^i (kHz, -10 °C) ^d	3.525	-1.910	1.420	4.895
ν_Q^i/ν_Q^4 (-10 °C) ^d	0.720	-0.390	0.290	1

^a Average values as computed from ref 20. ^b $R^i = (3 \cos^2 \gamma^i - 1)/2 - [(e^2qQ)/(e^2qQ)^4]$, taking for e^2qQ/h 186 kHz for olefinic deuterons and 165 kHz for aliphatic deuterons. ^c The chemical shifts are given relative to deuteron 4 which was taken as zero. A negative sign indicates shift to high field. ^d The sign of ν_Q^i was arbitrarily taken as positive while the other signs are relative to ν_Q^4 and are based on the signs of the R^i values.

whether this was the case, several spectra with different *t* values were recorded. There was in fact a narrow temperature range where such an effect was observed. The time interval between the pulses was then varied until the *t* dependence was essentially eliminated.

The probe temperature was controlled by using the Bruker B-VT1000 unit, and its absolute value was calibrated with a Fluke 2190 digital thermometer (estimated accuracy ± 1 °C).

Results and Discussion

Low-Temperature Spectrum and Peak Assignment. In Figure 1 are shown examples of deuterium NMR spectra of partially deuterated bullvalene in two liquid crystals. The upper spectrum (trace d) is of a 4.7 wt % solution in DHAB at 114.3 °C. At this temperature, the bond shift process of the Cope rearrangement is sufficiently high so that almost complete averaging of all quadrupole interactions occurs resulting in a single sharp doublet whose splitting is the average of all the different deuterons interaction in the bullvalene molecule. The lower three traces correspond to a 3.8 wt % solution in ZLI2452 at 19 °C and -5 °C as indicated in the figure. At the latter temperature the bond shift process is too slow to significantly affect the spectrum, and therefore separate signals are observed for the various groups of equivalent nuclei. Each group contributes a doublet to the spectrum, whose intensity is proportional to the number of deuterons in it. Hence, one obtains four doublets with relative intensities 3:3:3:1. The assignment of the various doublet is indicated on the lower trace of the figure, and their splittings, together with additional data, are summarized in Table I.

The assignment of deuteron 4 (see Figure 2 for the numbering system) is straightforward because its relative intensity is one-third of that of the others. Also because of its position along the

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symmetry axis of the molecule it must be associated with the largest splitting in the spectrum, as it actually does. Close examination of these spectra shows that they are slightly asymmetric, i.e., the various doublets do not share a common center. The effect is due to small chemical shift differences between the different types of deuterons and may be used to distinguish between the peaks due to the aliphatic deuterons 1 and 4 and those of the olefinic deuterons 2 and 3, which are shifted to lower field relative to the former. This observation allows the assignment of deuteron 1, but it cannot be used to distinguish between the doublets due to deuterons 2 and 3. This can however be done by comparing the experimental quadrupole splitting with estimates based on the molecular structure of bullvalene. Such an analysis will also confirm the assignment of deuterons 1 and 4 and in addition will allow us to determine the relative signs of the various quadrupolar interactions. This is important for the dynamic line-shape computations described below.

The overall doublet splitting of a particular deuteron, ν_Q^i , depends on the orientational ordering of the bullvalene and its molecular geometry.¹⁹ Since bullvalene has a C_3 symmetry axis, only one motional constant is required to describe its orientation in the nematic solvent, so that

$$\nu_Q^i = \frac{3}{2} \left(\frac{e^2qQ}{h} \right)^i \frac{1}{2} (3 \cos^2 \gamma^i - 1) S \quad (1)$$

where $(e^2qQ)/h$ is the principal quadrupole interaction constant for the particular deuteron and where axial symmetry of the quadrupole tensor about the C-D bond direction is assumed, γ^i is the angle between the molecular C_3 axis and the C-Dⁱ bond direction, and S is the orientational order parameter $\langle P_2(\cos \theta) \rangle$ of the molecular symmetry axis. It is clear from eq 1 that the relative splittings of the various deuterons must be constant and independent of the solvent or temperature, provided of course that the molecular geometry, i.e., the set of γ^i 's, remains unchanged. Taking deuteron 4 as reference, the relative splittings are given by

$$R^i = \frac{1}{2} (3 \cos^2 \gamma^i - 1) \frac{(e^2qQ)^i}{(e^2qQ)^4} \quad (2)$$

To compute these ratios from the molecular geometry we have used the crystallographic X-ray data of Amit et al.²⁰ Since in the crystal the molecule is slightly distorted from C_3 symmetry we took average values of the γ^i 's for each group of "equivalent" deuterons. These are indicated in Figure 2 and Table I. Also given in Table I are the calculated R^i values (where we have used for $(e^2qQ)/h$ 186 kHz for the olefinic deuterons and 165 kHz for the aliphatic ones²¹ as well as experimental ν_Q^i/ν_Q^4 determined from the low-temperature spectra in the ZLI2452 and Phase V solvents. Note that the experimental ratios ν_Q^i/ν_Q^4 in the two solutions are essentially the same, but they differ somewhat from the calculated R^i values. This discrepancy results from the fact that the R^i 's are extremely sensitive to the angles γ^i which are not very accurately determined by X-ray experiments and at any rate may be slightly different in solid and the liquid crystalline solutions. Also, there is considerable uncertainty in the values of e^2qQ/h . Nevertheless the similarity between the sets of R^i and ν_Q^i/ν_Q^4 values certainly allows us to complete the peak assignment of the liquid crystalline spectra and to determine the relative signs of the ν_Q^i as given in Table I.

Finally, we comment on the weak splittings observed in trace a of Figure 1. These splittings result from dipolar interactions

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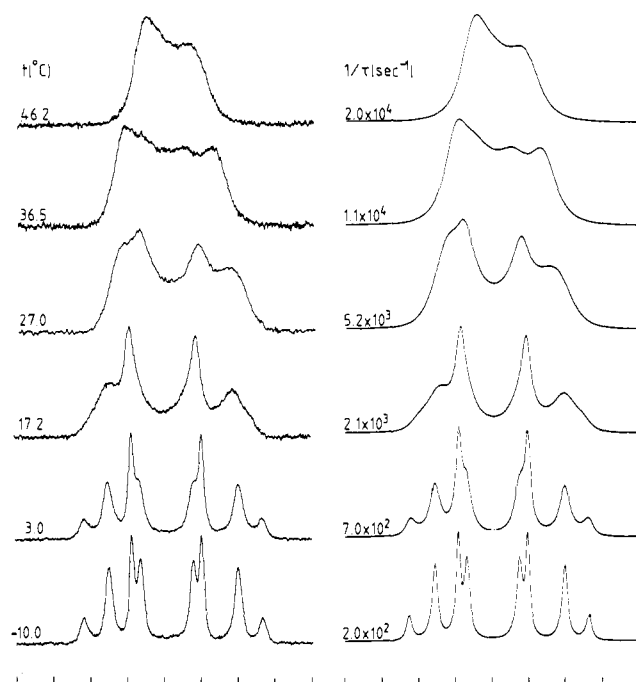


Figure 3. Experimental and simulated deuterium spectra of bullvalene in a nematic liquid. The left column corresponds to a 5.7 wt % solution in phase V at the temperatures indicated in the figure. The spectra on the right are calculated by using the inserted τ values and the ν_Q^4 results of Figure 4. The line-width parameter, $1/T_2$, varied between ~ 60 Hz at low temperatures to ~ 25 Hz at the high-temperature range. The frequency markers are 1 kHz apart.

with the residual protons in the partially deuterated bullvalene. They can be eliminated from the spectrum by proton decoupling as shown in trace b of the figure. For the dynamic studies proton decoupling was performed only at temperature at which the initial exchange broadening was observed, however, over the rest of the dynamic range proton decoupling did not affect the line shape.

Exchange Broadened Spectrum and Its Analysis. In Figure 3 are shown examples of spectra of deuterated bullvalene dissolved in phase V (5.7 wt %) in the temperature range -10 to $+50$ °C. The spectra show conspicuous changes in their line shape with increasing temperatures which we interpret in terms of the dynamic effect of the Cope rearrangement. To derive kinetic parameters from these results we compare them with simulated spectra computed for various specific rates of the reaction. The procedure is analogous to that adopted for the interpretation of the ^{13}C spectra using the Bloch-McConnell equations. In the present case the dynamic process "mixes" separately the four lines corresponding to the $(M \rightarrow M - 1)$ subspectrum, $+1 \rightarrow 0$, and the four lines of the $0 \rightarrow -1$ subspectrum.

The line shape can thus be obtained by solving two sets of four coupled equations. Were it not for the chemical shift differences between the different deuterons, the two sets would give line shapes related to each other by mirror symmetry (about the common Larmor frequency). However the chemical shift effect breaks this symmetry. The dynamic line shape $I(\omega)$ is thus calculated from²²

$$I(\omega) = \text{Re}\{\mathbf{P} \cdot [i\Omega^\pm + \mathbf{R} + \mathbf{A}]^{-1} \cdot \mathbf{\Pi}\} \quad (3)$$

where $\mathbf{\Pi}$ is the unit vector, \mathbf{P} is the population vector whose components are $3/10$, $3/10$, $3/10$, and $1/10$ for the deuteron sites 1, 2, 3, and 4, respectively; Ω^\pm is a diagonal matrix with elements characterizing the frequencies of the four sites

$$\Omega_{ii}^\pm = \delta^i \pm \pi \nu_Q^i \quad (4)$$

where δ^i is the chemical shift (in radians) and the \pm sign refers

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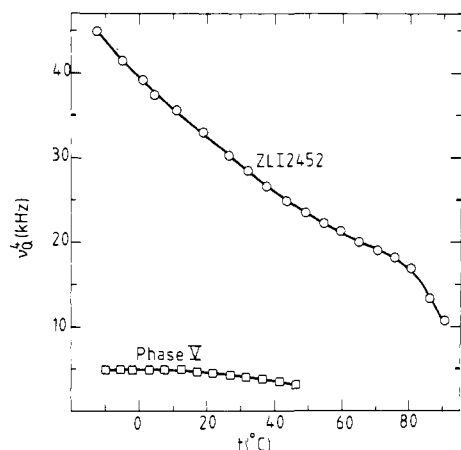


Figure 4. Plot of ν_Q^4 for bullvalene obtained by best fitting the experimental spectra to eq 3 for the two solvents as indicated in the figure.

to the two subspectra (note that in eq 4 the relative signs of the ν_Q^i 's enter the calculation); \mathbf{R} is a diagonal relaxation matrix

$$R_{ii} = 1/T_2^i \quad (5)$$

and \mathbf{A} is the exchange matrix

$$A = \frac{1}{\tau} \begin{pmatrix} -1 & 0 & 2/3 & 1/3 \\ 0 & -1/3 & 1/3 & 0 \\ 2/3 & 1/3 & -1 & 0 \\ 1 & 0 & 0 & -1 \end{pmatrix} \quad (6)$$

where τ is the mean lifetime between successive bond shifts.

The form of the exchange matrix, \mathbf{A} , may serve to confirm the assignment of deuterium 2: In the slow exchange region, before excessive overlap between the peaks sets in, the line broadening of the various peaks is proportional to the diagonal elements of the relaxation matrix. It may be seen from eq 6 that for deuterium 2 this element is one-third the value for the other peaks, so that its initial broadening should be less than for the others. The spectrum shown in trace c of Figure 1 was taken under the condition of slow exchanges, and it may indeed be seen that the pair of lines identified with deuterium 2 is considerably less broadened than the others, as predicted by the above arguments.

For the simulation of the dynamic spectra we need to take into account that the ν_Q^i , $1/T_2$, δ^i , and $1/\tau$ values are in general temperature dependent. In practice we used the δ^i value determined at low temperatures and assumed them to be temperature independent (c.f. Table I). Also, we used the same value of $1/T_2$ for all peaks ($1/T_1^i = 1/T_2$ for all i 's) but assumed its value to be temperature dependent. Finally, since the ν_Q^i values are all related via a single orientational order parameter (eq 1), the fit of the spectrum could be made by using just the three parameters ν_Q^4 , $1/T_2$, and $1/\tau$. Examples of such best fit spectra are shown on the right column of Figure 3. By comparing such spectra with the experimental results the temperature dependence of $1/\tau$ and ν_Q^4 could be determined. The results for ν_Q^4 for the two liquid crystalline solvents are shown in Figure 4. It may be seen that in ZLI2452 the splittings are quite large and strongly temperature dependent. From eq 1 and the results of Figure 4 order parameters from 0.18 to 0.04 can be estimated in the temperature range -13 to $+90$ °C. The low-temperature estimate for S is surprisingly large considering the size and shape of the bullvalene molecule.

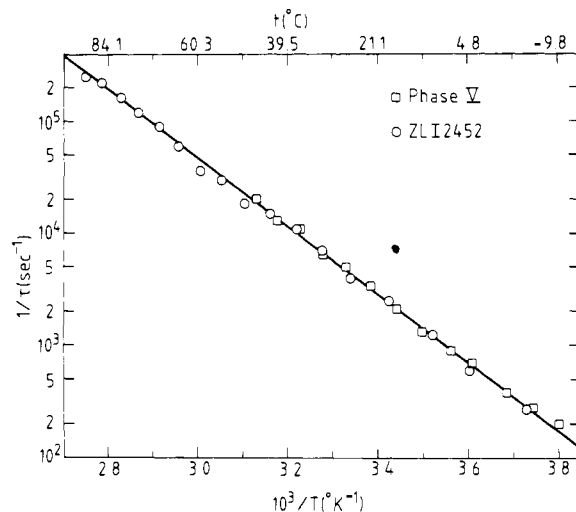


Figure 5. Arrhenius plot of the bond shift reaction rate, $1/\tau$, of bullvalene in the two liquid crystalline solvents as indicated in the figure.

On the other hand, the splittings in phase V are considerably smaller and much less dependent on temperature. The orientational order in this phase ranges between 0.02 and 0.013 over the temperature range studied (cf. Figure 4).

The temperature dependence of $1/\tau$ for the bond shift reaction is given as an Arrhenius plot in Figure 5. From this plot the following activation parameters are calculated: $E_a = 13.9$ kcal/mol; $\Delta H^\ddagger = 13.3$ kcal/mol; $\Delta S^\ddagger = +2.5$ eu; $1/\tau(300 \text{ °C}) = 4.6 \times 10^3 \text{ s}^{-1}$. These results are essentially identical with those obtained previously using ^{13}C NMR^{3,15} spectroscopy in isotropic solvents, indicating that the energetics of the reaction depend predominantly on intramolecular parameters rather than on interaction with the solvent. This is not surprising since the bond rearrangement is expected to occur without interference of the surrounding molecules. It is interesting that the weak anisotropic ordering potential of the liquid crystalline solvents also does not affect the kinetics of this reaction.

Summary

It was demonstrated by using the example of bullvalene that detailed dynamic information can be obtained from deuterium NMR spectroscopy of deuterated molecules dissolved in liquid crystalline solvents. Since the quadrupole splittings are large, wide dynamic ranges may be covered by this technique. Thus, for bullvalene, between -10 and $+80$ °C the reaction rate changes by more than a factor of 10^3 . Because of the simplicity of the deuterium NMR spectra in liquid crystalline solvents it is believed that this approach will find many applications in organic and inorganic systems. It will be particularly useful if liquid crystals of sufficiently low viscosities will be discovered that would allow measurements to be made even below -40 °C.

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Registry No. Bullvalene, 1005-51-2; bullvalene- d_8 , 91210-71-8.