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^{1}H NMR Study of 2,3-Dicyanobicyclo[2.2.2]octa-2,5,7-triene Partially Oriented in a Nematic Phase

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Synopsis. The ^{1}H NMR spectra of the title compound dissolved in a nematic phase of ZLI1167 have been analyzed, and the structure of the proton skeleton has been determined.

NMR spectroscopy has become a useful means of obtaining structural information about molecules dissolved in liquid crystal solvents.[1]

One of the present authors (K.S.) studied the photoreactions of 2,3-dicyanobarrelene (**1**).[2] In the reactions, two different isomeric products have mainly been obtained. One is 1,2-dicyanocyclooctatetraene and the other is 1,5-dicyanosemibullvalene. Two routes of the reactions were presented earlier via different intermediates which were derived from singlet and triplet excited states of **1**, respectively. Therefore, the geometry and structure of **1** is interesting and is supposed to be concerned with two reaction mechanisms. Three double bonds in **1** will be differently affected by the substituents introduced. The relative internuclear distances of **1** have been obtained and compared with those of unsubstituted barrelene (**2**).

Experimental

Dicyanobarrelene (2,3-dicyanobicyclo[2.2.2]octa-2,5,7-triene, **1**) was prepared by a method described by Ciganek.[3] ZLI1167 was of commercial origin, and was used without further purification. The ^{1}H NMR spectra of **1** in both the isotropic and nematic phases were recorded at 200 MHz on a Varian XL-200 spectrometer. The measurements were carried out for a 1.13 wt% solution in $CDCl_3$ at 21.8 °C and 2.19 wt% solution in ZLI1167 at 39.8 °C, respectively. The nematic solution was stable for a month during the NMR measurements. The calculations for spectral and structural analyses were carried out using either a HITAC-2020 computer system or an NEC PC-9801 VX personal computer system.

Results and Discussion

Analyses of the Spectra. The ^{1}H NMR spectrum of **1** in the 1.13 wt% solution in $CDCl_3$ was separated into two regions at about 5.1 and 6.9 ppm. The entire ^{1}H spectrum is shown in Fig. 1, along with expanded parts. The numberings of the nuclei of **1** are given in Fig. 2. The determined NMR parameters are given in Table 1. Although the chemical shifts are consistent with those given by Ciganek,[3] he did not give any values of the coupling constants of this molecule. The determined coupling constants were thus compared with the corresponding values of unsubstituted barrelene (**2**).[4] The values for **1** are similar to those for **2**. An example of the ^{1}H spectra observed in the nematic phase is shown in Fig. 3. The absorption lines spread over a region of

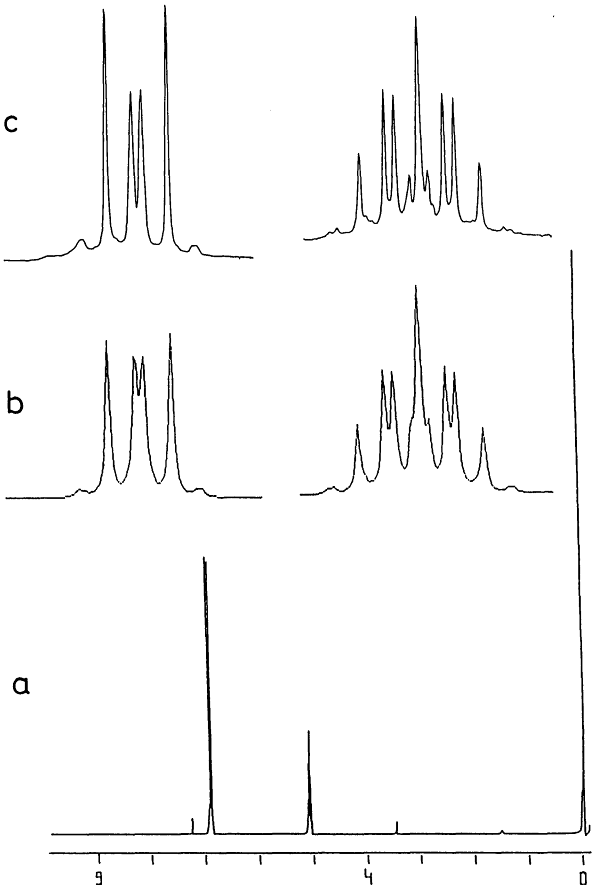

Fig. 1. Observed and calculated ^{1}H NMR spectra of **1** in a 1.13 wt% solution in $CDCl_3$ at 200 MHz and 21.8 °C; a) the entire observed spectrum, b) calculated expanded sections at 5.1 and 6.9 ppm, c) observed expanded sections.

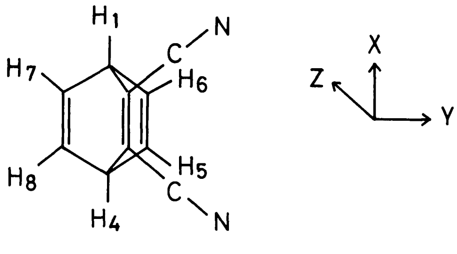

Fig. 2. Numbering for protons in **1**.

Table 1. Spectral Parameters for **1** in Hz

Isotropic phase[a]		Nematic phase[b]	
J_{14}	—(—)[c]	D_{14}	93.9±0.2[d]
J_{15}	1.6 (1.6)	D_{15}	60.0±0.1
J_{16}	5.7 (5.5)	D_{16}	−319.3±0.1
J_{56}	6.3 (6.3)	D_{56}	563.8±0.1
J_{57}	0.3 (—)	D_{57}	−46.4±0.1
J_{58}	0.5 (—)	D_{58}	−181.5±0.1
ν_1	1020.6 (1020)[e]	$\nu_5-\nu_1$	278.1±0.4
ν_5	1383.8 (1380)[e]		

a) Observed for a 1.13 wt% solution in $CDCl_3$. b) Observed for a 2.19 wt% solution in ZLI1167. c) The values in parentheses are those for **2** cited from Ref. 4. d) The errors are standard deviations taken from the output of a modified version of the iterative program of LAOCN3. e) Evaluated from Ref. 3.

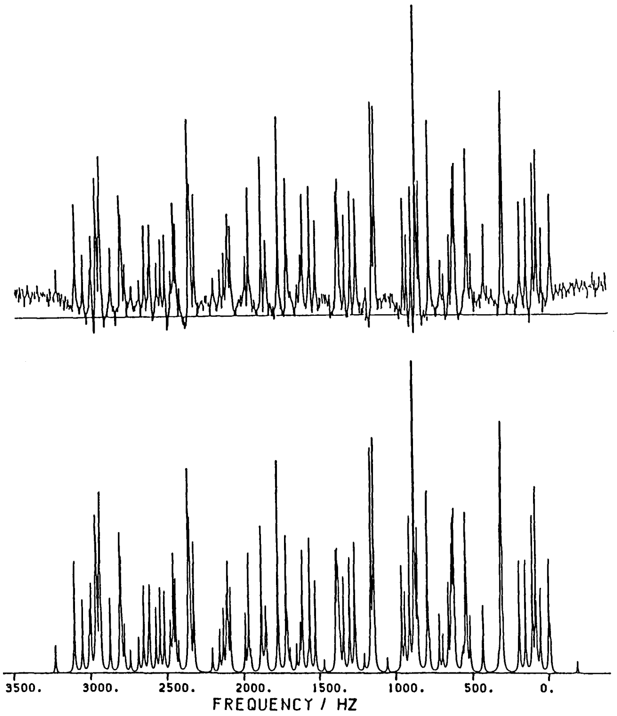

Fig. 3. Observed (upper) and calculated (lower) ^{1}H NMR spectra of **1** in a 2.19 wt% solution in ZLI1167 at 200 MHz and 39.8 °C.

about 3200 Hz. However, no specifically large splitting appeared in the spectrum. The spectrum is thus rather difficult to analyze. The structure of **2** obtained by an electron diffraction study[5] was used to estimate the direct coupling constants D_{ij}, while assuming various orientations of the molecule in the nematic phase. From a spectrum width of 3200 Hz, the D values were limited to be smaller than about 1000 Hz. After many trials, the parameters were obtained, as shown in Table 1. A calculated spectrum in the nematic phase is also shown in Fig. 3. An iteration of the spectrum was carried out for 74 lines in the spectrum with an RMS error of 0.96 Hz by using a modified version of the iterative program of LAOCN3.[6]

Table 2. Structural and Orientation Parameters for **1** Dissolved in ZLI167

i, j	$(R_{i,j}/R_{56})_{\mathrm{nmr}}$	$(R_{i,j}/R_{56})_{\mathrm{ed}}$
1,4	1.817[a] ±0.001[b]	1.822[c]
1,5	1.658 ±0.001	1.669
1,6	0.9663 ±0.0005	0.9823
5,7	1.827 ±0.001	1.840
5,8	1.529 ±0.001	1.545
S_{xx}	−0.08293±0.00040	
S_{zz}	−0.01235±0.00012	

a) R_{56} is assumed to be 2.604 Å. b) The errors are standard deviations derived from the output of a modified version of the iterated program SHAPE. c) Evaluated for **2** from the data in Ref. 5.

Analyses of the Molecular Structure. Since compound **1** has a structure with C_{2v} symmetry, there are only two diagonal orientation parameters necessary to describe the molecular orientation. The following assumptions were made before analyzing the molecular structure: (1) the molelcule has C_{2v} symmetry; (2) molecular vibrational corrections are not applied because of the lack of force constants and; (3) anisotropies of the proton–proton indirect couplings are negligible. Under these assumptions, the relative positions of the protons for **1** can be determined from the direct proton–proton couplings with the aid of a modified version of the iterative program SHAPE.[7] Thus, the derived geometrical and orientation parameters are given in Table 2. The distance ratios obtained are given in the second column. They can be compared with those of **2** in the third column calculated from the electron diffraction data.[5] From the values given in Table 2, all of the proton–proton distance ratios of **1** are found to be smaller than those of the unsubstituted barrelene (**2**). The largest effect appears at R_{16}. It is thus considered that two cyano groups apparently repel the two adjacent hydrogens, H_1 and H_4. Two reasons are considered. One is that the double bond between C_2 and C_3 is elongated by its conjugation with two adjacent cyano groups. The other is that the polarization of the C–N bond tends to repel H_1 or H_4 because of its positive nature caused by polarization of the C–H bond.

Among the orientation parameters of **1**, S_{yy} has the largest positive value. The direction of the molecule-fixed y-axis thus tends to be in the magnetic field direction.

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