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C. L. Khetrapal^{a b} & A. V. Patankar^{a c}

^a Tata Institute of Fundamental Research, Bombay 5, India

^b Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242, U.S.A.

^c Biology Group, Bhabha Atomic Research Centre, Trombay, Bombay, India

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The Structure of 2,1,3-Benzothiadiazole from the NMR Spectrum in the Liquid Crystalline Phase

C. L. KHETRAPAL† and A. V. PATANKAR‡

Tata Institute of Fundamental Research
 Bombay-5, India

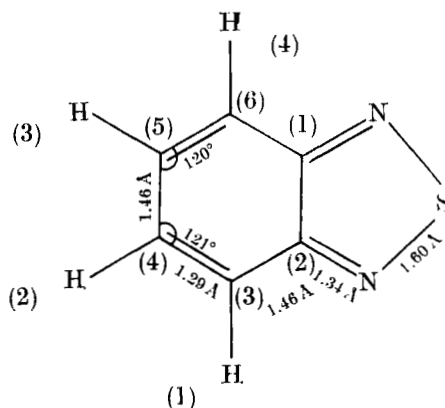
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Abstract—The NMR spectrum of 2,1,3-benzothiadiazole has been studied in the nematic phase of a mixture of 50% 4-methoxybenzylidene-4-amino- α -methyl cinnamic acid-*n*-propyl ester and 50% anisole-*p*-azophenyl-*n*-caproate. Geometry of the proton skeleton is determined. Values of the HCC angles are calculated from the known CC and CH bond lengths.

The preferred molecular orientation is with the C_2 -axis along the direction of the magnetic field and this resembles the way in which most of the aromatic molecules are oriented under such conditions.

1. Introduction

The X-ray data and the chemical properties of 2,1,3-benzothiadiazole (I) indicate that in the benzenoid ring, there is a considerable



Structure (I)

† Present address: Liquid Crystal Institute, Kent State University, Kent, Ohio 44242 (U.S.A.).

‡ Address: Biology Group, Bhabha Atomic Research Centre, Trombay, Bombay (India).

fixation of the double bond and the diene system is deactivated by electron-withdrawing properties of the fused heterocyclic ring.⁽¹⁾ This results in a considerable shortening of C₃—C₄ bond compared to C₄—C₅.⁽²⁾ The view is further supported from the fact that the indirect H—H couplings, J₁₂ and J₂₃ are respectively greater and smaller than typical for ortho disubstituted compounds.⁽¹⁾ However, no data are available on positions of protons. It was, therefore, thought worthwhile to study the shape of the proton skeleton of the molecule with the help of NMR in the nematic phase.

2. Experimental

2,1,3-benzothiadiazole was obtained from Aldrich Chemical Company and used without further purification. An 11.5 mole % solution of the compound was prepared in the nematic phase of a mixture of 70% 4-methoxybenzylidene-4-amino- α -methyl cinnamic acid-*n*-propyl ester⁽⁶⁾ (a) and 30% anisole-*p*-azophenyl *n*-capronate (b). The proton spectrum of the solution was recorded at 28 °C with the help of a Varian HR-spectrometer operating at 56.445 MHz. Several traces were taken on the field increasing and decreasing directions and the mean line positions were determined. The error in the measurement of line positions was ± 1.0 Hz and the average line width was 15 Hz.

3. Results and Discussions

The spectrum of the compound (Fig. 1) shows 12 lines similar to the spectra of the other compounds⁽³⁾ of the AA' BB' type with C_{2v} symmetry. It was, therefore, analyzed in the same manner, with the help of the LAOCONNOR program⁽⁴⁾ and the CDC-3600 computer. Values of the indirect coupling constants used were taken from the literature.⁽¹⁾ The signs of the indirect couplings were found to be the same as those of the direct ones from the fact that this sign combination gave a much smaller r.m.s. error (0.6 Hz) compared to the other (3.3 Hz) between the observed and the calculated line positions. Values of the dipolar couplings thus derived are given in Table 1. Errors of these values were determined as described earlier.⁽³⁾

The shape of the proton skeleton of the molecule can be determined

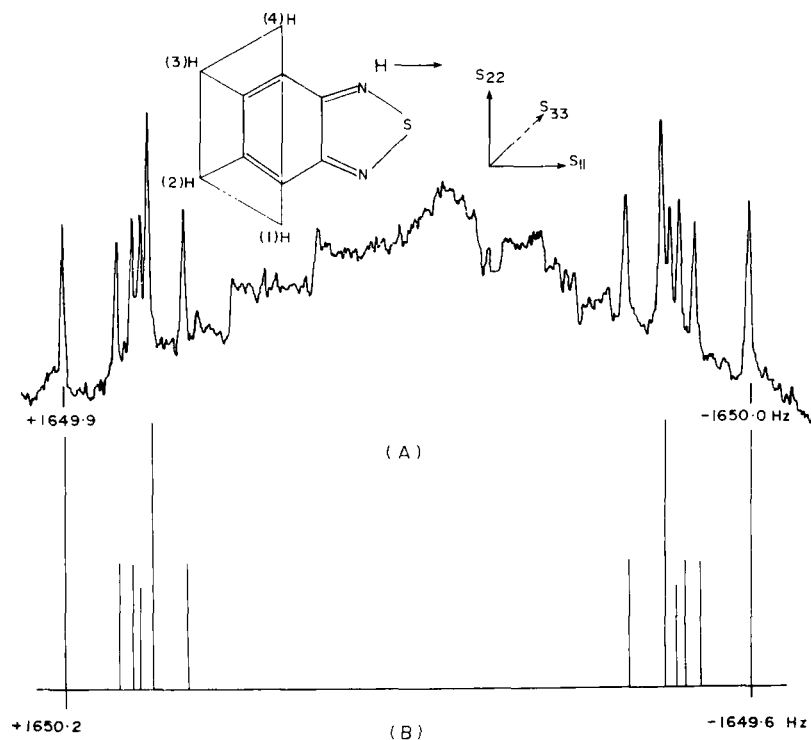


Figure 1. (A) Observed. (B) Calculated NMR spectra of 2,1,3-benzothiadiazole oriented in the nematic phase of a mixture of 70% (a) and 30% (b). Solute concentration = 11.5 mole%. Temperature = 28°C.

TABLE 1 Parameters Derived from the NMR Spectrum of 2,1,3-Benzothiadiazole Oriented in the Nematic Phase of (a) + (b). The numbering of nuclei corresponds to that given in Structure (I)

Parameter	Value	Parameter	Value
$D_{12}(=D_{34})$	-898.5 ± 0.2 Hz	S_{33}	-0.167
$D_{13}(=D_{24})$	-82.0 ± 0.1 Hz	r_{12}/r_{23}	0.991 ± 0.007
D_{23}	-193.1 ± 0.8 Hz	r_{13}/r_{23}	1.722 ± 0.011
D_{14}	-24.8 ± 0.8 Hz	r_{14}/r_{23}	1.982 ± 0.025
S_{11}	0.142 ± 0.006	$\angle H_1 C_3 C_4$	$(125 \pm 2)^\circ$
S_{22}	0.025 ± 0.001	$\angle H_2 C_4 C_5$	$(118.6 \pm 1)^\circ$

with the help of equations reported in the literature⁽²⁾ in connection with the spectra of the type AA' BB' with C_{2v} symmetry. The values are reproduced in Table 1. Surprisingly, they do not differ significantly from the values expected for the similar undistorted phenyl protons.⁽⁵⁾ These results combined with those obtained from X-ray crystallographic studies⁽²⁾ would indicate an appreciable distortion of the CCH bond angles from the normal value of 120° . Assuming that the C—H bond length is equal to 1.084 \AA , the various CCH angles calculated are given in Table 1. The values were determined with the help of a computer. It must be emphasized that the precision of these angles will be quite low ($\simeq 3^\circ$) if the errors of all the C—C and C—H bond lengths and also those of the ratios of interproton distances are taken into consideration. The error reported for these angles (Table 1) includes only the error of the NMR measurements.

The two orientation parameters S_{11} and S_{22} can be determined if one of the interproton distances is known. The NMR and the X-ray data with CH bond length equal to 1.084 \AA give $r_{23} = 2.50 \text{ \AA}$. This value of r_{23} was used to determine S_{11} and S_{22} (given in Table 1) with the help of the equations reported in the literature.

The magnitude and the sign of the S-values indicate that the preferred orientation of the molecule is with the six-membered ring and the C_2 -axis along the direction of the magnetic field and this resembles the manner in which most of the aromatic molecules orient under such conditions.

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