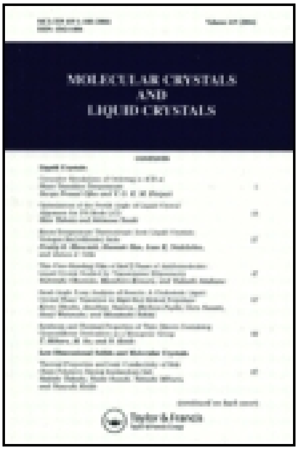

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Absolute Signs of the Order Parameters and the Structures of Benzo[C]bisisothiazoles

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Absolute Signs of the Order Parameters and the Structures of Benzo[C]bisisothiazoles

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Proton NMR spectra including the ^{13}C-satellites of two benzobisisothiazoles, namely, benzo (1, 2-C : 4, 3-C′)- and benzo (2, 1-C : 3, 4-C′)bisisothiazoles (referred to as (I) and (II) repsectively) have been studied in the nematic phase of *N*-(*p*′-ethoxybenzylidene)-*p*-*n*-butylaniline. The derived HH and ^{13}CH direct dipolar couplings have been corrected for harmonic vibrations and the r_α-structures derived. The results indicate that the molecules are planar and there is a considerable bond fixation in (II). As some of the dipolar couplings could not be derived precisely in (I), it was hard to conclude anything definite about the bond fixation.

In (I) the magnitude of the order parameter of the axis perpendicular to the C_2-symmetry axis and in the molecular plane is larger than 0.5 and hence its absolute sign is positive. In analogy with (I), the signs of the order parameters in (II) have also been derived.

INTRODUCTION

Studies of molecular structure of tricyclic compounds using NMR spectroscopy of oriented molecules have so far been restricted to

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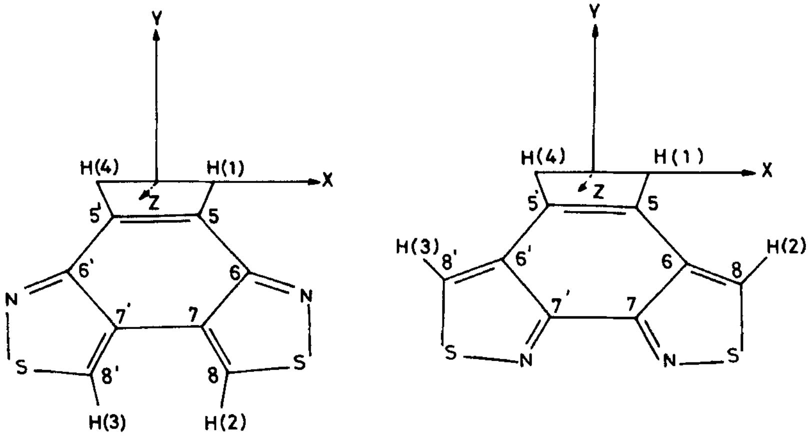
systems, such as phenazine[1], dibenzo-*p*-dioxin[2], thianthrene[3] and dibenzo-furan and thiophene[4], containing 8 interacting protons. For these, relative arrangements of protons have been derived and distortions from planarity estimated whenever present, from the proton NMR spectra without the ^{13}C-satellites. When the number of interacting nuclei decreases to 4, it may be possible to determine relative interproton distances if the molecule has at least C_{2v}-symmetry. However, the distortions from planarity, if any, cannot be detected. This is because in such cases the number of derived dipolar couplings (D_{ij}'s) between the interacting nuclei i and j becomes less than the sum of the number of independent interproton-distance-ratios needed to describe the molecular shape and the number of order parameters (S_{ij}'s) required to specify the orientation of the molecule. However, if the proton NMR spectra of such systems are studied including the ^{13}C-satellites etc., the number of derived dipolar couplings increases substantially. This makes it possible to determine the dihedral angles in addition to relative internuclear distances. Such studies have been undertaken for two different benzo[c]bisisothiazoles (I and II in figure 1) and the results are presented in the present paper. It is well known[5] that the ^{13}C-H direct dipolar couplings, as derived from the NMR experiments, provide larger ^{13}C-H distances due to vibrational influences. Accordingly, harmonic vibrational corrections have been ap-



I

II

FIGURE 1 The structures of benzo(1,2-C : 4,3-C')bisisothiazole (I) and benzo(2,1-C : 3,4-C')bisisothiazole (II) along with the Cartesian coordinate system and the numbering of the nuclei.

plied to the experimental dipolar couplings and the r_α-structures of both (I) and (II) have been obtained.

EXPERIMENTAL

The compounds (I) and (II) were dissolved in *N*-(*p*′-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA) and the spectra were recorded on the Bruker WH-270 FT-NMR spectrometer. The solute concentrations were 3.2 and 3.6 mole per cent respectively for (I) and (II) and the temperature at which the spectra were recorded was 294 K. Nine hundred and sixty Free-induction-decays (FID's) were accumulated and the FID was Fourier transformed with the help of a dedicated BNC-12 computer. The proton spectra under these conditions provided the ^{13}C-satellites in addition to the proton lines associated with the species containing ^{12}C-nuclei (nearly 99%).

A typical spectrum of (II) without ^{13}C-H satellites is shown in figure 2.

RESULTS AND DISCUSSION

Spectral analysis

The spectra were of the type $AA'BB'X$ and $AA'BB'$ with and without the ^{13}C-H-satellites, respectively. There were 4 sub-spectra corre-

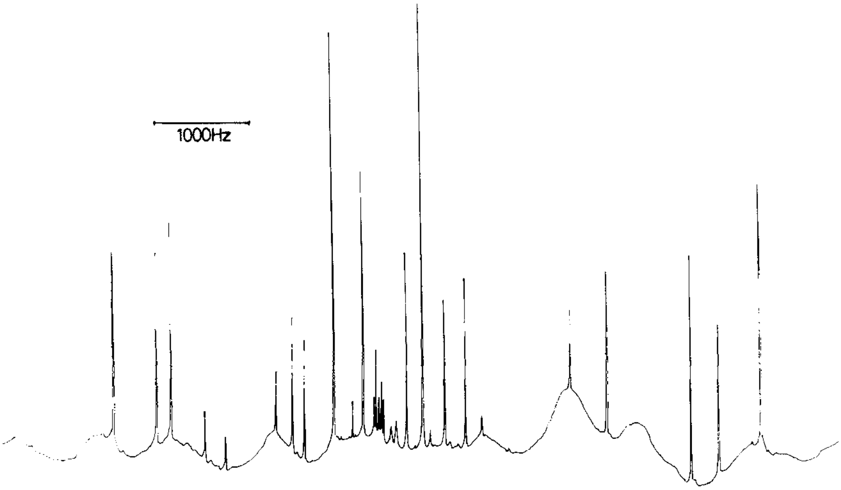


FIGURE 2 Proton NMR spectrum of (II) in EBBA without ^{13}C-H satellites. Solute concentration: 3.6 mole per cent. Temperature: 294 K. Spectrometer: WH-270.

sponding to 4 non-equivalent carbon atoms when the ^{13}C-H satellites were observed. All the spectra were analysed with the help of the LAOCOONOR programme[6] on a DEC-1090 computer. Iterations on the dipolar couplings and the chemical shifts ($\nu_A - \nu_B$) were carried out. The indirect HH and the ^{13}CH couplings were determined from the spectra in the isotropic media and their values were fixed during the iterative process except in (II) where J_{14} was determined as 9.5 ± 0.3 from the iterative analysis. The values of the indirect spin–spin couplings used are included at relevant places in Tables I and II which give the "best-fit" values of D_{ij} and ($\nu_A - \nu_B$). All the 16 observed lines were fitted to a root-mean-square (rms) error of 0.89 in (I) and 23 lines to an rms error of 0.45 Hz in (II) for the analysis of the spectra corresponding to *AA′BB′* types, i.e., for the proton spectra without the ^{13}C-satellites. The lines assigned were 27, 26, 31, 37 for (I) and 26, 14, 20, 23 for (II) and the corresponding rms errors were 1.25, 0.92, 0.94 and 0.94 for (I) and 1.57, 0.78, 1.08 and 1.10 Hz for (II) for the analysis of the 4 sub-spectra due to 4 nonequivalent ^{13}C-nuclei at

TABLE I

Vibrationally corrected and uncorrected dipolar couplings in (I) oriented in the nematic phase of EBBA. Numbering of the nuclei corresponds to that given in figure 1. Fixed J-values used are: $J_{14} = 8.0$, $J_{15} = J_{28} = 160.0$, $J_{45} = J_{16} = J_{38} = 5.0$ Hz and other J-values are zero. $(\nu_2 - \nu_1) = 449.43 \pm 0.40$ Hz at 270 MHz.

Parameter	Value (Hz) without vibrational corrections	with vibrational corrections
D_{12}	162.96 ± 0.80	164.40
D_{13}	44.62 ± 0.81	43.80
D_{14}	− 4043.67 ± 0.20	− 4113.41
D_{23}	− 2523.90 ± 0.19	− 2530.33
D_{15}	636.16 ± 0.68	610.20
$D_{25} + D_{35}$	84.02 ± 0.23	84.10
D_{45}	− 1161.40 ± 0.68	− 1189.79
D_{16}	653.94 ± 0.50	662.66
$D_{26} + D_{36}$	157.01 ± 0.06	158.20
D_{46}	− 157.87 ± 0.50	− 160.24
$D_{17} + D_{47}$	177.69 ± 0.17	178.79
D_{27}	415.20 ± 0.65	417.14
D_{37}	− 174.42 ± 0.76	− 179.80
$D_{18} + D_{48}$	76.35 ± 0.38	76.40
D_{28}	4781.09 ± 0.19	5176.53
D_{38}	− 385.23 ± 0.24	− 387.08

TABLE II

Vibrationally corrected and uncorrected dipolar couplings in (II) oriented in the nematic phase of EBBA. Numbering of the nuclei corresponds to that given in figure 1. Except for J_{14} all other J-values were fixed as:
$J_{28} = J_{15} = 160.0$; $J_{16} = J_{26} = J_{45} = 5.0$ Hz and other J-values are zero.
$\nu_1 - \nu_2 = 685.47 \pm 0.15$ Hz at 270 MHz.

Parameters	Value (Hz) without vibrational corrections	Value (Hz) with vibrational corrections
D_{12}	− 726.93 ± 0.10	− 739.23
D_{13}	− 168.09 ± 0.11	− 169.03
D_{14}	− 1594.26 ± 0.10	− 1628.06
D_{23}	− 67.37 ± 0.08	− 67.64
D_{15}	− 1547.79 ± 0.53	− 1711.78
D_{25}	− 216.91 ± 0.41	− 219.23
D_{35}	− 75.93 ± 0.47	− 76.33
D_{45}	− 519.17 ± 0.59	− 533.94
D_{16}	− 73.73 ± 0.59	− 78.51
D_{26}	− 501.03 ± 0.53	− 518.37
D_{36}	− 51.87 ± 0.43	− 52.10
D_{46}	− 97.04 ± 0.66	− 98.12
D_{17}	− 18.20 ± 1.16	− 18.50
D_{27}	− 114.00 ± 0.57	− 115.88
D_{37}	− 52.94 ± 0.56	− 53.31
D_{47}	− 34.30 ± 1.17	− 34.54
D_{18}	− 98.06 ± 0.67	− 100.21
D_{28}	− 2585.45 ± 0.52	− 2888.90
D_{38}	− 26.70 ± 0.51	− 26.78
D_{48}	− 48.32 ± 0.62	− 48.62
J_{14}	9.5 ± 0.3	

positions 5, 6, 7 and 8 respectively (figure 1). Errors of the parameters reported in Tables I and II correspond to the probable errors given by the computer programme.

The dipolar couplings D_{25}, D_{35}, D_{26}, D_{36}, D_{17}, D_{47}, D_{18} and D_{48} could not be determined precisely in (I) but the sums ($D_{25} + D_{35}$), ($D_{26} + D_{36}$), ($D_{17} + D_{47}$) and ($D_{18} + D_{48}$) were reasonably accurate. Hence, these values are reported in Table I rather than the individual coupling constants.

Molecular structure

If the molecules are planar, they have C_{2v}-symmetry. In such a situation, 10 relative internuclear distances completely define the relative positions of the protons as well as the carbons and 2 order parameters (S_{ij}'s) specify the molecular order.

The systems (I) and (II) provide 16 and 20 different dipolar coupling parameters respectively which can be used to determine 10 relative internuclear (HH, HC, CC) distances and the 2 order parameters for planar molecules. A satisfactory fit between the observed and the 'best-fit' calculated dipolar coupling parameters and reasonable relative bond lengths thus computed establish the validity of the assumption of the planar structure of the molecules. If the 'fit' is not satisfactory, the additional parameters, namely, the dihedral angles between the phenyl and the isothiazole planes and the extra order parameter can be computed from the observed dipolar parameters. The calculations were performed with the help of the SHAPE programme[7] suitably modified so as to include the sums of some of the dipolar couplings instead of the individual coupling constants. Before carrying out these calculations, the dipolar couplings were corrected for the harmonic vibrations. The required force fields for these molecules are not reported in the literature to our knowledge and hence the available values for benzene and isothiazole[8] were used. The computer programme VIBR[9] was used for such a purpose. The "best fit" vibrationally corrected (r_α) structure and the order parameters were thus derived. They are reported in Table III. The rms errors between the observed and the best fit calculated dipolar couplings

TABLE III

Order parameters and vibrationally corrected (r_α) relative internuclear distances in (I) and (II); r_{12} = 2.481 Å (assumed). The numbering of nuclei and the indexing of the S-values correspond to those given in figure 1. Errors of the relative internuclear distances are less than 0.01 Å in all the cases except for r_{56} and r_{67} in (I) due to reasons mentioned in the text.

Parameter	Value		Parameter	Value	
	In (I)	In (II)		In (I)	In (II)
r_{12}	5.516 Å	2.875 Å	r_{28}	1.075	1.094 Å
r_{15}	1.087 Å	1.095 Å	r_{56}	1.333	1.440 Å
$r_{55'}$	1.349 Å	1.352 Å	r_{67}	1.305	1.493 Å
r_{16}	2.184 Å	2.194 Å	r_{i8}[a]	1.355	1.401 Å
r_{17}	3.462 Å	3.553 Å	S_{XX}	0.5232	0.2068
r_{18}	4.465 Å	2.849 Å	S_{YY}	− 0.2928	− 0.2334

[a] i = 7 for (I) and 6 for (II)

were of the same order of magnitude as the errors of the individual dipolar couplings ($\simeq 0.6$ Hz). This indicates that the results are consistent with the planar structures of both the molecules within experimental error. Values of the vibrationally corrected C-H bond lengths are as expected (1.075–1.095 Å). It is interesting to note that carbon-carbon bond lengths r_{67} and r_{56} in (II) are similar to those expected for the single bonds whereas the bond length between the carbon atoms 5 and 5′ is the one expected for a double bond ($\simeq$ 1.35 Å). This indicates a considerable fixation of the double bond in the phenyl ring. This is further substantiated by the larger value (9.5 Hz) of the indirect HH coupling between the protons 1 and 4 compared to the value normally expected for the ortho protons (6–9 Hz) in substituted benzenes. The bond-fixation effect could not be established in (I) due to larger errors arising from the fact that some of the dipolar couplings could not be determined individually. This was particularly so for the nuclear positions 6 and 7 with the result that r_{56} and r_{67} were quite imprecise.

The order parameters determined with respect to the Cartesian coordinate system shown in figure 1 are included in Table 3. In (I) the magnitude of S_{XX} is larger than 0.5 and hence it must have a positive sign. In analogy with this, the sign of the order parameters in (II) are as shown in Table 2. The X-axis has the largest positive S-value in both the cases.

CONCLUSIONS

Both the benzo[C]bisisothiazoles are planar and there is a considerable fixation of the double bond in benzo(2, 1-C : 3, 4-C′)bisisothiazole. The r_α-structures of both the molecules have been determined. The sign of the order parameters in the molecular plane and perpendicular to the C_2-axis of symmetry are positive in both the systems.

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