Conformational Investigation of Cyclobutanone and Thietan in Liquid Crystalline Solvents

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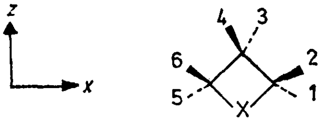
The n.m.r. spectra of cyclobutanone and thietan partially oriented in the nematic phases of liquid crystalline solvents have been obtained. They show that in these solutions cyclobutanone is planar whereas thietan experiences an appreciable ring puckering vibration. An approximate estimate of the mean amplitude of these vibrational modes (10°) has been obtained, the results being in qualitative agreement with microwave studies in the gaseous phase.

N.M.R. spectroscopy of molecules partially oriented in the nematic phases of liquid crystalline solvents is a useful tool in conformational studies of molecules with internal motions. A number of derivatives have been examined and information on conformational preferences in solution, which cannot be obtained with comparable accuracy by other methods, has been procured.[1,2] Four-membered rings have been investigated and it was shown that cyclobutane has a bent conformation[3] whereas oxetan is essentially planar:[4] in the latter case evidence has been found for ring puckering vibrations, in agreement with microwave,[5] far i.r.,[6] and Raman[7] findings in the gaseous phase. Microwave studies were also carried out on cyclobutanone[8] and thietan[9,10] and it has been predicted that the latter should experience a much larger ring puckering effect than the corresponding oxygen derivative whilst in cyclobutanone this effect should be much smaller or even negligible.

In order to see whether these results also hold in solution, a n.m.r. investigation was undertaken for both molecules dissolved in a liquid crystalline medium. This study was also expected to give information on the as yet unavailable geometrical parameters of thietan, and complete the knowledge of the structure of cyclobutanone by determining the positions of the hydrogen atoms.

RESULTS AND DISCUSSION

Both cyclobutanone (I) and thietan (II) are six-spin systems and their oriented spectra (Figures 1 and 2) were interpreted in terms of six dipolar couplings ($D_{i,j}$) and two chemical shifts. In the case of thietan, the four larger $J_{H,H}$ values were iterated; the spectral analysis thus allowed determination of absolute sign of these couplings. Since flat molecules are known to orient with their plane parallel to an applied magnetic field, the term S_{yy} of the orientation matrix is expected to be negative; the signs obtained for the $J_{H,H}$ according to this hypothesis (negative for the geminal and positive for the vicinal) should be therefore regarded as absolute.



(I) X = CO
(II) X = S

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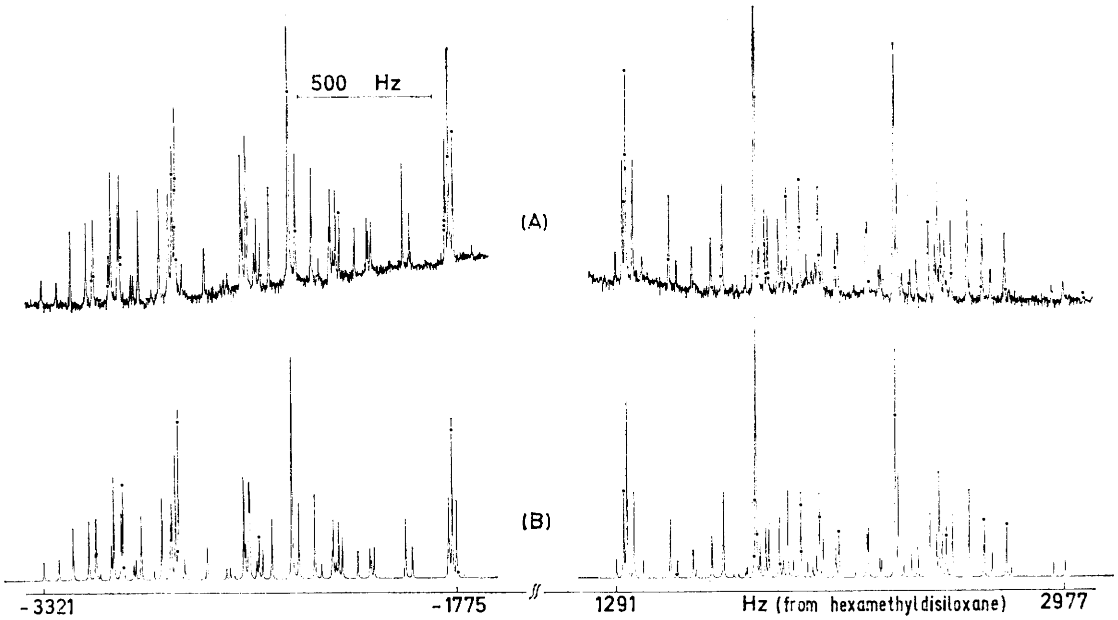

FIGURE 1 Experimental (A) and simulated (B) 100 MHz spectrum of cyclobutanone (I) partially oriented in the nematic phase of 4-n-butyl-4′-methoxyazoxybenzene (Merck Licristal Phase IV)

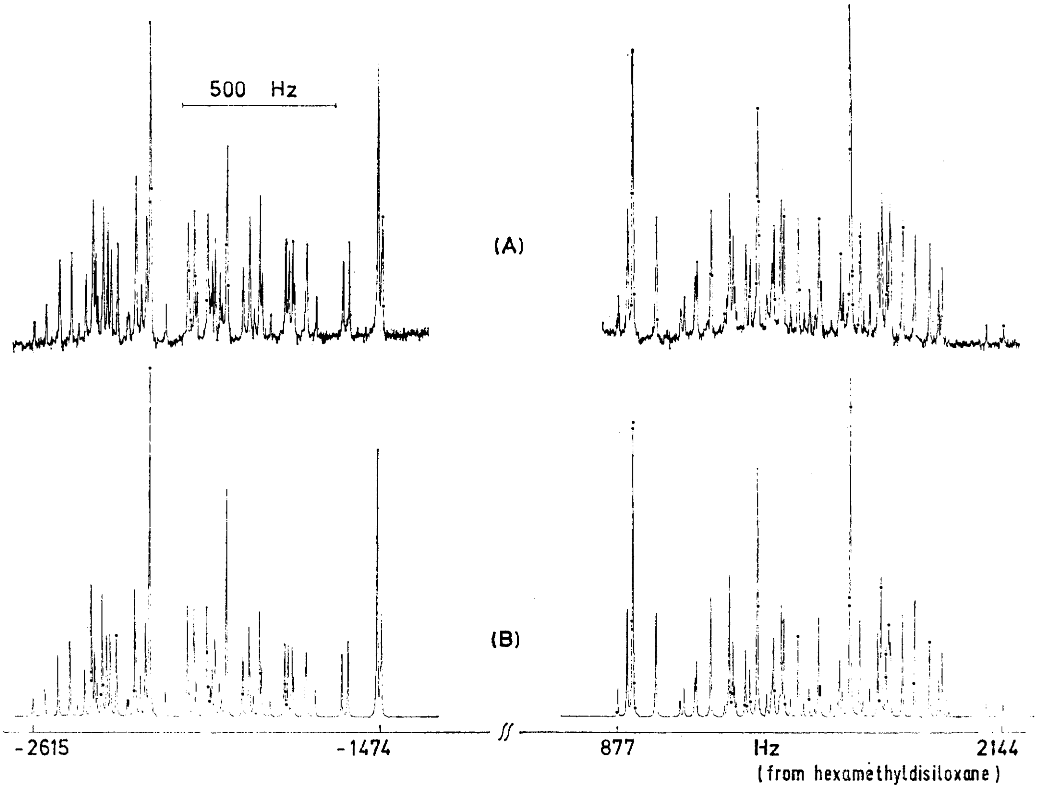

FIGURE 2 Experimental (A) and simulated (B) 100 MHz spectrum of thietan (II) partially oriented in the nematic phase of *N*-(*p*-ethoxybenzylidene)-*p*-n-butylaniline (EBBA)

The $D_{i,j}$ values of cyclobutanone were well accounted for by assuming a rigid planar structure (Table 1): the deviation between experimental and calculated dipolar couplings only slightly exceed the experimental errors. The proton co-ordinates giving such a result correspond to those of a molecule having carbon–carbon distances equal to those measured by microwave spectroscopy,[8] the $\mathrm{C}(\alpha)\widehat{\mathrm{C}}(\beta)\mathrm{C}(\alpha)$ angle of 89° 30′ (*cf.* the microwave value [8] of 90° 54′), $\mathrm{H}\widehat{\mathrm{C}}\mathrm{H}$ angles of 112° 4′ and 110° 22′ for the α and β positions respectively, and C–H bond lengths (1·091 and 1·100 Å for the α and β positions respectively) equal to those reported in ref. 5. The line bisecting the $\mathrm{H}(\beta)\widehat{\mathrm{C}}(\beta)\mathrm{H}(\beta)$ angle also bisects the corresponding $\mathrm{C}(\alpha)\widehat{\mathrm{C}}(\beta)\mathrm{C}(\alpha)$ angle, whereas the line bisecting the $\mathrm{H}(\alpha)\widehat{\mathrm{C}}(\alpha)\mathrm{H}(\alpha)$ angle is shifted by 12° (towards the CO group) with respect to the line joining the two C(α) atoms (*x*-axis).

TABLE 1

Experimental and computed data (Hz) obtained from the n.m.r. spectrum (100 MHz) of cyclobutanone (I) partially oriented in a nematic phase. (The calculated couplings have been derived assuming the carbon–carbon bond distances quoted in the text. The J_{HH} values are those of ref. 13, $\nu_1 = -283{\cdot}16 \pm 0{\cdot}05$, $\nu_2 = -192{\cdot}60 \pm 0{\cdot}07$)

	Experimental	Computed for planar conformation
$D_{1,2}$	1513·84 ± 0·10	1513·83
$D_{1,3}$	−284·35 ± 0·07	−284·74
$D_{1,4}$	4·09 ± 0·08	2·35
$D_{1,5}$	−103·74 ± 0·12	−103·99
$D_{1,6}$	−20·10 ± 0·11	−20·06
$D_{3,4}$	1522·97 ± 0·18	1522·90
R.m.s. deviation (Hz)		0·73
S_{xx}		0·0335
S_{zz}		0·0412
$r_{1,2}$ (Å)		1·810
$r_{1,3}$		2·515
$r_{1,4}$		3·097
$r_{1,5}$		3·382
$r_{1,6}$		3·836
$r_{3,4}$		1·806 *

* Assumed.

The interprotonic distances corresponding to this structure are reported in Table 1. The geometrical data of the carbon skeleton and the C–H bond lengths are the same as those obtained by the microwave method; the $\mathrm{H}\widehat{\mathrm{C}}\mathrm{H}$ angles and the deviation of the H(α)C(α)H(α) plane with respect to the *x*-axis are new data. The most important point, however, lies in the fact that ring puckering effects are negligible since the experimental data are satisfactorily matched by a rigid planar structure; structures bent even by few degrees lead to worse fitting of the experimental data. If the present results are compared with those obtained in the n.m.r. experiment for oxetan,[4] the discrepancy between computed and experimental data is halved when a rigid structure is considered; this is consistent with the observation, in the gaseous phase, of an almost negligible ring puckering barrier for cyclobutanone [8] (7·6 ± 2 cm^{-1}) with respect to oxetan.[5] Accordingly the conformation of cyclobutanone in solution can be regarded as rigidly planar.

On the other hand the spectral data of thietan cannot be matched with the same accuracy when the rigid planar structure is assumed (Table 2). The value of the best fit for the six $D_{i,j}$ couplings (3·1 Hz) is four times larger than in cyclobutanone and for some of the couplings the deviation largely exceeds the accuracy which the present technique may yield in case of rigid structures. The geometrical parameters corresponding to the planar conformation giving the best fit are given below and, although less accurate than for cyclobutanone, are worth mentioning since no structural information was given in the microwave investigation. The C–H bond lengths were assumed equal to those of cyclobutanone and oxetan;[4,5] we used a C(α)–C(β) bond length of 1·58 Å, $\mathrm{H}(\alpha)\widehat{\mathrm{C}}(\alpha)\mathrm{H}(\alpha) = 109°\ 4'$, $\mathrm{H}(\beta)\widehat{\mathrm{C}}(\beta)\mathrm{H}(\beta) = 109°\ 22'$, and $\mathrm{C}(\alpha)\widehat{\mathrm{C}}(\beta)\mathrm{C}(\alpha) = 95°\ 6'$. The line bisecting the $\mathrm{H}(\beta)\widehat{\mathrm{C}}(\beta)\mathrm{H}(\beta)$ angle also bisects the corresponding ring carbon angle, whereas the line bisecting the $\mathrm{H}(\alpha)\widehat{\mathrm{C}}(\alpha)\mathrm{H}(\alpha)$ angle is shifted by 3° [towards C(β)] with respect to the line joining the two C(α) atoms (*x*-axis): both the bisecting lines lie in the *xz*-plane. These data are in reasonable agreement with those of oxetan [4,5] and of a similar sulphurated molecule studied by *X*-ray diffraction (*i.e.* $\mathrm{C}(\alpha)\widehat{\mathrm{C}}(\beta)\mathrm{C}(\alpha) = 99°$ and C(α)–C(β) = 1·57 Å).[11]

TABLE 2

Experimental and computed data (Hz) obtained from the n.m.r. spectrum (100 MHz) of thietan (II) partially oriented in a nematic phase. (The calculated couplings have been derived assuming the carbon–carbon bond distances quoted in the text; $\nu_1 = -317{\cdot}23 \pm 0{\cdot}04$, $\nu_2 = -269{\cdot}35 \pm 0{\cdot}06$, $J_{1,2} = -11{\cdot}89 \pm 3{\cdot}23$, $J_{1,4} = 6{\cdot}25 \pm 0{\cdot}06$, $J_{1,3} = 8{\cdot}95 \pm 0{\cdot}06$, $J_{3,4} = -14{\cdot}72 \pm 3{\cdot}21$)

		Computed		
	Experimental	Planar	10° Bent along C(β)–S axis	10° Bent along C(α)–C(α) axis
$D_{1,2}$	1165·96 ± 0·08	1165·2	1166·8	1167·0
$D_{1,3}$	−212·09 ± 0 05	−216 3	−212·6	−212·7
$D_{1,4}$	7·11 ± 0·06	6·4	5·7	5·9
$D_{1,5}$	52·46 ± 0·10	−48·5	−49·6	−49·5
$D_{1,6}$	−3·30 ± 0·13	−8·2	−8·0	−8·3
$D_{3,4}$	1130·35 ± 0·13	1130·5	1129·4	1129·3
R.m.s. deviation (Hz)		3·1	2·4	2·5
S_{xx}		0·0188	0·0188	0·0189
S_{zz}		0·0356	0·0363	0·0362
$r_{1,2}$ Å		1·777	1·777*	1·777*
$1/2(r_{1,3} + r_{2,4})$		2·453	2·458	2·458
$1/2(r_{1,4} + r_{2,3})$		3·035	3·034	3·034
$1/2(r_{1,5} + r_{2,6})$		3·596	3·582	3·591
$1/2(r_{1,6} + r_{2,5})$		4·011	3·996	4·003
$r_{3,4}$		1·795*	1·795*	1·795*

* Assumed.

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The fact that the rigid planar structure does not give such satisfactory results as did cyclobutanone reflects the existence of relatively large vibrational effects, most likely involving ring puckering. In order to have an approximate estimate of the mean amplitude of the ring puckering vibrations of (II) we examined a number of bent conformations rapidly interconverting about the C(β)–S or the C(α)–C(α) axes, keeping unchanged the geometrical parameters mentioned above. As the time for interconversion is expected to be smaller than the reorientation time in the liquid crystal, the C_{2v} symmetry is dynamically preserved,[12] so that two ordering matrix elements can still be employed. If the third term is introduced, its value is found to be negligible and the r.m.s. deviation is almost unaffected.

For dihedral angles of *ca.* 10° either between the planes C(α)C(β)C(α) and C(α)SC(α), or C(α)C(β)S and SC(α)C(β) a better fitting of the experimental dipolar couplings is achieved (Table 2); angles larger than 20° lead to exceedingly large deviations. The improvement mainly affects the four couplings which are more sensitive to the ring puckering effects, whereas $D_{1,2}$ and $D_{3,4}$ essentially depend upon the values of the corresponding $\widehat{\mathrm{HCH}}$ angles.

It seems therefore that slightly puckered conformations (*ca.* 10°) are, in (II), more populated than the planar, although none of them can be obviously regarded as the single preferred conformer; this is in qualitative agreement with the microwave investigation which indicated large ring puckering vibrations in the direction of both the x- and z-axes.[9]

The mean amplitude of these vibrational modes seems to be smaller in solution than in the gaseous phase;[9] this might reflect the coarse approach employed in the present investigation for estimating the vibrational amplitudes, but could be also indicative of a flattening effect in the liquid (particularly in the viscous and anisotropic nematic medium) with respect to the gaseous phase.

In both cyclobutanone and thietan the element of the ordering matrix S_{zz} exceeds S_{xx}, which is the opposite of what is observed in oxetan.[4] This means that in the xz-plane these two molecules have the z-axis more oriented than the x-axis in the direction parallel to the magnetic field. Such an effect depends upon the more elongated shape of (I) and (II) in the z-direction due to the length of the C–S bonds or to the presence of the CO group, whereas in oxetan the greater molecular length is along the x-axis, which is thus more oriented.

Finally we conclude that the n.m.r. spectra of (I) and (II) in nematic media give results in agreement with those for the gas phase and allow confirmation of a ring puckering effect in solution for thietan and the lack of such an effect in cyclobutanone.

EXPERIMENTAL

N.m.r. spectra were recorded at 100 MHz in the frequency sweep mode at the probe temperature; internal lock was performed by using the signal of hexamethyldisiloxane sealed in a capillary tube coaxial with the conventional n.m.r. sample. Chemical shifts (in Hz) are referred to this external reference (see Tables 1 and 2).

Cyclobutanone (17·7 mol %) was dissolved in 4-n-butyl-4′-methoxyazoxybenzene (Licristal Merck Phase IV); its oriented spectrum (Figure 1) displayed 99 lines that were matched in the iterative theoretical calculation with a r.m.s. deviation of 0·7 Hz. The $J_{\mathrm{H,H}}$ values of ref. 13 were assumed to be unaffected by the nematic solvent.

Thietan (15·6 mol %) was dissolved in *N*-(*p*-ethoxybenzylidene)-*p*-n-butylaniline (EBBA); all the observed 107 lines of the oriented spectrum (Figure 2) were matched with a r.m.s. deviation of 0·5 Hz. The four larger J_{HH} values were also iterated and found to be equal, within error, to those determined in isotropic solution.[14] To the smaller couplings ($J_{1,5}$ and $J_{1,6}$) the values of ref. 14 were attributed.

The spectral analysis was carried out with a LAOCOONOR program and the spectral simulation of Figures 1 and 2 was performed assuming a Lorentzian line shape with a width at half-height of 2·8 Hz.

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