# An Investigation into the Structure and Conformation of *N*-(4-Bromophenyl)[$^{15}$N]maleimide by $^1$H Nuclear Magnetic Resonance Spectroscopy of Liquid Crystalline Solutions

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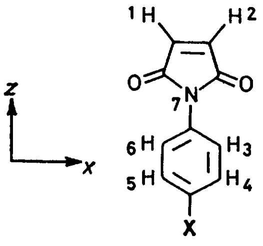
The set of dipolar couplings obtained by analysis of the $^1$H n.m.r. spectrum of *N*-(4-bromophenyl)[$^{15}$N]maleimide are used to investigate the conformation of the molecule. It is shown that the conformation derived previously from interproton dipolar couplings alone, and which has coplanar CN bonds, is incorrect. The dipolar couplings to $^{15}$N in addition to those between protons do show that inversion about nitrogen takes place, but cannot determine the minimum energy configuration of the molecule.

THE structure of *N*-phenylmaleimide or of phenyl-substituted derivatives is unknown, a surprising fact considering the important uses of these compounds in many aspects of chemistry and biology. The phenyl and maleimide parts of the molecule are unlikely to deviate considerably from their structures in other compounds, but their relationship to one another is uncertain. There is hindered rotation about the N–phenyl bond, and also the possibility that this bond does not lie in the plane of the other two C–N bonds. The conformation is therefore specified by the probability distributions $P_\phi(\phi)$ and $P_\alpha(\alpha)$, where $\phi$ refers to phenyl–N rotation, and $\alpha$ to nitrogen inversion. A study of *N*-(4-chlorophenyl)maleimide (I; X = Cl) by $^1$H n.m.r. of nematic solutions has been reported by Khetrapal *et al.*[1] This molecule yields three dipolar couplings: $D_{12}$, $(D_{13} = D_{23} = D_{16} = D_{26})$, and $(D_{14} = D_{15} = D_{24} = D_{25})$ which can be used to test models chosen for $P_\phi(\phi)$ and $P_\alpha(\alpha)$. They assumed that $\alpha$ is always zero, and found that the n.m.r. data are consistent with $P_\phi(\phi)$ having a maximum at $\phi$ 54.5° and at the three other positions determined by the symmetry of the rotation potential energy about the phenyl–N bond. The coplanar conformation has $\phi$ 0. The $^1$H spectrum of this molecule does not yield enough dipolar couplings to fix all the structural parameters even with the assumption that $\alpha$ is always zero. Consequently Khetrapal *et al.*[2] examined the $^1$H spectrum of the *N*-phenylmaleimide itself. The dipolar couplings for this molecule were consistent with the same model, *i.e.* $P_\phi(\phi)$ a maximum close to 53° and $\alpha$ 0. The set of dipolar couplings sensitive to the nature of internal rotation is increased by one, the coupling $D_{1X} = D_{2X}$ (X = H), whose magnitude, however, is not very sensitive to models chosen for $P_\phi(\phi)$ and $P_\alpha(\alpha)$. To overcome this problem we have synthesised $^{15}$N labelled *N*-(4-bromophenyl)maleimide (I; X = Br). The $^1$H spectrum of this molecule contains three extra dipolar couplings compared with the unlabelled compound, one of which, $D_{17} = D_{27}$, is useful in testing the possible natures of $P_\phi(\phi)$ and $P_\alpha(\alpha)$.



(I)

## EXPERIMENTAL

*N*-(4-Bromophenyl)maleimide labelled with $^{15}$N was prepared by reaction of 95% enriched 4-bromo[1-$^{15}$N]-aniline with maleic anhydride. The product was carefully purified by recrystallisation before use.

Two $^1$H spectra were recorded, one using the nematogen Merck Phase IV as solvent, and the other using 4,4′-di-n-heptylazoxybenzene (HAB), which has a nematic and smectic A phase. The spectrum of the HAB solution was recorded in the smectic A phase. The spectra were recorded at ambient temperature (30 °C) on a Varian XL 100, using $^{19}$F external lock, and in the pulse mode of operation. The spectra were analysed using the program LEQUOR, and the results are shown in Table 1. The isotropic constants, $J_{ij}$, were obtained by analysing the spectrum of a sample dissolved in CDCl$_3$ and were kept fixed at the values shown in Table 1 during the iterative analysis of the anisotropic spectra. The signs of the $^3J_{NH}$ and $^4J_{NH}$ were taken to be identical to those found for 2-chloroaniline.[3]

## RESULTS AND DISCUSSION

The dipolar couplings in the fragment $C_6H_4Br^{15}N$ were used to determine the order parameters $S_{zz}$ and $(S_{xx} - S_{yy})$, and the values of the co-ordinates $x_3 = -x_6$, $x_4 = -x_5$, and $z_7$ relative to $r_{34}$ 2.48 Å, with the results shown in Table 2. It should be noted that our analysis give $D_{45} > D_{36}$, whereas Khetrapal *et al*[1,2] found the reverse. We find that it is possible to obtain analyses of the spectra of the two samples used with either of the assignments of the relative values of $D_{36}$ and $D_{45}$. Thus the spectra do not distinguish between these two couplings, but they do determine them to be different. However, only the assignment $D_{45} > D_{36}$

gives a set of order parameters and co-ordinates which give calculated couplings to $^{15}N$ in satisfactory agreement with those observed for the $C_6H_4Br^{15}N$ fragment.

TABLE 1

Dipolar couplings and chemical shifts determined from proton spectra of *N*-(4-bromophenyl)maleimide dissolved in nematic and smectic solutions

| Nuclei | $D_{ij}$/Hz | | $\delta_{ij}$/p.p.m. | | $J_{ij}$/Hz |
|---|---|---|---|---|---|
| *ij* | Nematic | Smectic | Nematic | Smectic | |
| 12 | 258.1 ± 0.1 | 1 072.1 ± 0.2 | | | |
| 13 | −163.1 ± 0.1 | −324.6 ± 0.4 | 0.397 ± 0.007 | 1.707 ± 0.002 | 0.0 |
| 14 | −64.1 ± 0.1 | −125.4 ± 0.4 | 0.189 ± 0.007 | 1.539 ± 0.002 | 0.0 |
| 17 | 67.1 ± 0.1 | 127.6 ± 0.3 | | | −1.5 |
| 34 | −2 068.1 ± 0.1 | −4 035.1 ± 0.2 | 0.208 ± 0.014 | 0.168 ± 0.004 | 8.5 |
| 35 | 20.8 ± 0.7 | 33.6 ± 0.2 | 0.208 ± 0.014 | 0.168 ± 0.004 | 0.5 |
| 36 | 173.7 ± 0.7 | 321.8 ± 2.1 | | | 1.5 |
| 37 | 10.9 ± 0.7 | 24.6 ± 2.1 | | | −2.3 |
| 45 | 177.0 ± 0.7 | 331.2 ± 2.0 | | | 1.5 |
| 47 | 21.6 ± 0.7 | 45.2 ± 2.1 | | | |

TABLE 2

Order parameters and co-ordinates (Å) derived from dipolar couplings in the phenyl ring of *N*-(4-bromophenyl)maleimide

| | Nematic | Smectic |
|---|---|---|
| $x_3$ | 2.168 ± 0.002 | 2.164 ± 0.002 |
| $z_3$ | 2.480 ± 0.007 | 2.480 ± 0.001 |
| $x_4$ | 2.152 ± 0.002 | 2.143 ± 0.002 |
| $z_4$ | 0.0 | 0.0 |
| $z_7$ | 3.998 ± 0.006 | 3.998 ± 0.006 |
| $S_{zz}$ | 0.2628 ± 0.0001 | 0.5127 ± 0.0001 |
| $S_{xx} - S_{yy}$ | 0.0276 ± 0.0006 | 0.0783 ± 0.0006 |

If we assume that $\alpha$ has a fixed value of zero, that is the nitrogen atom has three coplanar C–N bonds, then we can examine five models for $P_\phi(\phi)$. In each case we take the geometry of the maleimide fraction to be close to that found for showdomycin by *X*-ray diffraction,[4] which fixes $r_{12}$ as 0.241 nm. In case (i) $P_\phi(0) = P_\phi(180) = 0.5$, that is, only the two conformations with the rings coplanar are populated. This model fails to give agreement between observed and calculated values of $D_{12}$ and can be rejected. In case (ii) $P_\phi(90) = P_\phi(270) = 0.5$, which corresponds to the two equivalent conformations having the rings orthogonal. Again $D_{12}$ (calculated) is very different from the observed value, and the model can be rejected. For (iii) $P_\phi(0) = P_\phi(180) = w$; $P_\phi(90) = P_\phi(270) = 0.5 - w$. The dipolar couplings determined by Khetrapal *et al.*[1] do fit such a mixture of planar and orthogonal forms, with separate order matrices, but a constant geometry for each form. However, the inclusion of couplings to $^{15}N$ destroys the internal consistency of this model. To show this, it is necessary to consider only the values of $S_{zz}$ and $S_{xx} - S_{yy}$ determined from the rigid fragment

$$a + b = S_{zz} \tag{1}$$

$$c + d = S_{xx} - S_{yy} \tag{2}$$

$C_6H_4Br^{15}N$, and the two couplings $D_{12}$ and $D_{17} = D_{27}$. Four variables $a$—$d$ characterise this model: $a = wS_{zz}{}^{p}$, $b = (1 - w)S_{zz}{}^{o}$, $c = w(S_{xx} - S_{yy})^{p}$, $d = (1 - w)(S_{xx} - S_{yy})^{0}$, where the superscripts p and o refer to planar and orthogonal forms. We derive equations (1)—(4); from (1)—(3), using the data from the nematic solution, $c = 0.116$, $d = -0.087$, and $a + b = 0.262\,7$. Substitution into (4) predicts $D_{17}$ to be 41 Hz compared with the experimental value of 67 Hz.

$$D_{12} = 4\,289\,(a - c + b + d) \tag{3}$$

$$D_{17} = 126\,(a + b) + 41\,(c - d) \tag{4}$$

Reasonable changes in the geometry of the maleimide fraction do not alter our conclusion that this model is incorrect. Case (iv) involves free rotation about $z$. This model is in fact identical in its consequences for dipolar coupling as model (iii) with $w = 0.25$, and hence is rejected on the same basis. In case (v) $P_\phi(\phi) = P_\phi(180 - \phi) = P_\phi(180 + \phi) = P_\phi(-\phi) = 0.25$. The angle $\phi$ is the only value where $P_\phi(\phi)$ has an appreciable magnitude. This model was examined by Khetrapal *et al.*[1] for 4-chlorophenylmaleimide and the three couplings $D_{12}$, $D_{13}$, and $D_{14}$ were used to determine $z_1 = z_2$, $\phi$, and $S_{zz}$, keeping $r_{12}$ fixed at 0.26 nm. The value of $\phi$ was found to be 54.5°. For phenylmaleimide Khetrapal *et al.*[2] found $\phi$ 52.9°. The latter molecule yields four couplings $D_{12}$, $D_{13}$, $D_{14}$, and $D_{1X}$ (X = H) which depend upon the variables $r_{12}$, $z_1 = z_2$; $\phi$ and $S_{zz}$, but Khetrapal *et al.*[2] found that these could not be used to fix all the parameters independently, so that $r_{12}$ was fixed at 0.255 nm. Repeating this type of calculation with the data on the $^{15}N$ labelled compound we find that a value for $\phi$ cannot be found which predicts $D_{12}$, $D_{13}$, $D_{14}$, *and* $D_{17} = D_{27}$. Thus, using only the proton–proton dipolar couplings with our data from the nematic sample gave $\phi$ 45.6°, but $D_{17}$ was predicted to be 82.9 Hz compared with the experimental value of 67.1°. Note that we have used $r_{12} = 0.241$ nm, but changing this value to 0.26 nm does not affect our conclusion that the model is incorrect. It is not possible to fit the set of dipolar couplings for this model with any value of $r_{12}$.

We cannot test more complex forms of $P_\phi(\phi)$ because they require more parameters than there are observed couplings, and therefore we cannot rule out the possibility that $\alpha$ is zero and some complex form for $P_\phi(\phi)$ will fit the data. However, it seems more reasonable to assume that the failure of the five models tested arises because $P_\alpha(\alpha)$ is finite for non-zero values of $\alpha$. There is insufficient data to test the general model of a distribution on both $\phi$ and $\alpha$, but some special cases are tractable. To identify these special cases we need to consider the nature of $P_\phi(\phi)$, $P_\alpha(\alpha)$, and $V$, the intermolecular potential determining the orientational ordering of the solute in the mesophase. Consider first extensions to cases (i), (ii), and (v), but which have variations in $P_\sigma(\alpha)$. In these cases if $P_\alpha(\alpha)$ is non-zero only for two values of $\alpha$ symmetrically disposed about the plane defined by the maleimide fraction when $\alpha = 0$, then $D_{12}$ is independent of both $P_\alpha(\alpha)$ and $V$, and depends only on $r_{12}$, $P_\phi(\phi)$, and the ordering matrix $S$. For cases (i) and (ii) $S$ is diagonal for the $xyz$ axes and these models can be rejected because they fail to predict the correct order of magnitude of $D_{12}$. For case (v) $S_{xy}$ has a non-zero value and fixing $r_{12}$ as 0.241 nm, the value found for this distance in showdomycin,[4] then $D_{12}$ is given by equation (5). The value of $S_{xy}$ must lie

$$D_{12} = -4\,289\,[-S_{zz} + (S_{xx} - S_{yy})(\cos^2\phi - \sin^2\phi) + 2S_{xy}\cos\phi\sin\phi] \quad (5)$$

in the range $\pm 0.75$, hence the experimental values of $D_{12}$ may be used to place limits on $\phi$, giving 7—81° from the nematic solution, and 7—77° for the smectic.

It is perhaps more probable that $P_\alpha(\alpha)$ is appreciable in magnitude for a range of values of $\alpha$, *i.e.* corresponding to a large amplitude oscillation. These cases will, in general, involve an intermolecular potential which is dependent on $\alpha$, so that $S$ and hence $D_{12}$ are dependent on $P_\alpha(\alpha)$. In the absence of any experimental or theoretical investigations into the dependence of ordering potentials on molecular structure we can do no more than conjecture that the dependence of $S_{zz}$, $S_{xx} - S_{yy}$, and $S_{xy}$ on $\alpha$ are small, and hence the limits on $\phi$ are realistically between 7 and 80°. No limits can be placed on $\alpha$.

*Conclusions.*—The $^1$H dipolar couplings from the unlabelled phenylmaleimides are insufficient to determine the conformational preference of the molecule. The $^{15}$N labelled molecule studied here highlights this problem, and establishes that the three CN bonds are probably not coplanar. We conclude by stressing the importance of basing firm conclusions about molecular conformation only when experiment yields a number of measured couplings which is in excess of that required by the model of internal rotation. This is a general observation and points to the importance of measuring such dipolar couplings as $^{13}$C–H to increase the size of experimental data sets.

[9/1511 *Received, 24th September,* 1979]

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