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On the Benzene Ring Rotations in Liquid Crystals

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By using IR correlation function analysis for benzene ring rotations of liquid crystal HOAB it has been found that these rotations occur in random angular jumps of 30° in the smectic phase and of 60° in the nematic and isotropic phases. The corresponding rotational correlation times are of the order of 10^{-12} s which appears to be comparable with those for benzene ring rotations in ordinary organic liquids.

ON THE BENZENE RING ROTATIONS IN LIQUID CRYSTALS

In a number of studies, translational and rotational motion in liquid crystals has been discussed on the basis of NMR, Rayleigh and neutron scattering[1–6] measurements.

However, the details of the motion of the molecules and the motion of their structural units, such as alkyl chains, azoxy groups and benzene rings, are still rather poorly understood.

For liquids it has been generally assumed that the rotation occurs through random angular steps which are short in comparison with the period of free rotation. According to Rothschild many organic molecules rotate in angular jumps of between 20° and 60°, and even higher than 60°, in very viscous media.[7] During a jump which is completed in 0.4×10^{-12} s (a usual value for many organic liquids), the molecules are thought to rotate freely.[7]

In the case of liquid crystals Samulski *et al*[8] have found that the molecules of PAA also rotate around the long axis in large jumps. They found that the reorientational jumps were higher than 60°.

In this letter an IR correlation function analysis of benzene ring rotations is given for liquid crystals HOAB (diheptyloxyazoxyanisole) on the basis of the free rotor model. In this way the subject of our study is not a whole molecule, but one of its structural units. However, the conclusions have been extended to the behaviour of the whole molecule.

The IR spectra of HOAB have been taken in the solid, smectic, nematic and isotropic phases, by using a Zeiss UR-20 IR prism spectrophotometer (400 cm^{-1}–4000 cm^{-1}) with automatic prism changing at the ranges: 400–750 cm^{-1} KBr prism, 750–2000 cm^{-1} NaCl prism and 2000–4000 cm^{-1} LiF prism. The IR spectra were studied also by using a Perkin-Elmer 521 double grating spectrophotometer. The spectral slitwidth was $\sim 1\ \text{cm}^{-1}$. The general conclusions regarding the temperature dependence of the IR lines are in agreement with Bulkin *et al.*[9]

It is well known that the IR absorption intensity $I(\omega)$ is given by the fluctuation-dissipation theorem:

$$I(\omega) = \int e^{-i\omega t}\langle \boldsymbol{\mu}(0)\boldsymbol{\mu}(t)\rangle \,\mathrm{d}t$$

$$= \int C(t)e^{-i\omega t}\,\mathrm{d}t,$$

where $\boldsymbol{\mu}(t)$ is a unit vector pointing into the direction of the transition dipole moment, and $C(t)$ is the correlation function. Once $I(\omega)$ is known, $C(t)$ can be obtained by means of Fourier inversion.

In the rotational-vibrational spectrum a contribution to spectral line shape will arise due to the time dependence of changes in the normal coordinate associated with the transition. Due to the interactions with neighbouring molecules as well as with other groups in the same molecule the corresponding power spectrum will be broader.[11]

Line broadening if IR absorption may arise from sources other than molecular reorientations. Such phenomena as vibrational relaxation, molecular diffusion, hot bands, as well as other mechanisms can also affect line broadening. All of them will contribute to the line broadening if their frequencies are comparable with the rotational frequency (inverse relaxation time). We shall briefly discuss these mechanisms, and show that all of them can be neglected in the case of benzene ring rotations of liquid crystals, with respect to the short time scale events.

If the vibrational events occur with frequency β_{VIB}, the complete correlation function can be written:[10]

$$C(t) = C_R(t)\,e^{-\beta_{\text{VIB}}t}$$

Evidently, this process is important only if $1/\beta_{\text{VIB}}$ is comparable with the rotational relax time. However, for the number of molecules it appears that the vibrational relaxation is too slow ($\beta_{\text{VIB}} \sim 10^{11}$–$10^{10}$ sec) to contribute significantly to the rotational relaxation.[10]

Strictly speaking, an additional contribution will arise if the number of molecules are in excited vibrational levels. The hot bands that result will be lightly displaced from the fundamental band by anharmonicity, and again give rise to broadening that is unrelated to rotational motion.[10,11]

Following a number of authors,[10,11] we have assumed that the rotational band shape is symmetrical and any anharmonic contribution will reflect itself as an asymmetry. However, we have not observed such effects for the band under consideration.

Finally, an additional contribution comes from the diffusion motion of benzene. However, the situation is here very simple to analyze, because the benzene ring is only a structural unit of the rather massive molecule of HOAB and has not its own diffusion, but that of the whole molecule. From a number of experiments[12] it is known that the diffusion jump frequency of the molecules is between (10^6–10^8 sec), and it holds for the benzene also. This is really too slow to seriously affect the result.

So taking into account what has been said above and following Bratosh *et al*[11] the correlation function $C(t)$ can be separated into two parts, C_v and C_R:

$$\begin{aligned}\langle \boldsymbol{\mu}(0)\boldsymbol{\mu}(t)\rangle &= \langle \mu(0)\mu(t)\rangle \cdot \langle \hat{\mu}(0)\hat{\mu}(t)\rangle \\ &= C_v(t)\cdot C_R(t).\end{aligned}$$

For symmetrical band profiles, C_v can be neglected and the free rotor model is the natural approach, i.e.,

$$C(t) \equiv C_R(t).$$

Since orientational motion occurs through random steps, a Gaussian form of the correlation function is to be expected, and, assuming a short-time behaviour, it can be expanded in a power series of $\omega_M t$, as shown by Bliot *et al.*[13] That is:

$$C_R(t) = 1 - \frac{1}{2}\omega_M^2 t^2 + \frac{1}{12}\left(1 + \frac{1}{14}\cdot\frac{B}{C}\right)\omega_M^4 t^4 + \cdots$$

where $\omega_M^4 = 2KT/I$ and I is the moment of inertia.

The ratio B/C gives the form of the ellipsoid of inertia, (for linear molecules $B/C = 0$, and for spherical ones $B/C = 1$). As we are looking at the rotational motion of the benzene ring, B/C can be taken to be about one. In fact, the rotational correlation function is rather independent of the B/C value in the interval $0 < \omega_M t < 2$ and the same $C_R(t)$ function is obtained for a number of B/C values. For details see Reference 13.

The moment of inertia of the benzene ring is calculated to be $\sim 2 \times 10^{-32}$ g-cm^2.

The upper formula has been used to fit the experimental correlation function for the rotational-vibrational line of 540 cm^{-1} in the smectic, nematic and isotropic phases.

For the rotational correlation times of the benzene ring which are given by[11] $\tau = \int \langle \mu(0)\mu(t) \rangle \, dt$ one finds:

$$\tau_{\text{smectic}} = 8.2 \times 10^{-12}\,\text{s}$$
$$\tau_{\text{nematic}} = 5.3 \times 10^{-12}\,\text{s}$$
$$\tau_{\text{isotropic}} = 4.1 \times 10^{-12}\,\text{s}$$

The calculated and the experimental $C(t)$ are identical (Figure 1) until the correlation function decreases to:

$$\langle \mu(0)\mu(t) \rangle_{\text{smectic}} = 0.85$$
$$\langle \mu(0)\mu(t) \rangle_{\text{nematic}} = 0.5$$
$$\langle \mu(0)\mu(t) \rangle_{\text{isotropic}} = 0.45$$

One finds that the average angular jumps of rotations are:

$$\text{arc cos } 0.83 \sim 30^\circ(\text{smectic})$$
$$\text{arc cos } 0.50 \sim 60^\circ(\text{nematic})$$
$$\text{arc cos } 0.45 \sim 63^\circ(\text{isotropic})$$

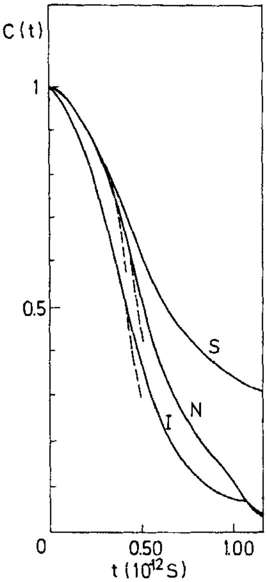

FIGURE 1 Correlation function of the liquid crystal HOAB in the smectic (S), nematic (N) and isotropic (I) phases. The dotted lines denote free rotor decay in every phase.

Now the following speculation is possible. If the whole molecule of the liquid crystal rotates like its benzene rings, then its angular jumps are 30° in the smectic phase, and 60° in the nematic and isotropic phases, which is in agreement with Samulski *et al.*[8]

For the rotational times of the whole *molecule* Samulski found a period of 10^{-9} s. From our calculations the rotational correlation times of benzene rings are of the order of 10^{-12} s, indicating that the benzene rings rotate between 10^2 and 10^3 times faster than the whole molecule. However, their jump angles are equal.

According to Spence *et al*,[14] the benzene groups rotate around the C–N axis more easily than the whole molecule can rotate about any axis, and our results confirm this.

We shall try to elucidate the reasons for such a behaviour.

In the smectic phase, where the benzene rings of two neighbouring molecules lie side by side, their rotation has to be a cooperative effect. So, the angular jumps have to be small, and correlation rotation times large. In this case a hindered rotation is a general feature. The molecular forces need only about 0.25×10^{-12} s to cause an observable effect on the molecular motion, which is reflected as a loss of correlation.

In the nematic phase the situation is rather different. The benzene rings of two molecules are not now in neighbouring positions, because translational order has collapsed.

Generally speaking, besides the effect of nematic order there can be cybotatic clusters, which appear in the nematic phase due to the residual order from the smectic phase.[3] Nevertheless, their role is highly reduced, and rotation is less hindered than in the smectic phase. The intermolecular forces need about 0.48×10^{-12} s to cause an observable effect, as in the isotropic phase.

To summarize, it can be said that the benzene rings rotate in angular jumps of 30° in 8.2×10^{-12} s, of 60° in 5.3×10^{-12} s, and higher than 60° in 4.1×10^{-12} s, in the smectic, nematic and isotropic phases, respectively.

For comparison, the rotational correlation time of the benzene ring in liquid toluene is about 3.5×10^{-12} s.[15] So, the rotational time of the benzene ring in liquid crystals appears to be of the same order as the rotational time of the benzene ring in ordinary organic liquids.

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References

1. C. C. Sung, *Chem. Phys. Lett.*, **10**, 35 (1971).
2. P. Pincus, *Solid St. Comm.*, **7**, 415 (1969).

3. R. Blinc, D. L. Hogenboom, D. E. O'Reilly, and E. M. Peterson, *Phys. Rev. Lett.*, **23**, 969 (1969).
4. M. Weger and B. Cabane, *J. Phys.*, **11–12**, C4-12 (1969).
5. D. McQueen, K. Edgren, and L. Einarson, *J. Appl. Phys.*, **6**, 885 (1973).
6. J. D. Litster and T. W. Stinson, *J. Appl. Phys.*, **41**, 996 (1970).
7. W. G. Rothschild, *J. Chem. Phys.*, **57**, 991 (1972), **53**, 990 (1971).
8. E. T. Samulski, C. R. Dybowski, and C. G. Wade, *Phys. Rev. Lett.*, **29**, 340 (1972).
9. B. J. Bulkin and D. Grundbaum, *Liquid Crystals and Ordered Fluids*, J. F. Johnson, Plenum Press, N.Y., 1970, p. 303.
10. P. van Konynenburg and W. A. Steele, *J. Chem. Phys.*, **56**, 4776 (1972).
11. S. Bratosh, J. Rios, and Y. Guissani, *J. Chem. Phys.*, **52**, 439 (1970).
12. W. Franklin, *Mol. Cryst. Liquid Cryst.*, **14**, 227 (1971).
13. F. Bliot, C. Abbar, and E. Constant, *Compt. Rend.*, **272B**, 1248 (1971).
14. R. D. Spence, H. G. Gutowsky, and C. H. Holm, *J. Chem. Phys.*, **21**, 1891 (1953).
15. Z. Pajak, E. Szcsesniak, J. Angerer, and K. Jurga, *Acta Phys. Pol.*, **A38**, 767 (1970).