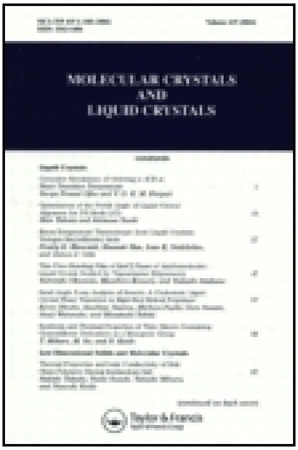


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Molecular Packing in the Nematic Phase of Cyano Compounds with Different Ring Systems

A. J. Leadbetter [a] & A. I. Mehta [a]
[a] Department of Chemistry, University of Exeter, Exeter, EX4 4QD, U.K.

Version of record first published: 21 Mar 2007.

To cite this article: A. J. Leadbetter & A. I. Mehta (1981): Molecular Packing in the Nematic Phase of Cyano Compounds with Different Ring Systems, Molecular Crystals and Liquid Crystals, 72:2-3, 51-57

To link to this article: http://dx.doi.org/10.1080/01406568108084036

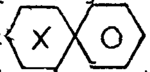
Mol. Cryst. Liq. Cryst. Vol. 72 (Letters), pp. 51-57
0140-6566/81/7202-0051$06.50/0

Printed in the United States of America

MOLECULAR PACKING IN THE NEMATIC PHASE OF CYANO COMPOUNDS WITH DIFFERENT RING SYSTEMS

A.J. LEADBETTER and A.I. MEHTA
Department of Chemistry, University of Exeter,
Exeter EX4 4QD, U.K.

(Submitted for publication June 9, 1981)

Abstract: The molecular packing in the nematic phase of three series of compounds R CN where  is  or  has been studied by X-ray diffraction. All have a preferred local structure based on overlapping cores but for the systems with bulky rings this differs significantly from the biphenyls in having only partial core overlap and a weaker longitudinal correlation. These results, together with studies of mixtures, have led to a qualitative correlation of structure and elastic constants.

An overlapping core packing is now widely accepted as the preferred local structure in nematic and smectic A phases of cyanobiphenyls[1]. In these structures the wavelength (d) of the density wave (highly damped for nematics) parallel to the director exceeds the molecular length (ℓ) by about the length of the molecular tail.

Recently a number of compounds have become available in which the core of the cyanobiphenyl is modified by replacing the phenyl ring adjacent to the tail by a cyclohexane or bicyclooctane group. Preliminary measurements[2] of the wavelengths of the damped density waves in some of these materials showed that $d/\ell \sim 1.4$ suggesting a core overlapping bilayer structure similar to the biphenyls. However, the substitution of a phenyl by a much bulkier ring system should have a marked effect on the packing, so we have now made a systematic study of the structure of these compounds by determining the wavelength, relative amplitude and correlation length of the density waves of a number of compounds of each type.

The X-ray measurements were made using monochromatic CuKα radiation and a single flat plate camera, as described previously.[3] The compounds investigated and the results of the measurements are given in Table 1. The diffraction patterns were typical of nematics in showing a strong equatorial arc, arising from lateral correlations between different molecules. The position of the peak maximum S ($S = 2\sin\theta/\lambda$) was used to define a spacing $d_\perp = S_\perp^{-1}$ which gives an approximate relative measure of the lateral intermolecular distance.[3] The other major feature of the diffraction pattern is a meridional peak which varies markedly in strength and sharpness and arises from (pseudo smectic A) damped density waves. The wavelength is given by $d_\parallel = S_\parallel^{-1}$. The amplitude of the wave (τ) is related to the intensity of the scattering ($\tau \propto I^{\frac{1}{2}}$) but this also depends on the structure factor for the system so is not easily compared between different substances. As a qualitative guide, however, we give in Table 1 the ratios $I_\parallel/I_\perp$ for the peak heights and also given in Fig.1 normalised plots of I (Q) for selected samples. The correlation length $\xi_\parallel$ of the density wave is related to the width of the scattering peak and while the details will of course depend on the correlation function, we use in Table 1 for comparative purposes $\xi_\parallel \sim (\Delta S\,(\mathrm{HWHM}))^{-1}$. (See Fig.1). The molecular lengths given in Table 1 are for the molecules in their most extended

TABLE 1. Summary of Data and Results for the Nematic Phases of Cyano Compounds having different ring systems: R - X -  CN

X	R	Code	T_{Cr} /°C	T_{NI}/°C	T_m/°C	ℓ/Å	$d_{\parallel}^{m}$/Å	$d_{\parallel}$/Å	$d_{\perp}$/Å	$\xi_{\parallel}$/Å	$I_{\parallel}/I_{\perp}$
	C_3H_7	3PCH	42	45	44	16	24	22.9	4.7	50	0.4
	C_5H_{11}	5PCH	30	55	50	18	29	26.3	4.7	80	0.45
	C_7H_{15}	7PCH	30	58	50	21	34	30.9	4.6	110	0.69
	C_3H_7	3BCO	64	88	74	16	24	22.3	5.1	50	0.27
	C_5H_{11}	5BCO	62	100	75	18	29	25.5	5.0	60	0.51
	C_8H_{17}	8BCO	50	90	75	22	36	31.0	5.0	200	0.89
	C_5H_{11}	5CB	22	35	30	18	-	25	4.3	130	0.98
	C_7H_{15}	7CB	29.0	42	29	21	-	29	4.3	150	1.90
Mixture	0.7 (3BCO)	0.3 (7CB)	-	52	51	-	-	24.9	4.8	90	0.32
	0.4 (3BCO)	0.6 (7CB)	-	64	39	-	-	28.2	4.6	130	0.75

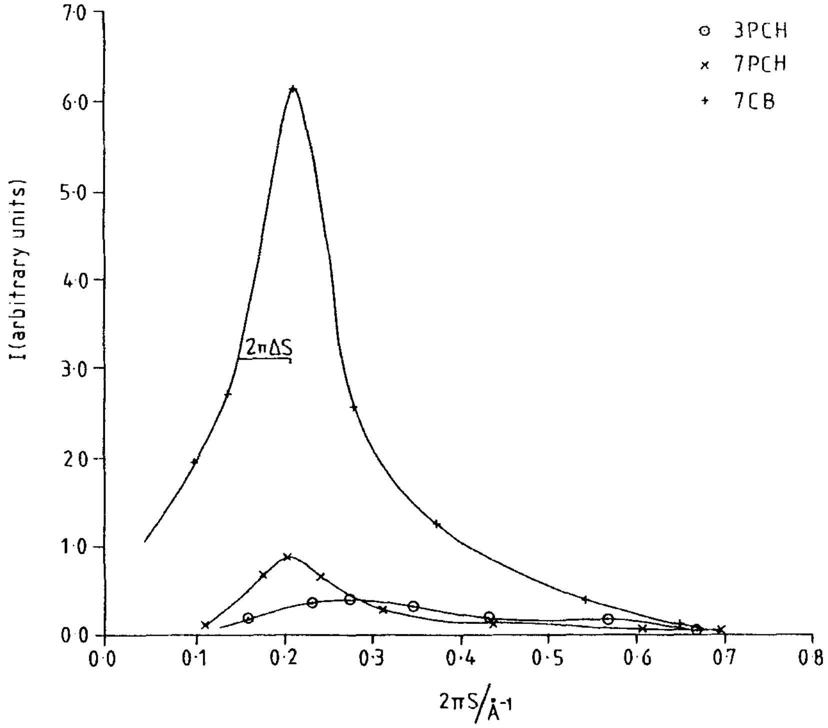


FIGURE 1. Intensity profiles I(S) parallel to the director of the first order meridional reflections in the nematic phases 7CB(+); 3PCH(O); 7PCH(X).

conformations as estimated using CPK molecular models.

The first point to note is that the lateral spacing ($d_\perp$) of the molecules increases with the bulkiness of the substituted ring from phenyl to cyclohexane to bicyclooctane - the average $d_\perp$/Å values being respectively 4.35, 4.7 and 5.0.

Consideration of the $d_{\parallel}$ values in conjunction with the molecular dimensions leads us to propose a model for the preferred local structures as shown schematically in Fig. 2 for 3BCO. The basis of the model is that the extra bulkiness of the cyclohexane and bicyclohexane rings dominates the packing and

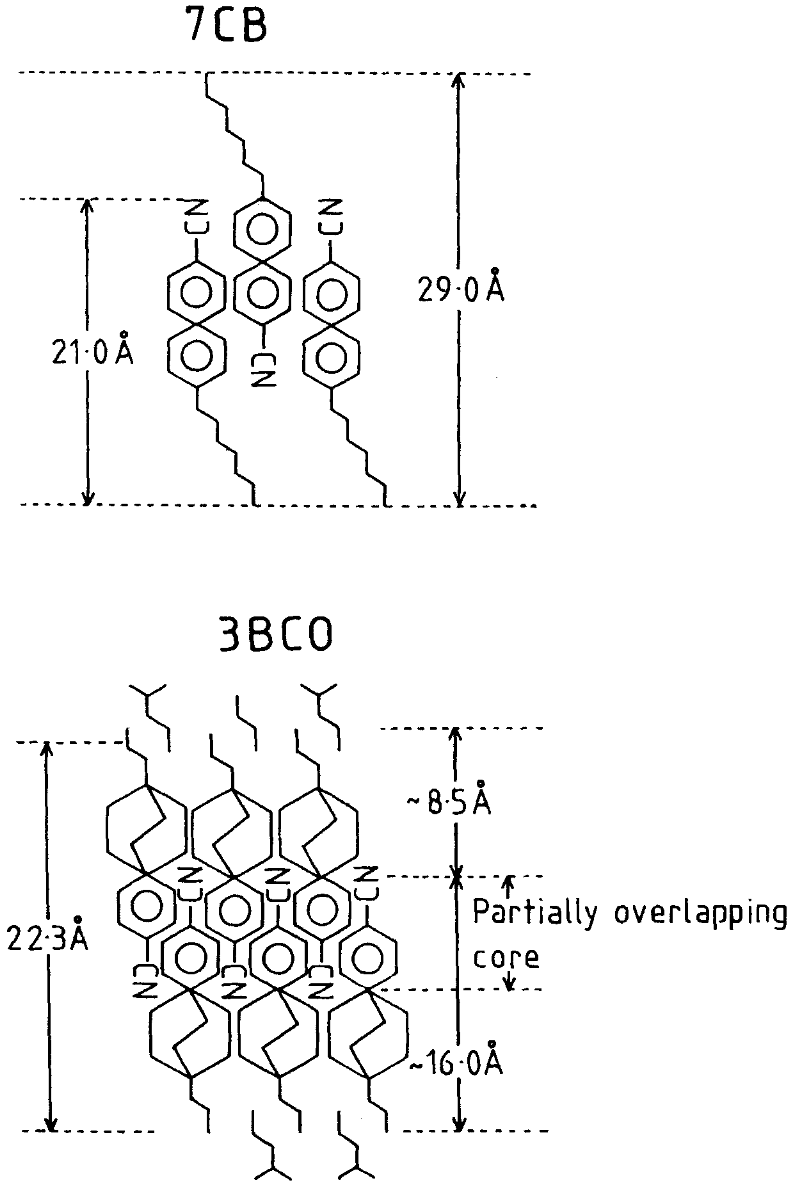


FIGURE 2. Schematic drawing of proposed local packing in 3BCO (and in similar n BCO and n PCH compounds) compared with the behaviour of cyanobiphenyls.

reduces the amount of core overlap from the essentially total overlap in the biphenyls. Opposed overlap of adjacent cyano and phenyl groups, close packing of bulky rings and some interdigitating of the alkyl tails then provides the most efficient means of filling space. The total length of an adjacent pair of oppositely oriented molecules (Fig.2) is given in Table 1 as $d_{\parallel}^{m}$, and $d_{\parallel}^{m} - d_{\parallel}$ gives a measure of the maximum interdigitation of alkyl tails which is probably less than 3 carbons of the tail. Note that this is a maximum because for a simple nematic $d < \ell$ on account of long axis fluctuations. Finally we emphasise that this is a model of the preferred local packing in a nematic which is still a liquid so there must always be very considerable disorder.

The strength of the correlations of this local structure along the director is indicated by the values of $I_{\parallel}/I_{\perp}$ and $\xi_{\parallel}$. These show that this is much less well-defined for the bulky ring systems than in the biphenyls. Furthermore, both the correlation length and amplitude of the correlations increases with increasing tail length for all types of ring systems which may be regarded as evidence for increasing tendency to smectic formation. The longitudinal correlations in the compounds with propyl tails are very weak, while 3CB does not in fact form a nematic phase.

An interesting correlation may be made with the elastic constants of these materials which have been measured by Bradshaw and Raynes.[4] They found that K_{33} is unusually large for 3BCO and, to a lesser extent also for 3PCH and approaches the more usual cyanobiphenyl values as the tail lengths in these series increase. This implies that lack of longitudinal correlation is associated with increased stiffness against bend distortions. In other words, a structure in which there are locally good end-to-tail correlations of molecules is easier to bend than one in which this correlation is weak - giving a less organised, more interdigitated type of structure. This is supported by the results given in Table 1 for mixtures of 3BCO and 7CB in which both structural and elastic properties vary smoothly across the composition range. At this stage the relationship between structural correlations and elastic properties is qualitative but it seems worth pursuing in other compounds and with a view to relating it to theories of elastic constants.

ACKNOWLEDGEMENTS

We thank BDH Ltd., Merck and Professor G.W. Gray of the University of Hull for supplying the compounds. Financial support from the ministry of Defence is also gratefully acknowledged. We also thank Mrs. M.J. Bradshaw and Dr. E.P. Raynes for sending us elastic constant results prior to publication.

REFERENCES

1. A.J. Leadbetter, J.C. Frost & J.P. Gaughan
J. de Phys. 40, 375 (1979)

2. G.J. Brownsey & A.J. Leadbetter,
J. de Phys. Letts. 42, L135 (1981).

3. A.J. Leadbetter & E.K. Norris,
Mol. Phys. 38, 669, (1979).

4. M.J. Bradshaw & E.P. Raynes,
Private communication, results to be published.