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Structural Arrangements of the Mesogenic Compounds 4-Ethyl-4′-(4″-pentylcyclohexyl)biphenyl and 4-Ethyl-2 ′-fluoro-4′ -(4″-pentylcyclo-hexyl)biphenyl (BCH's) in the Crystalline State

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Structural Arrangements of the Mesogenic Compounds 4-Ethyl-4′-(4″-pentylcyclohexyl)biphenyl and 4-Ethyl-2′-fluoro-4′-(4″-pentylcyclohexyl)biphenyl (BCH's) in the Crystalline State

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The crystal and molecular structures of 4-ethyl-4′-(4″-pentylcyclohexyl)biphenyl (BCH52) and its fluoro derivative, 4-ethyl-2′-fluoro-4′-(4″-pentylcyclohexyl)biphenyl (BCH52F) are described. The crystal data are: a = 31.564(5), b = 5.511(1), c = 25.243(4) Å, β = 104.904(4)°, space group C2/c for BCH52 and a = 17.156(3), b = 6.792(1), c = 37.334(6) Å, space group Pbcn for BCH52F. The structures refined to R values of 0.0711 (BCH52) and 0.0836 (BCH52F) using 2624 reflections for BCH52 and 2781 reflections for BCH52F. The torsion angles between the phenyl rings are radically different, being 3.9° in BCH52 and 41.9° in BCH52F. The torsion angles between the alkyl, phenyl, and cyclohexyl subunits of the molecules are compared and the influence of the fluoro substitution is discussed. The patterns of packing of the crystal structures are discussed, especially in terms of short-range ordering. Comparisons with similar compounds are made.

Keywords: crystal structure, biphenyl mesogens, fluorine substitution

INTRODUCTION

Details of the molecular and conformational structure as well as of the crystal packing are necessary if we are to obtain a deeper under-

†Hydrogen atom coordinates, anisotropic thermal parameters and listings of observed and calculated structure factors are available from the authors on request.

standing of the relationship between crystalline and liquid crystalline states.[1,2] Our previous investigations of this topic involve studies of the molecular structures and crystal packings of compounds with biphenyl,[3] phenylcyclohexane[4,5] or cyclohexylcyclohexane[6] units.

The compounds with biphenylcyclohexane cores were first described by Eidenschink *et al.*[7-9] Data concerning the phase transitions, some physical properties and X-ray structural data on the liquid crystalline and the solid crystalline states have been reported.[10-12]

Investigations of the syntheses and characterizations of mesogenic compounds containing lateral polar groups are becoming more frequent.[2,9,13] Such investigations have been carried out in the search for new compounds with some specific properties. A principal point of interest is the relative influence of the lateral substituent changes on the molecular conformations.

The present study reports the crystal and molecular structure of 4-ethyl-4′-(4″-pentylcyclohexyl)biphenyl (BCH52) and its fluoro derivative 4-ethyl-2′-fluoro-4′-(4″-pentylcyclohexyl)biphenyl (BCH52F). Since these compounds differ only by a fluoro substitution in the biphenyl unit, they enable the effect of such a substitution to be gauged.

Comparisons of the observed structural features with those of molecules having the same neighbouring subunits are made in order to reveal more about the flexibility of such partially-rigid systems. The results obtained from the crystalline state should help in our understanding of the liquid crystalline state.

EXPERIMENTAL

Substances

The two compounds investigated were kindly supplied by Dr. Eidenschink, E. Merck AG, Darmstadt. Their transition temperatures have been previously reported[7,9] and are:

BCH52 C 34 S_B 146 N 164 I (°C)
BCH52F C 37 N 117 I (°C)

Crystal data

Crystals suitable for X-ray analyses were obtained by slow evaporation of alcoholic solutions. Intensity measurements were made at

ambient temperature on an automatic STOE-STADI-4 four-circle-diffractometer with graphite monochromated CuKα-radiation (λ = 1.54178 Å). Lattice dimensions were obtained by a least-squares refinement with a number of strong reflections. The basic crystal data are given in Table I.

Structure determination and refinement

The structures of both compounds were solved by direct methods with the program package SHELX-76[14] without absorption corrections. The hydrogen atom positions were calculated (C—H = 1.08 Å)[14] and their isotropic thermal parameters were fixed using a factor of about 1.1 times the average value of the diagonal elements of the carrying atom. The refinement procedures converged at R = 0.0711 for BCH52 and at R = 0.0836 for BCH52F.

The atomic parameters for both compounds are given in Table II for all non-hydrogen atoms.

TABLE I

The basic crystal data

	BCH52	BCH52F
Formula weight ($g \cdot mol^{-1}$)	334.54	352.51
Space group (No. of Int. Tables)	*C2/c* (15)	*Pbcn* (60)
a (Å)	31.564(5)	17.156(3)
b (Å)	5.511(1)	6.792(1)
c (Å)	25.243(4)	37.334(6)
β (°)	104.904(4)	
V ($Å^3$)	4243.27	4350.28
Number of strong reflections used for lattice parameter refinement	52	44
Z	8	8
D_c ($g \cdot cm^{-3}$)	1.047	1.076
μ(Cu-K_α)(cm^{-1})	3.67	4.43
F(000)	1472	1536
Number of measured reflections	4202	4476
Number of independent reflections	2907	3027
Merging R	0.0448	0.0317
Number of unobserved reflections ($F_o < 2\sigma(F_o)$)	283	246
R (R_w with $w = 1/\sigma^2(F_o)$)	0.0711 (0.0774)	0.0836 (0.0827)

Note: In a previous publication[12] the preliminary single crystal data given for BCH52 were in fact those of BCH52F.

TABLE II

Positional and thermal parameters $\left(U_{eq.} = \frac{10^3}{3}\left(\sum_i\sum_j U_{ij}\, a_i^* a_j^* (a_i \cdot a_j)/\text{Å}^2\right)\right)$ with e.s.d.'s in parentheses (not for $U_{eq.}$) for BCH52 and BCH52F

Atom	BCH52				BCH52F			
	x	y	z	$U_{eq.}$	x	y	z	$U_{eq.}$
F(1)	—	—	—	—	0.4240(1)	0.0882(3)	0.2153(1)	96
C(2)	0.3640(1)	0.3737(5)	0.2619(1)	78	0.3515(2)	0.0983(7)	0.0829(1)	84
C(3)	0.3620(1)	0.5535(6)	0.2981(1)	120	0.3751(2)	0.2938(7)	0.0875(1)	65
C(4)	0.3296(1)	0.5645(6)	0.3259(1)	115	0.3802(2)	0.3768(6)	0.1206(1)	72
C(5)	0.2970(1)	0.3946(4)	0.3184(1)	63	0.3625(2)	0.2684(5)	0.1515(1)	57
C(6)	0.2981(1)	0.2188(5)	0.2803(1)	103	0.3400(2)	0.0728(5)	0.1469(1)	61
C(7)	0.3309(1)	0.2087(6)	0.2530(1)	113	0.3342(2)	−0.0083(6)	0.1132(1)	75
C(8)	0.2623(1)	0.4030(4)	0.3485(1)	62	0.3644(2)	0.3610(4)	0.1874(1)	52
C(9)	0.2599(1)	0.5885(4)	0.3849(1)	79	0.3354(2)	0.5505(5)	0.1932(1)	58
C(10)	0.2281(1)	0.5925(4)	0.4134(1)	82	0.3348(2)	0.6385(4)	0.2264(1)	56
C(11)	0.1969(1)	0.4104(4)	0.4077(1)	68	0.3643(2)	0.5418(4)	0.2564(1)	51
C(12)	0.1993(1)	0.2293(5)	0.3713(1)	88	0.3931(2)	0.3526(4)	0.2511(1)	54
C(13)	0.2307(1)	0.2233(4)	0.3425(1)	86	0.3920(2)	0.2688(4)	0.2179(1)	55
C(14)	0.1631(1)	0.4047(4)	0.4405(1)	74	0.3697(2)	0.6350(5)	0.2931(1)	52
C(15)	0.1356(1)	0.6335(5)	0.4361(1)	98	0.3157(2)	0.8092(5)	0.2995(1)	65
C(16)	0.1007(1)	0.6125(6)	0.4679(1)	93	0.3248(2)	0.8914(6)	0.3370(1)	69
C(17)	0.1194(1)	0.5482(5)	0.5274(1)	76	0.4085(2)	0.9547(5)	0.3448(1)	61
C(18)	0.1482(1)	0.3278(6)	0.5323(1)	118	0.4633(2)	0.7818(6)	0.3379(1)	70
C(19)	0.1828(1)	0.3476(6)	0.5002(1)	97	0.4545(2)	0.6966(6)	0.3008(1)	65
C(20)	0.0844(1)	0.5148(5)	0.5586(1)	84	0.4182(2)	1.0362(5)	0.3828(1)	73
C(21)	0.0566(1)	0.7354(5)	0.5614(1)	93	0.3767(3)	1.2273(6)	0.3902(1)	95
C(22)	0.0262(1)	0.7016(5)	0.5990(1)	94	0.3870(3)	1.3090(8)	0.4270(1)	109
C(23)	−0.0004(1)	0.9201(7)	0.6033(1)	129	0.3421(5)	1.4936(10)	0.4348(2)	167
C(24)	−0.0278(1)	0.8966(9)	0.6439(1)	153	0.3552(7)	1.5855(14)	0.4693(2)	227
C(25)	0.4000(1)	0.3642(6)	0.2323(1)	103	0.3451(4)	0.0018(10)	0.0461(1)	132
C(26)	0.4287(1)	0.1537(8)	0.2456(2)	175	0.4156(6)	−0.1087(19)	0.0368(2)	238

H-atoms geometrically idealized positioned (C—H = 1.08 Å)

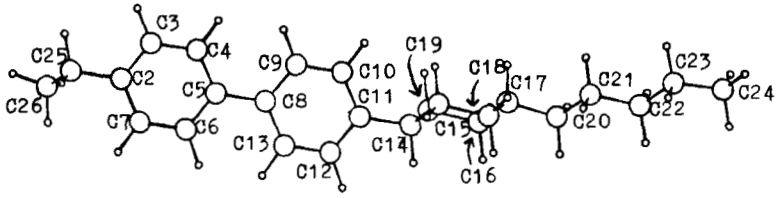

FIGURE 1 Molecular structure of BCH52 projected on the plane C(2), C(4), C(6).

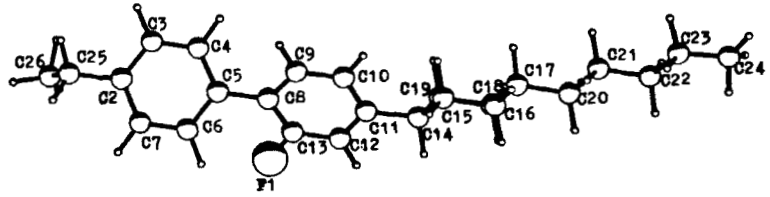

FIGURE 2 Molecular structure of BCH52F projected on the plane C(2), C(4), C(6).

RESULTS AND DISCUSSION

Molecular structures

The molecular structures of BCH52 and BCH52F are presented in Figures 1 and 2, respectively. Both molecules occur in their fully extended forms due to the *trans* configuration of the pentyl groups.

Some bond distances and angles of interest are listed in Table III. All distances and angles lie within the range of values found for other similar compounds.

The major point of the structural interest concerns the conformation of the molecules. Table IV compares the dihedral angles

TABLE III

Some interatomic distances (Å) and angles (°) of interest for BCH52 and BCH52F (e.s.d.'s in parentheses)

	BCH52	BCH52F
C(5)—C(8)	1.487(3)	1.482(4)
C(13)—F(1)	—	1.347(3)
C(2)—C(25)	1.512(4)	1.529(6)
C(17)—C(20)	1.522(4)	1.534(4)
C(17)—C(20)—C(21)	115.7(2)	115.4(3)
C(2)—C(25)—C(26)	114.6(3)	111.9(5)

TABLE IV

Dihedral angles (°) between best planes of the different subunits in BCH52 and in BCH52F and in related compounds

I II III IV V
$R_1—C_6H_4—C_6H_4—C_6H_{10}—R_2$

Compound	I/II	II/III	[e]III/IV	[e]IV/V	Ref.
BCH52	65.2	3.9	89.7	36.3	this work
BCH52F	84.1	41.9	48.7	35.0	this work
BCH30	—	22.0	76.5	58.7	12
BCH5CN	—	3.1	82.4	[f]—	12
[a]K6A	74.1	1.5	—	—	21,27
[a]K6B	72.0	0.7	—	—	21,27
[a]K9	87.7	42.8	—	—	3
[b]T15	78.2	40.4/29.5	—	—	21,28
[c]BP	[f]—	17.7/29.6	—	—	29
[d]PCH3	—	—	81.5	34.1	5
[d]PCH8A	—	—	64.9	33.3	6
[d]PCH8B	—	—	36.5	38.4	21,30
[d]PCH9A	—	—	46.0/41.3	43.7/40.1	21,30
[d]PCH9B	—	—	65.9	33.4	21,30

[a]K-series: $R—(C_6H_4)_2—CN$.
[b]$C_5H_{11}—(C_6H_4)_3—CN$.
[c]$C_4H_9—C_6H_4—COO—(C_6H_4)_2—C_3H_7$.
[d]PCH-series: $R—C_6H_{10}—C_6H_4—CN$.
[e]Best planes using only C(2), C(3), C(5), C(6).
[f]Dynamic disorder of the alkyl group.

between the best planes of the different subunits in BCH52 and in BCH52F with those found for other similar compounds.

Considering first the torsion angle in the biphenyl unit, different experimental approaches have given a value of approximately 42° in the vapour state,[15] and of about 20–25° in solutions[16,17] and in the melt.[18] This angle varies from 0–47° in the crystalline solid, showing that the small energy barriers between the realized geometries can be overridden by packing effects.[3,12,19–21] Various calculations have been carried out to explain these conformational changes. Lindner in 1974,[22] in a study of molecular geometries of strained hydrocarbons with a combined π-SCF-LCAO-MO and force field method, obtained an angle of ~26° for the energy minimum in biphenyl. The energy barrier calculated was 2 kcal mol^{-1}. Charbonneau *et al.* have used molecular models to explain the apparent planarity in the crystalline state.[23] PCILO conformational calculations carried out on model

compounds by Meurisse *et al.*[24] gave an absolute conformational energy minimum at a torsion angle of 40° in the case of an unsubstituted biphenyl and a height of 1.9 kcal · mol^{-1} for the energy barrier for a coplanar arrangement. The torsion angles between the phenyl rings are 3.9° in BCH52 and 41.9° in BCH52F. These two examples clearly illustrate that in the case of an unsubstituted biphenyl unit, the energy barrier can be overcome. This is also confirmed by BCH5CN (see Table IV). A resulting intramolecular H· · ·H distance of about 1.9 Å observed for BCH52 is of course smaller than twice the hydrogen van der Waals radius but the repulsion remains weak anyway. In a hypothetical coplanar arrangement of BCH52F, the intramolecular distances between the contacting atoms would be shorter and the repulsions would increase, principally due to the greater van der Waals radius of the fluorine atom. Calculations[25] with a modified version of the above mentioned force field method[22] suggest an energy barrier approximately twice as high. However, the dihedral angle for the energy minimum stays nearly unchanged (~45°). This energy barrier is too high to be countered by packing effects. Dihedral angles up to 90° are expected for 2,2′-disubstituted biphenyls with large substituents as reported, e.g., by Lesser *et al.*[26] in case of a 2,2′-dibromobiphenyl derivative (80.1°).

All the same, Table IV shows that, for some other molecules with unsubstituted biphenyl subunits, twist angles up to 43° occur. With the exception of the two modifications of K6, it can be seen that larger and more extended molecules have a greater tendency to be planar in the crystalline state. Following this trend, we conclude that within the liquid crystalline state, the forces involved in the dense packing can also overcome the rotation barrier in the biphenyl subunits.

Considering the dihedral angle between the alkyl group and the phenyl group (I/II) we observe, as for other studied compounds, angles between 60° to 90° which seems us to be typical. The dihedral angle between the cyclohexyl ring and the phenyl ring (III/IV), which can vary over a wide range for the PCH's, correlates with the phenyl-phenyl angle (II/III) in the BCH's series giving a total of approximately 90°. The dihedral angles between the cyclohexyl moiety and the alkyl group (IV/V) for BCH52 and BCH52F are found to be very close to the mean value usually found for this structural element (38 ± 6°). The only exception is BCH30. Recently we showed that an angle between 35° and 40° eliminates hydrogen-hydrogen repulsions.[31]

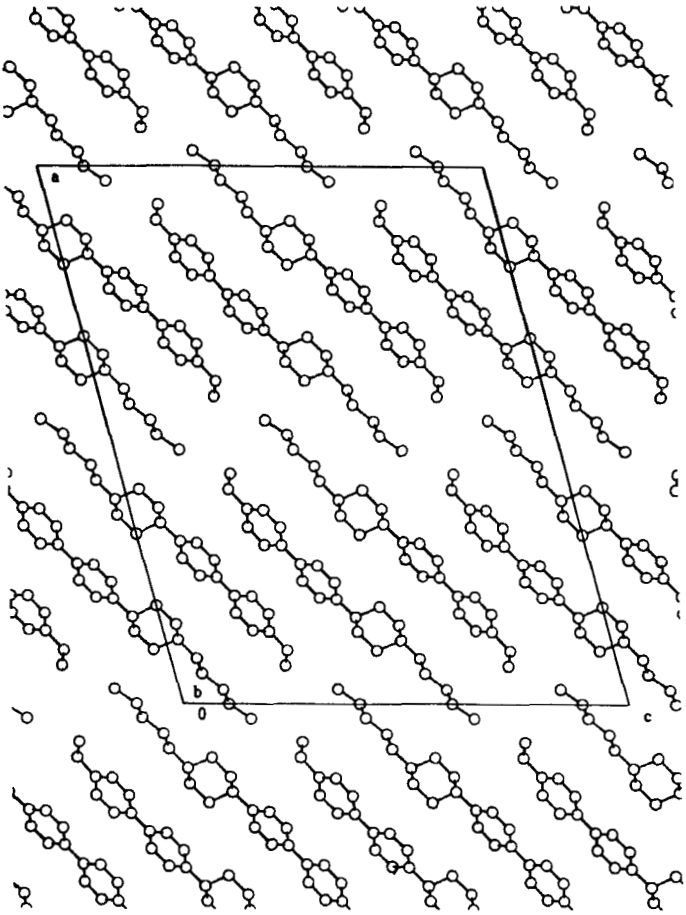

FIGURE 3 Crystal structure of BCH52, viewed along [010].

Molecular packing

The pattern of molecular packing in the crystalline state is shown in Figure 3 for BCH52 and in Figures 4 and 5 for BCH52F.

The line C(25)—C(2)—C(5)—C(8)—C(11)—C(14) in BCH52 lies virtually in the ac plane. The nearly coplanar biphenyl unit makes an angle of about 66° with this plane. The biphenyl group lies along the 101 diagonal. The biphenyl moieties form an infinite stack along the 2_1 axis at 1/4, y, 1/4. This stacking is comparable with that found in BCH5CN.[12] Additional to this infinite arrangement, the cyano groups in BCH5CN are also infinitely stacked along the [010] direc-

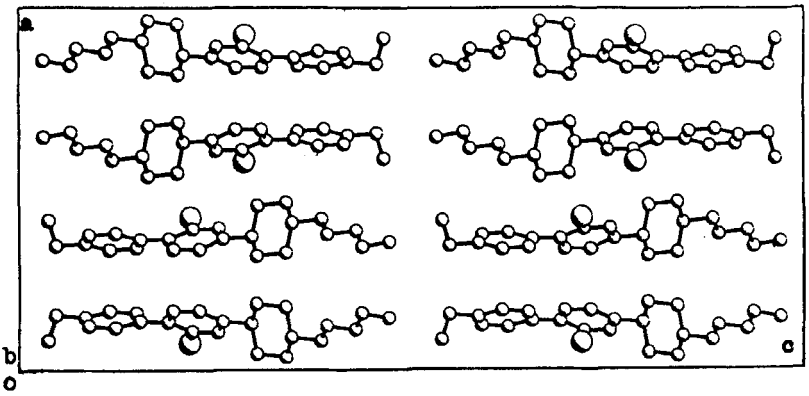

FIGURE 4 Crystal structure of BCH52F, viewed along [010].

tion (CN· · ·CN ~ 3.5 Å). Ethyl groups can not be packed so close together and the substitution of a cyano group by an ethyl group leads therefore, to an elongation of the [101] direction. Losing the specific short-range ordering caused by cyano groups in BCH5CN,[12] the same principal arrangement is repeated. At this point it should be noted that BCH52 forms a smectic B phase in contrast to BCH5CN which melts directly to the nematic phase.

The molecules in BCH52F lie in the (100) plane with $x \sim 1/8$, 3/8, 5/8, 7/8; as shown in Figure 4. The F(1) – C(13) bond is nearly parallel to the b-axis. Note that there is no contact between the

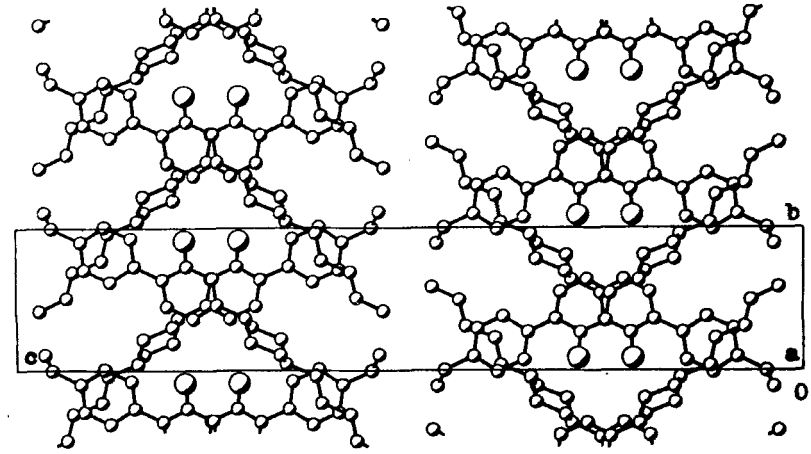

FIGURE 5 Crystal structure of BCH52F, viewed along [100] from $x = 1/4$ to $x = 3/4$.

fluorine atoms and other atoms of the neighbouring molecules, e.g. the phenyl ring. The packing in the crystalline state is completely different to that of BCH52 and BCH5CN.[12] In these compounds and in BCH30[12] the molecules lie with their long axes nearly parallel in a head-to-tail arrangement, but in BCH52F, the molecules lie perpendicular to [100] and are inclined at an angle of $\sim 40°$ to each other in the projection onto the (100) plane (see Figure 5).

CONCLUSIONS

The crystal and molecular structures of BCH52 and BCH52F which differ only by the replacement of a hydrogen by a fluorine atom, show marked differences. Similar observations have been described earlier for the liquid crystalline state. The effects arising from the fluoro substitution are responsible for the different physical properties of the crystalline and the liquid crystalline state.

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References

1. R. F. Bryan, Proceedings of the Pre-congress Symposium on Organic Crystal Chemistry, Poznan, Poland, 105 (1979).
2. D. Demus, *Z. Chem.*, **26**, 6 (1986).
3. W. Haase, H. Paulus and R. Pendzialek, *Mol. Cryst. Liq. Cryst.*, **100**, 211 (1983).
4. H. Paulus and W. Haase, *Mol. Cryst. Liq. Cryst. Lett.*, **92**, 237 (1983).
5. J. K. Foitzik, H. Paulus and W. Haase, *Mol. Cryst. Liq. Cryst. Lett.*, **1**, 1 (1985).
6. W. Haase and H. Paulus, *Mol. Cryst. Liq. Cryst.*, **100**, 111 (1983).
7. R. Eidenschink, W. Erdmann, J. Krause and L. Pohl, 10th Freiburger Arbeitstagung Flüssigkristalle, (2) (1980).
8. R. Eidenschink, *Kontakte* (Merck), **1**, 15 (1979).
9. R. Eidenschink, *Mol. Cryst. Liq. Cryst.*, **123**, 57 (1985).
10. H. J. Müller and W. Haase, *Mol. Cryst. Liq. Cryst.*, **92**, 63 (1983).
11. H. J. Müller and W. Haase, *J. Phys.*, **44**, 1209 (1983).
12. W. Haase, H. Paulus and H. J. Müller, *Mol. Cryst. Liq. Cryst.*, **97**, 131 (1983).
13. J. E. Fearon, G. W. Gray, A. D. Ifill and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **124**, 89 (1985).
14. G. M. Sheldrick, SHELX-76, Program for crystal structure determination, University of Cambridge, England (1976).
15. A. Almenningen and O. Bastiansen, *Skr., K. Nor. Vidensk. Selsk*, **4**, 1 (1958).
16. H. Suzuki, *Bull. Chem. Soc. Jpn.*, **32**, 1340 (1959).

17. B. D. Schmidt and B. Brosa, *J. Chem. Phys.*, **56**, 6267 (1972).
18. O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962).
19. A. Hargreaves and S. H. Rizvi, *Acta Cryst.*, **15**, 365 (1962).
20. C. P. Brock, M. S. Kuo and H. A. Levy, *Acta Cryst.*, **B34**, 981 (1978).
21. W. Haase, L. Walz and H. Paulus, 15th Freiburger Arbeitstagung Flüssigkristalle, (5) (1985).
22. H. J. Lindner, *Tetrahedron*, **30**, 1127 (1974).
23. G.-P. Charbonneau and Y. Delugeard, *Acta Cryst.*, **B33**, 1586 (1977).
24. P. Meurisse, F. Laupretre and C. Noël, *Mol. Cryst. Liq. Cryst.*, **110**, 41 (1984).
25. H. J. Lindner, private communication.
26. D. P. Lesser, A. de Vries, J. W. Reed and G. H. Brown, *Acta Cryst.*, **B31**, 653 (1975).
27. W. Haase and H. Paulus, to be published.
28. W. Haase, I. H. Ibrahim and M. A. Mokles, *Mol. Cryst. Liq. Cryst.*, Submitted for publication.
29. L. Walz, to be published.
30. W. Haase, H. Paulus and M. A. Mokhles, to be published.
31. L. Walz and W. Haase, *Mol. Cryst. Liq. Cryst. Lett.*, submitted for publication.