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DSC and thermomicroscopic analysis of 4-cyano-4′-*n*-propylbiphenyl (CB 3) revealed solid crystalline polymorphism. Thus the compound exhibits two solid phases subsequent to appropriate thermal treatment. The melting points are K_I: 338.4 (5) K and K_{II}: 326.3(3) K. The enthalpies of fusion for K_I and K_{II} are 19.9(5) kJ/mol and 16.7(7) kJ/mol, respectively. The compound also possesses a monotropic nematic phase, its clearing point being 303.3(2) K and $\Delta H_{N-I} = 0.3(2)$ kJ/mol. The crystals of the higher melting modification are monoclinic, with $a = 6.259$ (3) Å, $b = 19.1216$ (9) Å, $c = 11.0473$ (5) Å and $\beta = 103.39$ (2)°. The space group is $P2_1/c$. For 1014 nonzero reflections, $R = 0.051$, $R_w = 0.042$. The dihedral angle between the phenyl rings was found to be 42.8°.

INTRODUCTION

The first results of X-ray investigations relating to the crystal and molecular structure of 4-cyano-4′-*n*-propylbiphenyl (CB 3) were presented in 1978.[1] It is now possible to present the final refinement and some more detailed information on the thermal behaviour of this compound.

Previous data[2] quoted CB 3 as having a melting point K-I at 341.2K with an enthalpy of fusion amounting to 26.8 kJ/mol. Besides this, the

compound was reported to possess a monotropic nematic phase with a clearing point at 298.7 K. Solid state polymorphism has briefly been reported for CB 3. This occurred when the compound was allowed to solidify *via* the nematic phase. The unstable crystal form reverted to the more stable form at ca. 305.2 K upon heating. Further to this, it has been observed and reported that some other members of the homologous series, namely 4-cyano-4′-*n*-heptylbiphenyl[3,4] and 4-cyano-4′-*n*-nonylbiphenyl[3,5] also exhibit solid state polymorphism.

A point of interest concerning the 4,4′-disubstituted biphenyls has been the dihedral angle between the two phenyl rings. Mention has previously been made[6] of a number of compounds, with halogen, cyano, or methyl groups as substituents, possessing a dihedral angle of 36° to 42°. These angles are indeed comparable with the dihedral angle of 42° found for biphenyl in the gaseous state.[7] For a homologe of CB 3, namely 4-cyano-4′-*n*-butylbiphenyl, a dihedral angle of 40.3° has been reported[8] for the solid state, whereas in solution it is postulated[9] to be 32.1° as determined by the NMR-method. It should be mentioned that in 4,4′-disubstituted biphenylcyclohexanes, the dihedral angle varies from 2.4° (BCH 5CN) to 23.8° (BCH 30)[10] in the solid crystalline state.

EXPERIMENTAL

Calorimetric and thermal analysis of the compound was carried out with a Du Pont 990 Thermal Analyzer and the appropriate DSC-cell. The system was calibrated for thermal analysis with *p*-nitrotoluene and naphthalene (Fisher Certified Thermometric Standards). Indium served as standard for the calorimetric work. The cooling rates were

TABLE I

Crystal data for the higher melting stable modification of CB 3

Molecular formula:	$C_{16}H_{15}N$
Molecular weight:	221.3 g/mol
Space group:	$P2_1/c$
a:	6.259(3) Å
b:	19.1216(9) Å
c:	11.0473(5) Å
β:	103.39(2)°
V_C:	1286.2 Å^3
Z:	4
$\mu(MoK_\alpha)$:	0.34

controlled by employing liquid nitrogen. All DSC-runs in the heating mode were performed at 2 K/min. Confirmation of some transition points was obtained by means of a polarizing microscope (Leitz–Orthoplan–Pol) in conjunction with a hot-stage (Mettler FP-52) and control unit (FP-5). The mass of the samples was determined with a micro-balance up to an accuracy of ± 0.01 mg, varying between 2 to 5 mg. The integration of the peak areas was carried out with a Haff-Planimeter, the error being ± 0.01 in.[2]

TABLE II

Positional parameters with e.s.d.'s in parentheses and U_{eq} values

Atom	x	y	z	U_{eq}[a]
N	0.0814(5)	0.6225(1)	0.4865(3)	96(2)
C(1)	0.1876(5)	0.5894(2)	0.4373(3)	71(2)
C(2)	0.3157(5)	0.5477(1)	0.3723(2)	58(2)
C(3)	0.5004(5)	0.5757(2)	0.3416(3)	67(2)
C(4)	0.6183(5)	0.5367(2)	0.2754(3)	65(2)
C(5)	0.5567(4)	0.4684(1)	0.2388(2)	52(2)
C(6)	0.3722(5)	0.4410(1)	0.2727(2)	60(2)
C(7)	0.2532(5)	0.4797(2)	0.3387(3)	63(2)
C(8)	0.6777(4)	0.4270(1)	0.1634(2)	52(2)
C(9)	0.7454(5)	0.4572(1)	0.0643(2)	58(2)
C(10)	0.8443(5)	0.4181(1)	−0.0120(3)	63(2)
C(11)	0.8832(5)	0.3479(1)	0.0079(3)	62(2)
C(12)	0.8230(5)	0.3180(2)	0.1088(3)	67(2)
C(13)	0.7209(5)	0.3563(2)	0.1853(3)	63(2)
C(14)	0.9857(6)	0.3051(2)	−0.0790(3)	79(2)
C(15)	1.2267(8)	0.2988(2)	−0.0400(4)	108(3)
C(16)	1.3275(6)	0.2549(2)	−0.1261(4)	123(3)
H(3)	0.556(4)	0.625(1)	0.364(2)	80
H(4)	0.757(4)	0.556(1)	0.255(2)	70
H(6)	0.328(4)	0.393(1)	0.245(2)	70
H(7)	0.123(4)	0.462(1)	0.361(2)	70
H(9)	0.717(4)	0.505(1)	0.048(2)	70
H(10)	0.890(4)	0.439(1)	−0.086(2)	70
H(12)	0.849(4)	0.269(1)	0.127(2)	80
H(13)	0.682(4)	0.335(1)	0.259(2)	70
H(141)	0.971(5)	0.329(1)	−0.167(2)	90
H(142)	0.920(5)	0.259(1)	−0.086(2)	90
H(151)	1.295(5)	0.346(1)	−0.025(3)	100
H(152)	1.233(6)	0.282(2)	0.039(3)	100
H(161)	1.245	0.205	−0.132	120
H(162)	1.503	0.247	−0.099	120
H(163)	1.286	0.281	−0.216	120

[a] $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta) \cdot 10^3$

Crystals for the purpose of X-ray investigations were obtained by evaporation of a methanolic solution. DSC-analysis confirmed that the modification obtained in this manner was the higher melting kind, namely K_I.

A suitable crystal for X-ray analysis was mounted on a goniometer head. Its lattice dimensions as well as the reflection intensities were obtained using the usual procedure by means of a STOE-four circle diffractometer. The symmetry independent reflections amounted to 1195; the relevant crystal data are given in Table I. The structure was solved by the direct method. The two phenyl rings and the carbon atoms adjacent to each ring were obtained from the E-map. The remaining non-hydrogen atoms were obtained from the Fourier maps. The successive refinement with 1014 non-zero reflections ($F_0 > 2\sigma(F_0)$) led to $R = 0.051$ ($R_w = 0.042$), at this stage the temperature factor of the hydrogen atoms was fixed. Furthermore, the atomic coordinates of the hydrogen atoms at the C(16)-atom were varied as a fixed group simultaneously with the C(16)-atom through a distance of C(16)-H = 1.08Å. The atomic parameters are given in Table II. The anisotropic temperature factors for the non-hydrogen atoms and a list of observed as well as calculated structure factors are available from the authors on request.

RESULTS AND DISCUSSION

Thermal properties

DSC-analysis of CB 3 samples revealed the occurrence of solid crystalline polymorphism, depending upon the thermal history of the samples. Thus, virgin samples melt at 338.4 (5) K, resulting in an isotropic liquid. The identical modification, denoted with K_I, was also obtained when isotropic samples were subjected to cooling rates of less than 1 K/min. When cooling rates in excess of 1 K/min are employed, using the same samples, a metastable solid modification termed K_{II} was obtained and melted at 326.3(3) K. This melting and crystallization behaviour is shown in Figure 1 with the aid of DSC-thermograms typical of CB 3. It should be mentioned that the metastable solid phase K_{II} can be stored over a period of several weeks at room temperature. On the other hand, even the slightest mechanical disturbance of the substance in the sample pan will cause phase K_{II} to revert instantaneously to K_I, i.e., the modification which is stable at and above room temperature. Furthermore, the nature of some DSC-

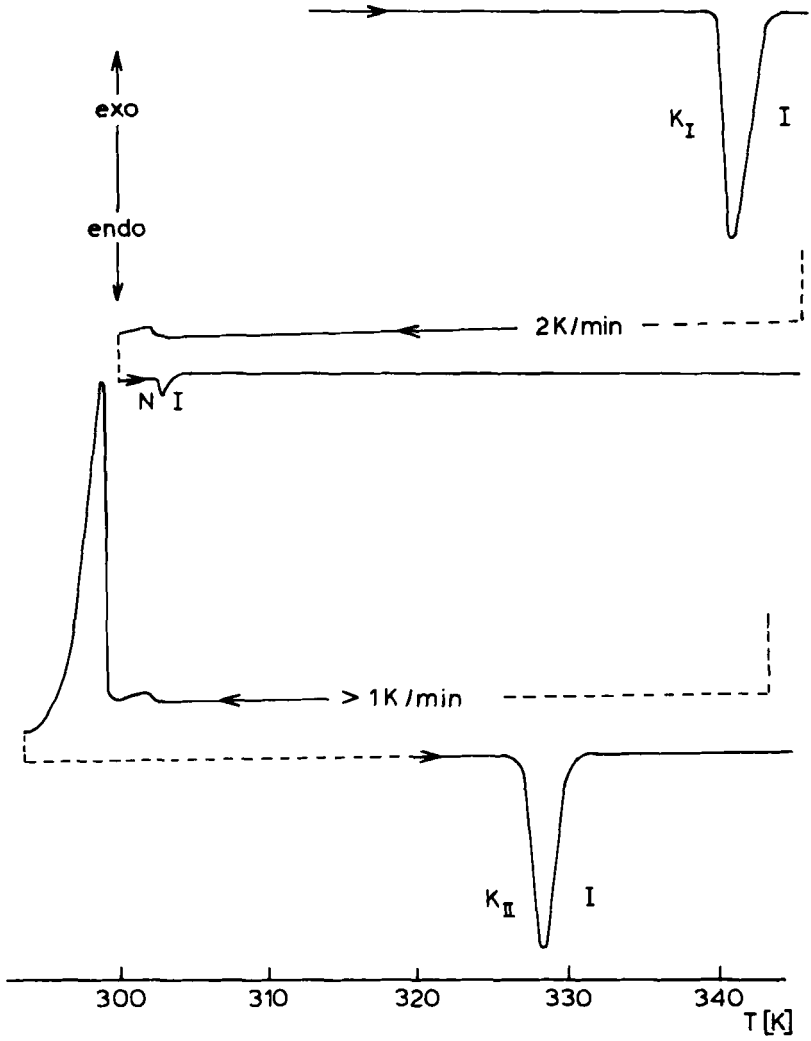

FIGURE 1 DSC-thermograms of melting and crystallization behaviour. Heating rate 2 K/min.

TABLE III

Transition temperatures and transition enthalpies for CB 3

Transition	Temperature [K]	Enthalpy [kJ/mol]
K_I–I	338.4 ± 0.5	19.9 ± 0.5
K_{II}–I	326.3 ± 0.3	16.7 ± 0.7
N–I	(303.3) ± 0.2	0.3 ± 0.2

thermograms was indicative of a third solid phase, which seemed to melt in the vicinity of the melting point of K_I. The probability of its occurrence can neither be entirely ruled out nor conclusively confirmed, despite the extensive analysis which was carried out. Similarly no evidence for a solid-solid transition between K_{II} and K_I could be secured. In addition to these solid phases, the compound also exhibits a monotropic nematic phase. Its clearing point was found to lie at 303.3(2) K. This temperature is well above the value of 298.7 K which had been given elsewhere.[2] The entire phase behaviour of CB 3 was duly confirmed by means of thermomicroscopic analysis. All observed transitions and their corresponding enthalpies are given in Table III.

Molecular structure

Some selected bond lengths and angles resulting from the X-ray investigations are presented in Table IV. Thus the bond N—C(1) and the adjacent angle N—C(1)—C(2) are indeed of normal magnitude

TABLE IV

Some selected bond lengths [Å] and angles [°] for the higher melting stable modification of CB 3

N—C(1)	1.142(5)
C(1)—C(2)	1.436(4)
C(5)—C(8)	1.479(4)
C(11)—C(14)	1.513(5)
C(14)—C(15)	1.474(6)
C(15)—C(16)	1.512(6)
C_{phenyl}—C_{phenyl}	1.383(8)[a]
N—C(1)—C(2)	178.3(3)
C(11)—C(14)—C(15)	114.5(3)
C(14)—C(15)—C(16)	114.2(3)
C—C_{phenyl}—C_{phenyl}	120.4(1.4)[a]

[a] standard deviation from the mean value

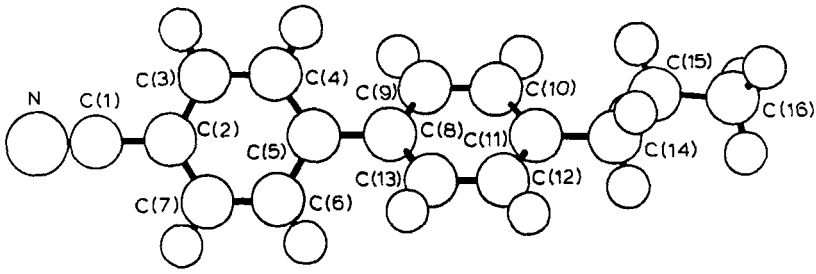

FIGURE 2 Molecule, projected perpendicular to the phenyl-ring, adjacent to the cyano group.

and comparable with the data obtained from other compounds.[11] The mean C—C bond length in the two phenyl rings is equal to 1.383 (8) Å and corresponds to known values for this ring as mentioned elsewhere.[6] The distance between the C(14) and C(15) atoms in the propyl chain, seems to be somewhat shorter. This behaviour can be attributed to thermal vibrations in general and to the anisotropy of the thermal vibrations of the relevant carbon atoms in particular. The molecule in question is depicted in Figure 2. A twist out of plane of the phenyl rings (best planes) results in a dihedral angle of 42.8°, which is comparable with previous data[6-8] for this angle in biphenyls with not too voluminous substituents in the 4, 4′-position. The entire length of the molecule was found to be 14.01 Å, i.e., from N to H (162). When the relevant van der Waal's radii are additionally included, the resultant length of 14.86 Å is in good agreement with the longest extension of 15.13 Å that was found for CCH 3.[11]

Packing in the crystalline state

The packing in the crystalline state is shown in Figure 3. As a consequence of an inversion centre, the related molecules align in a collinear manner, resulting in a layer which is subsequently perpendicular to the projection in Figure 3. With consideration of the 2_1-axis along the crystallographic *b*-axis, in the next layer the adjacent molecules are practically perpendicular to the molecules in the former layer. These layers are 9.56 Å thick, that is to say $b/2$.

A second type of layer is formed, which is perpendicular to the former, as a result of the molecular alignment parallel to the (102) plane, which can be shown in Figure 4. These layers possess a thickness of approximately 3.7 Å.

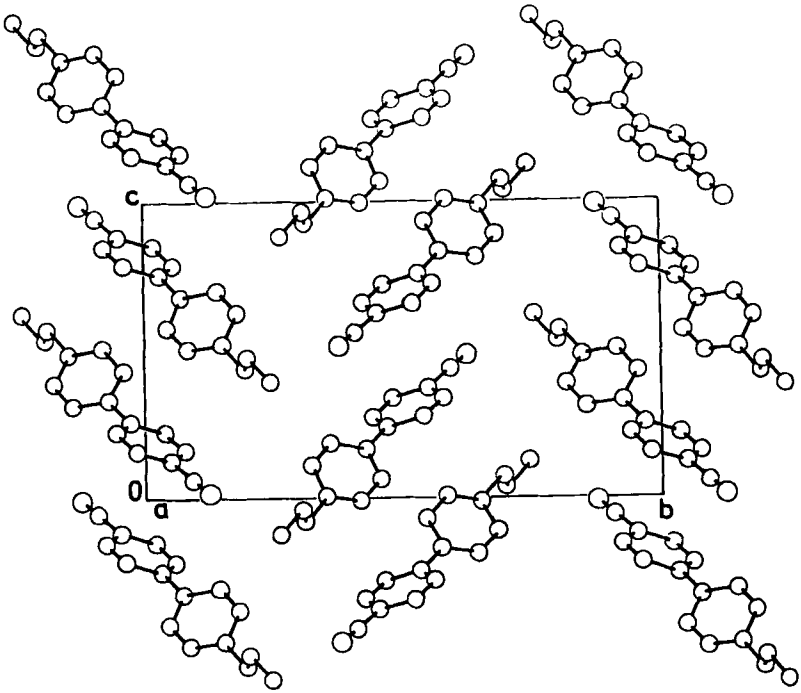

FIGURE 3 Projection along [100].

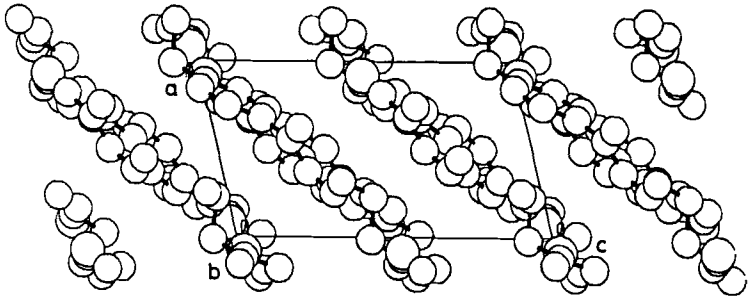

FIGURE 4 Projection along [010].

TABLE V

Selected intermolecular distances [Å] between two neighbouring centrosymmetric molecules $x' = 1 - x, y' = 1 - y, z' = 1 - z$

	C(2)′	C(3)′	C(4)′	C(5)′	C(6)′	C(7)′	C(8)′
N	4.95	4.75	4.17	3.77	4.00	4.60	3.93
C(1)	4.23	4.19	3.95	3.73	3.76	4.01	4.31

With regard to packing, one finds that the cyano group of one molecule overlaps the phenyl ring adjacent to the cyano group of the neighbouring centrosymmetric molecule in such a manner that the normal of this ring is nearly perpendicular to the C(1)—C(2) bond. This relationship can be seen in Figure 3 and the relevant distances are given in Table V. The mean N-C'_{phenyl} distance is 4.37 Å and the analogous C(1)—C'_{phenyl} distance is 3.98 Å. These distances are not in support of a dipole-dipole contact but represent rather a precursor arrangement to the transition resulting in the nematic state. The longest distance between the outermost atoms of two related molecules, namely H(163)—H(163)′ is 22.26 Å and 22.86 Å when the covalent radii are taken into account.

When one considers the covalent radius of 0.55 Å for nitrogen, the distance between N and the centre of the bond C(5)—C(8) and C(11)—C(14) is found to be 6.65 Å and 10.95 Å, respectively.

Molecular dimension related to the $d_{\parallel}$-values for CB 5 and CB 7

In view of the overlapping that is encountered in the solid crystalline state of CB 3 and in the liquid crystalline state of other cyano substituted compounds, namely the core-type[12-15], it follows that one can discuss at least two schematic modes of overlapping in the nematic state. Thus in case I (Table VI) the cyano group of a molecule overlaps with the cyano substituted phenyl ring of its neighbour and *vice versa*. In the second model the cyano group of one molecule now overlaps the alkyl substituted phenyl ring of its neighbour, and conversely. This is denoted as case II in Table VI, where various calculated molecular lengths for CB 3, CB 5 and CB 7 are compared with their $d_{\parallel}$-values in the nematic state, in those cases where it is applicable.[16] Whereas the molecular dimensions in the direction of the longest axis in biphenyl, phenylcyclohexane and cyclohexylcyclohexane are practically equivalent from series to series – the values for CCH 3 and CB 3 are

TABLE VI

Calculated lengths [Å] for some CBs, as a result of overlapping between the CN-group and the phenyl rings of the neighbouring centrosymmetric molecules, compared with $d_{\parallel}$-data for the nematic phase[16]

Compound	Case I		Case II		$d_{\parallel}$
	Phenylalkyl	"Dimer"	Alkyl	"Dimer"	
CB 3	8.21	23.07	3.91	18.77	
CB 5	10.74	28.13	6.44	23.83	25
CB 7	13.27	33.19	8.97	28.89	29

Molecular data from the crystalline state, including the covalent radii: N-H (162): 14.86 Å; N to the centre of the bond C(5)-C(8): 6.65 Å; N to the centre of the bond C(11)-C(14): 10.95 Å; Fixed distance between each next but one C-atom in the alkyl group: 2.53 Å.

presented above–a comparison of calculated molecular dimensions (Table VI) with $d_{\parallel}$-data for the nematic phase should be of some interest.

Let us say for a moment that only case I is the valid arrangement in the CB series, then the difference between the calculated data for some CBs in Table VI and the appropriate $d_{\parallel}$-values should be in some manner related to the tail conformation and to a reasonable extent of ordering in the relevant liquid crystalline phase. In this context it seems worth mentioning, that Bradshaw *et al.*[16] found for the nematic phases of PCH 7 and PCH 5, $d_{\parallel}$-values of 31 Å and 26 Å respectively, which do not contradict our view point, assuming identical lengths as for CBs.

In the same sense is the observation of Leadbetter *et al.*[15] that the calculated length with respect to case II for various cyano-substituted compounds proves to be 7–8% greater than the experimental $d_{\parallel}$-values for their S_A-phases. If one now also takes a realistic $\overline{P_2}$ of approximately 0.65 (with $\overline{\cos\beta} \sim 0.875$) into account for the nematic phases of both CB 5 and CB 7, then the $d_{\parallel}$-values should be 24.6 Å and 29.0 Å respectively for case I as compared with 20.9 Å and 25.3 Å for case II.

If we were now to assume that only the idealized cases I and II can be distinguished for the sake of discussion, then the above mentioned data are in support of case I being the more realistic model for the nematic state. If this is true this should depend on the dihedral angle between the two phenyl groups in the biphenyl unit being unequal to 0°. This should lead to a lower degree of conjugation in the cyano-

biphenylyl groups in comparison with that in a fully conjugated core showing a dihedral angle of 0°.

This does in a way invalidate the interpretation of Leadbetter *et al.*[15] that the $d_{\parallel}$-dependence is related to the tail conformation, the degree of overlap and the angular distribution function of the long axis, thus not permitting further detailed inferences about the molecular packing. The same is of course also true and even more applicable to the individual aggregations.

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