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Structure of the Nematogenic Compound 2-Cyano-*N*-[4-(4-*n*-pentyloxybenzoyloxy)-benzylidene]aniline

By U. Baumeister and H. Hartung

Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, DDR-4020 *Halle, Mühlpforte* 1, *German Democratic Republic*

and M. Gdaniec

Faculty of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6, 60–780 *Poznań, Poland*

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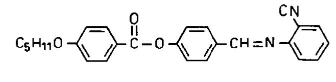
Abstract. 4-[(*o*-Cyanophenyl)iminomethyl]phenyl 4-(pentyloxy)benzoate, $C_{26}H_{24}N_2O_3$, $M_r = 412{\cdot}5$, triclinic, $P\bar{1}$, $a = 8{\cdot}454\ (2)$, $b = 11{\cdot}879\ (2)$, $c = 12{\cdot}141\ (2)$ Å, $\alpha = 103{\cdot}86\ (1)$, $\beta = 101{\cdot}98\ (1)$, $\gamma = 101{\cdot}59\ (2)°$, $V = 1116{\cdot}9\ (3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}22$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 5{\cdot}7$ cm^{-1}, $F(000) = 436$, $T = 293$ K, final $R = 0{\cdot}044$ for 1988 observed reflections. The molecule adopts a fully extended form. The phenyl benzoate and benzylideneaniline moieties both exhibit energetically favoured non-planar conformations. The crystal structure is characterized by a perfectly parallel alignment of the molecules which are arranged in a head-to-tail fashion.

Introduction. This paper continues a series of structural investigations on mesogenic compounds in their crystalline state carried out in our laboratories. The title compound, abbreviated CPBBA in the following, was first prepared and characterized by Weissflog (1983). It forms a nematic mesophase in a very narrow temperature range, 396·5–397 K. According to the classification of mesogens given by Kelker & Hatz (1980), CPBBA belongs to the aromatic compounds with two different bridging groups. Suitably substituted aromatic azomethines as well as phenyl benzoates have been known as mesogens for a long time and their molecular geometry and packing have been studied in detail. In the CPBBA molecule the above-mentioned structural fragments share a common benzene ring. The present X-ray analysis of CPBBA continues our previous investigations on the conformational behaviour of phenyl benzoates (Hartung, Baumeister & Jaskólski, 1986, and references therein).



Experimental. CPBBA first synthesized by Weissflog (1983). Crystal 0·3 × 0·26 × 0·2 mm. Syntex $P2_1$ diffractometer, Cu $K\alpha$ radiation, graphite monochromator. Lattice parameters from least-squares refinement of the setting angles of 15 reflections, $2\theta \leq 115°$, h, k, l range $-9, -12, 0$ to $8, 12, 13$. Check reflections $10\bar{3}$ and $\bar{2}0\bar{2}$ [intensity variations 6·55 (4)–6·81 (4) × 10^5 and 8·25 (5)–8·52 (5) × 10^5, respectively]. Total of 3024 independent reflections, 1998 observed [$|F_o| \geq 3{\cdot}92\sigma(F)$]. Lp correction, absorption and extinction ignored. Direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Anisotropic full-matrix least-squares refinement on F^2, H atoms (from difference electron density map) with fixed positional and isotropic thermal parameters. Ten F_o's with large $||F_o| - |F_c||/\sigma(F)$ omitted in last cycles. Final $R = 0{\cdot}044$, $wR = 0{\cdot}044$, unit weights throughout refinement. $(\Delta/\sigma)_{\max} = 0{\cdot}46$. Max. and min. heights in final $\Delta\rho$ map 0·143 and $-0{\cdot}134$ e Å^{-3}. All calculations performed on the ESER 1040 computer of Halle University using programs *SHELX*76 (Sheldrick, 1976), *MULTAN*80, *PRARA* (Jaskólski, 1980), *GEOME* (Jaskólski, 1981*a*) and *PLANE* (Jaskólski, 1981*b*). Atomic scattering factors those of *SHELX*76.

Discussion. Final atomic parameters are listed in Table 1.* Selected bond lengths and angles are given in Table 2. Atomic numbering and the molecular geometry are shown in Fig. 1. As can be seen from Fig. 1, the CPBBA molecule has a fully extended form. This nearly linear shape is based on the stereochemistry of both bridging groups: the azomethine as well as the carboxylic group are planar bridging groups with parallel configuration both introducing only a parallel displacement of the moieties they connect. They force the 1,4-axes of the adjacent benzene rings to lie parallel

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43693 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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and give the molecule the stretched configuration necessary for generating the liquid crystalline state. The observed geometric bonding parameters of CPBBA agree well with standard values. For a more detailed discussion it is useful to undertake separate considerations of the phenyl benzoate and benzylideneaniline moieties of the molecule.

Table 1. *Positional parameters* (× 10^4) *and equivalent isotropic temperature factors* (Å^2, × 10^3) *for the non*-H *atoms*

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	*y*	*z*	U_{eq}
C(1)	17865 (5)	8875 (4)	9565 (4)	114 (2)
C(2)	16068 (4)	8835 (3)	9411 (3)	92 (1)
C(3)	14839 (4)	7689 (3)	8570 (3)	80 (1)
C(4)	13022 (4)	7683 (3)	8525 (3)	78 (1)
C(5)	11822 (4)	6543 (3)	7682 (3)	83 (1)
C(6)	8846 (3)	5669 (3)	7045 (3)	73 (1)
C(7)	7290 (4)	5762 (3)	7192 (3)	78 (1)
C(8)	5869 (4)	4856 (3)	6553 (3)	78 (1)
C(9)	5960 (3)	3833 (3)	5761 (3)	67 (1)
C(10)	7520 (4)	3769 (3)	5602 (3)	81 (1)
C(11)	8955 (4)	4680 (3)	6239 (3)	81 (1)
C(12)	4510 (4)	2796 (3)	5124 (3)	76 (1)
C(13)	1538 (4)	2136 (3)	4864 (3)	65 (1)
C(14)	549 (4)	2003 (3)	5614 (3)	67 (1)
C(15)	−1033 (3)	1214 (3)	5168 (2)	68 (1)
C(16)	−1613 (3)	551 (2)	3995 (2)	60 (1)
C(17)	−574 (4)	704 (3)	3258 (3)	71 (1)
C(18)	991 (4)	1499 (3)	3689 (3)	74 (1)
C(19)	−3289 (3)	−285 (3)	3551 (3)	66 (1)
C(20)	−5456 (3)	−1773 (3)	2123 (2)	63 (1)
C(21)	−5710 (3)	−2977 (3)	1502 (2)	66 (1)
C(22)	−7319 (4)	−3743 (3)	1045 (3)	77 (1)
C(23)	−8671 (4)	−3303 (4)	1184 (3)	85 (1)
C(24)	−8432 (4)	−2123 (3)	1788 (3)	85 (1)
C(25)	−6837 (4)	−1352 (3)	2260 (3)	74 (1)
C(26)	−4276 (4)	−3422 (3)	1357 (3)	76 (1)
N(1)	−3800 (3)	−1021 (2)	2523 (2)	66 (1)
N(2)	−3163 (4)	−3798 (3)	1240 (3)	106 (1)
O(1)	10161 (2)	6597 (2)	7743 (2)	80 (1)
O(2)	4540 (3)	1857 (2)	4490 (2)	93 (1)
O(3)	3071 (2)	3009 (2)	5354 (2)	73 (1)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

C(5)—O(1)	1·435 (4)	C(16)—C(19)	1·464 (4)
O(1)—C(6)	1·356 (3)	C(19)—N(1)	1·270 (3)
C(9)—C(12)	1·471 (4)	N(1)—C(20)	1·414 (3)
C(12)—O(2)	1·203 (4)	C(21)—C(26)	1·443 (5)
C(12)—O(3)	1·361 (4)	C(26)—N(2)	1·139 (5)
O(3)—C(13)	1·397 (3)		
C(5)—O(1)—C(6)	118·7 (2)	C(15)—C(16)—C(19)	119·9 (3)
C(9)—C(12)—O(2)	126·2 (3)	C(17)—C(16)—C(19)	121·6 (2)
C(9)—C(12)—O(3)	111·4 (3)	C(16)—C(19)—N(1)	122·3 (3)
O(2)—C(12)—O(3)	122·4 (3)	C(19)—N(1)—C(20)	119·8 (3)
C(12)—O(3)—C(13)	121·4 (3)	N(1)—C(20)—C(21)	118·2 (3)
		N(1)—C(20)—C(25)	122·9 (3)
		C(21)—C(26)—N(2)	178·5 (4)

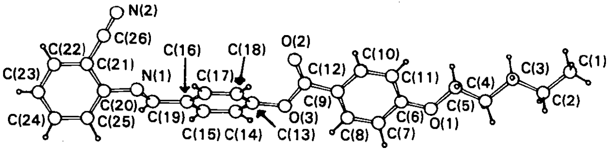

Fig. 1. *INTMOL* plot (Schrauber, 1986) of the CPBBA molecule.

The C(6)···C(11) benzene ring is roughly coplanar with the pentyloxy group (interplanar angle 5·1°) and with the carboxylic group (interplanar angle 5·3°). On the other hand, the twist of the carboxylic-group plane with respect to the C(13)···C(18) benzene ring amounts to 44·6°. The orientation of the carboxylic bridge with respect to the C- and O-bonded neighbouring ring systems can be described by the torsion angles τ_1 [C(10)—C(9)—C(12)—O(2)] 2·5 (4), τ_2 [C(9)—C(12)—O(3)—C(13)] −178·5 (3), τ_3 [C(12)—O(3)—C(13)—C(18)] −47·5 (3)°. The τ_1 and τ_2 values observed in CPBBA agree well with the results of experimental and theoretical conformational analyses performed for substituted phenyl benzoates (Baumeister, Brandt, Hartung & Jaskólski, 1983: Birner, Kugler, Simon & Náray-Szabó, 1982), whereas the τ_3 value is significantly out of the normal range of 60–90°. A similar τ_3 value has only been reported by Hartung, Baumeister & Jaskólski (1986) for molecule *A* in the mesogenic 4′-(2,2-dicyanoethenyl)phenyl-4-*n*-nonyloxybenzoate.

The conformation of the benzylideneaniline moiety is characterized by a different twist of the N—C and C—C bonded phenyl rings with respect to the plane of the central four-atom azomethine group [C(16), C(19), N(1), C(20)]. The corresponding interplanar angles are 45·1 and 10·6°, respectively. These values lie within the limits observed for other benzylideneanilines and are in agreement with the results of theoretical conformational analyses which indicate that the minimum energy

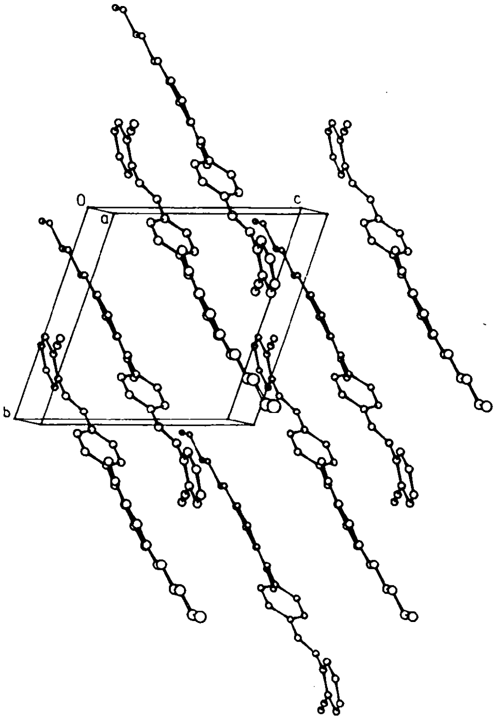

Fig. 2. Molecular packing of CPBBA.

conformation has these dihedral angles at 45 and 0°, respectively (Bernstein, Engel & Hagler, 1981). The four atoms C(16), C(19), N(1) and C(20) are displaced from the least-squares plane defined by them by 0·014 (3), −0·017 (3), −0·010 (3) and 0·015 (3) Å. The conformation of the azomethine bridge is completely described by the torsion angles C(17)—C(16)—C(19)—N(1) 9·3 (4), C(16)—C(19)—N(1)—C(20) −177·4 (3) and C(19)—N(1)—C(20)—C(25) 46·6 (4)°.

A large number of benzylideneanilines, including more than ten mesogenic compounds, have been examined by X-ray analysis. From these results a consistent pattern of bond lengths and angles with the following relatively small ranges was derived by Bryan & Forcier (1980): 1·398–1·460 Å for N(1)—C(20), 1·237–1·287 Å for C(19)—N(1), and 1·430–1·496 Å for C(16)—C(19). As a result of intramolecular steric repulsions, the angles N(1)—C(20)—C(25), C(16)—C(19)—N(1), and C(17)—C(16)—C(19) should be enlarged, and the angles N(1)—C(20)—C(21), C(19)—N(1)—C(20) and C(15)—C(16)—C(19) should be reduced from 120°. The observed bond lengths and angles in CPBBA (Table 2) conform to this pattern.

Fig. 2 illustrates the molecular arrangement in the crystal structure of CPBBA. The packing is characterized by a perfectly parallel alignment of the molecules along their long axes generated by the inversion centres and translations of the space group. Neighbouring molecules are arranged in a head-to-tail fashion. The crystal structure of CPBBA is typical of nematogens (nematic precursors), and could transform to the nematic phase by means of a simple displacive transition (Bryan & Forcier, 1980).

There are no unusually short intermolecular contacts in the structure.

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Structures of (−)-Cytisine and (−)-*N*-Methylcytisine: Tricyclic Quinolizidine Alkaloids

By Andrew A. Freer,* David J. Robins and Gary N. Sheldrake

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

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Abstract. (−)-1,2,3,4,5,6-Hexahydro-1,5-methano-8*H*-pyrido[1,2-*a*][1,5]diazocin-8-one, $C_{11}H_{14}N_2O$, $M_r = 190·3$, orthorhombic, $P2_12_12_1$, $a = 7·178$ (2), $b = 9·966$ (1), $c = 26·619$ (2) Å, $V = 1904·3$ Å^3, $Z = 8$, $D_m = 1·28$, $D_x = 1·33$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1·5418$ Å, $\mu = 6·55$ cm^{-1}, $F(000) = 816$, $T = 291$ K, final $R = 0·047$ for 1999 unique observed reflections. (−)-1,2,3,4,5,6-Hexahydro-3-methyl-1,5-methano-8*H*-pyrido[1,2-*a*][1,5]diazocin-8-one, $C_{12}H_{16}N_2O$, $M_r = 204·3$, orthorhombic, $P2_12_12_1$, $a = 9·065$ (2), $b = 10·824$ (3), $c = 11·206$ (2) Å, $V = 1099·5$ Å^3, $Z = 4$, $D_m = 1·13$, $D_x = 1·15$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0·71069$ Å, $\mu = 0·75$ cm^{-1}, $F(000) = 440$, $T = 291$ K, final $R = 0·035$ for 1014 unique observed reflections. The structures of each of the two molecules in the asymmetric unit of cytisine and that of *N*-methylcytisine are almost identical. Both (−)-cytisine (1) and (−)-*N*-methylcytisine (2) adopt the same conformations with ring *A* essentially planar; ring *B* has an envelope conformation with the bridgehead atom, C(8), out of the plane by

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* To whom correspondence should be addressed.