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Crystal Structure of Mesogenic Material.
I. Nematogenic 4-(4′-Ethoxyphenylazo)phenyl Hexanoate

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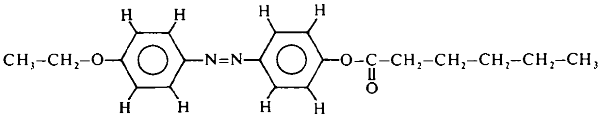
Abstract

$C_{20}H_{24}N_2O_3$ is monoclinic, space group $P2_1/c$, with $a = 5{\cdot}526\ (3)$, $b = 14{\cdot}101\ (8)$, $c = 23{\cdot}951\ (13)$ Å, $\beta = 82{\cdot}178\ (2)°$, $Z = 4$. The structure was refined to $R = 0{\cdot}079$ for 2038 counter intensities. The molecule is linear and the angle between the two phenyl rings is 10·16°. The crystalline cohesion is a result of a large number of feeble dispersion forces and dipole–dipole interactions.

Introduction

Investigation of crystals of mesogenic materials (compounds that exhibit a smectic, nematic or cholesteric liquid-crystalline phase on heating) shows the nature of the packing of the molecules in the solid state and other molecular characteristics which could give insight into the nature of liquid crystals. For example, to interpret such bulk properties of the liquid-crystalline phase as optical anisotropy or diamagnetic anisotropy one has to know the anisotropy of the polarizability or susceptibility of a single molecule, which can be determined from measurements on the solid state only if the crystal structure is known. It may also provide an answer to the problem as to why only a few organic substances exhibit a liquid-crystalline state and why some of them exhibit more than one phase. Attention was drawn to this problem by Bernal & Crowfoot (1933) in preliminary studies on some esters of cholesterol and a few other nematic substances, but little subsequent work has been performed.

To study the molecular packing in a homologous series, and to achieve greater insight regarding the imbricated packing [*i.e.* a molecular arrangement in which the end of one molecule is near the middle of its neighbour (Bernal & Crowfoot, 1933; Gray, 1962)], necessary for the formation of the nematic phase, the present study has been undertaken. In this paper the structure of 4-(4′-ethoxyphenylazo)phenyl hexanoate (I) is reported. Subsequent papers will deal with 4-(4′-ethoxyphenylazo)phenyl valerate, undecylenate and heptanoate. The compound was supplied by Eastman Kodak (USA). The crystalline solid gives a nematic phase at 348 K. The nematic–isotropic transition temperature is 399 K.



(I)

Experimental

Orange needles were obtained from toluene. The density was measured by flotation in a mixture of xylene and tetrabromoethane. Photographs gave the space group $P2_1/c$ from systematic extinctions $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$. Other data are $M_r = 340{\cdot}42$, $V = 1848{\cdot}95$ Å^3, $D_{\rm obs} = 1{\cdot}205$ Mg m^{-3}; Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}089$ mm^{-1}.

The accurate cell dimensions and orientation matrix were obtained by a least-squares fit to the setting angles of 28 reflections on a Hilger & Watts PDP8-controlled four-circle diffractometer (M. Dobler & B. Dürr, personal communication). Intensities were collected to $\sin\theta/\lambda \le 0{\cdot}6$ Å^{-1} by an $\omega/2\theta$-scan ordinate-analysis method (Watson, Shotton, Cox & Muirhead, 1970) with 60 steps of 0·03°. Three reference reflections measured after every 50 reflections showed no deterioration of the crystal. 2807 independent reflections were measured, of which 2038 were considered to be observed [$\bar{I} > 3\sigma(\bar{I})$ where $\sigma(\bar{I})$ is the standard deviation derived from counting statistics]. Reflections whose aparent centres were more than 0·2° from the predicted positions were excluded. Lorentz and polarization corrections and an empirical absorption correction (North, Phillips & Mathews, 1968) were applied.

Determination and refinement of the structure

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) for 250 reflections with $E >$

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1·45. An E map computed for the solution with the highest combined figure of merit obtained by the tangent formula revealed all the non-hydrogen atoms (R = 0·33). Their parameters were refined by full-matrix least squares to an R of 0·23 with isotropic temperature factors. Further refinement was by least squares with a two-block approximation: one block contained the positional parameters, the other the corresponding anisotropic temperature factors. At this stage an isotropic extinction correction was applied which reduced R to 0·117. A difference map revealed the positions of 19 out of 24 H atoms. The rest were placed in theoretical positions. After additional blocked-matrix least-squares refinement (individual isotropic temperature factors for H atoms), six intense low-angle reflections affected by the non-linearity of the counter were removed. Final refinement with the weighting scheme $W = 1/[\sum_{r=1}^{n} A_r T_r^*(X)]$ where n is the number of coefficients A_r for a Chebyshev series, T_r^* is the polynomial function and X is $(F_o/F_{o(\max)})$ (three coefficients A_r were used with values 173·94, 223·44, and 57·01) (Carruthers, 1975), gave a final R of 0·079[†] for 2032 reflections. The extinction parameter is 1489·176 (Larson, 1970). A final difference map revealed no extraneous peaks. In the final parameters, U_{11} and U_{33} for C(7) and C(8) are unsatisfactorily large. A similar problem was encountered by Krigbaum & Barber (1971) in ethyl p-azoxybenzoate and neither can be rationalized in terms of a conventionally disordered structure. All calculations were performed on the Oxford University ICL 1906A computer with the Oxford package of programs (Carruthers, 1975). Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final positional parameters for the non-hydrogen atoms and their estimated standard deviations are listed in Table 1. Table 2 gives the bond distances and angles for the non-hydrogen atoms. C—H distances range from 0·70–1·15 Å with a mean of 0·96 Å.

Table 1. *Final fractional atomic coordinates for the non-hydrogen atoms*

	x	y	z
O(1)	0·6463 (5)	0·4940 (2)	0·1021 (1)
O(2)	−0·5442 (5)	1·0301 (2)	−0·1153 (2)
O(3)	0·3879 (5)	0·4479 (3)	0·1761 (2)
N(1)	−0·0587 (6)	0·7423 (2)	−0·0174 (1)
N(2)	0·0757 (6)	0·7694 (2)	0·0179 (1)
C(1)	−0·8080 (10)	1·1064 (4)	−0·1692 (1)
C(2)	−0·700 (10)	1·0122 (4)	−0·1558 (3)
C(3)	−0·4327 (7)	0·9549 (3)	−0·0932 (2)
C(4)	−0·4610 (9)	0·8645 (3)	−0·1041 (2)
C(5)	−0·3356 (9)	0·7946 (3)	−0·0787 (2)
C(6)	−0·1826 (7)	0·8182 (3)	−0·0414 (2)
C(7)	−0·1550 (10)	0·9104 (4)	−0·0300 (4)
C(8)	−0·2760 (10)	0·9792 (4)	−0·0549 (4)
C(9)	0·2042 (6)	0·6941 (3)	0·0406 (2)
C(10)	0·3879 (7)	0·7229 (3)	0·0711 (2)
C(11)	0·5293 (7)	0·6547 (3)	0·0928 (2)
C(12)	0·4841 (6)	0·5619 (3)	0·0852 (2)
C(13)	0·2956 (8)	0·5310 (3)	0·0560 (2)
C(14)	0·1577 (7)	0·5997 (3)	0·0342 (2)
C(15)	0·5816 (6)	0·4402 (3)	0·1465 (2)
C(16)	0·7792 (6)	0·3722 (3)	0·1557 (2)
C(17)	0·7280 (7)	0·3143 (3)	0·2093 (2)
C(18)	0·9268 (7)	0·2427 (3)	0·2155 (2)
C(19)	0·8801 (8)	0·1849 (3)	0·2690 (2)
C(20)	1·080 (10)	0·1141 (4)	0·2763 (3)

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *involving non-hydrogen atoms*

C(1)–C(2)	1·509 (7)	C(9)–C(14)	1·367 (5)
C(2)–O(2)	1·404 (6)	C(10)–C(11)	1·383 (5)
O(2)–C(3)	1·368 (5)	C(11)–C(12)	1·349 (6)
C(3)–C(4)	1·315 (6)	C(12)–C(13)	1·400 (6)
C(3)–C(8)	1·389 (7)	C(13)–C(14)	1·379 (5)
C(4)–C(5)	1·391 (6)	C(12)–O(1)	1·408 (4)
C(5)–C(6)	1·351 (6)	O(1)–C(15)	1·316 (5)
C(6)–C(7)	1·342 (6)	C(15)–O(3)	1·205 (5)
C(7)–C(8)	1·360 (7)	C(15)–C(16)	1·492 (5)
C(6)–N(1)	1·432 (5)	C(16)–C(17)	1·516 (6)
N(1)–N(2)	1·259 (4)	C(17)–C(18)	1·514 (5)
N(2)–C(9)	1·426 (5)	C(18)–C(19)	1·511 (6)
C(9)–C(10)	1·390 (5)	C(19)–C(20)	1·516 (7)

C(1)–C(2)–O(2)	106·7 (5)	C(10)–C(9)–C(14)	120·3 (4)
O(2)–C(3)–C(4)	127·2 (4)	C(9)–C(10)–C(11)	119·0 (4)
C(2)–O(2)–C(3)	118·6 (4)	C(10)–C(11)–C(12)	120·0 (4)
O(2)–C(3)–C(8)	114·8 (4)	C(11)–C(12)–C(13)	122·2 (4)
C(4)–C(3)–C(8)	118·1 (4)	C(12)–C(13)–C(14)	117·3 (4)
C(3)–C(4)–C(5)	121·4 (4)	C(13)–C(14)–C(9)	121·2 (4)
C(4)–C(5)–C(6)	120·5 (4)	C(11)–C(12)–O(1)	118·9 (4)
C(5)–C(6)–C(7)	118·2 (4)	C(13)–C(12)–O(1)	118·6 (4)
C(6)–C(7)–C(8)	121·6 (5)	C(12)–O(1)–C(15)	120·8 (3)
C(7)–C(8)–C(3)	120·2 (5)	O(1)–C(15)–O(3)	123·0 (4)
C(5)–C(6)–N(1)	117·2 (4)	O(1)–C(15)–C(16)	111·5 (3)
C(7)–C(6)–N(1)	124·6 (4)	O(3)–C(15)–C(16)	125·5 (4)
C(6)–N(1)–N(2)	113·7 (3)	C(15)–C(16)–C(17)	114·5 (3)
N(1)–N(2)–C(9)	113·6 (3)	C(16)–C(17)–C(18)	112·8 (3)
N(2)–C(9)–C(10)	114·8 (3)	C(17)–C(18)–C(19)	113·6 (4)
N(2)–C(9)–C(14)	124·8 (4)	C(18)–C(19)–C(20)	114·2 (4)

Description

(*a*) *Distances and angles*

The bond distances and angles (Table 2) show good agreement with those in p-azodiphenetole (Galigné, 1970) and propyl 4-(4′-methoxybenzylideneamino)-α-methylcinnamate (Cotrait, Sy & Ptak, 1975).

(*b*) *Least-squares planes*

The best planes for the two benzene rings are given by $-2·91916x - 0·01246y + 18·42524z = 0·157$, and

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[†] Lists of structure factors, thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34301 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$-3{\cdot}65717x - 0{\cdot}81068y + 15{\cdot}57862z = 0{\cdot}641$, where x, y, and z are fractional coordinates with respect to the crystallographic axes. The rings are planar but not coplanar, the angle between the two normals being 10·16°. The C–N=N–C group is not planar as it is in *p*-azodiphenetole (Galigné, 1970). The group C(12)–O(1)–O(3)–C(15) is planar and its plane ($-2{\cdot}61748x - 9{\cdot}47341y - 15{\cdot}05635z = -7{\cdot}906$) forms an angle of 94·22° with the neighbouring benzene ring.

(*c*) *Conformation*

The projection of the molecule with probability thermal ellipsoids on the best plane excluding O(3) ($-3{\cdot}12026x + 1{\cdot}94593y + 17{\cdot}46731z = 1{\cdot}453$) is shown in Fig. 1. The conformation is defined by the torsion angles −179·14, −178·32 and −178·35°, respectively, about C(6)–N(1), N(1)–N(2) and N(2)–C(9).

(*d*) *Molecular packing*

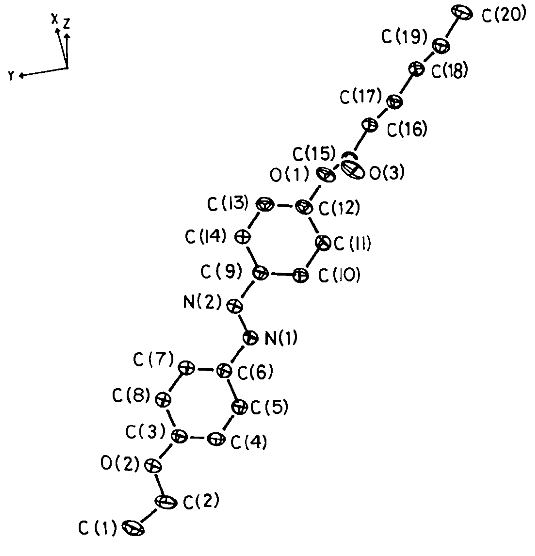

Fig. 1. Projection of the non-hydrogen atoms with their thermal ellipsoids on to the best plane of the molecule.

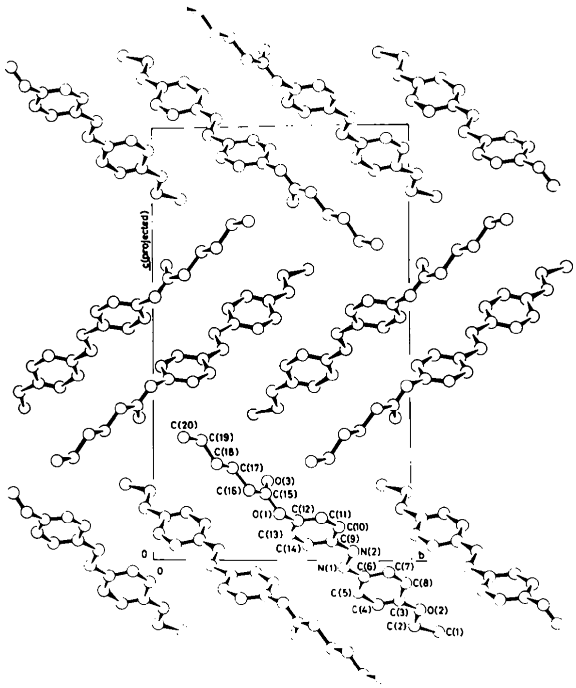

Fig. 2. Projection of the structure down x.

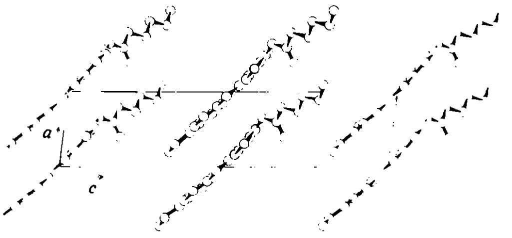

Fig. 3. Projection of the structure down y. Only part of the structure is shown. The missing part is related to that shown by the inversion centres of the space group.

Table 3. *Intermolecular contacts less than* 3·600 Å

O(1)···C(14)$^{(i)}$	3·406 (4) Å	C(7)···C(7)$^{(iii)}$	3·472 (5) Å
O(1)···C(14)$^{(ii)}$	3·552 (5)	C(8)···C(8)$^{(iv)}$	3·408 (4)
C(1)···N(1)$^{(i)}$	3·470 (5)	C(13)···C(13)$^{(v)}$	3·378 (3)
C(10)···N(1)$^{(i)}$	3·486 (5)	O(3)···C(20)$^{(vi)}$	3·560 (5)

Symmetry code

(i)	$1 + x, y, z$	(iv)	$-x - 1, 2 - y, -z$
(ii)	$1 - x, 1 - y, -z$	(v)	$1 - x, 1 - y, -z$
(iii)	$-x, 2 - y, -z$	(vi)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$

The molecules are almost linear. The molecular axis is inclined to x and y, and makes an angle of 45° with the xOz plane. The interactions in the direction Oy are of the ring–chain type for the molecules which are related to one another by the 2_1 axis (Fig. 2 gives the projection down x) and of the chain–chain type for the molecules related by $\bar{1}$ (Fig. 3 gives the projection down y). The molecules appear to form a two-dimensional arrangement parallel to Oy and Oz, lying in the planes (104) and (120), in accordance with the intense reflections 104 and 120. The cohesion is a result of a large number of feeble dispersion forces, as is evidenced by several intermolecular distances less than the sum of the van der Waals radii (Table 3). The dipoles of the carbonyl groups in the two-dimensional arrangements form the main forces in the crystalline cohesion. The distance between the antiparallel C=O dipoles is about 3·8 Å for molecules related by a centre of symmetry. The molecules are not imbricated to the extent predicted as necessary for the formation of a nematic liquid crystal. This may be why the thermal stability of the compound under study is considerably less than those in which strong imbricated packing has been observed.

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Crystal Structure of Mesogenic Material.
II. Nematogenic 4-(4′-Ethoxyphenylazo)phenyl Valerate

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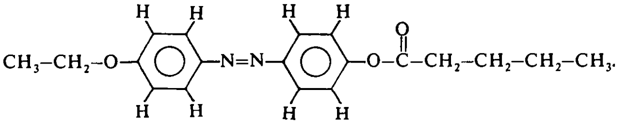
Abstract

$C_{19}H_{22}N_2O_3$, M_r = 326·39, triclinic, $P\bar{1}$, a = 11·558 (6), b = 9·028 (5), c = 8·668 (5) Å, α = 76·54 (2), β = 91·83 (2), γ = 77·35 (2)°, V = 854·99 Å^3, Z = 2, D_m = 1·221, D_c = 1·235 Mg m^{-3}, μ = 0·0929 mm^{-1}, Mo $K\alpha$ radiation, final R = 0·12. The molecule is almost linear and planar. The molecule axis is almost in the xy plane and makes an angle of 27° with y. Pairs of molecules related by a centre of symmetry form an imbricated arrangement.

Introduction

In the previous paper (Shashidhara Prasad, 1979) the structure of 4-(4′-ethoxyphenylazo)phenyl hexanoate has been reported. In this paper, the structure of 4-(4′-ethoxyphenylazo)phenyl valerate (I), obtained from Eastman Kodak (USA), is described.


(I)

Orange crystals were obtained from a solution in toluene. The crystals melt to form a nematic phase at 352 K and become isotropic at 401 K. The density was measured by flotation in a mixture of xylene and tetrabromoethane. Photographs showed that the crystal is triclinic with Z = 2. The crystal was mounted on a Hilger & Watts PDP8-controlled four-circle diffractometer fitted with a monochromator. Accurate cell dimensions and the orientation matrix were obtained by least squares from the setting angles of 18 reflections (M. Dobler & B. Dürr, personal communication). Intensities were collected with Mo $K\alpha$ radiation to $\sin\theta/\lambda \leq$ 0·63 Å^{-1} by an $\omega/2\theta$-scan ordinate-analysis method (Watson, Shotton, Cox & Muirhead, 1970) with 60 steps of 0·02°. Filters were used to measure the intense low-angle reflections. Of the 2913 independent reflections measured, 2409 were

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