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.

The author thanks Professor D. Hodgkin who suggested his visit to Oxford, Dr K. Prout for facilities, Drs D. J. Watkin and J. C. Daran for helpful dicussions, the Commonwealth High Commission for an Academic Fellowship, and the UGC (India) and the University of Mysore for leave.

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

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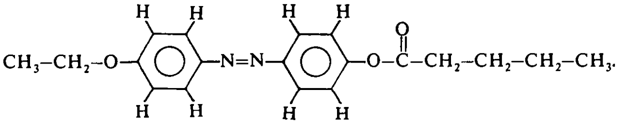
Abstract

$C_{19}H_{22}N_2O_3$, 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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considered to be observed $[\hat{I} > 3\sigma(\hat{I})]$. Lorentz, polarization and empirical absorption corrections (North, Phillips & Mathews, 1968) were applied. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) for 250 reflections with $E > 1{\cdot}56$. E maps were computed for two of the solutions with the lowest Ψ_0. One gave the complete set of expected non-hydrogen atoms ($R = 0{\cdot}50$). Refinement in $P\bar{1}$ (E statistics suggested $P\bar{1}$) failed to reduce R. Poor intermolecular contacts indicated that the molecule was properly oriented but in the wrong position. With the assumption that the space group was $P1$, a second molecule was generated by a weighted F_o synthesis from which the required translation was calculated* (Karle & Karle, 1971; Flippen, 1973). The shifts for x, y and z were $0{\cdot}075a$. $0{\cdot}185b$ and $0{\cdot}02c$. These values agree with the shifts estimated by a program which could calculate the structure factors for a group of atoms at a series of points that fall on a grid in the unit cell for 200 strong reflections (Carruthers, 1975). Full-matrix refinement with isotropic temperature factors reduced R to 0·21. Further refinement with a two-block approximation, one for the positional parameters, the other for the anisotropic temperature factors, gave an R of 0·17. An isotropic extinction correction reduced R to 0·15. A difference map then revealed 19 of the 22 H atoms. The rest were placed in theoretical positions. Refinement of all positional and thermal parameters (individual isotropic temperature factors for H atoms), after eliminating four intense low-angle reflections affected by non-linearity of the counter, gave a final R of 0·12. Unit weights were used. The extinction parameter is 523·82 (Larson, 1970). 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). 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 vary from 0·78 to 1·28 Å with a mean of 1·05 Å.

Discussion

The bond lengths and angles are in good agreement with those in *p*-azodiphenetole (Galigné, 1970) and 4-

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

	x	y	z
O(1)	0·4291 (4)	−0·0082 (5)	0·2255 (6)
O(2)	0·8944 (4)	1·0321 (6)	0·1821 (6)
O(3)	0·2632 (5)	0·0392 (6)	0·3455 (6)
N(1)	0·6798 (5)	0·5438 (6)	0·1580 (7)
N(2)	0·6134 (5)	0·5034 (6)	0·2612 (7)
C(1)	0·9498 (7)	1·2323 (9)	0·277 (1)
C(2)	0·8795 (7)	1·1090 (9)	0·3081 (9)
C(3)	0·8380 (6)	0·9137 (8)	0·1870 (9)
C(4)	0·7702 (7)	0·8593 (9)	0·3030 (9)
C(5)	0·7160 (7)	0·7399 (8)	0·2961 (9)
C(6)	0·7314 (6)	0·6685 (8)	0·1742 (8)
C(7)	0·8006 (7)	0·7236 (9)	0·0549 (8)
C(8)	0·8553 (7)	0·8432 (9)	0·0599 (9)
C(9)	0·5643 (6)	0·3777 (7)	0·2442 (8)
C(10)	0·5054 (7)	0·3147 (8)	0·3634 (9)
C(11)	0·4552 (7)	0·1897 (9)	0·3614 (9)
C(12)	0·4666 (6)	0·1243 (7)	0·2385 (8)
C(13)	0·5255 (7)	0·1872 (8)	0·1147 (8)
C(14)	0·5760 (7)	0·3113 (8)	0·1168 (8)
C(15)	0·3278 (6)	−0·0403 (8)	0·2769 (8)
C(16)	0·3093 (7)	−0·1859 (8)	0·2389 (9)
C(17)	0·2128 (7)	−0·251 (1)	0·315 (1)
C(18)	0·1912 (9)	−0·388 (1)	0·249 (1)
C(19)	0·101 (1)	−0·464 (1)	0·336 (1)

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

C(1)—C(2)	1·497 (10)	C(10)—C(11)	1·380 (9)
C(2)—O(2)	1·421 (7)	C(11)—C(12)	1·330 (9)
O(2)—C(3)	1·362 (7)	C(12)—C(13)	1·367 (9)
C(3)—C(4)	1·362 (9)	C(13)—C(14)	1·376 (9)
C(3)—C(8)	1·394 (9)	C(9)—C(14)	1·370 (8)
C(4)—C(5)	1·371 (9)	C(12)—O(1)	1·385 (7)
C(5)—C(6)	1·358 (8)	O(1)—C(15)	1·332 (8)
C(6)—C(7)	1·394 (9)	C(15)—O(3)	1·191 (7)
C(7)—C(8)	1·374 (9)	C(15)—C(16)	1·484 (9)
C(6)—N(1)	1·416 (8)	C(16)—C(17)	1·475 (10)
N(1)—N(2)	1·239 (7)	C(17)—C(18)	1·540 (11)
N(2)—C(9)	1·409 (8)	C(18)—C(19)	1·498 (13)
C(9)—C(10)	1·340 (9)		

C(1)—C(2)—O(2)	107·4 (6)	C(9)—C(10)—C(11)	123·1 (6)
C(2)—O(2)—C(3)	117·2 (5)	C(10)—C(11)—C(12)	119·9 (7)
O(2)—C(3)—C(4)	126·4 (6)	C(11)—C(12)—C(13)	118·2 (6)
O(2)—C(3)—C(8)	114·6 (6)	C(12)—C(13)—C(14)	122·0 (6)
C(3)—C(4)—C(5)	121·9 (6)	C(14)—C(9)—C(10)	117·4 (6)
C(4)—C(5)—C(6)	120·5 (7)	C(13)—C(14)—C(9)	119·5 (7)
C(5)—C(6)—C(7)	117·9 (6)	C(13)—C(12)—O(1)	115·5 (6)
C(6)—C(7)—C(8)	122·3 (6)	C(11)—C(12)—O(1)	126·3 (7)
C(7)—C(8)—C(3)	118·4 (7)	C(12)—O(1)—C(15)	123·7 (5)
C(8)—C(3)—C(4)	119·0 (6)	O(1)—C(15)—O(3)	122·9 (6)
C(5)—C(6)—N(1)	124·4 (7)	O(1)—C(15)—C(16)	111·1 (6)
C(7)—C(6)—N(1)	117·7 (6)	O(3)—C(15)—C(16)	126·0 (7)
C(6)—N(1)—N(2)	116·1 (5)	C(15)—C(16)—C(17)	116·6 (6)
N(1)—N(2)—C(9)	115·2 (5)	C(16)—C(17)—C(18)	111·8 (7)
N(2)—C(9)—C(10)	117·9 (6)	C(17)—C(18)—C(19)	112·0 (9)
N(2)—C(9)—C(14)	124·7 (6)		

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* The author thanks Professor M. M. Woolfson and Dr P. Main of York University for valuable discussions about this problem, and also for a copy of the private communication by J. Karle entitled *Partial Structures and the Use of Tangent Formula and Translation Functions.*

* Lists of structure factors, thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34302 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

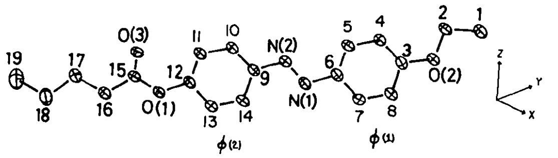

Fig. 1. Projection of the non-hydrogen atoms (with thermal ellipsoids) on to the best plane of the molecule.

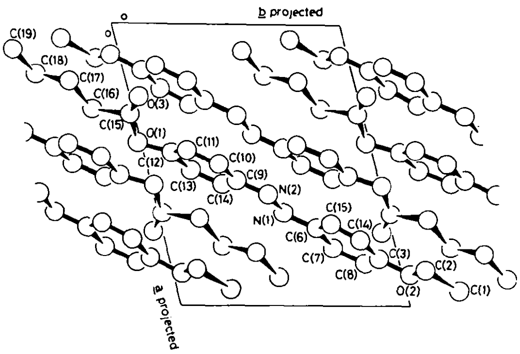

Fig. 2. Projection of the structure down z.

(4′-ethoxyphenylazo)phenyl hexanoate (Shashidhara Prasad, 1979). The two benzene rings are planar; the best planes are given by $-7\cdot65834x + 3\cdot53097y - 2\cdot91935z = 3\cdot743$ [$\varphi(1)$] and $-8\cdot28970x + 3\cdot29804y - 2\cdot46691z = -4\cdot023$ [$\varphi(2)$], where x, y and z are fractional coordinates with respect to the crystallographic axes. The two rings make an angle of 4·84°. The C—N=N—C group is planar; the equation of the best plane is $7\cdot35946x - 3\cdot40918y + 3\cdot39874z = 3\cdot691$. The C—N=N—C plane makes an angle of 3·48° with $\varphi(1)$ and 8·01° with $\varphi(2)$. The group O(1)—O(3)—C(15)—C(16) is also planar and forms an angle of 145·3° with the adjacent benzene ring $\varphi(2)$.

The projection, with probability thermal ellipsoids, on to the best plane of the molecule given by $7\cdot50755x - 3\cdot57205y + 3\cdot64297z = 3\cdot629$ is shown in Fig. 1. The molecules are linear, with the molecular axis lying in the xy plane and making an angle of 27° with y (Fig. 2). The packing consists of chains of molecules that run across z (Fig. 3). The crystalline cohesion is mainly dipolar owing to the carbonyl groups (Table 3). Pairs of molecules related by a centre of symmetry form an imbricated arrangement; this is more pronounced than in 4-(4′-ethoxyphenylazo)phenyl hexanoate.

The more pronounced imbricated packing and the smaller angle between the two benzene rings are the reasons for the greater thermal stability when compared to that of 4-(4′-ethoxyphenylazo)phenyl hexanoate, and these are consistent with the views that imbricated packing is a necessary requirement to form a nematic liquid crystal and the explanation that the mesomorphic stability is a function of interplanar angle.

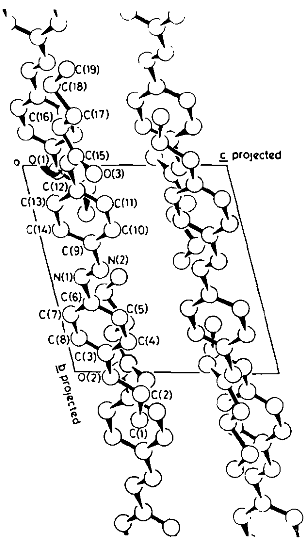

Fig. 3. Projection of the structure down x.

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

O(1)···C(5)$^{(i)}$	3·530 (9) Å	O(3)···C(8)$^{(iii)}$	3·560 (9) Å
O(3)···C(2)$^{(ii)}$	3·597 (10)	N(1)···C(13)$^{(iii)}$	3·400 (7)
O(3)···C(4)$^{(ii)}$	3·390 (7)	C(7)···C(15)$^{(iii)}$	3·562 (9)
O(3)···C(7)$^{(iii)}$	3·586 (9)	C(8)···C(15)$^{(iii)}$	3·421 (8)

Symmetry code

(i) $x, y-1, z$

(ii) $1-x, 1-y, 1-z$

(iii) $1-x, 1-y, -z$

The author thanks Professor D. Hodgkin who suggested the visit to Oxford, Dr K. Prout for facilities, Drs D. J. Watkin and J. C. Daran for discussions, the Commonwealth High Commission for an Academic Fellowship, and the UGC (India) and the University of Mysore for leave.

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