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Crystal Structure of Mesogenic Material III Nematogenic 4-(4′-Ethoxyphenylazo)Phenyl Undecylenate

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The crystal structure of 4-(4′-ethoxyphenylazo)phenyl undecylenate has been determined by direct methods. The compound crystallizes in space group $P2_1/n$ with $a = 5.914(1)$, $b = 15.143(3)$, $c = 25.819(2)$A° and $\beta = 91.450(2)°$. The structure was refined to $R = 0.0412$ for 1998 observed reflections. The molecule is almost linear and planar. The angle between the two phenyl rings is 3.996°. The pairs of molecules related by a centre of symmetry form an imbricated arrangement.

INTRODUCTION

It is very well established that a knowledge of the crystal and molecular structure of liquid crystal forming substances is an essential prerequisite for a proper understanding of structure and bonding in the mesophases. The present investigation has been taken up to study the molecular packing in a homologous series, and to achieve greater insight regarding the imbricated packing. The crystal structure of 4-(4′-ethoxyphenylazo)phenyl undecylenate has been discussed in detail.

EXPERIMENTAL

The compound was procured from Eastman Kodak (USA). The orange crystals were obtained from a solution in toluene. The crystals

TABLE I

Crystal data for 4-(4′-ethoxyphenylazo) phenyl undecylenate

Molecular formula = $C_{25}H_{32}N_2O_3$
Molecular weight = 408.54
Crystal system = Monoclinic
Space group = $P2_1/n$
$a = 5.914(1)$ Å
$b = 15.143(3)$
$c = 25.819(2)$
$\beta = 91.45(2)°$
$V = 2311.66$ Å^3
$Dc = 1.1736$ gm/cc
$Z = 4$
$F(000) = 880.00$
$(\mathrm{MoK}_\alpha) = 0.71069$ Å

melt to form a nematic phase at 339.2 K and become isotropic at 383 K. The density was measured by flotation in a mixture of xylene and tetrabromoethane. The preliminary cell parameters were obtained by oscillation and Weissenberg photographs, and the space group was determined to be $P2_1/c$.[1] The accurate cell parameters were determined by least squares calculations from 25 reflections measured on an 'Enraf Nonius' CAD-4 Computer controlled diffractometer using MoK_α radiation at 20 °C. The diffracted intensities were measured on the same instrument employing $\omega - 2\theta$ scanning mode. There are not much changes in the intensity of the standard reflections during the entire period of data collection. A total of 4169 reflections were collected in the interval $2 < \theta < 24$ of which 1998 reflections were classified as observed reflections ($I > 3\sigma(I)$). Lorentz and polarization corrections were applied and absorption correction was not made. The crystallographically important parameters are tabulated in Table I.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved with automatic centrosymmetric direct methods routine in the SHELX-76 crystallographic programme system[2] for 295 reflections with $E > 1.20$. E-maps were computed by taking both $P2_1/c$ and $P2_1/n$ space group symmetries. The refinement failed to reduce R for $P2_1/c$. The careful observation of diffractometer data suggests the space group $P2_1/n$. The 30 highest peaks in the map revealed the positions of all the non-hydrogen atoms. The atoms were

TABLE II

Refined atomic parameters for non-hydrogen atoms

Atom	*X/A*	*Y/B*	*Z/C*
C(1)	0.2294(7)	0.3394(3)	0.7363(1)
C(2)	0.0232(6)	0.3295(3)	0.7007(1)
O(1)	0.0813(4)	0.3685(2)	0.6525(1)
C(3)	0.9248(5)	0.3651(2)	0.6124(1)
C(4)	0.7185(6)	0.3234(2)	0.6140(1)
C(5)	0.5777(6)	0.3250(2)	0.5710(1)
C(6)	0.6415(5)	0.3662(2)	0.5239(1)
C(7)	0.8516(5)	0.4069(2)	0.5239(1)
C(8)	0.9915(5)	0.4068(2)	0.5673(1)
N(1)	0.4811(4)	0.3639(2)	0.4829(1)
N(2)	0.5466(5)	0.4036(2)	0.4432(1)
C(9)	0.3838(5)	0.4022(2)	0.4010(1)
C(10)	0.1784(6)	0.3592(3)	0.4016(1)
C(11)	0.0313(6)	0.3642(3)	0.3590(1)
C(12)	0.0949(6)	0.4116(3)	0.3163(1)
C(13)	0.3003(6)	0.4530(3)	0.3145(1)
C(14)	0.4462(5)	0.4486(3)	0.3574(1)
O(2)	−0.0708(4)	0.4221(2)	0.2761(1)
C(15)	−0.0381(6)	0.3894(2)	0.2286(1)
O(3)	0.1286(4)	0.3496(2)	0.2176(1)
C(16)	−0.2369(6)	0.4098(2)	0.1937(1)
C(17)	−0.2318(6)	0.3718(2)	0.1398(1)
C(18)	−0.4413(6)	0.3975(2)	0.1082(1)
C(19)	−0.4508(6)	0.3627(2)	0.0527(1)
C(20)	−0.6660(6)	0.3899(2)	0.0236(1)
C(21)	−0.6847(6)	0.3571(3)	−0.0318(1)
C(22)	−0.9044(6)	0.3844(3)	−0.9592(1)
C(23)	−0.9209(6)	0.3582(3)	−0.1159(1)
C(24)	−0.1250(7)	0.4019(4)	−0.1433(2)
C(25)	−0.2638(8)	0.3686(5)	−0.1738(2)

refined by full matrix least squares to an R of 0.1443 with isotropic temperature factors using the same programme SHELX. Anisotropic refinement of the non-hydrogen parameters converged to $R = 0.1033$. A difference electron density map revealed 29 of the 32 hydrogen atoms. The positional and isotropic temperature factors were refined which reduced R to 0.0774. The final difference map revealed the position of remaining 3 hydrogen atoms. The final refinement of two more cycles with unit weights converges R to 0.0412.† All calculations were performed on IBM 370/155 and DEC-1090 computers. Scattering factors were taken from International Tables for X-ray crystallog-

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†Structure factor tables may be obtained from the authors.

TABLE III

Refined anisotropic thermal parameters for non-hydrogen atoms

Atom	*U*11	*U*22	*U*33	*U*23	*U*13	*U*12
C(1)	0.0845(28)	0.1092(37)	0.0520(24)	0.0049(23)	−0.0167(21)	0.0188(26)
C(2)	0.01715(26)	0.0925(32)	0.0480(22)	0.0004(21)	−0.0013(19)	0.0173(23)
O(1)	0.0632(15)	0.0818(19)	0.0509(15)	0.0060(14)	−0.0140(12)	−0.0023(14)
C(3)	0.0495(20)	0.0567(23)	0.0459(20)	−0.0037(28)	−0.0072(16)	−0.0058(18)
C(4)	0.0514(21)	0.0752(26)	0.0442(20)	0.0079(18)	0.0030(17)	−0.0005(19)
C(5)	0.0490(20)	0.0701(26)	0.0583(24)	0.0065(20)	−0.0037(18)	−0.0100(19)
C(6)	0.0484(20)	0.0572(23)	0.0415(19)	0.0016(17)	−0.0011(15)	−0.0006(17)
C(7)	0.0537(21)	0.0569(23)	0.0507(21)	0.0071(18)	−0.0014(17)	−0.0038(18)
C(8)	0.0509(20)	0.0613(25)	0.0528(22)	0.0041(18)	−0.0031(17)	−0.0050(18)
N(1)	0.0534(17)	0.0672(21)	0.0505(19)	0.0018(16)	−0.0048(15)	−0.0001(15)
N(2)	0.0579(18)	0.0655(22)	0.0484(18)	0.0015(16)	−0.0060(15)	0.0018(16)
C(9)	0.485(20)	0.0599(24)	0.0449(21)	−0.0047(18)	−0.0033(16)	0.0065(16)
C(10)	0.0588(22)	0.0770(28)	0.0465(21)	0.0003(19)	−0.0032(17)	−0.0015(26)
C(11)	0.0551(21)	0.0807(29)	0.0558(23)	−0.0048(21)	−0.0052(18)	−0.0020(20)
C(12)	0.0509(21)	0.0743(27)	0.0474(21)	−0.0100(20)	−0.0069(17)	0.0158(20)
C(13)	0.0617(24)	0.0839(30)	0.0487(22)	0.0066(20)	0.0006(19)	0.0079(21)
C(14)	0.0512(21)	0.0743(27)	0.0512(22)	0.0048(19)	−0.0034(18)	−0.0003(19)
O(2)	0.0622(15)	0.1052(22)	0.0469(15)	−0.0184(14)	−0.0121(12)	0.0250(15)
C(15)	0.0556(22)	0.0611(26)	0.0529(22)	−0.0077(19)	−0.0030(18)	0.0061(20)
O(3)	0.0677(17)	0.1182(25)	0.0682(17)	−0.0283(17)	−0.0105(14)	0.0286(18)
C(16)	0.0612(22)	0.0704(26)	0.0454(20)	−0.0082(18)	−0.0062(17)	0.0071(20)
C(17)	0.0605(22)	0.0702(26)	0.0452(19)	0.0002(19)	−0.0016(16)	0.0004(19)
C(18)	0.0595(22)	0.0704(27)	0.0499(21)	0.0011(19)	−0.0055(17)	0.0017(19)
C(19)	0.0588(22)	0.0727(26)	0.0469(19)	0.0039(19)	−0.0036(16)	−0.0003(20)
C(20)	0.0663(23)	0.0762(27)	0.0476(21)	0.0023(19)	−0.0043(17)	0.0039(21)
C(21)	0.0620(23)	0.0764(27)	0.0486(20)	0.0024(20)	−0.0054(17)	0.0013(20)
C(22)	0.0686(25)	0.0953(34)	0.0576(24)	0.0017(22)	−0.0084(20)	0.0031(23)
C(23)	0.0674(25)	0.1030(34)	0.0562(23)	0.0018(23)	−0.0102(19)	−0.0038(24)
C(24)	0.0671(28)	0.1899(59)	0.0629(27)	0.0035(33)	−0.0154(23)	−0.0078(34)
C(25)	0.0833(33)	0.2259(70)	0.0861(35)	0.0220(41)	−0.0055(29)	0.0041(40)

raphy.[3] The final positional and thermal parameters for all atoms are presented in Tables II and III using the numbering scheme of the molecule in Figure 1. Table IV gives the bond distances and angles.†

DISCUSSION

The C–H distances vary from 0.87 to 1.28A°. The bond lengths and angles are in good agreement with those in 4-(4′-ethoxyphenylazo)phenyl valerate[4] and hexanoate.[5] The best planes for the two benzene rings are given by $0.4218x - 0.8521y - 0.3099z =$

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†Hydrogen atom parameters may be obtained from the authors.

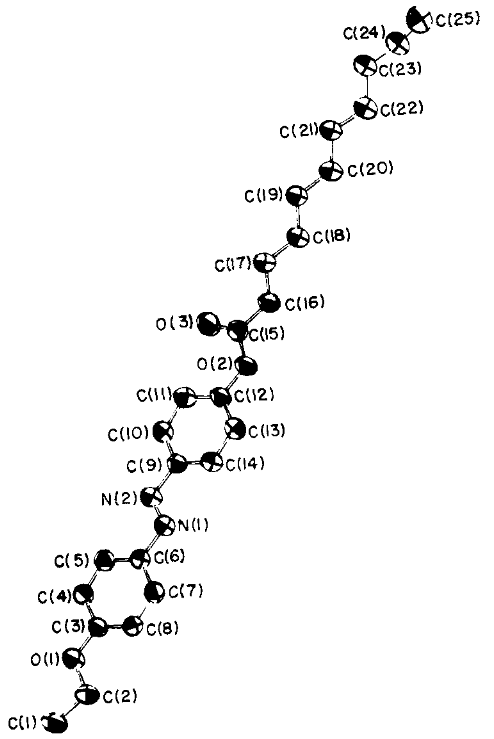

FIGURE 1 Projection of the molecule with probability thermal ellipsoid on the best plane of the molecule.

-7.4672 [$\phi(1)$], and $0.4234x - 0.8251y - 0.3741z = -8.0387$ [$\phi(2)$], where x, y and z are fractional coordinates with respect to the crystallographic axes. The two benzene rings are planar, but not coplanar, the angle between the two normals being 3.996°. It was shown earlier[4,5] that the change in stability within the homologs valerate and hexanoate could be explained by the varying difference in the angles between the benzene planes. The angle should have been higher for undecylenate compared with valerate and hexanoate, but it is less, and may be attributed to the existence of additional dipole at the end of the chain, viz., $CH_2{=}CH$. This strongly alters the intermolecular interaction as evident from packing coefficient studies[6] and which in turn influences the conformation of the benzene groups. The C—N = N—C group is planar; the equation of the best plane is $0.4140x - 0.8482y - 0.3303z = -7.7485$. The C—N = N—C plane makes an angle of 1°30′ with $\phi(1)$ and 2°54′ with $\phi(2)$. The group O(2)—O(3)—C(15)—C(16) is planar and its plane ($0.4415x$ +

TABLE IV

Bond lengths (Å) for non-hydrogen atoms

C(1)—C(2)	1.516(5)	C(13)—C(14)	1.389(5)
C(2)—O(1)	1.427(4)	C(14)—C(9)	1.383(5)
O(1)—C(3)	1.373(4)	C(12)—O(2)	1.417(4)
C(3)—C(4)	1.375(5)	O(2)—C(15)	1.342(4)
C(4)—C(5)	1.391(5)	C(15)—O(3)	1.196(5)
C(5)—C(6)	1.375(5)	C(15)—C(16)	1.495(5)
C(6)—C(7)	1.388(5)	C(16)—C(17)	1.507(5)
C(7)—C(8)	1.376(5)	C(17)—C(18)	1.517(5)
C(8)—C(3)	1.390(5)	C(18)—C(19)	1.527(5)
C(6)—N(1)	1.432(4)	C(19)—C(20)	1.518(5)
N(1)—N(2)	1.256(4)	C(20)—C(21)	1.516(5)
N(2)—C(9)	1.437(4)	C(21)—C(22)	1.521(5)
C(9)—C(10)	1.379(5)	C(22)—C(23)	1.517(5)
C(10)—C(11)	1.389(5)	C(23)—C(24)	1.533(6)
C(11)—C(12)	1.376(5)	C(24)—C(25)	1.232(7)
C(12)—C(13)	1.370(5)		

Bond angles (°) for non-hydrogen atoms

C(1)—C(2)—O(1)	106.2(3)	C(10)—C(12)—C(13)	121.8(3)
C(2)—O(1)—C(3)	118.0(3)	C(12)—C(13)—C(14)	119.0(3)
O(1)—C(3)—C(4)	125.1(3)	C(13)—C(14)—C(9)	120.0(3)
C(3)—C(4)—C(5)	118.7(3)	C(11)—C(12)—O(2)	116.5(3)
C(4)—C(5)—C(6)	121.5(3)	C(13)—C(12)—O(2)	121.4(3)
C(5)—C(6)—C(7)	119.2(3)	C(12)—O(2)—C(15)	120.9(3)
C(6)—C(7)—C(8)	119.9(3)	O(2)—C(15)—O(3)	122.9(3)
C(7)—C(8)—C(3)	120.3(3)	O(2)—C(15)—C(16)	110.2(3)
C(8)—C(3)—O(1)	114.5(3)	O(3)—C(15)—C(16)	127.0(3)
C(8)—C(3)—C(4)	120.4(3)	C(15)—C(16)—C(17)	116.3(3)
C(5)—C(6)—N(1)	116.2(3)	C(16)—C(17)—C(18)	111.3(3)
C(7)—C(6)—N(1)	124.6(3)	C(17)—C(18)—C(19)	115.3(3)
C(6)—N(1)—N(2)	113.5(3)	C(18)—C(19)—C(20)	112.5(3)
N(1)—N(2)—C(9)	113.4(3)	C(19)—C(20)—C(21)	114.8(3)
N(2)—C(9)—C(10)	124.8(3)	C(20)—C(21)—C(22)	113.0(3)
N(2)—C(9)—C(14)	115.0(3)	C(21)—C(22)—C(23)	114.2(3)
C(10)—C(9)—C(14)	120.2(3)	C(22)—C(23)—C(24)	111.3(3)
C(9)—C(10)—C(11)	119.9(3)	C(23)—C(24)—C(25)	128.6(6)
C(10)—C(11)—C(12)	119.1(3)		

$0.8567y - 0.2665z = 3.3118$) forms an angle of 6°52′ with the adjacent benzene ring.

Figure 1 shows the projection of the molecule with probability thermal ellipsoids on the best plane of the molecule ($0.0971x - 0.9938y - 0.0539z = -6.1534$). The conformation is defined by the torsion angle $-179.041°$ about N(1)—N(2). The torsional angle $C_{(22)}$—$C_{(25)}$—$C_{(24)}$—$C_{(25)}$ is $-135.551°$ and it is in preferred range.

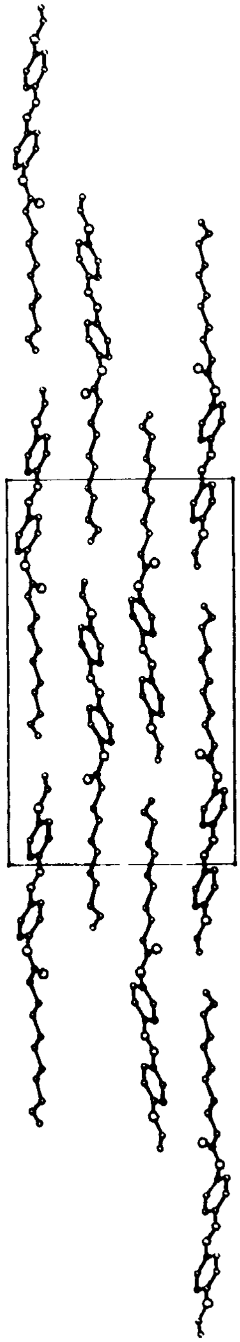

FIGURE 2 Projection of the structure down the *X*-axis.

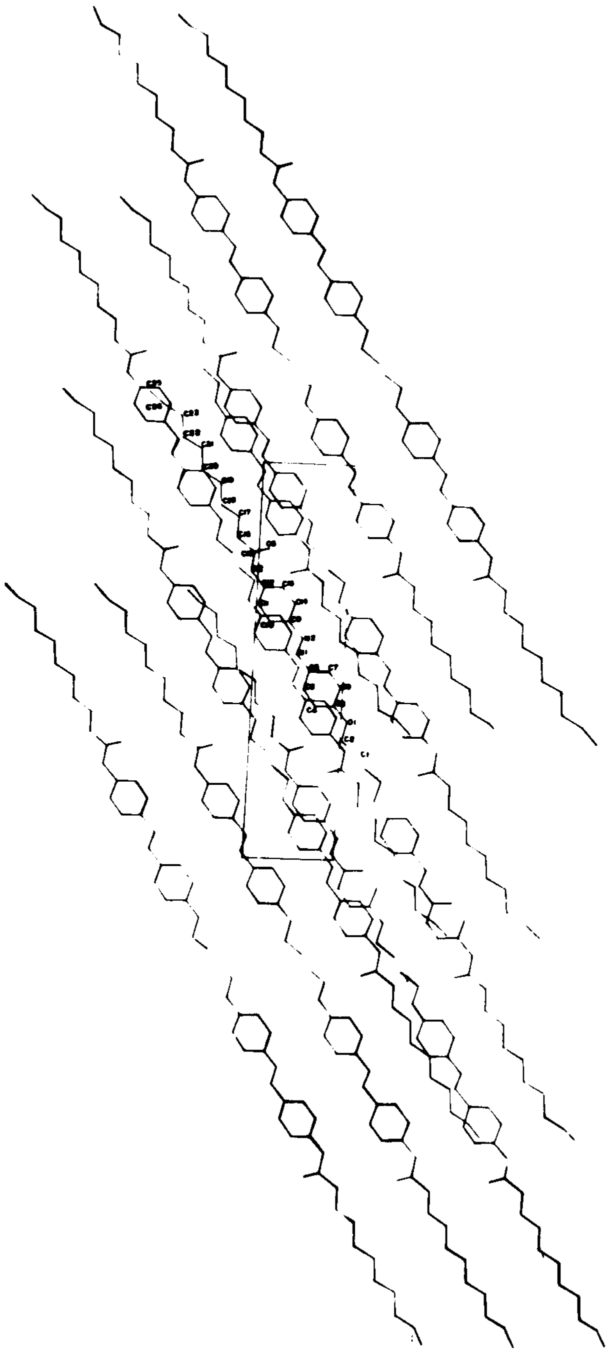

FIGURE 3 Projection of the structure down the Y-axis.

The molecules are almost fully extended. The projection of the molecular packing down *x* is shown in Figure 2. The molecules are almost parallel to *c*-axis. The molecular axis is inclined to *xz* plane and makes an angle of about 30 ° (Figure 3).

We have found that there are no intermolecular distances less than the sum of the Van der Waals radii. The dipoles of the carbonyl groups in the two dimensional arrangement form the main forces in the crystalline cohesion. The molecules are not imbricated to the extent predicted as necessary for the formation of a nematic liquid crystal.

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