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# Crytal and Molecular Structure of n-p-Cyanobenzylidene-p-n-octyloxyaniline (CBOOA)

G. V. Vani [a] & Kalyani Vijayan [b]
[a] Raman Research Institute, Banglore, 560006, India
[b] Materials Science Division, National Aeronautical Laboratory, Bangalore, 560017, India
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# Crystal and Molecular Structure of *n*-*p*-Cyanobenzylidene-*p*-*n*-octyloxyaniline (CBOOA)

G. V. VANI

*Raman Research Institute, Bangalore 560006, India*

and

KALYANI VIJAYAN

*Materials Science Division, National Aeronautical Laboratory, Bangalore 560017, India*

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Smectogenic CBOOA crystallizes in a tetramolecular monoclinic unit cell of dimensions $a = 15.994 \pm 0.006$, $b = 15.935 \pm 0.008$, $c = 7.663 \pm 0.008$ Å, $\beta = 91°48' \pm 04'$. The space group is $P2_1/c$. Three dimensional photographic intensity data have been used for the structure analysis. The structure was solved by direct methods and has been refined to $R = 0.089$ by iterative block-diagonal structure factor least-squares method using 1654 reflections. All the hydrogen atoms in the structure have been located and their coordinates have been refined. In the unit cell, the CBOOA molecules associate in antiparallel pairs. The interaction between the neighbouring molecules if of the van der Waal's type.

## INTRODUCTION

*n*-*p*-Cyanobenzylidene-*p*-*n*-octyloxyaniline (CBOOA) is known to exhibit the following liquid crystalline phases;

$$\text{Solid} \xrightarrow{73°C} \text{Smectic A} \xrightarrow{82.5°C} \text{Nematic} \xrightarrow{106.9°C} \text{Isotropic}$$

Results of the single crystal X-ray analysis of CBOOA presented in this paper form part of a programme of X-ray structural investigations on liquid crystalline materials.[1] A preliminary note on this analysis has already been reported.[2]

## EXPERIMENTAL

Transparent, yellow, rectangular-prismatic crystals of CBOOA were obtained by slow evaporation from a solution in *n*-heptane. From oscillation and Weissenberg photographs, the crystals were found to be monoclinic. From systematic absences of the type $h01$, 1 odd and $0k0$, $k$ odd, the space group was fixed to be $P2_1/c$. The density of the crystal as measured by flotation in aqueous potassium iodide solution indicated that the unit cell contained four molecules of CBOOA. The unit cell dimensions have been refined by least-squares method, using 23 high angle reflections from the $hk0$ and $h01$ projections. In Table I these values are presented along with other relevant crystal data.

TABLE I

Crystal date

| | |
|---|---|
| Molecular formula | $C_{22}H_{26}ON_2$ |
| Molecular weight | 334.45 |
| $a = 15.994 \pm 0.006$ Å | |
| $b = 15.935 \pm 0.008$ | |
| $c = 7.663 \pm 0.008$ | |
| $\beta = 91°48' \pm 04'$ | |
| Space group $P2_1/c$ | |
| $z = 4$ | |
| $\rho_{calc} = 1.14$ gm cm$^{-3}$ | |
| $\rho_{exp} = 1.14$ gm cm$^{-3}$ | |

Intensity data were collected on multiple films employing the equi-inclination Weissenberg geometry and copper $K\alpha$ radiation. 1654 independent reflections were recorded from the reciprocal levels $h01$ and $hkL$, $L = 0$ to 5 and were estimated visually by comparison with a standard calibrated strip. The intensities were corrected for Lorentz-polarisation factors and spot-shape. Absorption correction was applied using Palm's[3] expression for cylindrical specimens.

## STRUCTURE DETERMINATION

The structure was solved by direct methods using normalised structure factors $E_{hkl}$'s conventionally defined as[4]

$$E_{hkl}^2 = \frac{|F_{hkl}|^2}{\varepsilon \sum_{j=1}^{N} f_j^2}$$

where $f_j$ is the atomic scattering factor of the $j$th atom, $N$ is the total number

of atoms in the unit cell. $\varepsilon$ is an integer which is generally 1, but in different space groups, it changes for special sets of reflections. In the space group $P2_1/c$, $\varepsilon = 2$ for the $h01$ and $0k0$ type of reflections and 1 for all others. While analysing the crystal structure of nematogenic *n-p*-methoxybenzylidene *p*-phenylazoaniline[1] we have found that when the molecule has planar aromatic rings it is appropriate if, in the expression for $E_{hkl}$, the individual atomic scattering factors are replaced by a spherical average for the entire ring, placed at the centre of the ring. Hence, while calculating the normalised structure factors of CBOOA, the $f_j$'s were replaced by molecular scattering factors for the two phenyl rings. Also, to avoid the effect of rational dependence[5] arising from the rigid, rod-like geometry of the molecule, the reflections were divided into five $\sin\theta/\lambda$ ranges and the average value of $|E^2_{hkl}|$ in each range was normalised to unity. Each of the eight parity groups of reflections was also normalised in a similar fashion. 300 normalised $E_{hkl}$'s $\geq 1.67$ were used with the MULTAN programme of Germain, Main and Woolfson.[6] The choice of reflections for specifying the origin and the symbols are given below:

| $h$ | $k$ | $l$ | $\lvert E_{hkl}\rvert$ | |
|---|---|---|---|---|
| 2 | 3 | $\bar{4}$ | 4.88 + | origin |
| 13 | 4 | 1 | 4.08 + | |
| 7 | 8 | 4 | 3.22 + | |
| 13 | 1 | 0 | 4.58 A | symbols |
| 7 | 6 | $\bar{1}$ | 3.41 B | |

Out of the four possible solutions of MULTAN, *E*-map was computed for the best solution and positional coordinates were assigned to all the non-hydrogen atoms in the molecule. However, subsequent structure factor least-squares calculations revealed that the positions of five carbon atoms in the octyloxy chain were wrong. From a difference electron-density map, synthesized after removing the contributions from these five carbon atoms, their correct positions were determined. The initial *R*-factor defined as $\sum ||F_o| - |F_c||/\sum |F_o|$ was 0.297 for the 25 non-hydrogen atoms and was refined to 0.145 by iterative structure factor least-squares using Cruickshank's weighting scheme[7] of the form $w = (a + bF_0 + cF_0^2)^{-1}$ where $a = -0.383$, $b = 0.316$ and $c = 0.0013$, and individual isotropic temperature factors. At this stage anisotropic thermal parameters of the form $[\exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2hk\,b_{12} + 2hl\,b_{13} + 2kl\,b_{23})]$ were introduced for all the atoms and the *R*-value reduced to 0.117. In the course of the least-squares refinement, the reflection 031 was found to be affected by extinction effect and was corrected for using Zachariasen's formula.[8] A difference electron density map computed at this stage had distinct peaks for all the hydrogen atoms in the structure. In further least squares refinement, the hydrogen

atoms were also included. They were assigned isotropic temperature factors which were same as the equivalent $B$ values of the carbon atoms to which they were attached. The equivalent $B$'s were calculated using the well known formula:[9]

$$B_{\text{equivalent}} = \frac{4}{3} \sum_{i=1}^{3} \sum_{j=1}^{3} b_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$$

where the $b_{ij}$'s are the components of the anisotropic thermal parameters, $a_1$, $a_2$, $a_3$ are direct cell lengths. When the least squares refinement converged, the $R$-value was 0.089.*

The structure-factor least-squares programme used by us was originally written by R. Shiono for the IBM 1130 computer and later modified by B. S. Reddy for the IBM 360/44. The scattering factors used were those of Cromer and Waber.[10]

## RESULTS AND DISCUSSION

The final positional and thermal parameters of all the atoms are listed in Tables II and III. The bond lengths and bond angles involving the non-hydrogen atoms are marked in Figure 1 and those involving the hydrogen atoms are listed in Table IV. The labelling of the hydrogen atom is the same as that of the heavy atom to which it is linked; where more than one hydrogen atom is attached to the heavy atom, a new sequence is started and is included as the last digit of the labelling number. Within limits of experimental error, ($\Delta \leq 3\sigma$), the molecular dimensions are normal. In the phenyl rings, the average value of the C–C lengths is 1.392 (0.015) Å and the C–C–C angles average to 120.0(0.9)°. In the octyloxy-chain the average $C_{sp^3}$–$C_{sp^3}$ distance is 1.522 (9.017) Å. The molecular dimensions involving the hydrogen atoms have comparatively larger standard deviations.

The least-squares mean plane through various groups of atoms have been calculated with respect to an orthogonal coordinate system. In Table V, the equations to the various planes and the displacements of atoms from the respective planes have been listed. The two phenyl rings and the group of atoms C(5), C(8), N(2) and C(9) are planar. The angle between the plane normals of the two phenyl rings is 17°43′. The cyano group is displaced slightly above the plane of the phenyl ring through atoms C(2) to C(7), the displacements being 0.03 Å for C(1) and 0.07 Å for N(1). The oxygen atom lies in the plane of the second phenyl ring.

* The tables of structure factors are available with the authors and can be supplied on request.

TABLE II

Final fractional positional coordinates and anisotropic thermal parameters ( $\times 10^4$) of non-hydrogen atoms. Estimated standard deviations for last decimal are given in parentheses

| Atom | $x$ | $y$ | $z$ | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 325(7) | −864(7) | −964(15) | 46(5) | 54(6) | 337(30) | 2(4) | −30(8) | −40(8) |
| C(1) | 937(7) | −654(8) | −311(15) | 43(6) | 48(6) | 202(30) | 1(4) | −5(8) | −2(7) |
| C(2) | 1734(7) | −400(7) | 486(13) | 37(5) | 50(5) | 129(26) | −2(4) | −3(6) | 5(7) |
| C(3) | 1828(7) | 387(6) | 1301(14) | 38(5) | 35(4) | 192(29) | −0(4) | 1(7) | −13(6) |
| C(4) | 2600(7) | 600(7) | 2007(14) | 41(5) | 35(5) | 205(29) | −3(4) | −10(7) | −1(6) |
| C(5) | 3282(6) | 59(6) | 1952(13) | 37(5) | 32(4) | 140(25) | −4(3) | −3(6) | 9(5) |
| C(6) | 3170(7) | −735(6) | 1164(13) | 48(5) | 35(4) | 121(24) | 2(4) | −0(7) | 4(6) |
| C(7) | 2397(7) | −963(7) | 428(15) | 46(6) | 43(5) | 193(29) | −2(4) | −8(7) | −1(7) |
| C(8) | 4122(6) | 280(6) | 2639(13) | 36(5) | 44(5) | 128(26) | 2(3) | −8(6) | 15(6) |
| N(2) | 4313(5) | 1029(6) | 3124(11) | 34(4) | 43(4) | 185(23) | 1(3) | −0(5) | 3(6) |
| C(9) | 5144(6) | 1205(6) | 3703(12) | 35(4) | 33(4) | 148(26) | −5(3) | −9(6) | 10(6) |
| C(10) | 5255(7) | 1892(6) | 4838(14) | 40(5) | 36(5) | 174(27) | 2(4) | 2(7) | −7(6) |
| C(11) | 6050(7) | 2112(7) | 5442(13) | 43(5) | 45(5) | 131(26) | −0(4) | −5(7) | −5(7) |
| C(12) | 6744(6) | 1680(6) | 4892(12) | 43(5) | 33(4) | 99(23) | −3(3) | −10(6) | 12(6) |
| C(13) | 6647(7) | 994(7) | 3743(14) | 38(5) | 40(5) | 185(28) | −5(4) | −3(7) | −10(6) |
| C(14) | 5837(7) | 779(7) | 3170(14) | 38(5) | 34(5) | 218(29) | 0(4) | −4(7) | −3(6) |
| O | 7507(5) | 1944(5) | 5549(10) | 41(4) | 39(3) | 210(19) | −2(3) | −17(5) | −4(5) |
| C(15) | 8237(7) | 1478(7) | 5102(15) | 34(5) | 42(5) | 221(30) | 5(4) | −3(7) | −1(7) |
| C(16) | 8981(7) | 1895(8) | 6046(15) | 33(5) | 46(6) | 241(31) | 1(4) | −14(7) | 5(7) |
| C(17) | 9798(7) | 1411(8) | 5740(15) | 42(6) | 53(7) | 205(31) | 3(4) | −9(8) | −9(8) |
| C(18) | 10545(7) | 1817(8) | 6682(15) | 39(6) | 47(6) | 239(32) | −8(4) | −7(8) | 3(7) |
| C(19) | 11355(8) | 1341(8) | 6456(15) | 46(6) | 57(7) | 188(32) | 3(5) | −2(8) | −3(8) |
| C(20) | 12109(8) | 1775(8) | 7376(16) | 40(6) | 56(6) | 213(31) | −4(5) | −7(8) | 2(8) |
| C(21) | 12920(8) | 1270(8) | 7322(17) | 41(6) | 52(7) | 301(37) | 11(5) | −11(9) | −21(9) |
| C(22) | 13633(9) | 1708(10) | 8342(20) | 44(7) | 61(8) | 353(41) | −9(6) | −38(10) | 8(11) |

TABLE III

Final fractional positional coordinates and isotropic thermal parameters of hydrogen atoms. e.s.d's are given in parentheses

| Atom | $x(\times 10^2)$ | $y(\times 10^2)$ | $z(\times 10^2)$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| H(3) | 13(1) | 8(1) | 14(2) | 4.1 |
| H(4) | 27(1) | 12(1) | 26(2) | 4.0 |
| H(6) | 37(1) | −12(1) | 11(2) | 3.7 |
| H(7) | 23(1) | −16(1) | −2(2) | 4.3 |
| H(8) | 47(1) | −2(1) | 27(2) | 3.6 |
| H(10) | 47(1) | 22(1) | 52(2) | 3.8 |
| H(11) | 61(1) | 26(1) | 63(2) | 3.9 |
| H(13) | 72(1) | 6(1) | 33(2) | 3.9 |
| H(14) | 58(1) | 2(1) | 23(2) | 4.0 |
| H(151) | 83(1) | 15(1) | 38(2) | 4.4 |
| H(152) | 82(1) | 9(1) | 55(2) | 4.4 |
| H(161) | 89(1) | 19(1) | 73(2) | 4.7 |
| H(162) | 90(1) | 25(1) | 56(2) | 4.7 |
| H(171) | 99(1) | 14(1) | 45(2) | 5.1 |
| H(172) | 97(1) | 8(1) | 62(2) | 5.1 |
| H(181) | 104(1) | 19(1) | 79(2) | 5.1 |
| H(182) | 106(1) | 24(1) | 62(2) | 5.1 |
| H(191) | 115(1) | 13(1) | 52(2) | 5.0 |
| H(192) | 113(1) | 8(1) | 69(2) | 5.0 |
| H(201) | 120(1) | 19(1) | 86(2) | 5.0 |
| H(202) | 122(1) | 23(1) | 69(2) | 5.0 |
| H(211) | 131(1) | 12(1) | 60(2) | 5.2 |
| H(212) | 128(1) | 7(1) | 78(2) | 5.2 |
| H(221) | 137(1) | 24(1) | 82(2) | 6.2 |
| H(222) | 141(1) | 13(1) | 87(2) | 6.2 |
| H(223) | 134(1) | 19(1) | 95(2) | 6.2 |

TABLE IV

Bond lengths in Å and bond angles in degrees involving hydrogen atoms. Standard deviations are given in parentheses

| | | |
|---|---|---|
| C(3) | H(3) | 1.1(0.2) |
| C(4) | H(4) | 1.1(0.2) |
| C(6) | H(6) | 1.1(0.1) |
| C(7) | H(7) | 1.1(0.1) |
| C(8) | H(8) | 1.1(0.2) |
| C(10) | H(10) | 1.1(0.1) |
| C(11) | H(11) | 1.1(0.2) |
| C(13) | H(13) | 1.1(0.2) |
| C(14) | H(14) | 1.1(0.2) |
| C(15) | H(151) | 1.0(0.1) |
| C(15) | H(152) | 1.0(0.1) |
| C(16) | H(161) | 1.0(0.1) |
| C(16) | H(162) | 1.0(0.2) |
| C(17) | H(171) | 1.0(0.1) |
| C(17) | H(172) | 1.0(0.1) |

Table IV (*continued*)

| | | | |
|---|---|---|---|
| C(18) | H(181) | 1.0(0.1) | |
| C(18) | H(182) | 1.0(0.2) | |
| C(19) | H(191) | 1.1(0.2) | |
| C(19) | H(192) | 1.1(0.2) | |
| C(20) | H(201) | 1.0(0.2) | |
| C(20) | H(202) | 1.0(0.2) | |
| C(21) | H(211) | 1.0(0.2) | |
| C(21) | H(212) | 1.0(0.2) | |
| C(22) | H(221) | 1.1(0.2) | |
| C(22) | H(222) | 1.1(0.2) | |
| C(22) | H(223) | 1.0(0.2) | |
| C(2) | C(3) | H(3) | 122(9) |
| C(4) | C(3) | H(3) | 120(9) |
| C(3) | C(4) | H(4) | 118(10) |
| C(5) | C(4) | H(4) | 120(10) |
| C(5) | C(6) | H(6) | 120(7) |
| C(7) | C(6) | H(6) | 119(7) |
| C(6) | C(7) | H(7) | 119(6) |
| C(2) | C(7) | H(7) | 122(6) |
| C(5) | C(8) | H(8) | 120(8) |
| N(2) | C(8) | H(8) | 118(8) |
| C(9) | C(10) | H(10) | 119(5) |
| C(11) | C(10) | H(10) | 121(5) |
| C(10) | C(11) | H(11) | 120(8) |
| C(12) | C(11) | H(11) | 120(8) |
| C(12) | C(13) | H(13) | 121(10) |
| C(14) | C(13) | H(13) | 121(10) |
| C(13) | C(14) | H(14) | 119(9) |
| C(9) | C(14) | H(14) | 119(9) |
| 0 | C(15) | H(151) | 110(9) |
| 0 | C(15) | H(152) | 110(5) |
| C(16) | C(15) | H(151) | 109(9) |
| C(16) | C(15) | H(152) | 110(5) |
| H(151) | C(15) | H(152) | 111(10) |
| C(15) | C(16) | H(161) | 109(5) |
| C(15) | C(16) | H(162) | 110(9) |
| C(17) | C(16) | H(161) | 110(5) |
| C(17) | C(16) | H(162) | 110(9) |
| H(161) | C(16) | H(162) | 108(10) |
| C(16) | C(17) | H(171) | 110(8) |
| C(16) | C(17) | H(172) | 109(7) |
| C(18) | C(17) | H(171) | 110(8) |
| C(18) | C(17) | H(172) | 109(7) |
| H(171) | C(17) | H(172) | 107(11) |
| C(17) | C(18) | H(181) | 110(9) |
| C(17) | C(18) | H(182) | 109(9) |
| C(19) | C(18) | H(181) | 110(9) |
| C(19) | C(18) | H(182) | 109(9) |
| H(181) | C(18) | H(182) | 106(13) |
| C(18) | C(19) | H(191) | 110(9) |
| C(18) | C(19) | H(192) | 110(10) |
| C(20) | C(19) | H(191) | 109(9) |
| C(20) | C(19) | H(192) | 110(10) |

Table IV (*continued*)

| | | | |
|---|---|---|---|
| H(191) | C(19) | H(192) | 106(13) |
| C(19) | C(20) | H(201) | 109(12) |
| C(19) | C(20) | H(202) | 110(9) |
| C(21) | C(20) | H(201) | 107(12) |
| C(21) | C(20) | H(202) | 110(9) |
| H(201) | C(20) | H(202) | 106(15) |
| C(20) | C(21) | H(211) | 107(8) |
| C(20) | C(21) | H(212) | 111(9) |
| C(22) | C(21) | H(211) | 110(8) |
| C(22) | C(21) | H(212) | 111(9) |
| H(211) | C(21) | H(212) | 107(12) |
| C(21) | C(22) | H(221) | 116(10) |
| C(21) | C(22) | H(222) | 112(11) |
| C(21) | C(22) | H(223) | 109(12) |
| H(221) | C(22) | H(222) | 127(15) |
| H(221) | C(22) | H(223) | 82(12) |
| H(222) | C(22) | H(223) | 103(12) |

TABLE V

Equations of various least-square mean planes and displacements Δ in Å of atoms from them

(a) Plane through atoms C(2), C(3), C(4), C(5), C(6), C(7).

$$0.28325x + 0.39088y - 0.87577z = 0.19546.$$

| Plane | Atom | Δ |
|---|---|---|
| (a) | C(2) | 0.011 |
| | C(3) | −0.010 |
| | C(4) | 0.001 |
| | C(5) | 0.006 |
| | C(6) | −0.005 |
| | C(7) | −0.004 |
| | C(1) | 0.031 |
| | N(1) | 0.068 |

(b) Plane through atoms C(9), C(10), C(11), C(12), C(13), C(14).

$$0.09915x + 0.61807y - 0.77985z = -0.21550.$$

| Plane | Atom | Δ |
|---|---|---|
| (b) | C(9) | −0.007 |
| | C(10) | 0.004 |
| | C(11) | −0.002 |
| | C(12) | 0.002 |
| | C(13) | −0.004 |
| | C(14) | 0.007 |
| | 0 | −0.001 |

Table V (*continued*)

(c) Plane through atoms C(5), C(8), N(2), C(9).

$$0.28830x + 0.22133y - 0.93161z = 0.11680.$$

| Plane | Atom | Δ |
|---|---|---|
| (c) | C(5) | 0.011 |
| | C(8) | −0.012 |
| | N(2) | 0.011 |
| | C(9) | −0.011 |

## TABLE VI

Intermolecular contact distances less than 4 Å

| | | Å | | | Å |
|---|---|---|---|---|---|
| C(1)[a] | N(1)[b] | 3.31 | C(7a)[a] | 0[c] | 3.46 |
| C(1)[a] | C(1)[b] | 3.67 | C(7)[a] | C(13)[f] | 3.59 |
| C(1)[a] | C(16)[c] | 3.82 | C(7)[a] | C(15)[c] | 3.69 |
| C(1)[a] | C(17)[c] | 3.92 | C(7)[a] | C(16)[c] | 3.84 |
| C(1)[a] | C(16)[d] | 3.96 | C(7)[a] | C(12)[c] | 3.96 |
| C(2)[a] | C(16)[c] | 3.77 | C(8)[a] | C(14)[c] | 3.63 |
| C(2)[a] | C(15)[c] | 3.79 | C(8)[a] | C(13)[c] | 3.67 |
| C(2)[a] | N(1)[b] | 3.89 | C(8)[a] | C(9)[c] | 3.82 |
| C(3)[a] | N(1)[b] | 3.54 | C(8)[a] | C(12)[c] | 3.92 |
| C(3)[a] | C(20)[e] | 3.78 | C(9)[a] | C(11)[g] | 3.97 |
| C(3)[a] | C(21)[e] | 3.82 | C(10)[a] | C(22)[h] | 3.60 |
| C(4)[a] | C(22)[e] | 3.74 | C(10)[a] | C(22)[i] | 3.80 |
| C(4)[a] | C(21)[e] | 3.79 | C(10)[a] | C(11)[g] | 3.98 |
| C(5)[a] | C(12)[c] | 3.67 | C(11)[a] | C(14)[j] | 3.98 |
| C(5)[a] | C(13)[c] | 3.69 | C(11)[a] | C(10)[j] | 3.98 |
| C(5)[a] | C(22)[e] | 3.87 | C(13)[a] | C(21)[k] | 3.76 |
| C(5)[a] | 0[c] | 3.95 | C(14)[a] | C(21)[k] | 3.85 |
| C(6)[a] | C(12)[c] | 3.37 | C(16)[a] | N(1)[l] | 3.74 |
| C(6)[a] | 0[c] | 3.38 | C(17)[a] | N(1)[f] | 3.77 |
| C(6)[a] | C(11)[c] | 3.60 | C(18)[a] | N(1)[c] | 3.91 |
| C(6)[a] | C(14)[f] | 3.73 | C(18)[a] | N(1)[l] | 3.98 |
| C(6)[a] | C(13)[f] | 3.81 | C(21)[a] | N(2)[m] | 3.99 |
| C(6)[a] | C(11)[d] | 3.86 | C(22)[a] | N(2)[n] | 3.77 |
| C(6)[a] | C(15)[c] | 3.88 | C(22)[a] | N(2)[p] | 3.94 |
| C(6)[a] | C(13)[c] | 3.92 | N(1)[a] | N(1)[b] | 3.31 |
| C(7)[a] | 0[d] | 3.42 | | | |

[a] $x, y, z$
[b] $-x, -y, -z$
[c] $1-x, -y, 1-z$
[d] $1-x, y-\frac{1}{2}, \frac{1}{2}-z$
[e] $x-1, y, z-1$
[f] $1-x, -y, -z$
[g] $x, \frac{1}{2}-y, z-\frac{1}{2}$
[h] $x-1, \frac{1}{2}-y, z-\frac{1}{2}$
[i] $x-1, y, z$
[j] $x, \frac{1}{2}-y, \frac{1}{2}+z$
[k] $2-x, -y, 1-z$
[l] $1-x, \frac{1}{2}+y, \frac{1}{2}-z$
[m] $x+1, y, z$
[n] $x+1, \frac{1}{2}-y, \frac{1}{2}+z$
[p] $x+1, y, z+1$.

FIGURE 1 Bond lengths and bond angles involving non-hydrogen atoms.

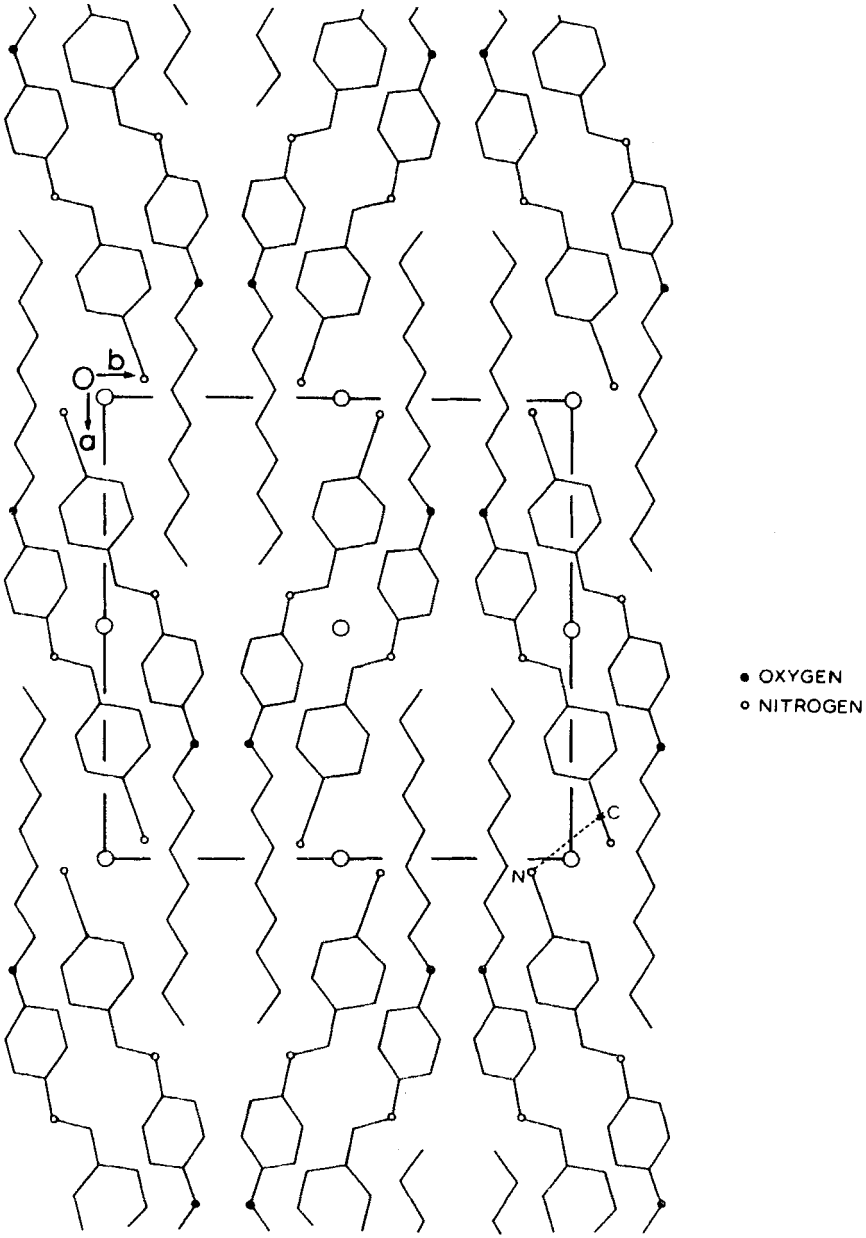


FIGURE 2 Molecular arrangement in the *ab*-plane. The short non-bonded C · · · N contact is indicated.

Figure 2 shows the molecular packing in the *ab*-plane. The CBOOA molecule lies nearly extended in this plane. The cyanobenzylidene group of the molecule is inclined to the *a*-axis by about 25° and the octyloxy chain runs parallel to the *a*-axis. In Figure 3, the arrangement of the molecules in the *bc*-plane has been shown. The cyano groups of the neighbouring molecules are at a distance less than the sum of the van der Waal's radii, with a non-bonded contact distance of 3.31 Å existing between the carbon and the nitrogen atoms (indicated in Figure 2). The CBOOA molecules associate in pairs about centres of inversion and hence, adjacent molecules in the unit cell are antiparallel to each other. The neighbouring pairs along the *c*-direction are related by the short *c*-cell translation. Along the *b*-direction they are related by the two-fold screw axis and the *c*-glide. If pairs of molecules related by an inversion centre are considered as one unit, the arrangement of these units in the *bc*-plane could be described as a herring-

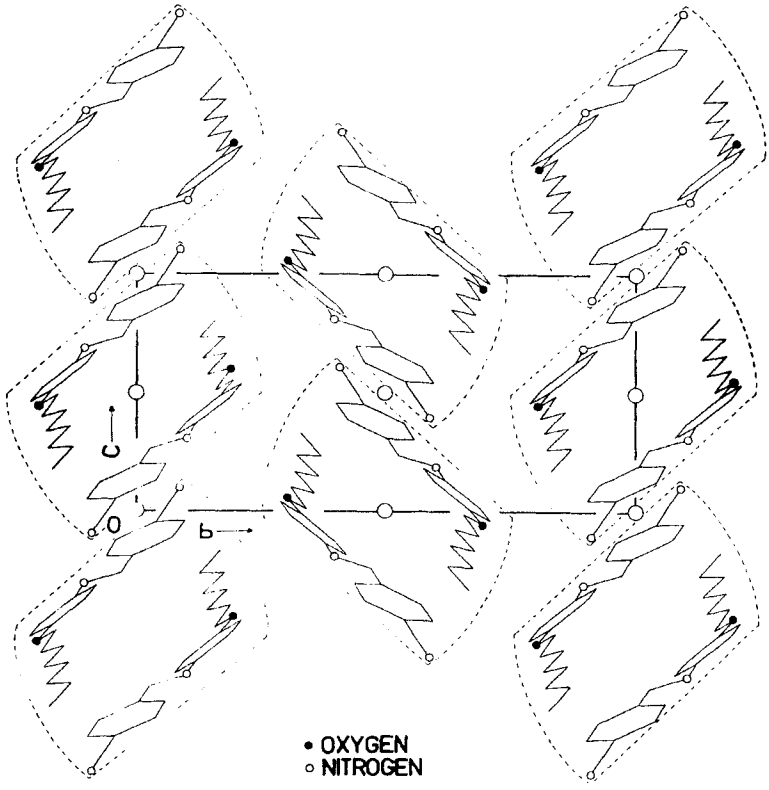


FIGURE 3 Molecular arrangement in the *bc*-plane. Pairs of antiparallel molecules have been enclosed to indicate herringbone-like packing.

bone-like pattern. In Figure 3, pairs of antiparallel molecules have been enclosed to indicate the herringbone-like packing.

All intermolecular contact distances less than 4 Å have been listed in Table VI. Of these, only two distances are less than the sum of the van der Waal's radii of the respective atoms. A striking feature regarding the contact distances is that they are crowded in some regions of the unit cell. There are some intermediate pockets where the contact distances are longer, indicating weaker interaction between neighbouring molecules. For example, the ring through the atoms C(9) to C(14) has many non-bonded contact distances less than 4 Å with the phenyl ring through atoms C(2) to C(7) of a neighbouring molecule on one side, whereas on the other side, there are very few interactions with the atoms of a neighbouring oxtyloxy chain. These pockets of weak interaction are contained in planes parallel to the ac-plane. The structure can, therefore, be described as consisting of layers of molecules parallel to the *ac*-plane, the layers being separated along the *b*-axis by the planes formed by these pockets of weak interaction. The molecules within a layer are related by centres of inversion and those in the adjacent layers by the *c*-glide and the two-fold screw axis. This layer-like stacking of molecules in the solid phase, probably explains the smectogenic nature of the compound.

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## References

1. K. Vijayan and G. V. Vani, Proceedings of the International Liquid Crystals Conference, Bangalore, 1973—*Pramana Supplement*, 1, p. 75.
2. G. V. Vani and K. Vijayan, *Current Science*, **45**, 857 (1976).
3. J. H. Palm, *Acta Crystallogr.*, **17**, 1326 (1964).
4. J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).
5. H. Hauptman and J. Karle, *Acta Crystallogr.*, **12**, 846 (1959).
6. G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, **A27**, 368 (1971).
7. D. W. J. Cruickshank, *Computing Methods in Crystallography*, Ed. J. S. Rollett, Pergamon, p. 114 (1965).
8. W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).
9. W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).
10. D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).