

CHAPTER 3

CRYSTAL AND MOLECULAR STRUCTURE OF N-n-CYANOBENZYLIDENE- p-n-OCTYLOXYANILINE (CBOOA)

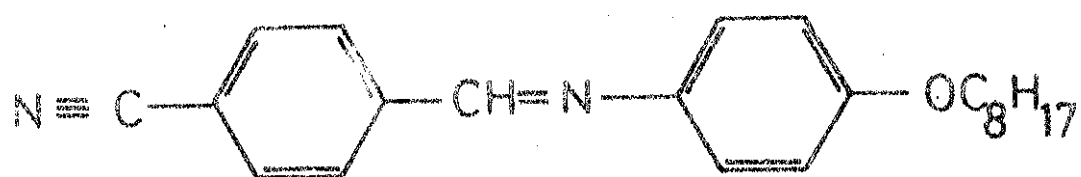
3.1 Introduction

N-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA),
 $C_{22}H_{26}OM_2$ (11) exhibits the following phase transitions:

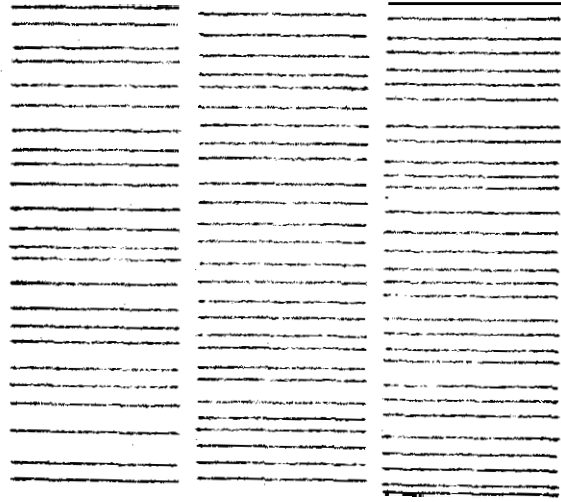
Solid $\xrightarrow{73^{\circ}C}$ Smectic A $\xrightarrow{82.5^{\circ}C}$ Nematic $\xrightarrow{106.9^{\circ}C}$ Isotropic

CBOOA is one of the most extensively studied **smecto-genic compounds** in recent years. A number of investigations have been **made** on **its** various physical properties in both its crystalline and liquid orystalline phases [1-22]. Current theories on liquid **crystals** [23,24,25] **indicate** that the smectic A-nematic phase transition could possibly be of the second order. Hence, the etudy of the critical **behaviour** of the **properties** of CBOOA in the vicinity of the smectic A-nematic transition has attracted considerable attention [26-36].

McMillan [37] has determined the interlayer spacing in the smectic A phase of CBOOA to be $\sim 35 \text{ \AA}$. But the length of the fully extended CBOOA molecule is **only** $\sim 27 \text{ \AA}$. The discrepancy between the molecular length and the layer **spacing** (or layer thickness) has been accounted for by



(II)



(a)



(b)

Figure 3.1: Schematic representation of the molecular arrangement in (a) ordinary smectic A phase, (b) bilayered smectic A phase.

proposing a bilayered structure for the smectic A phase of CBOOA, Fig. 3.1(a) and Fig. 3.1(b) are the **schematic** representations of the molecular arrangements in an ordinary **smectic** A phase and a bilayered smectic A phase **respectively**. In Fig. 3.1(a), the layer spacing is equal **to** the length of the **molecule**. In Fig. 3.1(b) the molecules within a layer are arranged **in** a staggered fashion, **and** hence the layer spacing is larger **than** the length of **the** molecule. Moreover, since the CBOOA molecule contains a strong polar group ($\text{C}\equiv\text{N}$) at one end, the nearest neighbours are likely to be oriented **antiparallel** to each other [38]. A **similar** bilayered **structure** has been observed in the smectic A phase of the compound 4-cyano-4'-octyl biphenyl [39]. **Experimental results** of the **impurity-dependence** studies [40], the high pressure **studies** [31] and the study of the transport properties [41] appear to support the existence of bilayers in the **smectic** A phase of CBOOA.

Details **of** the X-ray analysis of CBOOA **in** the crystalline phase have been described in this chapter.

3.2 Experimental

Transparent, faint yellow **coloured**, rectangular, **prismatic** crystals of CBOOA were obtained by slow evaporation **from** a **solution** in **n-heptane**. Oscillation and Weissenberg photographs were recorded with **a** crystal

mounted along the c-axis, using nickel filtered copper radiation. The diffraction pattern indicated that the crystals were monoclinic. The Weissenberg photographs were found to contain systematic extinctions for the reflections of the type $h0l$, l odd, and $0k0$, k odd. The presence of these extinctions unambiguously determined the space group to be $P2_1/c$.

The value of the direct cell axial dimension c was measured from the rotation photograph. The values of b^* (and hence b) and a^* were obtained from the c-axis zero level Weissenberg photograph. The monoclinic angle β was measured from higher level Weissenberg photographs by the method of angular lag [42]. The cell dimension a was then calculated using the values of a^* and β .

The density of the compound as determined by flotation in aqueous potassium iodine solution indicated that the unit cell contained four molecules of CB00A.

The cell constants a , b , c and β were refined by the method of least-squares. 23 high angle projection reflections (14 of the hko type and 9 of the hol type) were used. The refinement converged at the end of two cycles, when the shifts were smaller than the standard deviations for all the four parameters. The preliminary crystal data of CB00A are listed in Table 3.4. Table 3.2

TABLE 3.1

Crystal Data

Unit cell dimensions	$a = 15.994 \pm 0.006$	$\overset{a}{\text{\AA}}$
	$b = 15.935 \pm 0.008$	$\bullet \text{\AA}$
	$c = 7.663 \pm 0.008$	$\bullet \text{\AA}$
	$\beta = 91^\circ 48' \pm 04'$	
Space group	$P2_1/c$	
Volume of the unit cell	$U = 1952.06$	$\text{\AA}^3$
Molecular weight	334.45	
Number of molecules per unit cell	$Z = 4$	
Calculated density	$\rho_c = 1.14$	gm. cm^{-3}
Measured density	$\rho_m = 1.14$	gm. cm^{-3}
Linear absorption coefficient for $\text{CuK}\alpha$ radiation	$\mu = 5.61$	cm^{-1}
Total number of electrons per unit cell	$F(000) = 720.$	

TABLE 3.2

A comparison of the measured and the calculated values of $\sin^2\theta$ at the end of the least-squares refinement of the cell parameters

<u>h</u>	<u>k</u>	<u>l</u>	<u>$\sin^2 \theta_{\text{meas}}$</u>	<u>$\sin^2 \theta_{\text{calc}}$</u>
6	8	0	0.2327	0.2335
13	1	0	0.3952	0.3953
13	5	0	0.4515	0.4515
9	11	0	0.4717	0.4715
3	12	0	0.3582	0.3579
6	10	0	0.3176	0.3178
7	9	0	0.3031	0.3035
1	10	0	0.2367	0.2364
6	7	0	0.1981	0.1984
6	6	0	0.1680	0.1680
7	8	0	0.2631	0.2637
7	6	0	0.1981	0.1982
12	2	0	0.3440	0.3442
8	3	0	0.1691	0.1699
12	0	2	0.3830	0.3827
11	0	2	0.3292	0.3286
5	0	4	0.2262	0.2263
4	0	4	0.2037	0.2042
6	0	$\overline{4}$	0.2380	0.2385
5	0	$\overline{2}$	0.0943	0.0956
8	0	2	0.1944	0.1942
7	0	2	0.1587	0.1587
6	0	2	0.1286	0.1279

lists the measured ($\sin^2 \theta_{\text{meas}}$) and the final calculated ($\sin^2 \theta_{\text{calc}}$) values of $\sin^2 \theta$, for all the 23 reflections, at the end of the refinement.

Intensity data collection

An approximately cylindrical crystal of mean radius = 0.35 mm mounted along the needle axis (c-axis) was used for the three-dimensional intensity data collection. Multifilm equi-inclination Weissenberg photographs were recorded using nickel-filtered copper radiation ($\lambda = 1.5418 \text{ \AA}$) from the reciprocal levels hkl , $l = 0$ to 5. A crystal of radius = 0.33 mm was mounted along the b-axis (perpendicular to the needle axis) and the $h0l$ projection intensity data were recorded by the same technique. Out of a possible total of 4465 reflections in the $\text{CuK}\alpha$ sphere 1654 independent, observable reflections could be recorded. The maximum θ recorded was 79° .

The intensities were visually estimated by comparison with a standard calibrated strip. The intensity of each reflection was estimated twice and averaged. The intensities were corrected for Lorentz-polarisation factors [43], absorption effects for cylindrical specimen [44] and spot shape effects [45].

The intensity data of each reciprocal level were

scaled independently by **computing** the individual layer Wilson's plot [46]. The **temperature** factor B for the **structure** was **determined as** the mean of the values obtained from the Wilson's plots of the different layers. The average value of B thus **calculated** was equal to $4.8 \pm 0.5 \text{ \AA}^2$. The **intensity** data were put on an **absolute** scale **using normalised structure factors**. Normalised structure factors, E 's, defined in section 2.3, were **computed** for each of the reciprocal levels, **using the** atomic **scattering** factors **given by Cromer and Waber** [47] and the B -value of $4.8 \text{ \AA}^2$. The absolute scale factors were then **determined** by normalizing the value of $\langle E^2 \rangle$ to unity for each layer.

3.3 Structure Determination

CBOOA being an all light atoms **structure**, the solution was initiated by using the direct methods.

While analysing the **crystal structure** of MBPAA (Chapter 2), **it** was found that for **calculating** the E 's, it was appropriate if the individual atomic scattering factors for the atoms **of** the planar **aromatic** rings were replaced by the spherical average for the entire ring placed at the **centre** of the **ring** (section 2.3). Hence, for CBOOA, which contains **planar aromatic rings** similar to the MBPAA molecule, **normalised structure factors**

were **calculated** using the spherically averaged molecular **scattering factors** for the two phenyl **rings**. Also, to avoid the effect of **rational** dependence, the **reflections** were divided into five $\sin \theta$ **ranges** and the $\langle E^2 \rangle$ value in each range was **renormalized** to unity. Each of the eight **parity groups** of reflections was also **renormalized** in a similar **fashion**. Table 3.3 lists the **three-dimensional E-statistics**.

The highest 300 E's (≥ 1.67) were next used with the **MULTAN** programme of Germain et al [48], described in section 2.3. Two symbols were used in the programme. The choice of the reflections **specifying** the origin and the symbols **axis** given in Table 3.4, which also lists the **details** of the four solutions obtained from the **MULTAN** programme. The best solution was found to have a combined **index** (C.I.) of 2.0. The E-map corresponding to this solution was next computed. The **cyanobenzylidene** aniline group of the molecule could be **clearly** identified from the distribution of **peaks** in this E-map (Fig. 3.2). The **molecular** model fitted on the E-map is also marked in Fig. 3.2. The initial H-factor for this model was 0.555 and in three **cycles** of **block-diagonal structure factor least-squares** refinement, it reduced to 0.386. At this stage of the least-squares **refinement**, five **carbon** atoms in the octyloxy chain, *viz.*, C(18) to C(22), were found

TABLE 3.3

Averages and distributions of normalized
structure factors

	Experi- mental value	Theoretical values	
		centrosymmetric	non- centrosymmetric
$\langle E \rangle$	0.766	0.798	0.886
$\langle E^2 - 1 \rangle$	1.067	0.968	0.736
$ E > 1.0$	26%	32%	37%
$ E > 2.0$	5.8%	5%	1.8%
$ E > 3.0$	1.2%	0.3%	0.01%

TABLE 3.4

MULTAN results

2	3	4	}	Origin
13	4	1		
7	8	4		
13	1	0	}	Symbols
13	5	1		

Set No.	ABSFOM A_F	RESID R	Combined Index C. I.
1	0.5920	47.91	0.0596
2	0.5656	47.83	0.0054
3	1.0083	33.0	2.0000
4	0.9322	35.16	1.6832

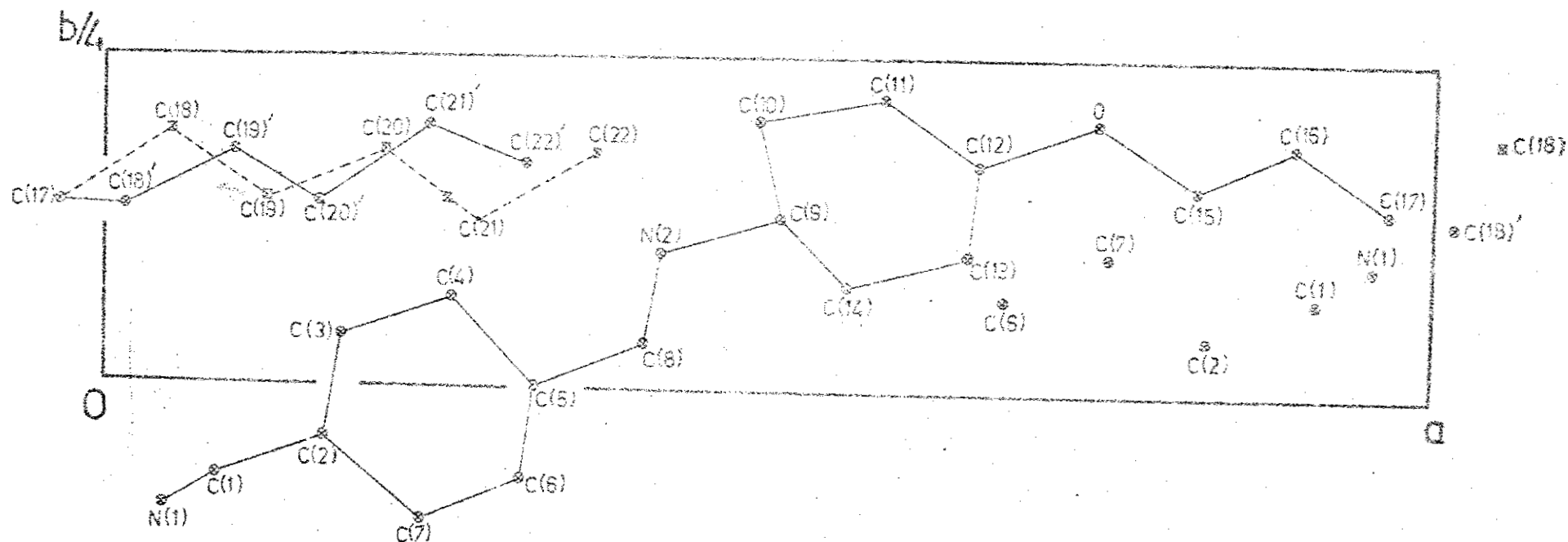
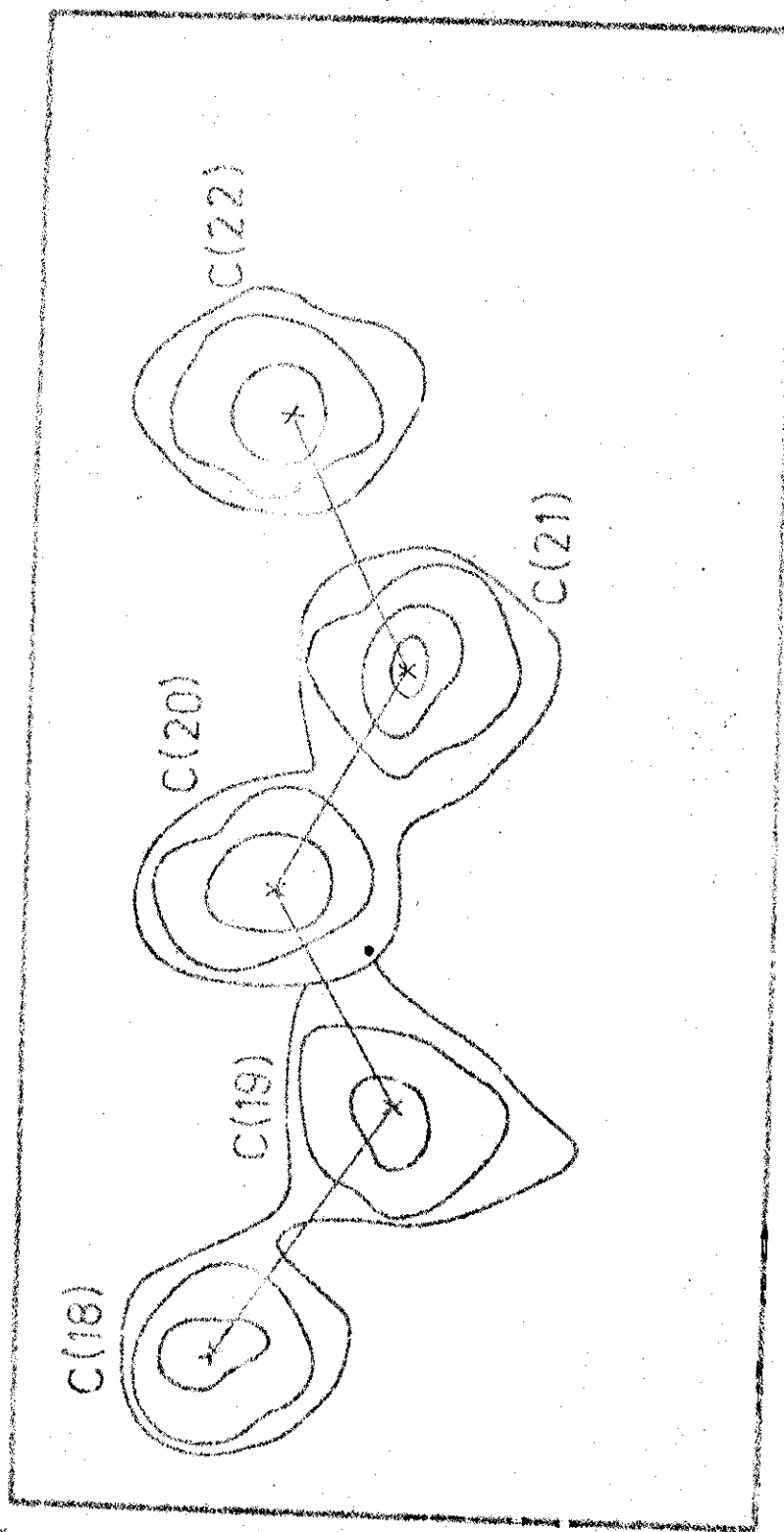


Figure 3.2: Molecular model fitted on the peak distribution in the E-map. The positions C(18)' ... C(22)' correspond to the initial incorrect model and C(18) ... C(22) to the correct model.

b/14



a/2

Figure 3.2

The composite difference electron density distribution from which the correct positions for the five atoms C(18) to C(22) were obtained.

to have very high thermal parameters, compared to the rest of the structure ($B = 10.9$ to $22.1 \text{ \AA}^2$). Also, the molecular dimensions in this region of the molecule were abnormal, suggesting that the positions of these atoms in the octyloxy chain could be wrong. Hence, a difference electron density map was computed after removing the contributions from these five carbon atoms. Fig. 3.3 gives the composite electron density of this map, from which the five carbon atoms could be easily identified. A comparison of the difference map and the E-map showed that there was a one-to-one correspondence between the maps for four of the carbon atoms. However, for the fifth carbon atom, viz., C(21), the peak in the E-map was slightly shifted from the position obtained from the difference map. The heights of the E-map peaks for these five carbon atoms were, however, considerably lower than those for the rest of the atoms and that was, in fact, the reason for not using them at the first instance. In Fig. 3.2, the positions C(18)' ... C(22)' correspond to the initial incorrect model and C(18) ... C(22) to the correct model. The initial R-factor for the correct model was 0.297. The structure was further refined to $R = 0.145$ by iterative block-diagonal structure factor least-squares procedure. Cruickshank's weighting scheme [49] of the form $w = (a + bF_0 + cF_0^2)^{-1}$ where $a = -0.383$, $b = 0.396$ and $c = 0.0015$ was used and the

atoms were oorrected individually for isotropic thermal motions. Anisotropic thermal parameters [50] of the form $[\exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$ were next introduced for all the non-hydrogen atoms. Three cycles of further least-squares refinement reduced the R-value to 0.117. In the course of the least-squares refinement, the reflection 031 was found to have a much higher value for F_{obs} than for F_{calc} and hence was corrected for secondary extinction effect, using the Zachariasen's formula [51], described in section 2.3.

A difference electron density map was computed at this stage and all the hydrogen atoms in the structure could be unambiguously located from this map. The peak heights in the difference map corresponding to the hydrogen atoms are listed in Table 3.5 while Fig. 3.4 gives the composite electron density of this map. In further least-squares refinement, the parameters of the hydrogen atoms were also refined. The hydrogen atoms were assigned isotropic temperature factors, equal to the equivalent B values of the carbon atoms to which they were attached. The equivalent B's oorreponding to the anisotropic thermal parameters were calculated using the formula [52]

$$B_{equivalent} = \frac{4}{3} \sum_{i=1}^3 \sum_{j=1}^3 b_{ij}(\vec{a}_i \cdot \vec{a}_j) \quad (3.1)$$

where the b_{ij} 's are the components of the anisotropic

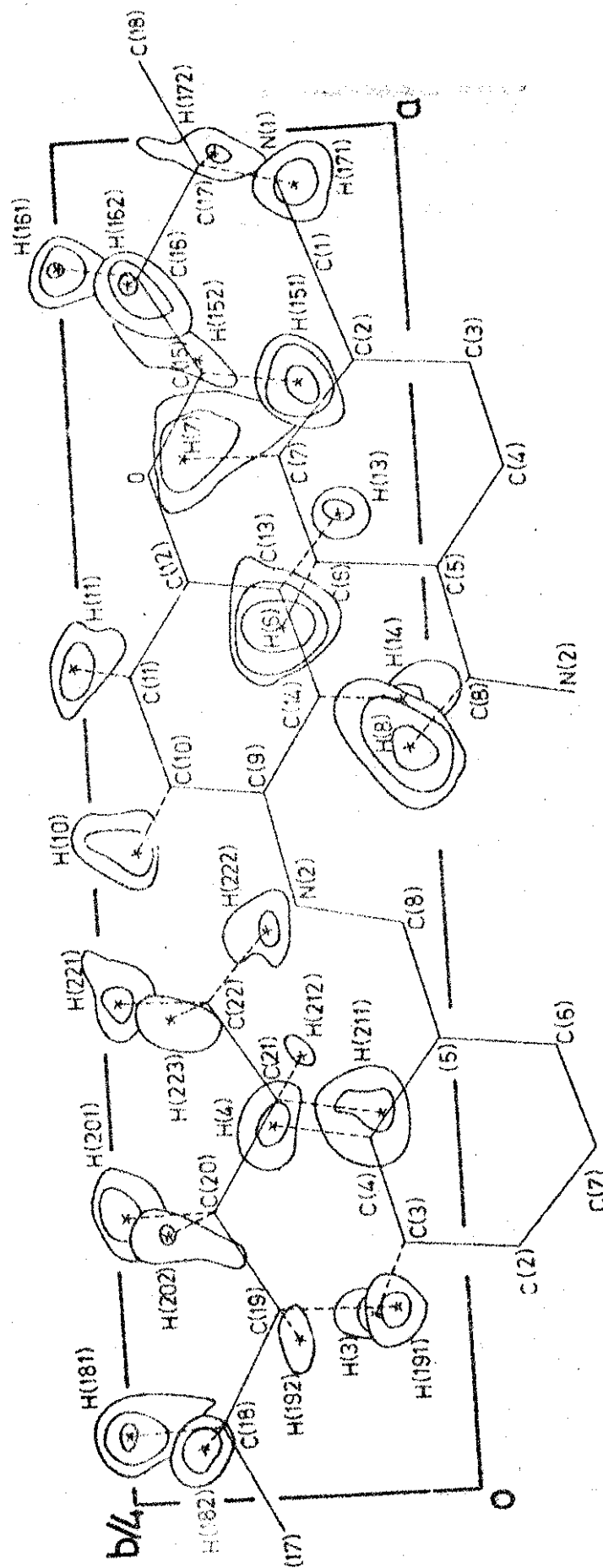


Figure 3.4

The composite difference electron density distribution from which the positions of the hydrogen atoms were obtained.

TABLE 3.5

Peak heights corresponding to hydrogen atoms in the
difference Fourier map

<u>Atom</u>	<u>Peak height in $e/\text{\AA}^3$</u>
	0.27
H(4)	0.30
H(6)	0.44
H(7)	0.35
H(8)	0.44
H(10)	0.33
H(11)	0.35
H(13)	0.27
H(14)	0.27
H(151)	0.41
H(152)	0.25
H(161)	0.38
H(162)	0.41
H(171)	0.33
H(172)	0.27
H(181)	0.38
H(182)	0.35
H(191)	0.30
H(192)	0.25
H(201)	0.33
H(202)	0.27
H(211)	0.30
H(212)	0.19
H(221)	0.30
H(222)	0.27
H(223)	0.25

thermal parameters and a_1 , a_2 , a_3 are the direct cell lengths. The least-squares refinement converged after two more cycles and the R-value at this stage was 0.089.

The observed and the calculated values of the structure factors of all the measured reflections are listed in Table 3.6.

3.4 Description of the structure

The final positional and thermal parameters, at the end of the refinement, of all the non-hydrogen atoms are listed in Table 3.7. [Table 3.8 lists the corresponding values for the hydrogen atoms. The numbering scheme for the non-hydrogen atoms is shown in Fig. 3.5, where the bond lengths and bond angles involving these atoms are also marked. The labelling of each hydrogen atom is the same as that of the heavy atom to which it is attached; where more than one hydrogen atom is linked to the same heavy atom, a new sequence is started and is included as the last digit of the labelling number. The bond lengths and bond angles involving the hydrogen atoms are given in Table 3.9. Within the 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

TABLE 3.6

The observed and calculated values of structure factors (x10)
for all the measured reflections of CBOQA.

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[illegible]

143	147	-5	-67	-84	2	41	37	4	-48	-54	3	-171	-165
206	196	-4	-137	-129	4	66	51	5	-151	-145	5	-315	-268
-75	-54	-2	-166	-168	5	54	46	6	-203	-179	6	82	75
-96	100	-1	-47	53				7	-41	-35	7	94	93
91	91	0	-60	-41	H	18	2	8	-25	-25	8	-176	-168
44	43	2	115	115				9	94	96	10	-75	-70
-709	-258	3	-66	60	-9	30	34	10	-189	-186	11	-146	-167
153	-170	4	-83	-45	3	43	44	12	244	227	12	-72	-77
304	317	5	-159	-142	4	-87	-104	13	93	95	13	196	204
-243	-266	7	114	111				14	-73	-71	14	25	18
45	-255	9	87	98	H	19	2	15	57	51			
-31	-15	10	-104	-102				16	41	30	H	5	3
-62	-50				-5	33	28	18	-37	-31			
-45	-46	H	13	2	-3	-34	-16				-15	-38	-40
					4	44	74	H	3	3	-13	57	56
H	10	2	-12	63							-12	-56	-57
			-11	54	H	1	3				-11	-55	-60
15	70		-10	55				-16	-52	-59		-58	-53
43	-39		-8	115		-92	-73	-15	-55	-47		-80	-65
-90	-100		-6	128		-114	-118	-14	-89	-97		-84	-92
115	112		-1	-80		235	227	-13	28	13		94	87
38	49		0	-87		-40	-44	-10	65	54		125	126
-151	-147		2	120		38	37	-9	-86	-81		-47	-30
-79	-98		3	-122		-26	-18	-8	-37	-32		61	78
231	308		4	40		-42	-60	-7	268	233		227	210
-219	-206		7	-69		-38	-28	-6	-51	-48		686	677
-199	-181		10	119		70	69	-5	-106	-88		-666	-659
78	67	H		57		130	141	-4	-190	-176		354	350
44	37					-225	-243	-2	85	77		-174	-178
63	44					-51	-75	-1	-579	-531		-72	-76
-248	-223					-225	-234	0	56	58		73	74
-102	-117					-764	-633	1	98	95		-89	-87
337	331					96	95	2	-114	-107		-160	-138
-84	-78					34	20	3	-63	-37		97	86
-90	-90					97	87	4	60	49		-225	-217
55	25					-442	-407	5	469	441		53	48
						84	76	6	195	182		64	49
H	11	2				-31	-28	7	-336	-309		-215	-217
						129	118	8	118	101		-36	-26
						125	135	9	-72	-79		34	21
						-134	-128	10	134	136		75	73
						36	21	11	169	174			
						29	23	12	98	78			
						18	-68	13	108	114	H	6	
								18	-36	-36			
											-14	-96	-100
											-12	-70	-81
											-10	54	56
											-9	25	36
											-8	-68	-60
											-5	79	65
											-4	111	99
											-3	73	87
											-2	-398	-383
											-1	-383	-372
											0	324	288
											1	-82	-74
											2	133	126
											3	94	99
											4	-122	-107
											5	-300	-268
											6	-198	-194
											7	80	76
											8	158	152

9	-249	-235		9	3	5	54	65	2	127	114	8	76	94
11	-103	-97	H			6	-102	-93	3	-70	-63	9	51	45
12	-267	280				7	231	224	4	-124	-119	10	126	140
13	-46	-51				11	56	47	5	-51	-41	11	113	94
17	44	37				12	71	59	6	-41	-38	12	199	198
									8	-38	-31	13	74	75
												14	48	39
												16		
H	7	3				H	12	3	H	16	3	H	1	4
-15	88	87				-13	-22	-19	-11	13	4	-15	126	109
-14	55	59				-12	-49	-48	-9	55	66	-14	36	34
-10	-68	-60				-8	-28	-25	-7	32	10	-11	34	32
-9	-37	-42				-7	-50	-61	0	80	85	-10	26	25
-7	-48	216				-6	-183	-173	1	-50	-51	-9	-66	-75
-7	127	122				-5	-166	-169	2	-66	-72	-8	-118	-114
-5	21	21				-4	-84	-85	3	72	70	-7	-85	-96
-5	299	269				-2	-53	-57	5	46	40	-6	-147	-175
-3	-54	-48				-1	-27	-38				-5	-44	-43
-3	122	118				3	-99	-99	H	17	3	-3	-42	-42
-2	-238	-226				5	-210	-199				4	-250	-273
-1	-64	-46				6	-121	-115				5	187	179
0	118	113				7	103	98				6	-52	-51
1	-155	-145				12	53	42				7	-94	-94
2	-78	-80										8	26	34
3	74	74										9	-114	-112
4	177	-175										10	-142	-151
5	-181	-184										11	-125	-120
6	-84	-60										12	68	58
7	-53	-60										13	30	26
8	125	118										14	52	45
9	-162	-164										17	60	71
11	-92	-102										18		
12	-231	-209												
13	91	87												
14	-47	-37												
H	8	3				H	10	3	H	18	3	H	2	4
-16	-37	-45				-12	-63	-61	-7	27	39	-16	-66	-56
-15	34	38				-11	34	48	-6	34	38	-15	-71	-68
-14	-37	-36				-8	55	55	-3	19	7	-14	85	-78
-12	-28	-34				-7	-134	-137	-2	-41	-44	-10	-40	-21
-10	56	44				-5	47	41	-3	-41	-44	-9	-25	-25
-8	-63	-57				-4	-81	-92	2	76	75	-8	167	177
-7	77	74				-3	-79	-92	3	-41	-50	-7	-29	-29
-7	91	83				-2	-85	-90	4	-41	-50	-6	89	84
-6	-23	-10				1	-83	-83				-5	-335	-307
-6	61	70				2	-121	-112				-4	302	240
-4	45	50				3	-127	-136				-3	45	45
-3	217	205				4	-93	-69				-2	47	41
-2	127	130				6	44	45				-2	-144	-135
-1	36	18				8						-2	-350	-341
0	76	77				10						-2	179	161
1	140	142				12						-2	19	23
2	114	109				13						-2	46	49
3	-63	-136				16						-2	60	71
4	30	28										-2	33	28
5	174	170										-2	-35	-38
6	37	33												
7	-92	-93												
10	78	79												
12	-104	-104												
13	53	34												
14	-29	-28												
15	-70	-61												
16														

[illegible]

[illegible]

Table 3.7: 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 3.8

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

Atom	x(x10 ²)	y(x10 ²)	z(x10 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

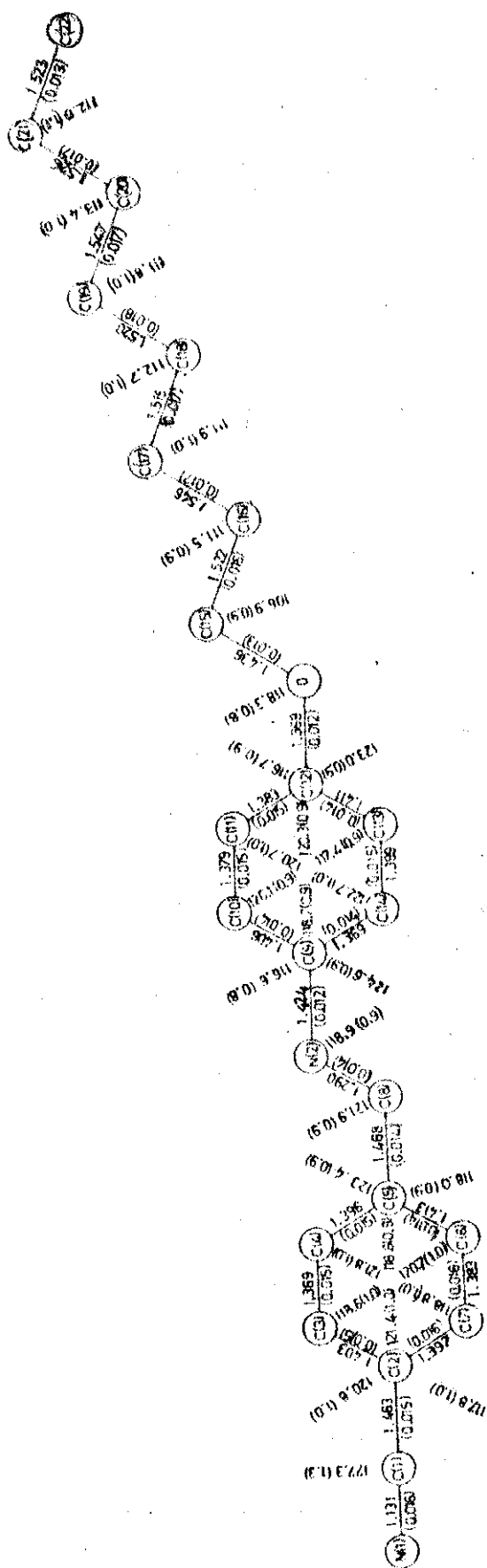


Figure 3.5: Interatomic bond lengths and angles involving non-hydrogen atoms.

TABLE 3.9

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(15)	1.0(0.1)	
C(15)	H(15)	1.0(0.1)	
C(16)	H(16)	1.0(0.1)	
C(16)	H(16)	1.0(0.2)	
C(17)	H(17)	1.0(0.1)	
C(17)	H(17)	1.0(0.1)	
C(18)	H(18)	1.0(0.1)	
C(18)	H(18)	1.0(0.2)	
C(19)	H(19)	1.1(0.2)	
C(19)	H(19)	1.1(0.2)	
C(20)	H(20)	1.0(0.2)	
C(20)	H(20)	1.0(0.2)	
C(21)	H(21)	1.0(0.2)	
C(21)	H(21)	1.0(0.2)	
C(22)	H(22)	1.1(0.2)	
C(22)	H(22)	1.1(0.2)	
C(22)	H(22)	1.0(0.2)	
C(2)			122(9)
C(4)			120(9)
C(5)			120(10)
C(5)			120(7)
C(7)			119(7)
C(7)			119(6)
C(6)			122(6)
C(2)			120(8)
C(5)			118(8)
C(9)			119(5)
C(11)			121(5)
C(10)			120(8)
C(12)			121(10)
C(14)			121(10)
C(13)			119(9)
C(9)			119(9)
O			110(9)

continue

Table 3.9 continued

O	C(16)	C(15)	H(152)	110(5)
C(16)	C(16)	C(15)	H(151)	109(9)
H(151)	C(15)	C(15)	H(152)	110(5)
C(15)	C(16)	C(15)	H(161)	111(10)
C(15)	C(16)	C(16)	H(162)	109(5)
C(17)	C(16)	C(16)	H(161)	110(9)
C(17)	C(16)	C(16)	H(162)	110(5)
H(161)	C(16)	C(16)	H(162)	110(9)
C(16)	C(17)	C(17)	H(171)	108(10)
C(16)	C(17)	C(17)	H(172)	110(8)
C(18)	C(17)	C(17)	H(171)	109(7)
C(18)	C(17)	C(17)	H(172)	110(8)
H(171)	C(17)	C(17)	H(172)	109(7)
C(17)	C(18)	C(18)	H(181)	107(11)
C(17)	C(18)	C(18)	H(182)	110(9)
C(19)	C(18)	C(18)	H(181)	109(9)
C(19)	C(18)	C(18)	H(182)	110(9)
H(181)	C(18)	C(18)	H(182)	109(9)
C(18)	C(19)	C(19)	H(191)	106(13)
C(18)	C(19)	C(19)	H(192)	110(9)
C(20)	C(19)	C(19)	H(191)	110(10)
C(20)	C(19)	C(19)	H(192)	109(9)
H(191)	C(19)	C(19)	H(192)	110(10)
C(19)	C(20)	C(20)	H(201)	106(13)
C(19)	C(20)	C(20)	H(202)	109(12)
C(21)	C(20)	C(20)	H(201)	110(9)
C(21)	C(20)	C(20)	H(202)	107(12)
H(201)	C(20)	C(20)	H(202)	110(9)
C(20)	C(21)	C(21)	H(211)	106(15)
C(20)	C(21)	C(21)	H(212)	107(8)
C(22)	C(21)	C(21)	H(211)	111(9)
C(22)	C(21)	C(21)	H(212)	110(8)
H(211)	C(21)	C(21)	H(212)	111(9)
C(21)	C(22)	C(22)	H(221)	107(12)
C(21)	C(22)	C(22)	H(222)	116(10)
C(21)	C(22)	C(22)	H(223)	112(11)
H(221)	C(22)	C(22)	H(222)	109(12)
H(221)	C(22)	C(22)	H(223)	127(15)
H(222)	C(22)	C(22)	H(223)	82(12)
				103(12)

is 1.52 (0.02) Å and the $C_{sp^3} - C_{sp^3} - C_{sp^3}$ angles average to 112(1)°. The molecular dimensions involving the hydrogen atoms have comparatively larger standard deviations.

The least-squares mean planes through the various groups of atoms have been calculated with respect to an orthogonal coordinate system [53]. In Table 3.10, the equations of 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 mean planes through the two phenyl rings is 17°43'. The phenyl rings through the atoms C(2) to C(7) and C(9) to C(14) are oriented at 10°14' and 26°53' respectively with respect to the plane formed by the central atoms C(5), C(8), N(2) and C(9). The cyano group is displaced slightly above the plane of the phenyl ring to which it is attached, 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 other phenyl ring through atoms C(9) to C(14). Fig. 3.6 gives a three-dimensional perspective view of the CBOOA molecule.

Fig. 3.7 shows the molecular packing in the ab-plane. The CBOOA molecule lies nearly extended in this plane. The cyano benzyldene group of the molecule is inclined to the a-axis by about 25° and the octyloxy

TABLE 3.10

Equations of various least-squares 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).

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

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

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

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

$$0.28830x + 0.22133y - 0.931618 = 0.11680.$$

<u>Plane</u>	<u>Atom</u>	<u>Δ</u>
(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)	C(9)	-0.007
	C(10)	0.004
	C(11)	-0.002
	C(12)	0.002
	C(13)	-0.004
	C(14)	0.007
	O	-0.001
(c)	C(5)	0.011
	C(8)	-0.012
	N(2)	0.011
	C(9)	-0.011

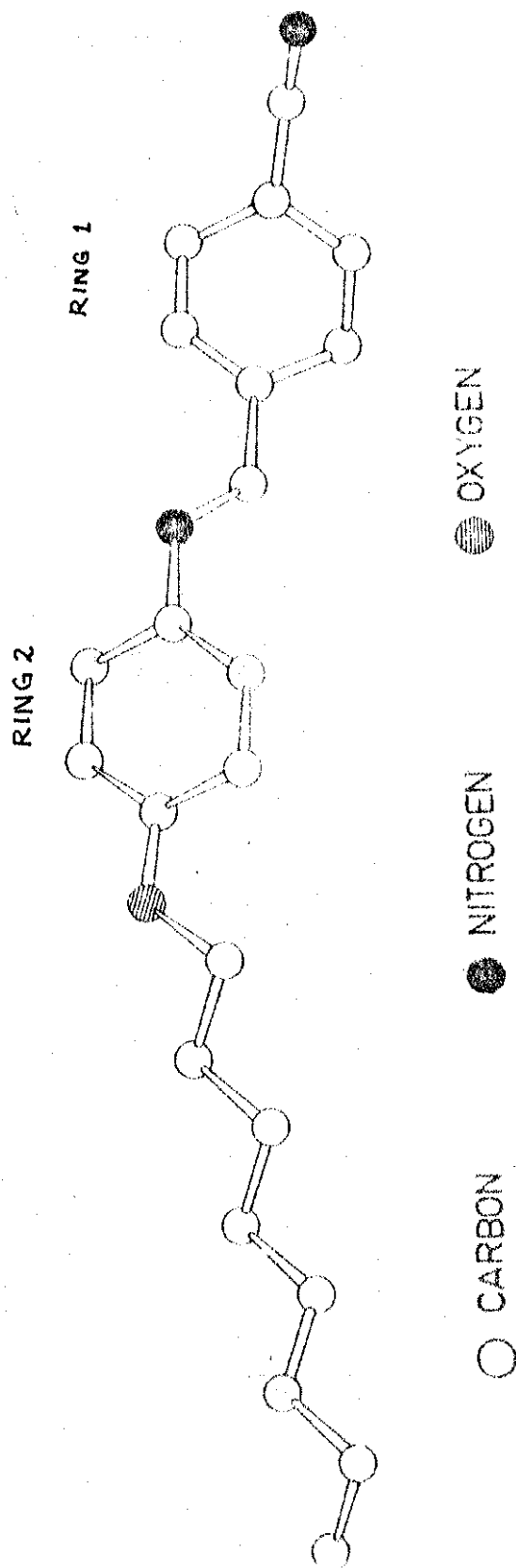


Figure 3.6: Perspective view of the CBOOA molecule as seen normal to the mean plane of ring 1.

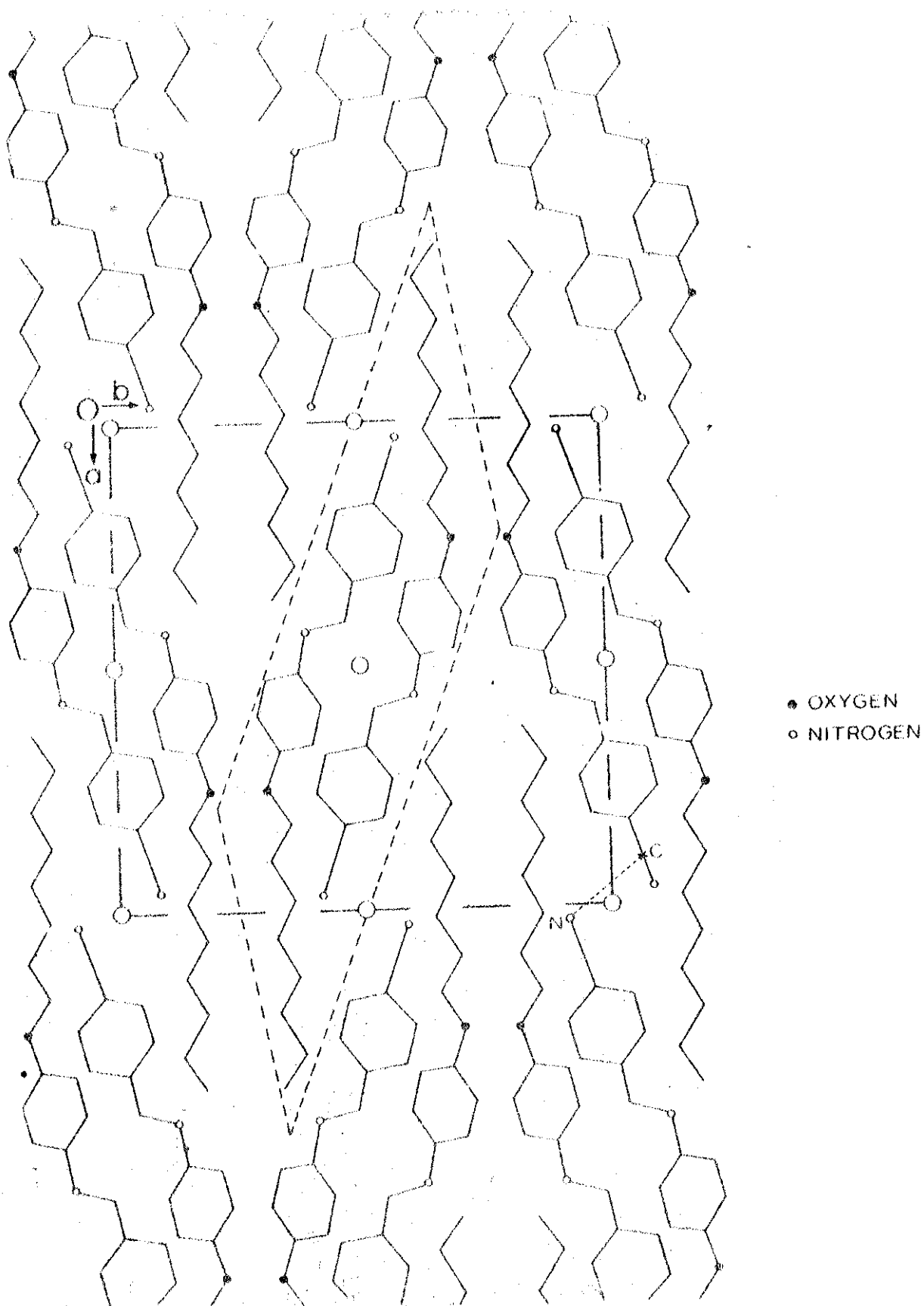


Figure 3.7: Molecular arrangement in the ab-plane. The molecular unit used for describing the packing is indicated.

chain runs almost parallel to the a-axis. In Fig. 3.8, the arrangement of the **molecules** in the bc-plane is shown. The **cyano** groups of the **neighbouring** molecules approach one another with a short contact distance of 3.31 Å between the carbon atom of **one** molecule and the nitrogen atom of the other (indicated in Fig. 3.7). The CBOOA molecules associate in pairs about centres of inversion and hence, the 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 herringbone-like pattern. In Fig. 3.8, pairs of **antiparallel** molecules have been enclosed to indicate the herringbone-like packing. (This molecular unit is shown in Fig. 3.7 **also**.) Similar herringbone-type of molecular packing has also been found in the crystal structures of the **nematogenic** compounds 2,2'-dibromo-4,4'-bis-(n-methoxy beneylidene amino) biphenyl [54], MBPAA (chapter 2) and the high temperature **polymorph** of the **smectogen** ethyl p-azoxybanzoate [55].

The three-dimensional crystal structure is **stabilised** by non-bonded van der **Waals interactions**. All **intermolecular**

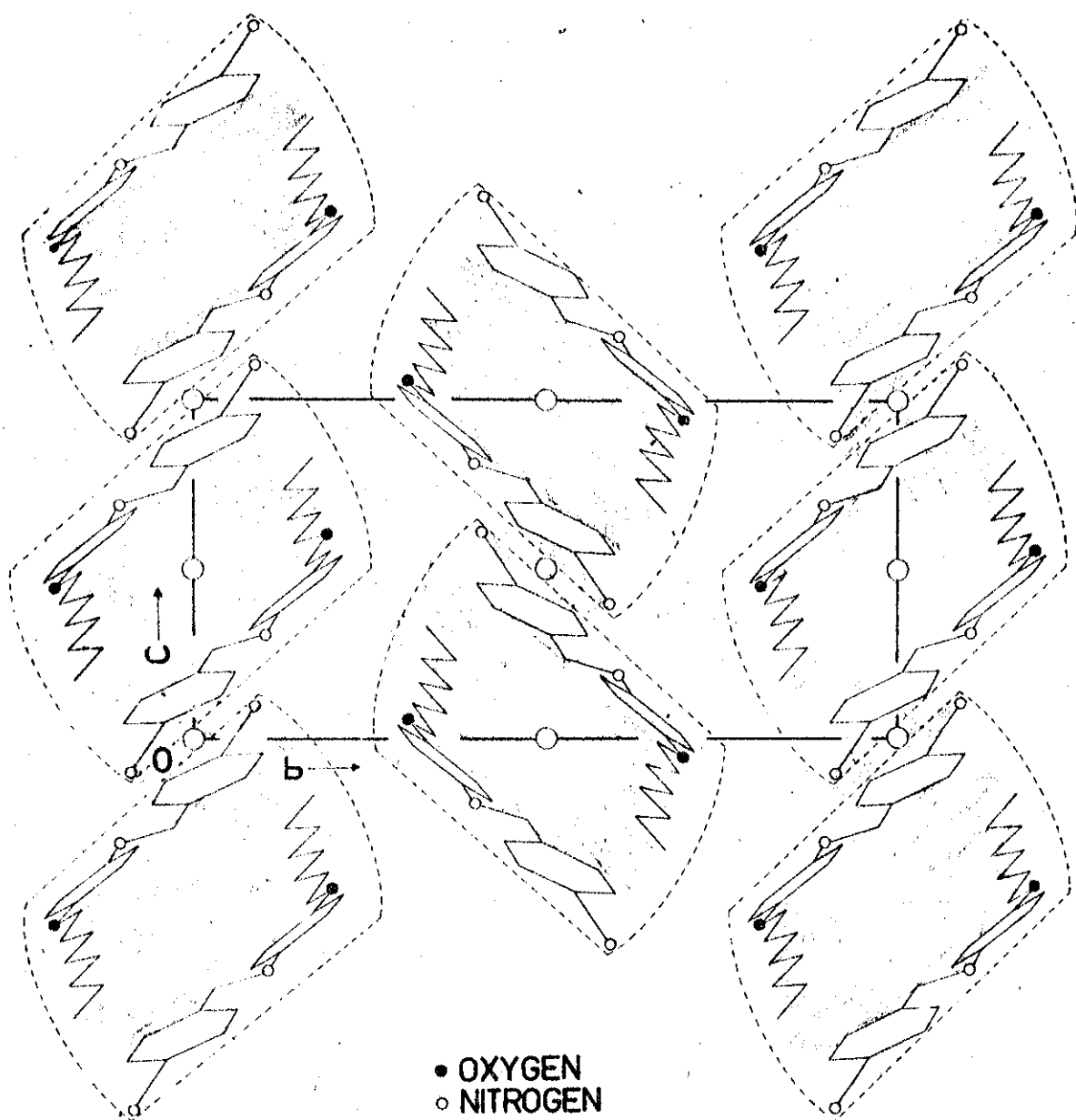


Figure 3.8

Molecular arrangement in ^{the} *bo*-plane. Molecular units formed by pairs of antiparallel molecules have been enclosed to indicate the herringbone type of packing. Regions of strong intermolecular interactions have been shaded.

contact distances less than $4 \text{ \AA}$ have been listed in Table 3.11. Of these, only two distances are less than the sum of the van der Waals 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 and fewer in number, indicating weaker interaction between neighbouring molecules. For example, the phenyl rings through the atoms C(9) to C(14) and C(2) to C(7) have a large number of non-bonded contact distances less than $4 \text{ \AA}$ on one side of the rings with the atoms of the phenyl rings through atoms C(2) to C(7) and C(9) to C(14) respectively of a neighbouring molecule; this is contrasted with the other side of the two phenyl rings, where there are very few interactions with the atoms of the octyloxy chains of the neighbouring molecules. These pockets of weak interaction are contained in planes parallel to the ac-plane. In Fig. 3.8, the regions of strong interactions have been shaded. 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 the 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-

TABLE 3.11

Intermolecular contact distances less than 4 Å

[illegible]

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

like stacking of molecules in the **solid** phase **has** been commonly found in the **crystal structures** of other smectogenic **compounds** reported so far [56,55,57,58,59,60], and can be correlated to the smectogenic nature of the compounds.

Molecular arrangement in the **smectic** A phase

The length of the fully extended molecule of CBOOA is $\sim 27 \text{ \AA}$. As mentioned in section 3.1 of this chapter, McMillan [37] has determined the inter-layer spacing in the smectic phase of CBOOA as $\sim 35 \text{ \AA}$. Gray and Lydon [39] have pointed out that some form of bilayered structure is mandatory to explain the **discrepancy** between the interlayer spacing and the molecular length in **smectics**. The molecular **arrangement** in the crystalline phase of CBOOA adds further support to the existence of bilayered **structure** in the **smectic** phase. As seen in Figures 3.7 and 3.8, the molecules related by the **centre** of inversion associate in pairs and **form** a molecular unit which repeats in a herringbone-like fashion. In **each** molecular unit, the molecules are arranged in a staggered **fashion**, so that the length of the unit as a whole is greater than that of the individual molecule. The effective length of the **molecular** unit is $\sim 35 \text{ \AA}$, in good agreement with the interlayer spacing of the **smectic** A phase of CBOOA.

given by **McMillan [37]**. Therefore, it appears that the molecular arrangement in the crystalline phase can be directly correlated with the structure of the **smectic A** phase. When the solid-smectic A transformation takes place, the molecules continue to associate in anti-parallel pairs, as in the solid phase, resulting in a bilayered **smectic** structure with a layer separation $\sim 35 \text{ \AA}$. As the **smectic A** phase corresponds to an upright molecular arrangement within the layer, the molecular pairs could be assumed to rotate so that their long axes become normal to the plane of the layer. **Fig. 3.1(b)** gives a schematic representation of the bilayered arrangement. The pockets of weak interaction separating the layers in the solid phase could be expected to persist in the smectic A phase also.

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