

4'-Nitrophenyl 4-Octyloxybenzoate (NPOB)

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Abstract. $C_{21}H_{25}NO_5$, monoclinic, $P2_1/c$, $a = 14.503$ (2), $b = 9.211$ (2), $c = 16.355$ (2) Å, $\beta = 114.67$ (1)°, $D_o = 1.21$ (1), $Z = 4$, $D_c = 1.241$ Mg m⁻³; $R = 0.085$ for 1771 reflexions with $I > 2\sigma(I)$. The molecule is completely stretched and forms an imbricated structure, typical of many mesogenic substances.

Introduction. NPOB is a mesogenic substance which forms a smectic *A* phase at 322.2 K, becomes nematic at 334.5 K and forms an isotropic liquid at 340.0 K. By calorimetric (Demus *et al.*, 1978), spectroscopic (Cavatorta, Fontana & Kirov, 1978; Schulz & Grande, 1978; Lösche & Grande, 1976; Kubitz, 1978) and dielectric measurements (Bata & Buka, 1977) the behaviour of NPOB has been characterized mainly in its liquid-crystalline phases.

The cell parameters were obtained by least squares from the 2θ values of 70 high-order reflexions measured on a diffractometer. The space group $P2_1/c$ was determined from systematic absences ($h0l$: $l = 2n + 1$, $0k0$: $k = 2n + 1$). The intensities were collected with an Enraf-Nonius CAD-4 diffractometer. Experimental conditions were: graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), ω - 2θ scan, $\theta_{\min} = 3^\circ$, $\theta_{\max} = 24^\circ$, 2θ scan width: $(0.6 + 0.2 \tan \theta)^\circ$, aperture: $(2.4 + 0.9 \tan \theta)$ mm, maximum scan time 20 s or a net count of 5000, background: one quarter of the scan time at each of the scan limits. 3117 independent reflexions were recorded; 1771 of these with $I > 2\sigma(I)$ were used in the analysis. Corrections were applied for Lorentz and polarization effects but not for absorption. The structure was solved with *MULTAN 77* (Main, Woolfson, Lessinger, Germain & Declercq, 1977) and refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms and with anomalous-dispersion corrections for N, O and C. The best *E* map (CFOM = 3.000) obtained with unit

weights (ABSFOM = 1.005, $\psi_0 = 0.760$ and RESID = 25.81 for 250 *E*'s) revealed the positions of all non-hydrogen atoms. The function minimized was $\sum w(|F_o| - k|F_c|)^2$ where the weighting function was determined empirically: $w = w_F w_S$ where $w_F (|F_o| < A) = (|F_o|/A)^C$, $w_F (|F_o| > B) = (B/|F_o|)^D$, $w_F (A < |F_o| < B) = 1.0$ and $w_S (\sin \theta < E) = (\sin \theta/E)^H$, $w_S (\sin \theta > G) = (G/\sin \theta)^J$, $w_S (E < \sin \theta < G) = 1.0$. The weighting-function parameters are: $A = 5.00$, $B = 15.00$, $C = 1.00$, $D = 1.50$, $E = 0.28$, $G = 0.35$, $H =$

Table 1. Final positional parameters ($\times 10^4$) with *e.s.d.*'s in parentheses

	x	y	z
O(1)	-1430 (6)	7980 (8)	6979 (5)
O(2)	-345 (5)	6441 (9)	7868 (4)
O(3)	1162 (3)	6728 (4)	4809 (3)
O(4)	1730 (3)	9031 (5)	5032 (3)
O(5)	3511 (3)	6493 (4)	2367 (3)
N(1)	-688 (6)	7170 (8)	7193 (5)
C(1)	-201 (5)	7056 (7)	6556 (4)
C(2)	525 (5)	6034 (8)	6698 (4)
C(3)	978 (5)	5940 (7)	6110 (5)
C(4)	692 (4)	6887 (7)	5405 (4)
C(5)	-47 (5)	7915 (8)	5253 (4)
C(6)	-505 (5)	7995 (8)	5830 (5)
C(7)	2125 (4)	7518 (6)	4048 (4)
C(8)	2669 (5)	8593 (6)	3834 (4)
C(9)	3131 (5)	8301 (6)	3272 (4)
C(10)	3063 (4)	6905 (6)	2907 (4)
C(11)	2514 (5)	5831 (7)	3097 (5)
C(12)	2054 (5)	6137 (6)	3673 (4)
C(13)	1668 (4)	7879 (6)	4674 (4)
C(14)	3963 (5)	7593 (7)	2019 (4)
C(15)	4440 (5)	6817 (7)	1477 (4)
C(16)	4854 (5)	7878 (6)	1007 (4)
C(17)	5467 (5)	7130 (6)	570 (4)
C(18)	5801 (5)	8116 (6)	-1 (4)
C(19)	6369 (5)	7342 (7)	-460 (4)
C(20)	6720 (6)	8282 (8)	-1029 (5)
C(21)	7171 (6)	7464 (9)	-1577 (5)

Table 2. Interatomic distances (Å) with e.s.d.'s in parentheses

N(1)—O(1)	1.23 (1)	C(7)—C(12)	1.40 (1)
N(1)—O(2)	1.21 (1)	C(8)—C(9)	1.37 (1)
N(1)—C(1)	1.49 (1)	C(9)—C(10)	1.40 (1)
C(1)—C(2)	1.36 (1)	C(10)—O(5)	1.35 (1)
C(1)—C(6)	1.38 (1)	C(10)—C(11)	1.38 (1)
C(2)—C(3)	1.38 (1)	C(11)—C(12)	1.39 (1)
C(3)—C(4)	1.37 (1)	O(5)—C(14)	1.45 (1)
C(4)—O(3)	1.41 (1)	C(14)—C(15)	1.51 (1)
C(4)—C(5)	1.37 (1)	C(15)—C(16)	1.51 (1)
C(5)—C(6)	1.36 (1)	C(16)—C(17)	1.52 (1)
C(13)—O(3)	1.36 (1)	C(17)—C(18)	1.52 (1)
C(13)—O(4)	1.20 (1)	C(18)—C(19)	1.51 (1)
C(13)—C(7)	1.47 (1)	C(19)—C(20)	1.51 (1)
C(7)—C(8)	1.40 (1)	C(20)—C(21)	1.51 (1)

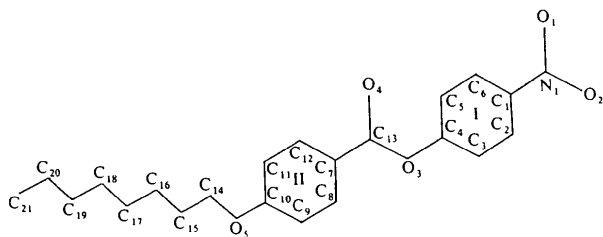


Fig. 1. Numbering of the atoms.

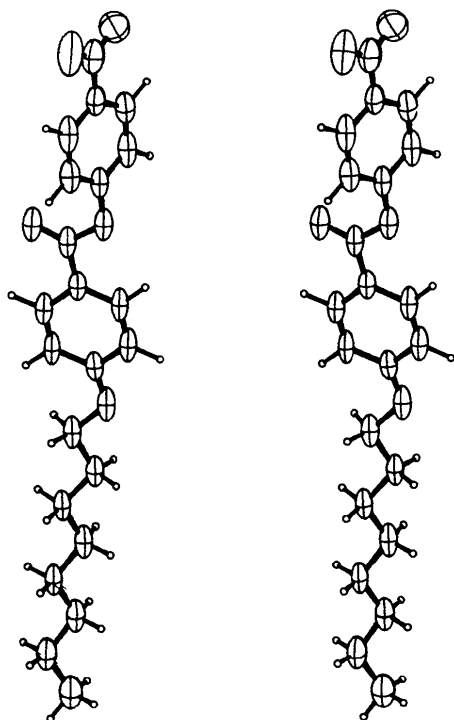
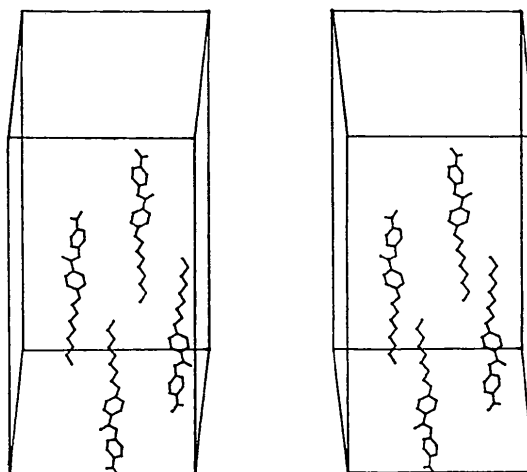


Fig. 2. Stereoscopic drawing of the molecule.

2.00, $J = 1.50$. The positional parameters of the H atoms were calculated and included with $U = 0.08 \text{ \AA}^2$, but were not refined. The final $R = \sum \|F_o\| - |F_c| / \sum |F_o| = 0.085$ and $R_w = 0.108$ for 1771 reflexions and 325 parameters. The final difference map was

Fig. 3. Packing of the molecules in the unit cell. From an origin at the lower left rear corner, x is vertical, y is to the right and z is towards the reader.

featureless. All calculations were performed on the CDC Cyber 172 computer of RRC Ljubljana with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Scattering factors for the non-hydrogen atoms were taken from Cromer & Mann (1968), anomalous-dispersion corrections from Cromer & Liberman (1970) and scattering factors for H from Stewart, Davidson & Simpson (1965). The positional parameters and the interatomic distances are listed in Tables 1 and 2 respectively. The numbering of atoms is shown in Fig. 1.* Stereoscopic drawings (Johnson, 1965) are given in Figs. 2 and 3.

Discussion. The molecules are arranged in a fully stretched configuration. Their largest extension, between H(213) and O(2), is 23.2 \AA .

The average C—C length in the alkoxy chain is 1.51 \AA , the same as in BOBA† (Bryan & Fallon, 1975), whereas in CBOOA (Vani & Vijayan, 1977) and TBBA (Doucet, Mornon, Chevalier & Lifchitz, 1977) it is 1.53 and 1.54 \AA respectively. C(14), O(5) and C(10) form a characteristic group for a number of liquid-crystal molecules. The C(14)—O(5) and O(5)—C(10) distances are 1.45 and 1.35 \AA respectively. Comparable values are found in PAA (Krigbaum, Chatani &

* Lists of structure factors, H atom parameters, bond angles and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34758 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Abbreviations used are: BOBA: *p*-(*n*-butoxy)benzoic acid; CBOOA: *N*-(*p*-cyanobenzylidene)-*p*-octyloxyaniline; TBBA: bis-*p*-butylanilino derivative of terephthalic acid; PAA: *p*-azoxyanisole; AAA: anisaldehyde azine; DMOBAP: 2,2'-dibromo-4,4'-bis(*p*-methoxybenzylideneamino)biphenyl; AOP: azoxyphenetole; EAOb: ethyl *p*-azoxybenzoate; MBNA: *N*-(*p*-methylbenzylidene)-*p*-nitroaniline; MOBA: *p*-methoxybenzoic acid; EOBA: *p*-ethoxybenzoic acid.

Barber, 1970) (1.44 and 1.36 Å), in CBOOA (1.44 and 1.37 Å), in AAA (Galigné & Falgueirettes, 1968) (1.45 and 1.39 Å), in DMOBAP (Lesser, de Vries, Reed & Brown, 1975) (1.44 and 1.37 Å), in BOBA (1.43 and 1.36 Å) and in deuterated AOP (Filipenko, Ponomarev & Atovmyan, 1978) (1.43 and 1.35 Å). The carboxylic group has bond distances of 1.36 [C(13)—O(3)] and 1.20 Å [C(13)—O(4)], where the latter corresponds to a C=O double bond. Comparable bond lengths (1.32 and 1.20 Å) within the carboxylic group can only be found in EAOB (Krigbaum & Barber, 1971). For the nitro group, N—O = 1.22 Å which approximately corresponds to a N=O double bond. The same distance has been found by Bürgi & Dunitz (1970) for the terminal nitro group of MBNA.

The average bond angle in the alkoxy chain is 113.8 (6)° for the sp^3 -hybridized C atoms. This value exceeds the tetrahedral angle by more than 4°. In BOBA, CBOOA and TBBA this angle is 113.3 (3), 112 (1) and 109.3 (6)° respectively. The angle C(14)—O(5)—C(10) is 118.8 (5)°; this is comparable with the corresponding bond in deuterated AOP [118.7 (3)°], in BOBA [118.5 (3)°], in AAA [118.4 (3)°], and in PAA [118.4 (3)°], and can have values down to 116.3 (8)° in CBOOA. The O—C—O bond angle of the carboxylic group in NPOB is 123.2 (7)°. In EAOB 124.8 (5)° was found for the same group. This angle can vary between 123.4 (6)° in MOBA (Bryan, 1967) and 121.9 (3)° in EOBA (Bryan & Jenkins, 1975). The O(1)—N(1)—O(2) angle in NPOB is 125 (1)°, whereas 123.6 (6)° was observed in MBNA.

The phenyl rings (planes I and II) form an angle of 57.1°. The distortion of these rings is in agreement with that in molecules of comparable structures. An exception is EAOB with a distortion of only 0.5°. O(5) and C(14) to C(21) are fairly planar (plane III), the maximum deviations being +0.10 Å for C(21) and -0.15 Å for C(17). Plane (III) forms an angle of 17.0° with plane (II). The result is an intramolecular distance between H(9) and H(142) of 2.18 Å which is shorter than the comparable distance (2.50 Å) between H(9) and H(141). In TBBA these planes form an angle of about 90° (89.3 and 85.4°). Values very different from 90° are also found in mesogenic substances. Thus the angle in molecule A of BOBA between the plane of the alkoxy C atoms and the plane of the phenyl ring is only 2.9°.

Fig. 2 shows the packing of the molecules in the unit cell. All intermolecular distances are greater than the sum of the van der Waals radii.

By proton relaxation-time measurements, in addition to the rotation of the methyl group a second motion of part of the molecule has been found, but no mechanism can yet be advanced. A flipping process of the phenyl ring (I) of 180° could possibly take place in the crystal without steric hindrance.

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