1-(−)-Menthyl 4-Bromo-2-nitrobenzoate

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Abstract. $C_{17}H_{22}NO_4Br$, triclinic, $P1$, $a=8\cdot123$ (2), $b=9\cdot523$ (2), $c=6\cdot353$ (2) Å, $\alpha=111\cdot44$ (4), $\beta=97\cdot84$ (2), $\gamma=92\cdot72$ (2)°, $U=450\cdot62$ Å^3, $Z=1$, $D_x=1\cdot403$ g cm^{-3}. In the ester grouping, the carbonyl group and H(C8)–C(8) bond are nearly eclipsed when viewed along the C(8)–O(4) bond. The planes of the carboxyl and nitro groups twist from the bromobenzene plane by 52·61 and 40·67°, respectively, in the same direction with a small out-of-plane displacement in the opposite direction.

Introduction. Nagai & Iga (1970) and Nagai, Abe & Sano (1974) found that a dissymmetric twisting of the nitro group in the *o*-nitrobenzoate causes optical activity which shows the Cotton effect at 330 nm. In order to determine the relation between the sign of the Cotton effect and the chirality of the twisted nitroben-

zoate, we have synthesized the title compound and elucidated the absolute molecular structure by an X-ray diffraction method.

Crystals were easily grown from methanol, as well as isopropanol solutions. Most of them were bundles or multiplex thin leaves. After many trials at recrystallization, we could obtain a single crystal with the dimensions 0·1 × 0·15 × 0·4 mm. Intensity data were collected using a Rigaku-automated four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation. The ω–2θ scan technique at a rate of $2\theta=4°$ min^{-1} was employed. Three standard reflexions were measured every fifty reflexions; they showed no significant change in intensity. A total of 1287 non-zero independent reflexions were observed up to $2\theta=140°$. The intensities were corrected for Lorentz and polarization factors, but no corrections for absorption and extinction were applied.

The structure was solved by the heavy-atom method and refined to an R index of 0·057 by the method of

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Table 1. *Atomic parameters*

(*a*) Non-hydrogen atoms

Atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^4$) with the estimated standard deviations in parentheses. The anisotropic thermal parameters for the non-hydrogen atoms are of the form $T=\exp[-B_{11}h^2-B_{22}k^2-B_{33}l^2-2B_{12}hk-2B_{13}hl-2B_{23}kl]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	0 (0)	0 (0)	0 (0)	273 (2)	196 (2)	358 (3)	−36 (1)	−56 (2)	52 (2)
O(1)	6313 (10)	−94 (10)	3981 (15)	221 (16)	230 (15)	570 (35)	80 (12)	117 (20)	26 (18)
O(2)	6824 (8)	2202 (9)	6425 (13)	130 (12)	212 (14)	544 (33)	−16 (10)	44 (16)	49 (17)
O(3)	5341 (9)	1683 (8)	10138 (12)	226 (15)	153 (11)	388 (26)	43 (10)	3 (15)	64 (14)
O(4)	4359 (8)	3926 (6)	10645 (10)	192 (12)	111 (9)	231 (18)	5 (8)	19 (12)	31 (10)
N	5909 (10)	1071 (10)	5197 (14)	174 (16)	174 (14)	359 (30)	19 (12)	95 (17)	69 (16)
C(1)	3500 (10)	1959 (9)	7126 (14)	113 (14)	95 (11)	281 (27)	−1 (10)	38 (16)	39 (14)
C(2)	4097 (11)	1201 (9)	5153 (15)	128 (15)	108 (12)	315 (30)	−18 (11)	70 (17)	55 (16)
C(3)	3108 (11)	570 (10)	3022 (14)	152 (16)	96 (11)	260 (28)	−2 (10)	56 (17)	−3 (15)
C(4)	1434 (11)	786 (10)	2949 (15)	178 (18)	103 (13)	293 (31)	−15 (12)	−26 (18)	26 (16)
C(5)	758 (11)	1536 (11)	4844 (17)	101 (15)	168 (16)	353 (34)	−26 (12)	20 (17)	44 (18)
C(6)	1782 (12)	2180 (11)	6962 (16)	160 (17)	155 (15)	288 (30)	−44 (13)	9 (18)	40 (18)
C(7)	4552 (11)	2502 (10)	9474 (15)	129 (15)	132 (13)	261 (28)	−15 (11)	25 (16)	39 (16)
C(8)	5125 (12)	4633 (10)	13093 (14)	177 (17)	139 (13)	194 (25)	11 (12)	−6 (17)	42 (15)
C(9)	3712 (12)	5106 (10)	14367 (15)	177 (18)	123 (13)	281 (29)	−15 (12)	−5 (18)	65 (16)
C(10)	4281 (12)	6022 (11)	16928 (15)	207 (20)	137 (14)	264 (30)	23 (13)	46 (19)	47 (16)
C(11)	5550 (13)	7331 (12)	17245 (17)	210 (21)	197 (19)	270 (31)	−30 (16)	4 (20)	25 (20)
C(12)	6986 (13)	6815 (12)	15964 (16)	174 (19)	194 (18)	283 (33)	−34 (14)	−29 (20)	30 (19)
C(13)	6398 (10)	5918 (11)	13372 (15)	102 (15)	160 (14)	264 (27)	−1 (12)	−13 (16)	75 (16)
C(14)	7820 (13)	5427 (12)	12020 (17)	178 (19)	164 (16)	360 (37)	3 (14)	−23 (21)	68 (21)
C(15)	8971 (16)	6730 (15)	12072 (23)	243 (26)	234 (23)	545 (51)	40 (19)	115 (29)	144 (28)
C(16)	8844 (14)	4302 (15)	12736 (23)	156 (20)	264 (24)	589 (52)	60 (17)	45 (26)	132 (29)
C(17)	2835 (16)	6494 (14)	18200 (19)	292 (28)	239 (22)	314 (37)	45 (19)	92 (26)	66 (23)

Table 1 (cont.)

(b) Hydrogen atoms
Atomic coordinates ($\times 10^3$) and thermal parameters ($\times 10^2$)

	x	y	z	B
H(C3)	361 (10)	12 (10)	169 (14)	438
H(C5)	−36 (11)	157 (10)	473 (15)	482
H(C6)	112 (12)	249 (11)	845 (17)	563
H(C8)	542 (12)	374 (11)	1362 (16)	574
H(C9)	317 (9)	581 (9)	1381 (13)	341
H'(C9)	305 (10)	421 (9)	1419 (13)	298
H(C10)	478 (11)	537 (10)	1739 (16)	489
H(C11)	478 (12)	795 (11)	1664 (16)	618
H'(C11)	591 (13)	794 (12)	1872 (18)	811
H(C12)	753 (11)	597 (10)	1634 (15)	519
H'(C12)	797 (9)	763 (9)	1609 (13)	328
H(C13)	591 (8)	658 (7)	1277 (11)	117
H(C14)	729 (10)	495 (9)	1038 (14)	462
H(C15)	847 (12)	760 (11)	1170 (17)	694
H'(C15)	941 (11)	746 (10)	1368 (15)	630
H''(C15)	988 (14)	631 (12)	1087 (19)	952
H(C16)	828 (13)	355 (12)	1352 (18)	757
H'(C16)	947 (14)	486 (14)	1428 (19)	854
H''(C16)	944 (13)	375 (12)	1168 (17)	781
H(C17)	231 (10)	719 (9)	1756 (13)	335
H'(C17)	213 (12)	571 (11)	1840 (12)	563
H''(C17)	319 (12)	705 (11)	1986 (16)	672

block-diagonal least squares. The final difference Fourier synthesis showed hydrogen atoms at appropriate positions. Further refinement by the least-squares method in which anisotropic thermal parameters were assumed for the non-hydrogen atoms and isotropic ones for the hydrogen atoms resulted in the R index of 0·045. The weight was $w = 1$ for all observed structure factors. The final values of the atomic coordinates and the thermal parameters are listed in Table 1.*

The absolute configuration was determined by the anomalous dispersion method. The data used were collected by the same apparatus as the above-mentioned, using Zr-filtered Mo $K\alpha$ radiation. The dispersion corrections for Mo $K\alpha$ radiation by bromine atoms ($\Delta f' = -0·3$, $\Delta f'' = 2·5$) were those given by Dauben & Templeton (1955). Comparison of the observed and calculated $|F(hkl)|/|F(\bar{h}\bar{k}\bar{l})|$ values for 25 Friedel pairs establishes the absolute configuration as shown in Fig. 1. The atomic scattering factors were those cited as SX-6, 7, 8 and 71 in International Tables for X-ray Crystallography (1962).

Discussion. The bond lengths and angles are listed in Table 2. The average C–C bond length in the benzene ring is 1·382 Å and in the menthyl group 1·517 Å. The six-membered ring of the menthyl group has a chair conformation with the three substituents (o-nitro-p-bromobenzoyl, methyl and isopropyl) in equatorial positions. The conformation about the ester bond C(8)–O(4) is such that H(C8) and the carbonyl group

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31568 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
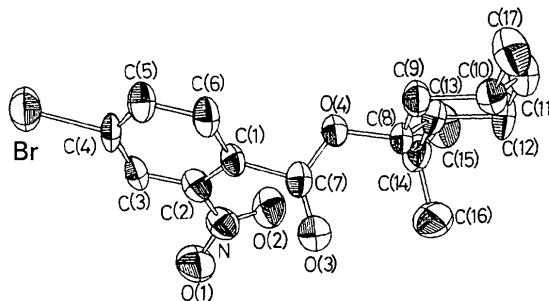

Fig. 1. An ORTEP (Johnson, 1965) drawing of the molecule with the thermal ellipsoids representing 50% probability; this diagram also shows the correct absolute configuration.
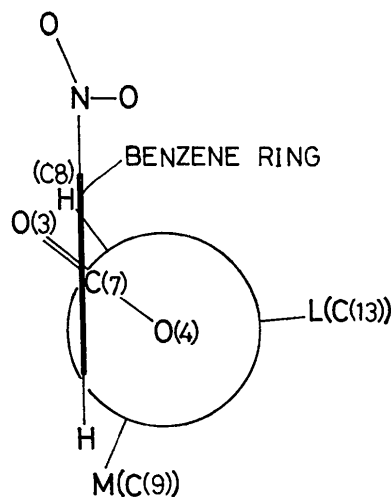

Fig. 2. Newman projection along the O(4)–C(8) bond; the bulky groups substituted at C(8) are represented by L $\left[C(13) < ^{\text{isopropyl}}_{C(12)-} \right]$ and M $\left[C(9) < ^{H}_{C(10)-} \right]$. L is more bulky than M.
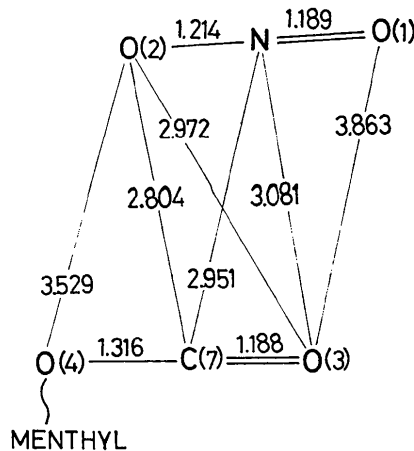
Fig. 3. Interatomic distances between the nitro and carboxyl groups.

Table 2. *Bond lengths* (Å) *and angles* (°)

Br——C(4)	1·929 (8)	C(16)–H′(C16)	0·98 (10)
O(1)—N	1·189 (11)	C(16)–H″(C16)	0·90 (11)
O(2)—N	1·214 (10)	C(17)–H(C17)	0·98 (9)
O(3)—C(7)	1·188 (13)	C(17)–H′(C17)	0·98 (11)
O(4)—C(7)	1·316 (10)	C(17)–H″(C17)	0·98 (9)
O(4)—C(8)	1·480 (9)		
N——C(2)	1·480 (12)	Br——C(4)—C(3)	118·0 (7)
C(1)—C(2)	1·366 (12)	O(1)—N——O(2)	127·0 (9)
C(1)—C(7)	1·506 (11)	O(3)—C(7)—O(4)	127·1 (9)
C(2)—C(3)	1·379 (11)	O(3)—C(7)—C(1)	122·3 (8)
C(4)—C(3)	1·382 (13)	O(4)—C(7)—C(1)	110·4 (7)
C(4)—C(5)	1·360 (13)	O(4)—C(8)—C(13)	108·3 (7)
C(5)—C(6)	1·386 (12)	N——C(2)—C(1)	120·3 (8)
C(6)—C(1)	1·417 (13)	C(1)—C(6)—C(5)	119·0 (9)
C(8)—C(9)	1·487 (14)	C(2)—N——O(1)	117·4 (9)
C(8)—C(13)	1·507 (14)	C(2)—N——O(2)	115·6 (8)
C(9)—C(10)	1·530 (12)	C(2)—C(1)—C(6)	118·2 (8)
C(10)–C(11)	1·515 (15)	C(2)—C(1)—C(7)	123·5 (8)
C(10)–C(17)	1·509 (16)	C(3)—C(2)—N	115·8 (8)
C(11)–C(12)	1·512 (15)	C(3)—C(2)—C(1)	123·8 (8)
C(12)–C(13)	1·545 (12)	C(4)—C(3)—C(2)	116·0 (8)
C(13)–C(14)	1·523 (14)	C(5)—C(4)—Br	118·7 (7)
C(14)–C(15)	1·505 (18)	C(5)—C(4)—C(3)	123·2 (9)
C(14)–C(16)	1·544 (19)	C(6)—C(1)—C(7)	118·3 (8)
C(3)—H(C3)	0·96 (9)	C(6)—C(5)—C(4)	119·7 (9)
C(5)—H(C5)	0·91 (9)	C(7)—O(4)—C(8)	119·3 (7)
C(6)—H(C6)	1·10 (11)	C(8)—C(13)–C(12)	108·2 (8)
C(8)—H(C8)	1·05 (11)	C(9)—C(8)—O(4)	105·6 (7)
C(9)—H(C9)	0·96 (9)	C(9)—C(8)—C(13)	114·4 (8)
C(9)—H′(C9)	0·94 (8)	C(9)—C(10)–C(17)	112·6 (9)
C(10)–H(C10)	0·88 (11)	C(10)–C(9)—C(8)	113·2 (8)
C(11)–H(C11)	1·01 (11)	C(11)–C(10)–C(9)	109·5 (8)
C(11)–H′(C11)	0·90 (9)	C(11)–C(10)–C(17)	113·8 (9)
C(12)–H(C12)	1·02 (10)	C(12)–C(11)–C(10)	112·3 (9)
C(12)–H′(C12)	1·06 (8)	C(13)–C(12)–C(11)	112·6 (9)
C(13)–H(C13)	0·93 (8)	C(13)–C(14)–C(16)	112·9 (9)
C(14)–H(C14)	0·99 (8)	C(14)–C(13)–C(8)	114·0 (8)
C(15)–H(C15)	1·03 (12)	C(14)–C(13)–C(12)	113·9 (8)
C(15)–H′(C15)	1·00 (8)	C(15)–C(14)–C(13)	113·8 (9)
C(15)–H″(C15)	1·12 (12)	C(15)–C(14)–C(16)	110·0 (10)
C(16)–H(C16)	1·13 (13)		

are in the eclipsed position. The internal rotational angle H(C8)-C(8)-O(4)-C(7) is 16·6° and that of C(8)–O(4)-C(7)-O(3) is −2·6°. A Newman projection along the C(8)-O(4) bond is shown in Fig. 2. The distances of C(7)-H(C8) and O(3)-H(C8) are 2·45 and 2·35 Å respectively. As expected in view of the steric hindrance, the benzene ring is arranged close to the *M* group (C9) and apart from the *L* group (C13). The equations of the three least-squares planes (benzene ring, nitro group and carboxyl group) and the interplanar angles between them are listed in Table 3. Because of the overcrowding of the substituent groups in the benzene ring, neither the nitro nor the carboxyl group can be coplanar with the benzene plane. In the present molecule, the planes of the nitro and the carboxyl groups twist by 40·7 and 52·6° from the benzene plane in the same direction. The corre-

sponding twist angles in *o*-nitrobenzoic acid are 55 and 23° respectively (Sacore, Tavale & Pant, 1967). The crystal of the latter compound is centrosymmetric while the present crystal consists of molecules having only one conformation. It is clear that the dissymmetry of the twisting of the nitro group is induced by the presence of an asymmetric carbon at C(8) in the (−)-menthyloxy group.

Table 3. *Least-squares planes and interplanar angles*

Equations of the planes

(1) Benzene ring	$0·0896x + 0·8517y − 0·5163z =$	$−0·06165$
(2) Nitro group	$0·1021x − 0·3328y + 0·9374z =$	$2·29763$
(3) Carboxyl group	$0·7805x + 0·2976y − 0·5498z =$	$0·77946$

Angles between the planes

	(2)	(3)
(1)	40·67°	′ 52·61°
(2)	—	57·67

The relation between the chirality of the twisting and the sign of the Cotton effect has been discussed by Nagai *et al.* (1974). The C(7) carbon atom and nitrogen atom are displaced out of the benzene plane in opposite directions by 0·15 and 0·11 Å. This situation is almost the same as that in *o*-nitrobenzoic acid, in which the corresponding values are 0·21 and 0·16 Å. The relative arrangements of the nitro and carboxyl groups are shown in Fig. 3. The bond length of N-O(1), 1·189 Å, is significantly shorter than that of N-O(2), 1·214 Å, indicating the left-weighted resonance between $O(1)=N^+-O(2)^- \leftrightarrow O(1)^- -N^+ =O(2)$. As the carboxyl group tends to have a partially charged structure $O(3)^{\delta-} -C(7)^{\delta+} -O(4)$, the arrangement shown in Fig. 3 would be the most stable in view of the steric as well as the electrostatic interactions between the nitro and carboxyl groups. There is neither intramolecular nor intermolecular hydrogen bonding in this crystal. Molecules adjoin each other only by van der Waals forces.

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