

ring is planar. The atom N(2), *cis* with respect to C(2) and C(4) and *trans* with respect to C(1), confirms the DL-form of the histidine moiety in the present work (Bennett *et al.*, 1970). The C(3)—C(2) conformation is such that C(1) is *trans* with respect to C(4) and N(1) is *gauche*.

The bond angles involving heavy atoms in the title compound are comparable with those in histidine dihydrochloride and histidine hydrochloride monohydrate. There are, in general, three single bonds in the histidine moiety which permit conformational freedom: C(4)—C(3), C(3)—C(2) and C(2)—C(1). A comparison of the torsion angles about these bonds in the histidine molecule in title compound, and in L-histidine dihydrochloride and L-histidine hydrochloride monohydrate, is given in Table 2. The difference in the torsion angle C(4)—C(3)—C(2)—C(1) of about 4.5° between the present work and L-histidine dihydrochloride is consistent with an 'open' conformation; the molecular conformation in L-histidine dihydrochloride monohydrate is 'closed' with the torsion angle about C(2)—C(3) equal to -52.8° (Oda & Koyama, 1972).

The crystal-packing diagram of DL-histidinium dinitrate is shown in Fig. 2. Ribbons of histidine cations, each straddling a glide plane, lie essentially in parallel channels along the crystallographic *a* axis. The head-to-tail alignment of the molecules is stabilized by a series of hydrogen bonds [N(1)—H(1)⋯O(12), N(2)—H(7)⋯O(22), N(1)—H(2)⋯O(21) *etc.*] running approximately parallel to *b*. The hydrogen-bond distances and their angles are given in Table 2. All protons attached to N and O atoms are involved in hydrogen bonding. However, there

seems to be a bifurcated hydrogen bond between the carboxylate O(2) atom and two O atoms [O(21) and O(231)] of the same nitrate group. The thermal parameters of O(231), O(2) and H(11) involved in this hydrogen bond are relatively high (0.0963, 0.1105 and 0.16 Å<sup>2</sup>, respectively). Similarly there is one more bifurcated hydrogen bond between the amino-group N atom and two O atoms [O(21) and O(22)] of the same nitrate group.

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## Structure of a *p*-Bromobenzoyl Derivative of Amyrinol\*

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**Abstract.** 5,6,9,9-Tetramethyl-10-oxatricyclo-[6.2.2.0<sup>1,6</sup>]dodec-2-yl *p*-bromobenzoate, C<sub>22</sub>H<sub>29</sub>BrO<sub>3</sub>,

$M_r = 420.9$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.038$  (1),  $b = 23.924$  (2),  $c = 24.84$  (1) Å,  $V = 4182.5$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.336$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,  $\mu = 26.2$  cm<sup>-1</sup>,  $F(000) = 1760$ ,  $T = 288$  K, final  $R = 0.053$  for 2830 reflections. The compound crystallizes with two molecules in the asymmetric unit where each molecule has two cyclohexane rings of which one is

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Table 1. Final atomic coordinates and equivalent isotropic thermal parameters of non-H atoms with their e.s.d.'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U <sub>eq</sub> (Å <sup>2</sup> )
<b>Molecule A</b>				
Br1	0.04601 (24)	0.21923 (6)	0.56333 (6)	0.0984
C2	-0.1150 (17)	0.1566 (4)	0.5545 (4)	0.0590
C3	-0.3108 (19)	0.1658 (5)	0.5498 (5)	0.0738
C4	-0.0447 (17)	0.1048 (4)	0.5511 (4)	0.0585
C5	-0.4289 (17)	0.1212 (4)	0.5404 (4)	0.0595
C6	-0.1620 (16)	0.0611 (4)	0.5404 (4)	0.0512
C7	-0.3600 (16)	0.0694 (4)	0.5354 (4)	0.0481
C8	-0.4925 (17)	0.0226 (4)	0.5228 (4)	0.0521
O9	-0.6614 (10)	0.0261 (3)	0.5258 (3)	0.0654
O10	-0.3996 (9)	-0.0236 (3)	0.5076 (3)	0.0662
C11	-0.5159 (15)	-0.0695 (4)	0.4855 (4)	0.0520
C12	-0.5328 (20)	-0.1141 (6)	0.5285 (5)	0.0798
C13	-0.3409 (28)	-0.1459 (8)	0.5390 (6)	0.0966
C14	-0.2647 (19)	-0.1692 (4)	0.4858 (6)	0.0789
C15	-0.2292 (14)	-0.1246 (4)	0.4441 (5)	0.0558
C16	-0.1882 (17)	-0.1531 (5)	0.3889 (6)	0.0800
C17	-0.3163 (17)	-0.1324 (5)	0.3434 (5)	0.0703
C18	-0.2988 (23)	-0.0689 (6)	0.3425 (6)	0.0959
C19	-0.3842 (26)	-0.0425 (5)	0.3947 (5)	0.0758
C20	-0.4177 (13)	-0.0902 (4)	0.4353 (4)	0.0490
O21	-0.5598 (9)	-0.1277 (2)	0.4136 (3)	0.0517
C22	-0.5290 (17)	-0.1460 (5)	0.3595 (4)	0.0661
C23	-0.0871 (29)	-0.2051 (6)	0.4984 (9)	0.1526
C24	-0.0645 (18)	-0.0868 (6)	0.4588 (6)	0.0838
C25	-0.5578 (21)	-0.2105 (5)	0.3598 (7)	0.0835
C26	-0.6706 (24)	-0.1185 (7)	0.3212 (6)	0.1119
<b>Molecule B</b>				
Br1	0.14497 (26)	-0.03417 (6)	0.65858 (7)	0.1103
C2	0.2932 (21)	0.0296 (5)	0.6707 (5)	0.0756
C3	0.4946 (20)	0.0219 (4)	0.6772 (6)	0.0813
C4	0.2191 (17)	0.0799 (5)	0.6730 (5)	0.0610
C5	0.5949 (24)	0.0685 (5)	0.6848 (7)	0.0773
C6	0.3283 (17)	0.1275 (4)	0.6803 (4)	0.0608
C7	0.5289 (16)	0.1208 (4)	0.6887 (4)	0.0480
C8	0.6476 (17)	0.1704 (4)	0.6971 (4)	0.0539
O9	0.8224 (11)	0.1661 (3)	0.6990 (3)	0.0717
O10	0.5562 (10)	0.2170 (3)	0.7031 (3)	0.0621
C11	0.6596 (17)	0.2694 (4)	0.7067 (6)	0.0526
C12	0.6987 (18)	0.2847 (5)	0.7683 (5)	0.0703
C13	0.5208 (19)	0.2995 (5)	0.7972 (4)	0.0723
C14	0.4288 (17)	0.3483 (4)	0.7706 (4)	0.0603
C15	0.3671 (14)	0.3351 (4)	0.7108 (4)	0.0501
C16	0.3002 (19)	0.3914 (5)	0.6805 (8)	0.0807
C17	0.4169 (22)	0.4002 (5)	0.6309 (5)	0.0772
C18	0.3938 (22)	0.3475 (6)	0.5971 (5)	0.0926
C19	0.4986 (20)	0.2987 (5)	0.6225 (5)	0.0658
C20	0.5474 (15)	0.3142 (3)	0.6790 (4)	0.0463
O21	0.6867 (9)	0.3597 (3)	0.6782 (3)	0.0485
C22	0.6381 (17)	0.4068 (5)	0.6453 (5)	0.0672
C23	0.2550 (21)	0.3694 (6)	0.8043 (6)	0.0917
C24	0.2074 (15)	0.2930 (3)	0.7080 (6)	0.0723
C25	0.6676 (22)	0.4584 (4)	0.6766 (6)	0.0876
C26	0.7594 (30)	0.4088 (9)	0.5952 (7)	0.1048

Table 2. Bond distances (Å) of non-H atoms with e.s.d.'s in parentheses

	Molecule A	Molecule B	Molecule A	Molecule B	
Br1—C2	1.892 (11)	1.873 (12)	C20—C19	1.541 (16)	1.491 (16)
C2—C4	1.337 (14)	1.312 (16)	C12—C13	1.573 (24)	1.487 (18)
C6—C4	1.358 (15)	1.386 (16)	C14—C13	1.531 (21)	1.491 (16)
C7—C6	1.413 (16)	1.436 (17)	C14—C15	1.506 (16)	1.580 (14)
C7—C5	1.335 (14)	1.339 (15)	C14—C23	1.549 (23)	1.565 (18)
C7—C8	1.491 (14)	1.466 (15)	C15—C24	1.515 (16)	1.511 (13)
C3—C5	1.374 (16)	1.332 (18)	C15—C16	1.559 (17)	1.612 (18)
C3—C2	1.401 (18)	1.439 (20)	O21—C22	1.429 (13)	1.434 (13)
O10—C11	1.475 (12)	1.453 (12)	C19—C18	1.562 (20)	1.520 (19)
O10—C8	1.339 (12)	1.295 (12)	C18—C17	1.525 (19)	1.524 (18)
O9—C8	1.194 (14)	1.236 (14)	C26—C22	1.526 (20)	1.510 (22)
C11—C20	1.511 (14)	1.498 (15)	C22—C17	1.584 (17)	1.605 (19)
C11—C12	1.512 (16)	1.598 (19)	C22—C25	1.556 (17)	1.474 (16)
C20—C15	1.576 (13)	1.576 (14)	C17—C16	1.528 (18)	1.496 (22)
O21—C20	1.448 (11)	1.466 (11)			

Table 3. Bond angles (°) with e.s.d.'s in parentheses

	Molecule A	Molecule B
Br1—C2—C3	118.3 (0.8)	117.6 (0.8)
Br1—C2—C4	112.3 (0.9)	122.2 (1.1)
C3—C2—C4	120.4 (1.1)	120.3 (1.1)
C2—C3—C5	119.1 (1.1)	115.5 (1.1)
C3—C5—C7	121.1 (1.1)	127.5 (1.5)
C5—C7—C6	118.7 (0.9)	115.5 (1.1)
C7—C6—C4	120.5 (0.9)	118.2 (1.0)
C6—C4—C2	120.0 (1.1)	122.6 (1.2)
C6—C7—C8	122.0 (0.8)	119.4 (0.9)
C7—C8—O9	123.8 (0.9)	120.3 (0.9)
O9—C8—O10	124.2 (0.4)	124.3 (1.0)
C11—O10—C8	116.7 (0.8)	120.0 (0.8)
C12—C11—C20	112.8 (0.8)	111.5 (0.9)
C11—C12—C13	113.0 (1.1)	111.5 (1.0)
C12—C13—C14	109.5 (1.2)	109.8 (1.0)
C13—C14—C15	113.2 (1.0)	112.3 (0.8)
C20—C15—C14	109.0 (0.9)	108.2 (0.8)
C20—C15—C16	105.1 (0.9)	105.5 (0.9)
C15—C16—C17	113.6 (0.9)	110.0 (1.0)
C16—C17—C22	107.7 (1.0)	111.2 (1.1)
C16—C17—C18	106.6 (1.0)	106.1 (1.1)
C18—C17—C22	106.5 (1.0)	108.0 (1.1)
C19—C18—C17	111.1 (1.1)	110.8 (1.1)
C20—C19—C18	107.6 (1.0)	108.2 (0.9)
C19—C20—O21	108.7 (0.9)	109.0 (0.8)
C19—C10—C15	110.4 (1.0)	111.4 (0.9)
C11—C20—C15	108.1 (0.7)	115.0 (0.9)
C20—O21—C22	115.8 (0.8)	115.7 (0.7)
O21—C22—C17	111.8 (1.0)	106.3 (0.8)
O21—C22—C26	110.8 (1.0)	111.0 (1.1)
C25—C22—C26	110.2 (1.1)	109.2 (1.1)

in the boat form (with a bridge) whereas the other, without a bridge, is in the chair form. The dihedral angle between the benzene plane and the plane of the carboxylate group is 12.8 (10)<sup>o</sup> in molecule A and 5.9 (10)<sup>o</sup> in molecule B.

**Introduction.** The wood distillate of the plant *Amyrsis* is a rich source of essential oils reported to be fungicidal (Maruzzella & Balker, 1959), antibacterial (Maruzzella & Bramnick, 1961) and toxic (Jenner, Hagan, Taylor, Cook & Fitzhugh, 1964). Six sesquiterpenes have recently been identified in the oil of *Amyrsis balsamifera* by gas chromatography/mass spectroscopy methods (Rohmer, Schwartz &

Anton, 1977). Other compounds such as amyrol, C<sub>15</sub>H<sub>26</sub>O, amyrolin and a coumarin, m.p. 430–432 K, C<sub>14</sub>H<sub>12</sub>O<sub>3</sub>, have also been isolated. The crystals of the parent compound amyrolin were found to be silky, flaky and unsuitable for X-ray analysis, hence a bromine derivative which is crystalline (Ray, 1986) was investigated to establish its conformation.

**Experimental.** Crystals of the title compound (received courtesy of Dr A. K. Barua, Bose Institute, India) were obtained from aqueous methanol with two molecules per asymmetric unit in the form of transparent needles at room temperature, dimensions 0.31 × 0.24 × 0.13 mm. Lattice parameters were determined from 15 intermediate axial reflections in the range 17 < 2θ < 38°.

Three standard reflections monitored periodically had no significant intensity variation. 2836 [2406

Table 4. Some selected torsional angles ( $^{\circ}$ ) with e.s.d.'s in parentheses

	Molecule A	Molecule B
C5—C7—C8—O9	-13.48 (1.58)	2.64 (1.76)
C5—C7—C8—O10	166.34 (0.98)	-176.07 (1.13)
C11—O10—C8—C7	-170.14 (0.78)	-174.41 (0.88)
C11—O10—C8—O9	9.64 (1.42)	6.94 (1.55)
C8—O10—C11—C12	-104.08 (0.98)	-93.49 (1.11)
C8—O10—C11—C20	134.12 (0.84)	143.94 (0.92)
O10—C11—C12—C13	-70.17 (1.29)	-68.89 (1.21)
O10—C11—C20—C15	72.27 (0.98)	74.09 (1.07)
C11—C12—C13—C14	-53.94 (1.55)	-59.24 (1.26)
C11—C20—C15—C14	49.14 (1.12)	48.91 (1.10)
C12—C13—C14—C23	-174.51 (1.26)	-173.00 (0.99)
C12—C13—C14—C15	59.04 (1.53)	62.73 (1.19)
C13—C14—C15—C20	-55.50 (1.31)	-55.63 (1.09)
C13—C14—C15—C16	-169.78 (1.10)	-170.76 (0.96)
C14—C15—C16—C17	125.95 (1.06)	122.67 (1.10)
C14—C15—C20—C19	177.51 (0.95)	177.78 (0.86)
C16—C15—C14—C23	66.69 (1.37)	64.92 (1.18)
C20—C15—C14—C23	-179.03 (1.09)	-179.95 (0.87)
C18—C17—C16—C15	53.53 (1.31)	56.53 (1.37)
C22—C17—C16—C15	-60.47 (1.23)	-60.64 (1.36)
C15—C20—C19—C18	54.01 (1.25)	52.26 (1.20)
C20—C19—C18—C17	12.37 (1.50)	14.57 (1.42)
C20—C15—C16—C17	9.19 (1.22)	5.85 (1.32)
C16—C17—C18—C19	-66.35 (1.36)	-71.57 (1.37)
C22—C17—C18—C19	48.47 (1.38)	47.77 (1.37)
C22—O21—C20—C19	49.72 (1.09)	51.07 (1.07)
C26—C22—C17—C18	56.51 (1.33)	57.06 (1.44)
C25—C22—C17—C18	178.67 (1.05)	178.19 (1.05)
C22—O21—C20—C11	167.33 (0.77)	169.00 (0.82)

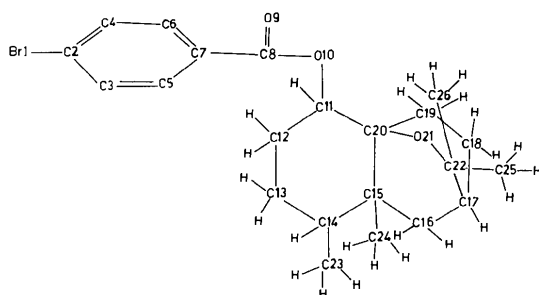


Fig. 1. Chemical diagram of the molecule.

with  $I > 3\sigma(I)$  unique reflections were collected on a CAD-4 diffractometer with Ni-filtered Cu  $K\alpha$  radiation in  $2\theta$ - $\omega$  step-scan mode.  $2\theta_{\max} = 120^{\circ}$ . Ranges of  $h, k, l$  were  $-15$  to  $15$ ,  $-5$  to  $5$ ,  $-2$  to  $17$ . Data were corrected for Lorentz-polarization factors but not for absorption. The structure was solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least squares with *SHELX76* (Sheldrick, 1976) on *F*. All the H atoms were located from  $\Delta F$  syntheses and refined isotropically. All non-H atoms were refined anisotropically. There are two molecules in the asymmetric unit. Final  $R = 0.053$  and  $wR = 0.053$ ;  $w = 1/\sigma^2(F_o)$ ;  $\Delta\rho$  peaks are  $0.3$  to  $-0.2$  e  $\text{\AA}^{-3}$ ,  $(\Delta/\sigma)_{\max} = 0.65$ . Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

**Discussion.** Final atomic parameters are given in Table 1.\* The bond lengths, bond angles and some dihedral angles of the molecules are in Tables 2, 3 and 4. Fig. 1 shows a chemical diagram of the title compound, Fig. 2 gives a comparative view of the two independent molecules as revealed from the X-ray study and Fig. 3 presents a packing diagram down the *a* axis.

Each molecule has two cyclohexane rings of which one (with a bridge) is in the boat form and the other

\* Lists of structure factors, anisotropic thermal parameters, least-squares planes, intermolecular bond contacts and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53652 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

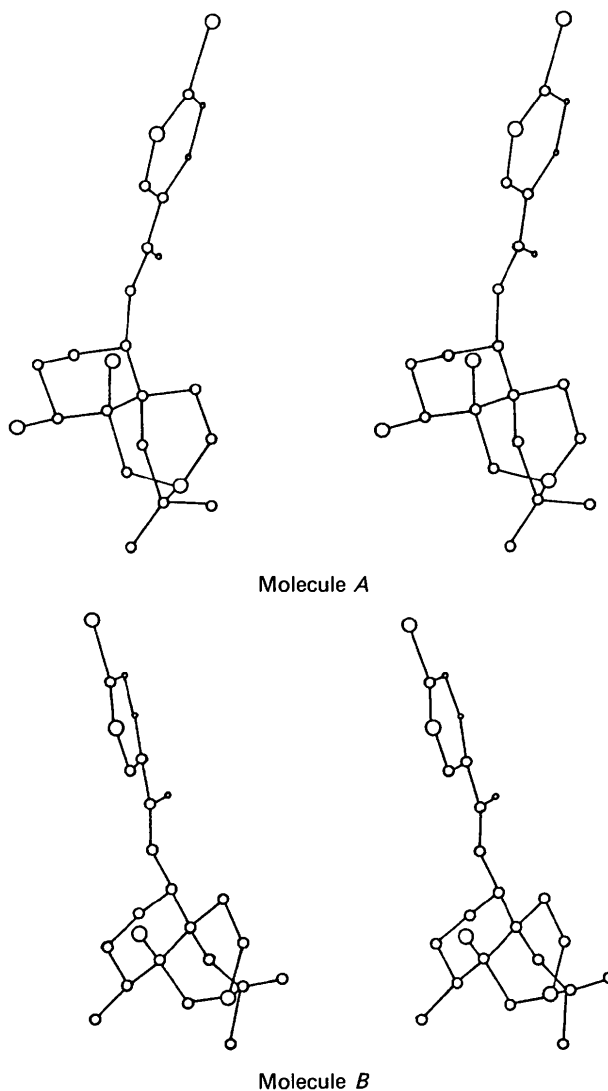


Fig. 2. Comparative stereoviews of conformations of the two molecules as revealed by X-ray study.

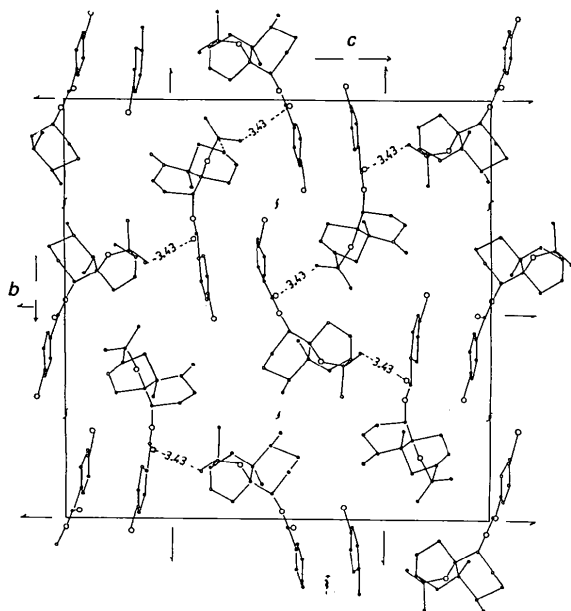


Fig. 3. Packing diagram of the molecules down the *a* axis with intermolecular short contacts (Å).

(without a bridge) is in the chair form. In the cyclohexane ring having the chair conformation, the distance between the planes containing alternate atoms is about 0.433 Å. In the cyclohexane ring having the boat conformation, the atoms forming the 'bottom' of the boat are not exactly coplanar. The deviations of C18 from the planes passing through C16, C15, C19 in molecule *A* and in molecule *B* are 0.296 (6) and 0.286 (5) Å, respectively.

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## Structure of 17-Epinimbocinol

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**Abstract.** 7 $\alpha$ -Hydroxy-4,4,8-trimethyl-21,23-epoxy-24-nor-5 $\alpha$ ,13 $\alpha$ ,17 $\beta$ -chola-1,14,20,22-tetraene-3,16-

dione, C<sub>26</sub>H<sub>32</sub>O<sub>4</sub>, *M<sub>r</sub>* = 408.51, m.p. = 526–528 K, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 6.7094 (9), *b* = 13.195 (1), *c* = 24.281 (3) Å, *V* = 2149.64 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.262 Mg m<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha)$  = 1.5418 Å,  $\mu$  =

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In molecule *A*, Br1 and O9 are on the opposite sides of the benzene plane, the distances of Br1, O9, O10 from this plane being –0.106 (1), 0.124 (7) and –0.354 (7) Å, respectively. In molecule *B*, however, Br1 and O9 are on the same side of the benzene plane, the distances of Br1, O9, O10 from this plane being –0.035 (2), –0.053 (8) and 0.173 (7) Å, respectively. The dihedral angle between the benzene plane and the plane of the (C8, O9, O10) group is 12.8 (10)° in molecule *A* and 5.9 (10)° in molecule *B*.

Many intramolecular short contacts are present but the intermolecular forces are apparently small [shortest contact C···O, 3.43 (2) Å]. This implies that the molecules are somewhat loosely bound to each other. It is therefore not surprising that the melting point of the compound is rather low (observed m.p. 395 K).

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