

Fig. 2. Stereoview of a single molecule.

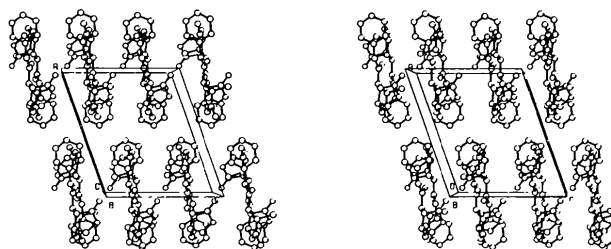


Fig. 3. Stereo packing diagram, viewed down *b*. H atoms are omitted.

Final atomic coordinates are given in Table 1, bond lengths and angles in Tables 2 and 3. Diagrams of the structure are given in Figs. 2 and 3.\*

**Discussion.** The stereochemistry at the asymmetric centres is established as (3a*SR*,4*RS*,5*SR*,7a*SR*). The chemical significance of this is discussed elsewhere (Owens & Raphael, 1978).

Several bond lengths and angles show some deviation from ideal geometry, the most marked being C(6)–C(7)–C(7a), 126.0°, and C(3a)–C(3)–O(31), 128.6°. This may be due to strain at the ring junctions.

\* Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33375 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The cyclohexene ring adopts the sofa conformation with C(4) 0.49 Å above and C(3a) 0.15 Å below the plane of the other four atoms.

C(3) (at *x,y,z*) is 3.12 Å from O(11) (at  $2-x, -0.5+y, 0.5-z$ ). There are no other unusually short non-bonded distances.

We thank the MRC for financial support and the SRC for provision of the diffractometer. The figures were drawn with *PLUTO* written by Dr W. D. S. Motherwell. All other crystallographic programs were written by Dr G. M. Sheldrick.

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*Acta Cryst.* (1978). **B34**, 2027–2030

## 5-(3-Dimethylammonio-prop-1-enylidene)-5*H*-dibenzo[*a,d*]cycloheptene Maleate, a Central Nervous System Depressant–Antidepressant

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(Received 30 January 1978; accepted 21 February 1978)

**Abstract.** C<sub>20</sub>H<sub>20</sub>N<sup>+</sup>C<sub>4</sub>H<sub>3</sub>O<sub>4</sub><sup>-</sup>, *M<sub>r</sub>* = 389.46, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.554 (2), *b* = 9.656 (2), *c* = 22.799 (6) Å, β = 96.06 (2)°, *U* = 2092 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.237, *D<sub>m</sub>* (floatation) = 1.24 g cm<sup>-3</sup>, μ = 6.0 cm<sup>-1</sup> (Cu *K*α). The structure was refined to *R* = 0.048 for 2553 diffractometer data. The cation and anion are

linked by a hydrogen bond. The structure is compared with that of the antidepressant imipramine.

**Introduction.** As part of our investigation of the structural and conformational properties of the tricyclic antidepressants (Post, Kennard & Horn, 1974, 1975; Rodgers, Kennard, Horn & Riva di Sanseverino, 1974; Rodgers, Horn & Kennard, 1975; Rodgers, Kennard,

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Sheldrick & Horn, 1976) we have determined the structure of the title analogue (DMPD, Fig. 1) (Roszkowski, Schuler, Marx & Edwards, 1975). This molecule is of interest because its allenic nature confers on it less molecular flexibility than previously examined derivatives such as imipramine (Post *et al.*, 1974, 1975) or iprindole (Rodgers *et al.*, 1974). This may, in principle, be useful in indicating the preferred conformation of this class of drugs at their biological receptors.

DMPD was crystallized from 2-propanol as pale-yellow crystals of irregular shape. One large crystal was partially redissolved in 2-propanol. The remaining fragment, 0.7 × 0.5 × 0.4 mm, was used for data collection on a Syntex P2<sub>1</sub> diffractometer with Cu K $\alpha$  radiation and graphite monochromator. Cell dimensions were obtained by least squares from 15 strong reflexions. 3743 reflexions were measured in the range  $0 < 2\theta < 116^\circ$ ; after Lp corrections were applied, averaging equivalent reflexions gave 2553 unique reflexions with  $F > 4\sigma(F)$ . Systematic absences  $0k0$ ,  $k$  odd and  $h0l$ ,  $l$  odd, indicated space group  $P2_1/c$ .

Multisolution  $\sum_2$  sign expansion with the program *SHELX* failed to give a solution. The program *XCSD* was therefore used; this incorporates a pseudotangent refinement to select the starting set (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973) and the negative quartet test NQUEST (De Titta, Edmonds, Langs & Hauptman, 1975). The best  $E$  map established positions for all the non-H atoms, all the top 29 peaks being correct. Figures of merit for this solution were NQUEST  $-0.549$ ,  $RA$  (a point atom  $R$  factor based on observed peaks)  $0.284$ ,  $R_\alpha$  (Roberts *et al.*, 1973)  $0.089$ ; all merit figures were substantially better than for any other  $E$  map. Isotropic least-squares refinement gave  $R = 0.17$ ; anisotropic refinement (to  $R = 0.10$ ), followed by a difference synthesis, gave sites for all H atoms. In the final cycles of refinement all H atoms refined freely, separate overall isotropic temperature factors being employed for methyl and non-methyl H. The final  $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.0622$ , with  $R = 0.0484$ ; the weighting scheme was  $w = 1/[\sigma^2(F) + 0.001F^2]$ , which gave mean values of  $w\Delta^2$  varying only slightly with  $\sin \theta$  or  $|F_o|$ . A final difference map had no peaks  $>0.21 e \text{ \AA}^{-3}$ . Final

atomic parameters are given in Table 1,\* bond lengths and angles in Tables 2 and 3. Diagrams of the structure are given in Figs. 2 and 3. The numbering scheme for

\* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving hydrogen atoms and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33425 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atom coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(11)	-242 (3)	2771 (2)	3664 (1)	
C(10)	-1580 (3)	2897 (2)	3444 (1)	
C(9a)	-2408 (2)	2102 (2)	2983 (1)	
C(5a)	-1818 (2)	1377 (2)	2523 (1)	
C(5)	-295 (2)	1456 (2)	2462 (1)	
C(4a)	753 (2)	1109 (2)	2973 (1)	
C(11a)	780 (2)	1781 (2)	3517 (1)	
C(9)	-3870 (3)	2073 (3)	2989 (1)	
C(8)	-4701 (3)	1383 (4)	2576 (2)	
C(7)	-4162 (3)	672 (4)	2138 (2)	
C(6)	-2681 (2)	648 (3)	2105 (1)	
C(4)	1735 (2)	76 (2)	2900 (1)	
C(3)	2758 (2)	-274 (2)	3346 (1)	
C(2)	2857 (2)	429 (2)	3872 (1)	
C(1)	1907 (3)	1439 (2)	3954 (1)	
C(1')	127 (2)	1697 (2)	1944 (1)	
C(2')	504 (2)	1914 (2)	1419 (1)	
C(3')	708 (2)	3313 (2)	1169 (1)	
N(1)	2096 (2)	3429 (2)	920 (1)	
C(26)	3297 (2)	3281 (3)	1384 (1)	
C(27)	2185 (3)	4744 (2)	587 (1)	
O(1)	1632 (2)	1377 (1)	126 (1)	
O(2)	3311 (2)	251 (2)	665 (1)	
C(21)	2451 (2)	387 (2)	208 (1)	
C(22)	2416 (3)	-661 (3)	-266 (1)	
C(23)	3231 (3)	-1738 (3)	-333 (1)	
C(24)	4471 (2)	-2297 (2)	30 (1)	
O(3)	5096 (2)	-3266 (2)	-146 (1)	
O(4)	4874 (2)	-1709 (2)	532 (1)	
H(1)	2040 (22)	2641 (22)	652 (9)	97 (2)
H(111)	115 (23)	3451 (22)	3987 (9)	97 (2)
H(101)	-2052 (24)	3572 (21)	3661 (10)	97 (2)
H(91)	-4368 (22)	2629 (23)	3354 (9)	97 (2)
H(81)	-5829 (23)	1219 (22)	2558 (9)	97 (2)
H(71)	-4446 (24)	143 (22)	1856 (10)	97 (2)
H(61)	-2179 (24)	23 (22)	1851 (10)	97 (2)
H(41)	1633 (23)	-350 (24)	2522 (10)	97 (2)
H(31)	3429 (23)	-999 (23)	3278 (10)	97 (2)
H(21)	3710 (24)	283 (23)	4178 (10)	97 (2)
H(11)	1993 (22)	1916 (25)	4300 (9)	97 (2)
H(2'1)	644 (24)	1164 (23)	1136 (10)	97 (2)
H(3'1)	690 (22)	4111 (24)	1474 (10)	97 (2)
H(3'2)	19 (23)	3565 (22)	853 (10)	97 (2)
H(261)	3269 (25)	4014 (26)	1716 (11)	109 (3)
H(262)	3182 (25)	2413 (25)	1581 (10)	109 (3)
H(263)	4199 (25)	3304 (26)	1192 (10)	109 (3)
H(271)	3064 (26)	4661 (24)	430 (11)	109 (3)
H(272)	1472 (27)	4709 (24)	283 (11)	109 (3)
H(273)	1975 (26)	5506 (26)	801 (11)	109 (3)
H(221)	1745 (23)	-485 (24)	-543 (10)	97 (2)
H(231)	3101 (23)	-2273 (23)	-660 (10)	97 (2)
H(2)	4376 (23)	-978 (23)	604 (9)	97 (2)

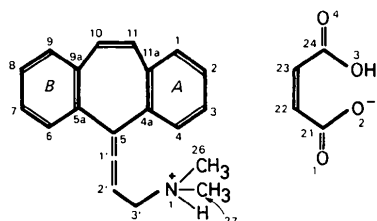


Fig. 1. Chemical structure of DMPD showing the numbering scheme for non-hydrogen atoms and labelling of rings A and B.

Table 2. Bond lengths (Å)

C(11)—C(10)	1.328 (4)	C(11)—C(11a)	1.431 (4)
C(10)—C(9a)	1.464 (4)	C(9a)—C(5a)	1.427 (4)
C(9a)—C(9)	1.398 (4)	C(5a)—C(5)	1.479 (4)
C(5a)—C(6)	1.384 (4)	C(5)—C(4a)	1.492 (3)
C(4a)—C(11a)	1.398 (3)	C(4a)—C(4)	1.391 (4)
C(11a)—C(1)	1.425 (4)	C(9)—C(8)	1.343 (5)
C(8)—C(7)	1.358 (6)	C(7)—C(6)	1.425 (5)
C(4)—C(3)	1.376 (4)	C(3)—C(2)	1.372 (4)
C(2)—C(1)	1.359 (4)	C(1')—C(5)	1.307 (4)
C(1')—C(2')	1.304 (4)	C(2')—C(3')	1.487 (4)
C(3')—N(1)	1.501 (5)	C(26)—N(1)	1.484 (4)
C(27)—N(1)	1.486 (4)	C(21)—O(1)	1.237 (3)
C(21)—O(2)	1.264 (3)	C(21)—C(22)	1.477 (4)
C(22)—C(23)	1.318 (5)	C(23)—C(24)	1.473 (4)
C(24)—O(3)	1.202 (4)	C(24)—O(4)	1.299 (4)

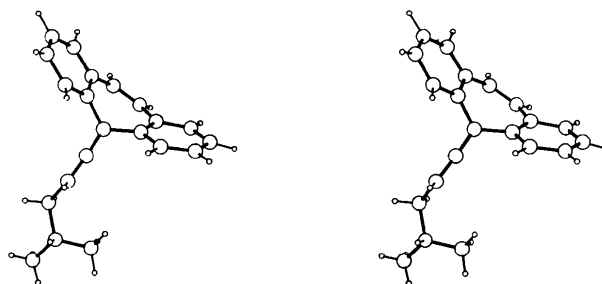
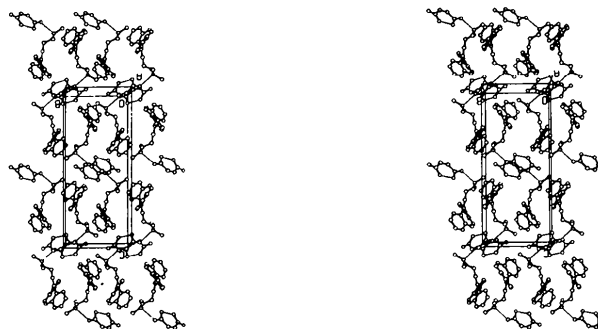
Table 3. Bond angles (°)

C(10)—C(11)—C(11a)	128.8 (3)	C(11)—C(10)—C(9a)	130.4 (2)
C(10)—C(9a)—C(5a)	124.0 (3)	C(10)—C(9a)—C(9)	118.0 (3)
C(5a)—C(9a)—C(9)	118.0 (3)	C(9a)—C(5a)—C(5)	120.9 (3)
C(9a)—C(5a)—C(6)	120.2 (3)	C(5a)—C(5a)—C(6)	118.8 (3)
C(5a)—C(5)—C(4a)	120.1 (3)	C(5a)—C(5)—C(1')	119.6 (3)
C(4a)—C(5)—C(1')	120.0 (3)	C(5)—C(4a)—C(11a)	122.5 (3)
C(5)—C(4a)—C(4)	118.2 (3)	C(11a)—C(4a)—C(4)	119.3 (3)
C(11)—C(11a)—C(4a)	124.6 (3)	C(11)—C(11a)—C(1)	118.4 (3)
C(4a)—C(11a)—C(1)	117.0 (3)	C(9a)—C(9)—C(8)	121.4 (4)
C(9)—C(8)—C(7)	121.7 (4)	C(8)—C(7)—C(6)	120.1 (4)
C(5a)—C(6)—C(7)	118.6 (3)	C(4a)—C(4)—C(3)	121.6 (3)
C(4)—C(3)—C(2)	120.1 (3)	C(3)—C(2)—C(1)	119.3 (3)
C(11a)—C(1)—C(2)	122.5 (3)	C(5)—C(1')—C(2')	177.8 (2)
C(1')—C(2')—C(3')	123.9 (3)	C(2')—C(3')—N(1)	111.7 (3)
C(3')—N(1)—C(26)	111.8 (2)	C(3')—N(1)—C(27)	110.9 (3)
C(26)—N(1)—C(27)	111.4 (3)	O(1)—C(21)—O(2)	123.4 (3)
O(1)—C(21)—C(22)	117.0 (3)	O(2)—C(21)—C(22)	119.6 (3)
C(21)—C(22)—C(23)	131.0 (2)	C(22)—C(23)—C(24)	132.4 (2)
C(23)—C(24)—O(3)	119.7 (3)	C(23)—C(24)—O(4)	118.7 (3)
O(3)—C(24)—O(4)	121.6 (3)		

non-H atoms is given in Fig. 1; H atoms on C are numbered such that H(*mn*) is the *n*th H atom on C(*m*). H(1) and H(2) are bonded to N(1) and O(4) respectively.

**Discussion.** In animal tests reflecting potential anti-depressant activity, DMPD was found to be 4 to 16 times more potent than imipramine; as a CNS depressant it was found to be more potent than meprobamate, phenobarbital or chlordiazepoxide (Roszkowski *et al.*, 1975). It has been suggested by these workers that this combination of depressant-anti-depressant activity may be useful clinically.

In DMPD the angle between the planes of the benzene rings (138°) and the distances of the N atom from the centroids of the benzene rings *A* and *B* (6.30, 6.94 Å) are roughly comparable with the values (130°, 6.25, 7.22 Å) previously found in one of the two

Fig. 2. Stereopair of the cation. Ring *A* is on the right.Fig. 3. Stereo packing diagram viewed down *a*. H atoms are omitted. Hydrogen bonds are indicated by thin lines.

crystallographically independent molecules of the conformationally more flexible imipramine (Post *et al.*, 1974, 1975). At present, however, it is difficult to assess fully the significance of these comparisons because of the lack of information concerning DMPD's activity *in vitro* in inhibiting biogenic amine uptake.

The cation and anion are linked by a hydrogen bond; associated distances are N(1)⋯O(1) 2.69, H(1)⋯O(1) 1.73 Å. There is also an intra-anionic hydrogen bond with O(2)⋯O(4) 2.45 and O(2)⋯H(2) 1.58 Å. There are no other unusually short interatomic contacts.

We thank Dr A. P. Roszkowski, Syntex Research, Palo Alto, California for providing the crystals, the MRC for financial support and the SRC for provision of the diffractometer. Figures were drawn with *PLUTO* written by Dr W. D. S. Motherwell; all other crystallographic programs were written by Dr G. M. Sheldrick.

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*Acta Cryst.* (1978). B34, 2030–2033

## Protonated 1-Methylcytosine Triiodide

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(Received 24 October 1977; accepted 13 January 1978)

**Abstract.**  $(C_5H_8N_3O)(I_3)$ , orthorhombic, *Pnma*,  $a = 12.980$  (3),  $b = 7.113$  (3),  $c = 13.415$  (4) Å,  $V = 1238.6$  Å<sup>3</sup>,  $Z = 4$ ,  $M_r = 506.84$ ,  $D_c = 2.718$ ,  $D_m = 2.729$  (4) g cm<sup>-3</sup>. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic with the inclusion, but no refinement, of the H atoms) based on 1881 counter-collected  $F_o$ 's led to a final  $R$  value of 0.051. The structure consists of protonated 1-methylcytosine cations and unsymmetrical and nonlinear triiodide anions [ $d_{1-1} = 2.794$  (1) and 3.123 (1) Å, and the intramolecular angle = 177.6 (1)°]. The structure is dominated by layers ( $y = \pm \frac{1}{4}$ ) of linear chains of cations (intermolecularly hydrogen bonded) and anions [with a triiodide I–I intermolecular distance of 3.755 (1) Å] generated by screw axes parallel to **a**. Within these layers, the coupling between the cationic and anionic chains is accomplished *via* hydrogen bonding between one of the terminal I atoms of the triiodide anion and the protonated cation. Interlayer interactions are clearly electrostatic in nature. A rationale for the instability of the crystals owing to the loss of  $I_2$  is presented on the basis of the crystal structure.

**Introduction.** Over the past several years, there has been considerable interest in crystalline polyhalides, not the least of which are the polyiodides. Crystalline polyiodides range in size from the  $I_3^-$  anion to discrete, macromolecular species such as  $I_{16}^{4-}$  (Herbstein & Kapon, 1975). Broadly speaking, the polyiodide salts may be classified into the following four categories (with examples given for each): (1) large-cation polyiodides [tetraphenylarsonium triiodide (Runsink, Swen-Walstra & Migchelsen, 1972), cesium triiodide (Run-

sink *et al.*, 1972), tetraethylammonium heptaiodide (Havinga & Wiebenga, 1958), ferricinium triiodide (Bernstein & Herbstein, 1968)]; (2) neutral organic alkali-metal triiodides [(xanthotoxin)<sub>2</sub>KI<sub>3</sub> (Kapon & Herbstein, 1974)]; (3) protonated organic heterocycles with polyiodides [(phenacetin)<sub>2</sub>HI<sub>5</sub> (Herbstein & Kapon, 1972), (theobromine)<sub>2</sub>H<sub>2</sub>I<sub>8</sub> (Herbstein & Kapon, 1975)]; (4) radical-cation (open-shell) polyiodides [hepta(tetrathiofulvalene) pentaiodide (Daly & Sanz, 1975; Johnson & Watson, 1976), bis(tetrathio-tetracene) triiodide (Isett & Perez-Albuerna, 1977; Smith & Luss, 1977; Buravov *et al.*, 1976)]. The radical-cation polyiodide salts in this last category fall into the range of quasi-one-dimensional conductors in which the linear (normally disordered) polyiodide chains may contribute to the conductivity properties.

Our continuing interest in the structural properties of protonated nucleic acid derivatives and their interaction with different types of anionic species (Kistenmacher, Rossi & Marzilli, 1978*a,b*) prompted us to report here a structural analysis of the salt formed from protonated 1-methylcytosine and the triiodide anion, which falls into category (3) above. The crystal structure is highly ordered (but unstable owing to the loss of  $I_2$  in air) and allows a detailed determination of the structural properties to be made.

Protonated 1-methylcytosine triiodide was prepared by the oxidation of 1-methylcytosine hemihydroiodide hemihydrate (Kistenmacher, Rossi & Marzilli, 1978*a*) in aqueous 1*N* perchloric acid. Multifaceted, red-orange crystals were obtained directly from the reaction mixture. The crystals decompose in air, owing to a loss of  $I_2$  (see below), so all further manipulations were performed on crystals coated with a thin film of low-