shorter than the expected van der Waals distance (Pauling, 1960), while the methyl hydrogen contact, $H(2C1) \cdots H(2C3)$, 2·46 (9) Å, is slightly greater. Presumably, the distortion of C(1) and C(3) out of the plane of the triazine ring results in a disruption of the aromaticity of the ring system.

Bugg et al. (1971) concluded that the nucleic acid constituents, in addition to base, overlap as a result of positioning a polar substituent over the ring system of an adjacent base, and interactions between oxygen substituents and adjacent base rings are important. The contacts between $O(4_c)$ and C(2) and N(3) of 3·975 (3) and 3·990 (3) Å are an example of this type of interaction. The distance of $O(4_c)$ from the triazine ring is 3·34 Å. C(2) is 0·39 Å out of the plane of the symmetry-related triazine ring. The angle $C(4_c)-O(4)_c \cdots C(2)$ is 124°. Thus this is apparently a dipole–dipole interaction with one of the unshared electron pairs of the sp^2-hybridized O pointing directly at C(2).

Another significant intermolecular contact involves the carbonyl O(2) which is involved in the dipole–dipole interaction with the triazine ring. It is also hydrogen bonded to H(1N7) in a typical $N-H \cdots O$ hydrogen bond of the amide type (Pimentel & McClellan, 1960). The $H(1N7) \cdots O(2)$ distance is 2·08 (3) Å, and $N(7) \cdots O(2)$ 2·932 (3) Å. The $N(7)-H(1N7) \cdots O(2)$ angle is 167°.

The intermolecular interactions described above link the molecules together in the bc plane. The shortest contact between the molecules in the general direction of the a axis is between O(6) and C(3) and at 3·121 (4) Å is slightly shorter than the van der Waals distance.

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11-anti-Ammonio-8-chlorobenzo[b]bicyclo[3.3.1]nona-3,6a(10a)-diene Hemiformate Hemiperchlorate: a Potent and Selective Inhibitor of Serotonin Uptake

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Abstract. $C_{13}H_{15}ClN^+ \cdot \frac{1}{2}CHO_2^- \cdot \frac{1}{2}ClO_4^-$, $M_r = 292·96$, orthorhombic, Pbcn, $a = 33·258$ (10), $b = 10·974$ (3), $c = 7·175$ (2) Å, $U = 2619$ Å^3, $Z = 8$, $D_x = 1·486$ Mg m^{-3}, μ(Cu $K\alpha$) $= 3·4$ mm^{-1}. $R = 0·042$ for 1537 unique reflexions. The ClO_4^- and formate ions are associated with special positions on twofold axes, the formate being disordered.

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Introduction. A common pharmacological feature of the tricyclic antidepressants imipramine and chlor-

imipramine (Post, Kennard & Horn, 1975; Post & Horn, 1977) is that they inhibit the neuronal uptake of both noradrenaline (NA) and 5-hydroxytryptamine (5-HT) (serotonin), *i.e.* they are not very selective (Horn, 1976). In recent years, however, more selective inhibitors of 5-HT uptake have been synthesized (Fuller & Wong, 1977); one of these is 11-*anti*-ammonio-8-chlorobenzo[*b*]bicyclo[3.3.1]nona-3,6a(10a)-diene chloride, also known by the trivial name Org.6582. Here we report the structure of the mixed formate/perchlorate salt of the same cation (I).

(I)
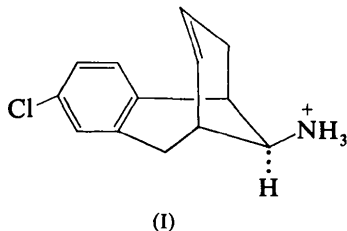
A sample of Org.6582 was kindly provided by Organon Laboratories Ltd. Repeated attempts to obtain suitable crystals from a wide variety of solvents were unsuccessful. Eventually colourless blades were obtained by diffusion of diisopropyl ether into a solution of Org.6582 in 85% formic acid. A crystal $0.4 \times 0.08 \times 0.04$ mm was used to collect data on a Syntex $P2_1$ diffractometer with monochromated Cu $K\alpha$ radiation. Cell dimensions were obtained by least squares from 15 strong reflexions. Systematic absences $0kl$, k odd; $h0l$, l odd; $hk0$, $h + k$ odd indicated space group $Pbcn$. 2124 reflexions were collected in the region $3° < 2\theta < 116°$; after application of Lp corrections, averaging equivalent reflexions gave 1785 unique reflexions with $F > 4\sigma(F)$.

Attempts to solve the structure by automatic multi-solution Σ_2 sign expansion (with *SHELX*) were unsuccessful because very few high E reflexions with $h + k$ odd were present. A solution was obtained with the program *XCSD*, with six such reflexions forced into the starting set, and with suitably renormalized E values. The cation was clearly shown on the best E map, but identification of the anions was less straight-forward. Three peaks corresponding to a tetrahedral species on a twofold axis were tentatively assigned as half a perchlorate ion (confirmed by successful refine-ment). Since the starting material contained only chloride anion (confirmed by elemental analysis), we are uncertain what has caused the presence of per-chlorate. Three other peaks, two of which lay on a two-fold axis, were identified as a disordered formate ion, consistent with overall electrical neutrality.

Least-squares refinement, in the course of which all H atoms of the cation were identified by difference syntheses, proceeded to a final R of 0.042. The formate H was not found. All non-H atoms were anisotropic;

Table 1. *Atom coordinates* $(\times 10^4)$

Overall isotropic temperature factor for H atoms: 0.052 (2) Å^2.

	x	y	z
C(1)	1176 (1)	1177 (2)	2826 (4)
C(2)	1116 (1)	1716 (3)	4793 (4)
C(3)	1088 (1)	3072 (3)	4751 (4)
C(4)	1048 (1)	3718 (3)	3193 (5)
C(5)	1033 (1)	3154 (3)	1295 (4)
C(6)	1448 (1)	3195 (3)	313 (4)
C(6a)	1739 (1)	2263 (3)	1092 (4)
C(7)	2144 (1)	2357 (3)	619 (4)
C(8)	2412 (1)	1481 (3)	1200 (4)
C(9)	2289 (1)	498 (3)	2269 (4)
C(10)	1888 (1)	425 (3)	2762 (4)
C(10a)	1610 (1)	1296 (2)	2200 (4)
C(11)	906 (1)	1821 (2)	1432 (4)
N(1)	474 (1)	1720 (2)	1998 (3)
Cl(1)	2917 (1)	1591 (1)	576 (1)
H(1)	1098	222	2890
H(2)	1367	1455	5658
H(3)	842	1353	5377
H(4)	1101	3557	6059
H(5)	1026	4697	3304
H(6)	818	3675	495
H(7)	1575	4093	491
H(8)	1405	3016	−1154
H(9)	2247	3119	−205
H(10)	2500	−193	2705
H(11)	1788	−330	3609
H(12)	938	1393	84
H(13)	299	1982	1031
H(14)	432	2207	3075
H(15)	421	891	2287
Cl(2)	5000	3592 (1)	2500
O(21)	4911 (1)	2806 (2)	879 (3)
O(22)	4651 (1)	4349 (2)	2955 (3)
C(30)	0	5042 (4)	2500
O(31)	0	3971 (3)	2500
O(32)	−292 (1)	5561 (4)	3264 (7)

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

C(1)–C(2)	1.543 (6)	C(1)–C(10a)	1.517 (6)
C(1)–C(11)	1.518 (6)	C(2)–C(3)	1.492 (5)
C(3)–C(4)	1.330 (6)	C(4)–C(5)	1.496 (6)
C(5)–C(6)	1.550 (6)	C(5)–C(11)	1.526 (6)
C(6)–C(6a)	1.514 (6)	C(6a)–C(7)	1.392 (5)
C(6a)–C(10a)	1.394 (5)	C(7)–C(8)	1.377 (5)
C(8)–C(9)	1.386 (5)	C(8)–Cl(1)	1.742 (5)
C(9)–C(10)	1.379 (5)	C(10)–C(10a)	1.391 (5)
C(11)–N(1)	1.497 (4)		

C(2)–C(1)–C(10a)	111.2 (3)	C(2)–C(1)–C(11)	110.3 (3)
C(10a)–C(1)–C(11)	109.1 (3)	C(1)–C(2)–C(3)	111.8 (3)
C(2)–C(3)–C(4)	123.7 (4)	C(3)–C(4)–C(5)	123.2 (4)
C(4)–C(5)–C(6)	111.8 (3)	C(4)–C(5)–C(11)	110.3 (3)
C(6)–C(5)–C(11)	107.6 (3)	C(5)–C(6)–C(6a)	112.4 (3)
C(6)–C(6a)–C(7)	118.5 (4)	C(6)–C(6a)–C(10a)	121.9 (3)
C(7)–C(6a)–C(10a)	119.5 (4)	C(6a)–C(7)–C(8)	120.1 (4)
C(7)–C(8)–C(9)	121.2 (4)	C(7)–C(8)–Cl(1)	119.9 (3)
C(9)–C(8)–Cl(1)	118.8 (3)	C(8)–C(9)–C(10)	118.2 (4)
C(9)–C(10)–C(10a)	121.9 (4)	C(1)–C(10a)–C(6a)	121.8 (3)
C(1)–C(10a)–C(10)	119.2 (3)	C(6a)–C(10a)–C(10)	118.9 (3)
C(1)–C(11)–C(5)	109.0 (3)	C(1)–C(11)–N(1)	110.7 (3)
C(5)–C(11)–N(1)	110.7 (3)		

$$C_{13}H_{15}ClN^{+}.\tfrac{1}{2}CHO_2^{-}.\tfrac{1}{2}ClO_4^{-}$$

Table 3. *Selected torsion angles* (°)

The sign convention is as defined by Klyne & Prelog (1960).

C(10a)–C(1)–C(2)–C(3)	78·8 (4)	C(10a)–C(1)–C(11)–N(1)	179·8 (3)	C(4)–C(5)–C(11)–N(1)	69·6 (4)
C(11)–C(1)–C(2)–C(3)	−42·3 (4)	C(1)–C(2)–C(3)–C(4)	11·1 (5)	C(6)–C(5)–C(11)–C(1)	69·8 (4)
C(2)–C(1)–C(10a)–C(6a)	−95·7 (4)	C(2)–C(3)–C(4)–C(5)	−0·9 (6)	C(6)–C(5)–C(11)–N(1)	−168·2 (3)
C(2)–C(1)–C(10a)–C(10)	83·5 (4)	C(3)–C(4)–C(5)–C(6)	−97·8 (4)	C(5)–C(6)–C(6a)–C(7)	−167·1 (4)
C(11)–C(1)–C(10a)–C(6a)	26·2 (4)	C(3)–C(4)–C(5)–C(11)	21·9 (5)	C(5)–C(6)–C(6a)–C(10a)	15·5 (5)
C(11)–C(1)–C(10a)–C(10)	−154·6 (3)	C(4)–C(5)–C(6)–C(6a)	75·1 (4)	C(6)–C(6a)–C(7)–C(8)	−175·7 (4)
C(2)–C(1)–C(11)–C(5)	64·2 (4)	C(11)–C(5)–C(6)–C(6a)	−46·2 (4)	C(10a)–C(6a)–C(7)–C(8)	1·8 (5)
C(2)–C(1)–C(11)–N(1)	−57·8 (4)	C(4)–C(5)–C(11)–C(1)	−52·4 (4)	C(6)–C(6a)–C(10a)–C(1)	−5·2 (5)
C(10a)–C(1)–C(11)–C(5)	−58·2 (4)				

C—H, N—H distances and H–X–H angles (X = N or C) were fixed at 1·08, 0·95 Å and 109·5° respectively. An overall isotropic temperature factor for H atoms was employed. The final $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$ was 0·048; the weighting scheme was $w = 1/[\sigma^2(F) + 0·001F^2]$. A final difference map showed no peaks >0·24 e Å^{-3}. Final atomic coordinates are given in Table 1,* bond lengths and angles and torsion angles in Tables 2 and 3. Diagrams of the structure are given in Figs. 1 and 2.

Discussion. We assume throughout that the structure of the cation reported here is identical to that in Org.6582.

Sugrue, Goodlet & Mireylees (1976) have shown that *in vivo* Org.6582 is five times more potent than chlorimipramine as an inhibitor of 5-HT uptake, whilst unlike the latter drug it does not inhibit NA uptake *in vivo*; it is thus more selective. A further advantage of Org.6582 is that, unlike chlorimipramine and imipramine, it is a rigid molecule; thus the values for interatomic distances found in the crystal should be virtually

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34283 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
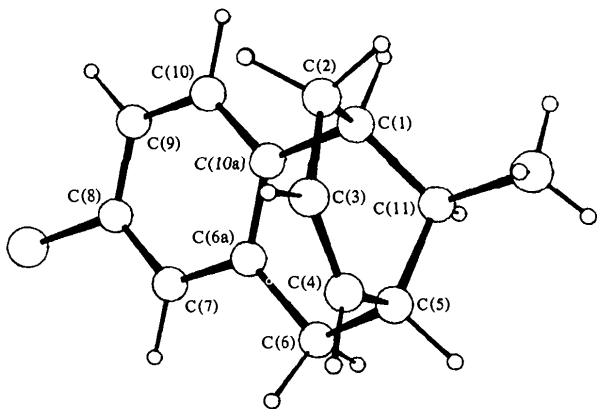
identical to those occurring at the biological receptor. In addition, it is known that Org.6582 is a competitive inhibitor of 5-HT uptake (Goodlet, Mireylees & Sugrue, 1977) and so possibly interacts with the same uptake site on the membrane as 5-HT itself. In connexion with its interaction at the 5-HT uptake site we have calculated the following parameters: N atom to benzene ring centroid, 5·14 Å; N···Cl distance, 8·19 Å; and the height of the N atom above the mean plane of the benzene ring, 0·55 Å. In future publications we intend to compare certain of these parameters with those in 5-HT, and also with those in other selective inhibitors of 5-HT uptake.

The —NH$_3^+$ group of the cation is hydrogen-bonded to the perchlorate anion, with N(1)···O(21) 2·84, H(13)···O(21) 1·90 Å (second atoms at $-\tfrac{1}{2} + x, \tfrac{1}{2} - y, -z$), N(1)···O(22) 2·72, H(15)···O(22) 1·78 Å (second atoms at $\tfrac{1}{2} - x, -\tfrac{1}{2} + y, z$). As a consequence of this strong hydrogen bonding, the perchlorate O atoms show no signs of disorder. The formate ion is, however, less satisfactory. High temperature factors for O(31) and an unsatisfactory length of 1·18 Å for C(30)–O(31) suggest that O(31) may be near, rather than on, the twofold axis; but no such model could be refined. There is no evidence for hydrogen bonding involving the formate ion; there is a fairly short N(1)···O(31) (at x,y,z) contact of 2·95 Å, but the corresponding H···O distance is large (2·45 Å). There is a short contact of 2·63 Å between O(21) and O(32) (at $\tfrac{1}{2} + x, -\tfrac{1}{2} + y, \tfrac{1}{2} - z$), but no H atoms are involved.

A projection of the structure down **c** (Fig. 2) shows that layers of anions run parallel to **b** at $x \simeq n/2$.

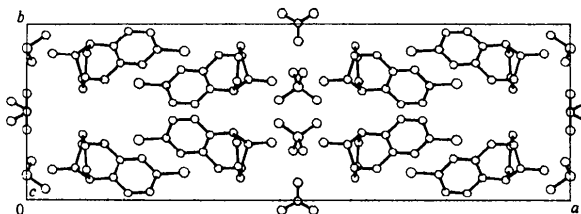Fig. 1. Perspective view of the cation, showing the C atom numbering.

Fig. 2. Packing diagram of the unit-cell contents projected down **c**. H atoms are omitted for clarity. Both positions of the disordered formate ion are shown. At the cell edges only half perchlorate ions are shown.

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3,4-Seco-3,5-cyclo-1,2-dihydro-N(1),N(4)-dimethylstrictamine Methiodide

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Abstract. $C_{23}H_{31}N_2O_2^+ \cdot I^-$, monoclinic, $P2_1$, $a = 6.577$ (5), $b = 12.194$ (6), $c = 13.342$ (6) Å, $\beta = 95.8$ (1)°, $Z = 2$, final R value 9.7%. The C and E rings form a bicyclic (3.2.1) system with the six-membered ring in a chair conformation. Both rings are joined on their *endo* face by a three-atom segment. The $15R$ configuration was established using the anomalous dispersion of iodine.

Introduction. A crystal of $0.2 \times 0.2 \times 0.4$ mm was mounted on a Philips PW 1100 diffractometer and 2547 reflections were collected using graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) for θ up to 68°. There were 401 Bijvoet pairs and 1891 independent reflections greater than $3\sigma(I)$ were finally retained for the calculations.

The position of the I anion was determined ($x = 0.007$, $y = 0.500$, $z = 0.393$) by an analysis of the Patterson function. Initial phases computed from the I, followed by successive full-matrix least-squares refinements of the three-dimensional electron density map led to the location of 28 atoms of the molecule. The O and N atoms were distinguished following simple mechanistic and biogenetic considerations. The H atoms directly attached to the C atom skeleton were introduced (C–H = 1.00 Å, C–C–H = 109 or 120°) and were assigned the B values of the bonded C atoms. Refinement was pursued considering all the atomic coordinates, isotropic temperature factors for the C, N, O atoms, and anisotropic temperature factors for iodine. After the anomalous dispersion was introduced, an unweighted agreement factor of 0.097 was obtained for the absolute configuration shown in Fig. 1. The enantiomer led to $R = 0.104$. At this stage the

difference Fourier map did not show any significant electron density which could be related to the H atoms of the methyl groups. The atomic coordinates are listed in Table 1, and the bond lengths and bond angles in Tables 2 and 3, respectively. Scattering factors for the non-hydrogen atoms were taken from Doyle & Turner (1968) while those for H atoms were from Stewart, Davidson & Simpson (1965).*
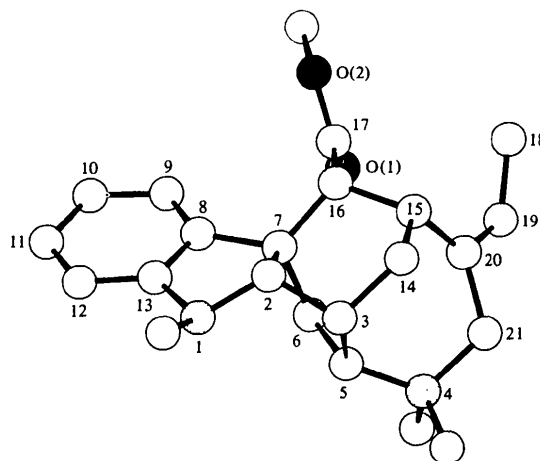

Fig. 1. Molecular structure and conformation.