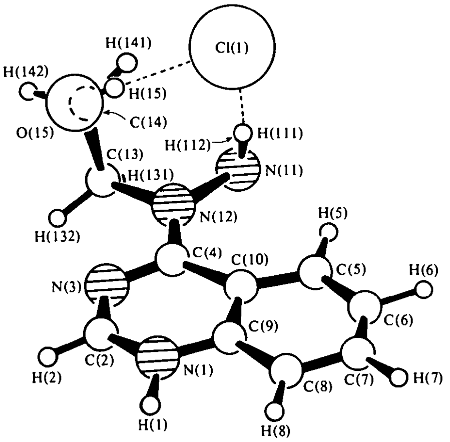

Fig. 1. A view of one molecule showing the atomic numbering. H atoms are numbered according to the atoms to which they are bonded.

syntheses) such that the lone pair of electrons on N(11) is directed towards the C(5)—H(5) bond. In this context we note that the NMR spectrum of (I) [hydrochloride in Me_2SO-d_6] contains an exceptionally low-field 5-proton signal at δ 9·52 (Barker & Taylor, 1976).

Consideration of the structural formula of (I) suggests three sites at which protonation could plausibly have occurred, namely N(1), N(3) and N(11). However, we have already noted the short separation between N(11) and the C(5)—H(5) bond, while N(3) is also in close proximity to the C(13)—H(132) bond. On steric grounds, therefore, N(3) and N(11) would appear to be less favourable sites for protonation than N(1), where, in addition, the interactions between H(1) and H(8) are partly relieved by the boat conformation of the pyrimidine ring.

The organic cations are linked to the Cl^- ions by a complex network of N—H···Cl^- and O—H···Cl^- hydrogen bonds. Other intermolecular distances correspond to, or are greater than, van der Waals contact distances.

We thank Dr A. Barker and Mr P. J. Taylor of Imperial Chemical Industries, Pharmaceuticals Division, who brought this problem to our attention, provided crystals, and who participated in many stimulating discussions.

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Acta Cryst. (1979). B**35**, 1509–1512

1,4,5,6-Tetrahydro-1,5,*N*-trimethyl-4,6-dioxo-1,3,5-triazine-2-carboxamide

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(*Received* 25 *July* 1978; *accepted* 13 *February* 1979)

Abstract. $C_7H_{10}N_4O_3$, M_r = 198·18, monoclinic, $P2_1/c$, a = 9·394 (2), b = 12·461 (4), c = 7·739 (2) Å, β = 93·45 (2)°, U = 904·2 (4) Å^3, Z = 4, d_m = 1·45 (flotation), d_c = 1·46 Mg m^{-3}, $F(000)$ = 416. The structure was solved by direct methods. Full-matrix least-squares refinement converged to R = 0·053 for 1297 observed reflections. The molecules dimerize, presumably as a result of a dipole–dipole interaction of the type found in nucleic acids. This interaction appears to be of sufficient strength to distort the aromaticity of

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the triazine ring. Hydrogen bonding and electrostatic interactions are discussed as possible forces affecting packing.

Introduction. This study was undertaken to elucidate the structure of a compound isolated as one major component in the complex product mixture resulting from the reaction of ozone with caffeine. The investigation of this component by mass spectrometry, infrared spectroscopy, proton magnetic resonance, and carbon magnetic resonance yielded much useful information, but did not permit characterization of the compound.

Crystals of the compound, grown by slow evaporation of a chloroform solution, were isolated as thin colorless plates. Preliminary examination using precession photography revealed monoclinic symmetry conforming to space group $P2_1/c$ (No. 14) with systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$.

Intensity data were collected at room temperature (295 K) on a Syntex $P\bar{1}$ autodiffractometer (Mo $K\alpha$ radiation, graphite monochromator, $2\theta_m = 12{\cdot}2°$). The cell dimensions were determined on the diffractometer and were refined by a least-squares fit of the parameters to 15 carefully centered reflections using programs supplied by Syntex. Intensity measurements were made using the θ–2θ scanning technique as programmed by Syntex.

Reflections were surveyed within a single unique quadrant over the range $2{\cdot}0° \leq 2\theta \leq 65{\cdot}0°$. The data were corrected for a decline of 5·5% in observed intensity and for Lorentz and polarization effects. Of the 3432 unique reflections surveyed, 1297 were determined to have intensity significantly above background and were used for the solution and refinement of the structure. A reflection was considered significant when $F_o^2 > 3{\cdot}0\sigma(F_o^2)$ where $\sigma(F_o^2) = (1/\text{Lp})\{\text{TSC} + \text{BACK} + [P(\text{TSC} - \text{BACK})]^2\}^{1/2}$. TSC is the total counts collected during the measurement cycle and BACK is the number of counts accumulated during the background-counting portion of the measurement cycle. For P, a damping factor to down-weight stronger intensities, a value of 0·04 was used (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967). No correction was made for absorption [μ(Mo $K\alpha$) = 0·1087 mm^{-1}].

The structure was solved by direct methods using the program *MULTAN* (Germain, Main & Woolfson, 1971). Phases were calculated for all of the 250 reflections with $|E|$'s greater than 1·75. An E map revealed the positions of 14 atoms in the top 15 unique peaks. After five cycles of full-matrix least-squares isotropic refinement, $R = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}34$, the thermal parameters for two atoms in the model were significantly greater than the rest of the model (10·3 and 12·3 *versus* 1·1 to 5·9 Å^2). These two atoms and an adjacent atom were removed from the model and a new difference map calculated. This map revealed three peaks, one which corresponded to the adjacent atom and two which were new. Isotropic refinement on this model with atom types assigned on the basis of isotropic thermal parameters, geometry, and chemical considerations converged with R = 0·120. Refinement with all atoms treated anisotropically converged with R = 0·073. The positions of all ten H atoms were located in the subsequent three-dimensional difference map. The H atoms were added to the model with isotropic thermal parameters and the entire model was refined using full-matrix least-squares procedures to convergence; R = 0·0530 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0{\cdot}0539$. The standard deviation of an observation of unit weight was 1·59. The maximum shift over error for all parameters was 0·296. The average value was 0·020 for all parameters. The ratio of observations to parameters was 7·5 to 1. A final three-dimensional difference map was featureless. The weighting scheme used for all refinements was based on counting statistics where $w = 1/\sigma^2(F_o) = 4{\cdot}0F_o^2/\sigma^2(F_o^2)$. The scattering factors used for O, N, C, and H were taken from *International*

Table 1. *Final atomic parameters*

The values of the atomic fractional coordinates and their estimated standard deviations (in parentheses here and in Table 2) are multiplied by 10^4 for non-hydrogen atoms and by 10^3 for hydrogen atoms.

	x	y	z		x	y	z
N(1)	863 (2)	4132 (2)	3014 (3)	C(1)	1664 (4)	4786 (3)	1819 (5)
O(2)	−1027 (2)	5253 (2)	2573 (3)	C(2)	−545 (3)	4430 (2)	3191 (3)
N(3)	−1336 (2)	3737 (2)	4124 (3)	C(3)	−2862 (3)	3963 (3)	4149 (5)
O(4)	−1573 (2)	2162 (2)	5537 (2)	C(4)	−813 (3)	2775 (2)	4802 (3)
N(5)	620 (2)	2555 (2)	4630 (3)	C(5)	2931 (3)	2924 (2)	3661 (3)
O(6)	3845 (2)	3605 (2)	3958 (3)	C(6)	1355 (3)	3203 (2)	3749 (3)
N(7)	3168 (2)	1903 (2)	3339 (3)	C(7)	4602 (4)	1467 (4)	3331 (7)
H(1N7)	245 (3)	146 (2)	318 (4)	H(2C3)	−328 (4)	380 (3)	310 (5)
H(1C1)	257 (4)	445 (3)	178 (5)	H(3C3)	−330 (4)	345 (3)	482 (5)
H(2C1)	117 (5)	483 (4)	75 (6)	H(1C7)	466 (4)	78 (4)	310 (5)
H(3C1)	181 (4)	543 (3)	218 (5)	H(2C7)	523 (5)	193 (4)	274 (6)
H(1C3)	−301 (3)	465 (3)	458 (4)	H(3C7)	504 (4)	154 (3)	443 (6)

Tables for X-ray Crystallography (1974). Table 1 gives the final parameters for the atoms.* All calculations except the data reduction were performed using the programs contained in the Northwestern University Crystallographic Computing Library of J. A. Ibers. The data reduction program, written in this laboratory, was based in part on routines supplied by Syntex Analytical Instruments. The function minimized in all least-squares procedures was $\sum w(|F_o| - |F_c|)^2$.

Discussion. Comparison of bond lengths of the chemically similar bonds, N(1)—C(2), C(2)—N(3), N(3)—C(4) and C(4)—N(5), in the triazine moiety (Fig. 1) with those tabulated for uracil (Voet & Rich, 1970) shows no significant differences. The N(1)—C(6) bond is significantly shorter than the other conjugated heterocyclic C—N bonds, indicating a greater π-bonding contribution. The N(5)—C(6) bond appears to be predominantly double in character, the length being within the range given by Sutton (1965) for C=N. Examination of the bonding in the carboxamide moiety reveals nothing unusual.

Equations for least-squares planes calculated by the method of Hamilton (1961) and the deviations from the planes are given in Table 2. The carboxamide group is planar within experimental limits. The triazine ring is not, with variations from planarity as high as 10 times the standard deviation. The deviations from planarity and the almost pure double-bond character of the N(5)—C(6) bond indicate that the ring is only partially aromatic.

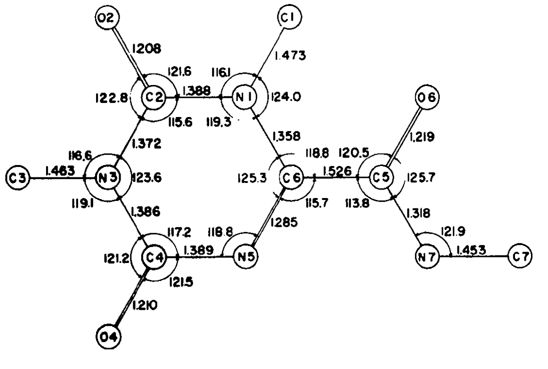

Fig. 1. Bond lengths (Å) and angles (°) for the title compound. Standard deviations are in the range 0·003 to 0·004 Å for bond lengths and 0·2 to 0·3° for bond angles. Distances and angles involving H atoms are omitted for clarity; they vary from 0·86 to 0·96 (5) Å, and 100 to 120 (3)°.

Table 2. *Least-squares planes through the triazine and methylcarboxamide moieties*

x, *y* and *z* are fractional cell coordinates. The atoms which are listed without errors were not included in the calculation of the plane. C(2)† is in the symmetry-related position $-x$, $1 - y$, $1 - z$. The dihedral angle between the two planes is 135·3°.

(*a*) Triazine ring

$2{\cdot}0535x + 6{\cdot}1153y + 6{\cdot}4137z - 4{\cdot}6432 = 0{\cdot}0$

N(1)	−0·006 (2) Å	C(1)	−0·208 A
C(2)	0·001 (2)	O(2)	0·009
N(3)	0·013 (2)	C(3)	−0·147
C(4)	−0·033 (3)	O(4)	−0·093
N(5)	0·016 (2)	C(5)	0·095
C(6)	−0·002 (2)	C(2)†	3·244

(*b*) Carboxamide moiety

$0{\cdot}65892x + 2{\cdot}4900y - 7{\cdot}5824z + 1{\cdot}8519 = 0{\cdot}0$

C(5)	−0·003 (3) Å	C(7)	−0·005 (5) Å
O(6)	0·001 (3)	C(6)	−0·104
N(7)	0·002 (2)	H(1N7)	−0·036

Fig. 2 shows four symmetry-related molecules, which have significant intermolecular contacts. The separation between triazine rings, related by centers of symmetry, is 3·24 Å. This close contact, which is the result of base stacking of the type reviewed by Bugg, Thomas, Sundaralingam & Rao (1971), provides a possible explanation for the deviations from planarity seen in the triazine ring. As a result of the close approach of the rings, C(2) and C(2_a) are separated by only 3·250 (5) Å and C(1) and C(3_a) as well as C(3) and C(1_a) are pushed away from each other and out of the plane of the triazine ring. The resulting contact between C(1) and C(3) is 3·607 (6) Å, considerably

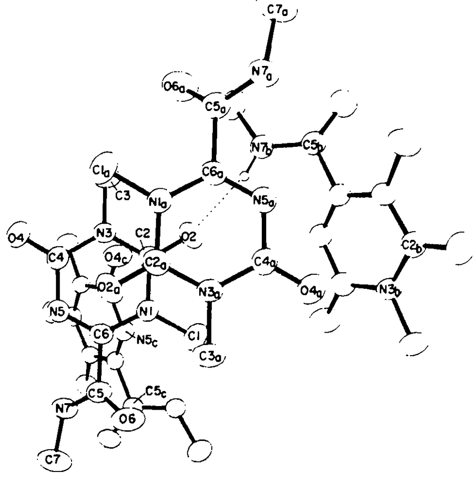

Fig. 2. Projection of the structure on to the plane of the triazine ring showing the base-stacking interactions and the N(7)—H··· O(2) hydrogen bond. Atoms in the molecule with no subscripts on the atom labels are in symmetry position *x,y,z*. Those subscripted are in symmetry positions (*a*) $-x$, $1{\cdot}0 - y$, $1{\cdot}0 - z$, (*b*) $-x, \frac{1}{2} + y, \frac{1}{2} - z$, and (*c*) $x, \frac{1}{2} - y, -\frac{1}{2} + z$.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34274 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

shorter than the expected van der Waals distance (Pauling, 1960), while the methyl hydrogen contact, H(2C1)···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···O hydrogen bond of the amide type (Pimentel & McClellan, 1960). The H(1N7)···O(2) distance is 2·08 (3) Å, and N(7)···O(2) 2·932 (3) Å. The N(7)–H(1N7)···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.

We wish to thank the University of Colorado Computing Center for their support of this project with CDC 6400 computing time. This research was also assisted by an Institutional Research Grant from the National Science Foundation for the purchase of the autodiffractometer. RCH wishes to thank Drs T. H. Koch, B. Ellison and C. G. Pierpont for many helpful discussions regarding this problem. The financial support of the Environmental Protection Agency (Grant R804472010) is gratefully acknowledged.

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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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(*Received* 16 *January* 1979; *accepted* 19 *February* 1979)

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

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

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