Structure of 2,4,6-Tris(*N,N*-dimethylamino)-1,3,5-oxadiazinium Chloride Dihydrate, C$_9$H$_{18}$N$_5$O$^+$.Cl$^-$.2H$_2$O*

By Philip Rushton, Carl H. Schwalbe and Malcolm F. G. Stevens

Department of Pharmacy, The University of Aston in Birmingham, Gosta Green, Birmingham B4 7ET, England

Abstract. $M_r = 283.75$, monoclinic, $P2_1/c$, $a = 7.608$ (4), $b = 16.099$ (7), $c = 12.127$ (8) Å, $\beta = 99.82$ (5)°, $U = 1463.7$ Å^3, $Z = 4$, $D_x = 1.29$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.214$ mm^{-1}, $F(000) = 608$. Final $R = 0.057$ for 1156 observed reflections. The cyclic system shows extensive delocalization to include the exocyclic nitrogen centres, thus maintaining the *N*-methyl substituents nearly coplanar with the ring.

Introduction. Reaction of *N,N*-dimethylcarbamoyl chloride (II) with *N,N*-dimethylcyanamide (III) results in the formation of 2,4,6-tris(*N,N*-dimethylamino)-1,3,5-oxadiazinium chloride (I) in excellent yield. The IR spectrum of the compound appeared, initially, contrary to the cyclic structure (I), *i.e.* a strong band occurred at $v = 1720$ cm^{-1}. However, this crystal-structure analysis revealed that (I) is correct, and the apparently anomalous IR band has been assigned to C=$\overset{+}{N}$Me$_2$ stretching frequencies by using Cl$_2$C=NMe$_2$Cl$^-$ as a model compound. Although other 1,3,5-oxadiazinium systems have been reported (Bredereck & Richter, 1966), the structural evidence has not been conclusive.

Me$_2$NCOCl + 2Me$_2$NCN $\xrightarrow{\Delta}$ (scheme showing ring product I)

(II)   (III)   (I)
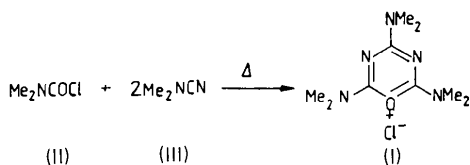
Experimental. Crystals of (I) grew from CH$_2$Cl$_2$ containing a trace of ether as florets of needles up to 3 mm long. A specimen $1.0 \times 0.5 \times 0.1$ mm was prepared.

Although the compound is deliquescent, data collection was successfully carried out with this crystal mounted on a glass fibre. A large evaporating basin containing anhydrous CaCl$_2$ was placed inside the standard Enraf–Nonius radiation enclosure, which then acted as a dry box.

Unit-cell dimensions determined by least-squares analysis of setting angles of 25 reflections, CAD-4

diffractometer, graphite-monochromated Mo $K\alpha$, data collected by ω–2θ scans, scan range in θ (1.00 + 0.35 tan θ)°, scan rate 0.5 to 5.0° min^{-1} depending on intensity; two intensity standards measured every 2 h showed an initial increase of *ca* 20% in first 8–10 h attributable to recrystallization from a liquid film present on the crystal, a negligible decrease in intensity followed; separate correction functions (linear with time) applied to intensities measured during these two phases, 2656 reflections measured with $2 \le \theta \le 25°$ of which 2403 were unique ($R_{int} = 0.042$) and 1156 classified as observed ($F > 3\sigma$), standard deviations assigned on basis of counting statistics and instrument instability, corrections made for Lorentz–polarization effects but not for absorption; structure solved by direct phasing with *SHELX* (Sheldrick, 1976).

For the initial least-squares refinement of non-H-atom positions and isotropic temperature factors, the ring system was treated as if it were a 1,3,5-triazine. An abnormally low temperature factor and a positive peak on a difference electron density map allowed the ring O atom to be distinguished. Two water molecules were also identified. H atoms were entered into calculated positons, assuming minimal steric hindrance for methyl groups and straight hydrogen bonds for water molecules. These were then allowed to refine. In the final least-squares refinement the coordinates and anisotropic thermal parameters of all non-H atoms were adjusted, together with the coordinates and isotropic temperature factors of all H atoms, except H(31) and H(32) which are attached to the water-molecule oxygen O(3). This water molecule may not occupy all available sites in view of the higher temperature factor found for O(3) compared with O(2) and the microanalytical data which indicate *ca* 1.25 H$_2$O.

F_o magnitudes were weighted by $w = 1/[\sigma^2(F_o) + 0.00239 F_o^2]$ and a small empirical extinction correction was applied. The final discrepancy indices are $R = 0.057$, $R_w = 0.052$ for observed data, goodness-of-fit ratio $S = 1.06$. No feature on a final difference electron density map exceeded 0.26 e Å^{-3}.

Discussion. The molecule and its numbering scheme are illustrated in Fig. 1. Atomic coordinates are given in

Table 1,* bond distances and bond angles in Table 2. The cyclic structure including the three exocyclic nitrogen centres has C—N bond lengths within a 0·07 Å range indicating extensive delocalization. This effect is favoured by the near coplanarity of the N-methyl substituents with the ring. The heterocyclic nucleus exhibits partial double bonds and the positive charge is not localized on the oxygen centre. Indeed, multiple bonding to O is relatively minor and the C—O distances of 1·366 (6) and 1·386 (5) Å exceed by 0·02 Å those in 4',6,7-trihydroxyflavylium chloride hydrate (IV) (Ueno & Saito, 1977) and are comparable with the 1·368 (6) Å in furan (V) (Fourme, 1972).
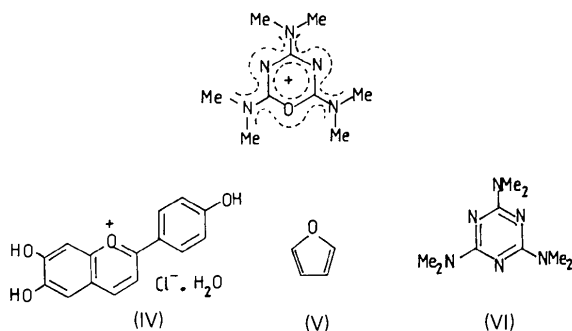
The D_{3h} symmetry observed within experimental error for crystalline hexamethylmelamine (VI) (Bullen, Corney & Stephens, 1972) is reduced here to a crude C_{2v} symmetry with related bond distances differing by 0·03 Å or less. A comparison of distances and angles in (VI) and (I), averaged over the approximate symmetry, shows markedly shorter ($>6\sigma$) ring C—N bonds adjacent to O in (I), little difference in other C—N ring bonds, shorter ($>5\sigma$) exocyclic C_{ring}—N distances in (I), and no clear trend in N-methyl distances. These effects

* Lists of structure factors, anisotropic thermal parameters, mean-plane calculations, and selected geometrical parameters involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38271 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
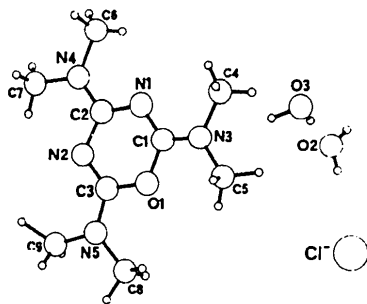

Fig. 1. *PLUTO* (Motherwell, 1972) drawing of the molecule in projection onto its least-squares plane showing the atom-numbering scheme.

Table 1. *Fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *and isotropic temperature factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	U_{eq}/U_{iso}
Cl	1620 (3)	−1207 (1)	−5664 (2)	75 (<1)
O(1)	7139 (5)	−537 (2)	−997 (3)	39 (1)
O(2)	2102 (6)	722 (3)	−4953 (4)	57 (2)
O(3)	4548 (7)	1879 (3)	−5662 (4)	92 (3)
N(1)	6688 (6)	741 (3)	−142 (3)	34 (2)
N(2)	8508 (8)	−321 (3)	874 (3)	36 (2)
N(3)	5614 (6)	475 (3)	−1998 (3)	37 (2)
N(4)	8020 (6)	922 (3)	1678 (4)	41 (2)
N(5)	8671 (2)	−1569 (3)	−53 (4)	37 (2)
C(1)	6472 (7)	265 (3)	−1021 (5)	31 (2)
C(2)	7722 (7)	445 (3)	774 (4)	34 (2)
C(3)	8122 (7)	−790 (3)	−5 (5)	34 (2)
C(4)	4900 (10)	1327 (4)	−2172 (6)	55 (4)
C(5)	5428 (9)	−73 (4)	−2981 (5)	46 (3)
C(6)	7169 (11)	1747 (4)	1688 (6)	60 (4)
C(7)	9229 (9)	659 (5)	2700 (5)	56 (4)
C(8)	8116 (10)	−2109 (4)	−1013 (6)	53 (4)
C(9)	9668 (10)	−1949 (4)	954 (6)	61 (4)
H(21)	199 (7)	14 (4)	−525 (5)	150 (54)
H(22)	108 (6)	87 (3)	−474 (4)	58 (29)
H(31)*	378	150	−544	105 (42)
H(32)*	562	168	−529	105 (44)
H(41)	373 (6)	130 (3)	−243 (4)	64 (31)
H(42)	539 (7)	154 (4)	−280 (5)	139 (50)
H(43)	498 (6)	165 (4)	−150 (4)	95 (38)
H(51)	417 (7)	6 (4)	−352 (5)	131 (50)
H(52)	537 (6)	−68 (4)	−278 (5)	107 (41)
H(53)	623 (6)	4 (4)	−338 (5)	120 (46)
H(61)	673 (6)	182 (4)	241 (5)	114 (42)
H(62)	665 (6)	182 (4)	100 (5)	96 (40)
H(63)	819 (6)	211 (3)	180 (4)	81 (34)
H(71)	875 (6)	74 (4)	328 (5)	101 (40)
H(72)	1038 (7)	90 (5)	275 (6)	212 (75)
H(73)	944 (7)	2 (4)	279 (5)	138 (47)
H(81)	907 (6)	−254 (4)	−102 (5)	117 (43)
H(82)	807 (6)	−188 (3)	−173 (4)	67 (31)
H(83)	689 (7)	−236 (4)	−96 (5)	152 (52)
H(91)	1048 (6)	−222 (4)	81 (5)	86 (38)
H(92)	881 (7)	−231 (4)	136 (5)	140 (48)
H(93)	1010 (6)	−156 (3)	160 (4)	80 (33)

* Positional parameters were not refined for these atoms.

Table 2. *Bond distances* (Å) *and bond angles* (°)

O(1)—C(1)	1·386 (5)		N(3)—C(5)	1·470 (7)
O(1)—C(3)	1·366 (6)		N(4)—C(2)	1·326 (6)
N(1)—C(1)	1·300 (6)		N(4)—C(6)	1·479 (7)
N(1)—C(2)	1·335 (6)		N(4)—C(7)	1·474 (7)
N(2)—C(2)	1·367 (6)		N(5)—C(3)	1·326 (6)
N(2)—C(3)	1·298 (6)		N(5)—C(8)	1·457 (7)
N(3)—C(1)	1·296 (6)		N(5)—C(9)	1·458 (7)
N(3)—C(4)	1·477 (7)			

C(1)—O(1)—C(3)	116·1 (4)		C(8)—N(5)—C(9)	117·2 (5)
C(1)—N(1)—C(2)	116·5 (5)		O(1)—C(1)—N(1)	122·5 (5)
C(2)—N(2)—C(3)	114·7 (5)		O(1)—C(1)—N(3)	112·8 (5)
C(1)—N(3)—C(4)	119·2 (5)		N(1)—C(1)—N(3)	124·7 (5)
C(1)—N(3)—C(5)	123·3 (5)		N(1)—C(2)—N(2)	125·6 (5)
C(4)—N(3)—C(5)	117·3 (5)		N(1)—C(2)—N(4)	118·3 (5)
C(2)—N(4)—C(6)	120·9 (5)		N(2)—C(2)—N(4)	116·0 (5)
C(2)—N(4)—C(7)	121·5 (5)		O(1)—C(3)—N(2)	124·3 (5)
C(6)—N(4)—C(7)	117·5 (5)		O(1)—C(3)—N(5)	111·9 (5)
C(3)—N(5)—C(8)	123·3 (5)		N(2)—C(3)—N(5)	123·9 (5)
C(3)—N(5)—C(9)	118·9 (5)			

are consistent with enhanced electron donation from the dimethylamino groups in (I) in response to the substitution of an O atom for one ring N atom in (VI).

Bond angles within the ring of (I) are increased from 120° at C and decreased at N but not to the same degree as in (VI), where the mean C—N—C and N—C—N angles are 127·3 (5) and 112·7 (5)° respectively.

Steric hindrance between methyl groups is relieved by a small movement (up to ±0·2 Å) out of the plane of the heterocycle,* but not by the obvious mechanism of a concerted series of twists about exocyclic C—N bonds. There is indeed a twist about C(2)—N(4) which depresses C(6) and elevates C(7) relative to the plane, but the entire dimethylamino group attached to C(1) is elevated whilst the entire group at C(3) is depressed. The sum of the bond angles at each of the dimethyl-amino N atoms is very close to 360°, suggesting that sp^2 hybridization of N occurs. Furthermore, efficient π overlap with the ring is encouraged by the lack of twisting.

The ions and solvent molecules are held together in the unit cell (Fig. 2) by hydrogen bonding and stacking. The Cl⁻ ion accepts hydrogen bonds from two symmetry-related O(2) water molecules and one O(3) water molecule with O···Cl distances of 3·227 (5), 3·148 (5), and 3·264 (5) Å. The remaining water hydrogen atom, H(31), forms a hydrogen bond to the other water O atom with O···O = 2·867 (6) Å. The heterocyclic cations are formed into stacks in the **a** direction by the action of centres of symmetry. This packing mode enables dimethylamino groups on successive molecules within the stack to interleave (Fig. 2). The closest interaction is between C(1) and N(1) of adjacent rings at 3·398 (6) Å.
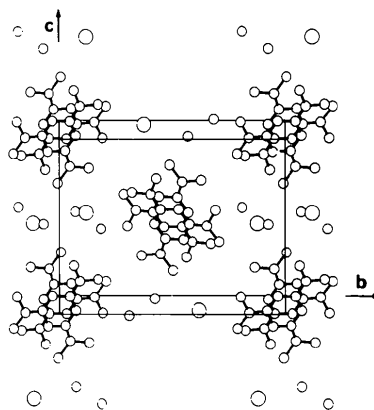
* See previous footnote.

Fig. 2. *PLUTO* (Motherwell, 1972) drawing of the unit-cell contents viewed down a.

References

BREDERECK, K. & RICHTER, R. (1966). *Chem. Ber.* **99**, 2454–2460.
BULLEN, G. J., CORNEY, D. J. & STEPHENS, F. S. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 642–646.
FOURME, R. (1972). *Acta Cryst.* B**28**, 2984–2991.
MOTHERWELL, W. D. S. (1972). *PLUTO*. A program for plotting molecular and crystal structures. Univ. of Cambridge, England.
SHELDRICK, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.
UENO, K. & SAITO, N. (1977). *Acta Cryst.* B**33**, 111–113.

Elementary Patterns in Protein–Nucleic Acid Interactions. VII.
Structure of *N*-[3-(9-Adeninyl)propionyl]-DL-tryptophan Ethyl Ester, C₂₁H₂₃N₇O₃*

By MIDORI TAKIMOTO, AKIO TAKENAKA AND YOSHIO SASADA

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

Abstract. $M_r = 421\cdot46$, triclinic, $P\bar{1}$, $a = 7\cdot734$ (2), $b = 22\cdot40$ (1), $c = 6\cdot798$ (3) Å, $\alpha = 112\cdot79$ (3), $\beta = 104\cdot10$ (4), $\gamma = 88\cdot69$ (4)°, $V = 1049\cdot7$ Å³, $D_m = 1\cdot32$, $D_x = 1\cdot333$ Mg m⁻³, $Z = 2$, λ(Cu $K\alpha$) = 1·54184 Å; $R = 0\cdot11$ for 1762 diffractometer-measured intensities. The molecule is extended so that there is no intramolecular stacking between the adenine and indole moieties. However, the adenine moieties related by the inversion are stacked with respect to each other, and the indolyl and ethyl groups are piled up alternately along