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## Complexes of the 'Proton Sponge' 1,8-Bis(dimethylamino)naphthalene (DMAN). III. Structure of [DMANH]<sup>+</sup>.[Pentachlorophenolate]<sup>-</sup>.[Pentachlorophenol]<sub>2</sub> at 100 K\*

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**Abstract.** (8-Dimethylamino-1-naphthyl)dimethylammonium pentachlorophenolate-pentachlorophenol (1/2), C<sub>14</sub>H<sub>19</sub>N<sub>2</sub><sup>+</sup>.C<sub>6</sub>Cl<sub>5</sub>O<sup>-</sup>.2C<sub>6</sub>HCl<sub>5</sub>O, *M<sub>r</sub>* = 1013.3, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 11.363 (2), *b* = 16.676 (2), *c* = 20.307 (2) Å, *V* = 3847.9 (4) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.749 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 11.2 cm<sup>-1</sup>, *F*(000) = 2024, *T* = 100 K, final *R* = 0.0271 and *wR* = 0.0231 for 7630 reflections with *I* ≥ 2.5σ(*I*). The 'proton sponge' 1,8-bis(dimethylamino)naphthalene (DMAN) accepts a proton from one of the three pentachlorophenols (PCPs) resulting in the formation of a strong asymmetric intramolecular [N—H⋯N]<sup>+</sup> hydrogen bond with N⋯N and N—H distances and N—H⋯N angle of 2.555 (3), 1.11 (2) Å and 162 (2)° respectively. The [PCP]<sup>-</sup> anion and the two neutral PCP residues form an isolated hydrogen-bonded cluster. The OH donors of these hydrogen bonds are each involved in an asymmetric three-center hydrogen bond with a strong O—H⋯O<sup>-</sup> intermolecular branch and a weak O—H⋯Cl intramolecular branch.

**Introduction.** Recently we reported the structure of the complex 8-dimethylamino-1-dimethylammonio-naphthalene hydrogen squarate ([DMANH]<sup>+</sup>.[HSQ]<sup>-</sup>; Kanters, Schouten, Kroon & Grech, 1991*a*) and the low- and room-temperature structures of the complex of DMAN and chloroanilic acid ([DMANH]<sub>2</sub><sup>+</sup>.[CAA]<sup>2-</sup>; Kanters, Schouten, Duisenberg, Głowiak, Malarski, Sobczyk & Grech, 1991).

In these complexes the strongly basic 'proton sponge' DMAN absorbs a proton from the acidic residue and a strong asymmetric intramolecular hydrogen bond is formed. In the literature seven other [DMANH]<sup>+</sup> complexes are known (Kanters *et al.*, 1991*a*; Woźniak, Krygowski, Kariuki, Jones & Grech, 1990) and in these structures, which were all determined at room temperature, the N⋯N distances are in the range 2.55–2.65 Å and the N—H distances cover the range 1.17–1.31 Å, well outside the normal range observed in N—H⋯N hydrogen bonds. On the other hand, in the low-temperature structures of [DMANH]<sup>+</sup>.[HSQ]<sup>-</sup> and [DMANH]<sub>2</sub><sup>+</sup>.[CAA]<sup>2-</sup> the N—H distances are significantly shorter, 1.08 (2) and 1.07 (3) Å respectively, whereas in the latter room-temperature complex the N—H distance again is elongated to 1.14 (3) Å. Assuming that the [N—H⋯N]<sup>+</sup> potential is not temperature dependent, the observed elongation of the N—H bond suggests that temperature increase is paralleled by a marked tendency of the H atom to occupy both minima of the potential well. However, a clear distinction should be made between structures where space-group symmetry requires the H atom to lie on a symmetry element and structures which have no such restriction. In the former case the [N—H⋯N]<sup>+</sup> potential is *ipso facto* symmetrical, either a double- or a single-well type. The double well will give rise to disorder, either static or dynamic, with normal N—H lengths and the single well to an ordered H atom with, as a consequence, very long N—H lengths. The effect of symmetry is nicely demonstrated in the two modifications of [DMANH]<sup>+</sup>.[OTeF<sub>5</sub>]<sup>-</sup>. In the room-temperature triclinic form

\* Part II: Kanters, Schouten, Duisenberg, Głowiak, Malarski, Sobczyk & Grech (1991).

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(Miller, Abney, Rappé, Anderson & Strauss, 1988) the  $[\text{N—H}\cdots\text{N}]^+$  bridge is asymmetric with  $\text{N—H}$  1.17 Å. On the other hand, in the low-temperature (143 K) orthorhombic form (Kellett, Anderson, Strauss & Abney, 1989), in which  $[\text{DMANH}]^+$  has a mirror plane through the central C—C bond, the ordered H atom is located on the mirror plane, at the expense of an unusual  $\text{N—H}$  distance of 1.37 Å and an unfavourable angle of  $140^\circ$ . A similar result was reported for the room-temperature structure of  $[\text{DMANH}]^+\cdot\text{Br}^-\cdot 2\text{H}_2\text{O}$  (Pyżalska, Pyżalski & Borowiak, 1983) where the H atom is also on a mirror plane with an  $\text{N—H}$  distance of 1.30 Å and an  $\text{N—H}\cdots\text{N}$  angle of  $153(3)^\circ$ . We now report the structure of the complex of DMAN and pentachlorophenol (PCP),  $[\text{DMANH}]^+[\text{PCP}]^- \cdot [\text{PCP}]_2$ , at liquid-nitrogen temperature (100 K) with special emphasis on the geometry of the intramolecular  $[\text{N—H}\cdots\text{N}]^+$  hydrogen bond.

**Experimental.** Crystals of the title compound were obtained from a solution in acetonitrile of a 1:3 mixture of 1,8-bis(dimethylamino)naphthalene and pentachlorophenol. A rod-shaped colourless crystal of dimensions  $0.2 \times 0.3 \times 0.06$  mm was used for collection of data at liquid-nitrogen temperature (100 K) on an Enraf-Nonius CAD-4 diffractometer with Zr-filtered  $\text{Mo } K\alpha$  radiation in the  $\omega$ - $2\theta$  scan mode. Lattice parameters were determined from the setting angles of 25 reflections in the range  $15.5 \leq \theta \leq 17.8^\circ$ . Intensity data of 8887 reflections ( $h = 14/14$ ,  $k = 0/21$ ,  $l = 26/0$ ;  $2\theta_{\text{max}} = 27.5^\circ$ ) were collected. After merging equivalent reflections ( $R_{\text{int}} = 0.034$ ) 7630 unique reflections remained with  $I > 2.5\sigma(I)$ , of which 3192 were Bijvoet pairs. Three standard reflections ( $30\bar{3}$ ,  $0\bar{1}4$ , 430) showed fluctuations of 3% during 48 h of X-ray exposure time. The data were corrected for  $L_p$  and absorption (*DIFABS*; Walker & Stewart, 1983;  $T_{\text{max}} = 1.09$ ,  $T_{\text{min}} = 0.96$ ). The variance  $\sigma^2(I)$  was calculated based on counting statistics plus an instability constant term ( $0.023I^2$ ) as derived from the excess variance in the standard reflections (McCandlish, Stout & Andrews, 1975). The space group was determined from the observed systematic absences. The structure was solved by direct methods (*SHELXS86*; Sheldrick, 1986) and refined on  $F$  by full-matrix least squares with *SHELX76* (Sheldrick, 1976). All H atoms were located in a difference Fourier map and included in the refinement with a general isotropic thermal parameter. Refinement of 534 parameters with weights  $w = [\sigma^2(F)]^{-1}$  converged to  $R = 0.0271$  [ $wR = 0.0231$ ;  $S = 1.39$ ;  $(\Delta/\sigma)_{\text{av}} = 0.019$ ,  $(\Delta/\sigma)_{\text{max}} = 0.36$ ]. An extinction correction of the form  $F' = F(1 - 0.0001gF^2/\sin\theta)$  was applied with  $g = 1.8 \times 10^{-4}$ . A final difference Fourier map did not show residual peaks outside  $-0.27$  and  $0.31 \text{ e } \text{Å}^{-3}$ . The

corresponding residuals of the refinement of the inverted structure were  $R = 0.0284$  and  $wR = 0.0244$ . Scattering factors were taken from Cromer & Mann (1968) and anomalous-dispersion corrections from Cromer & Liberman (1970).

The program package *EUCALID* (Spek, 1982) was used for geometrical calculations and illustrations. All calculations were carried out on a MicroVAXII. The final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.\*

**Discussion.** The atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1, bond distances and angles in Table 2. The asymmetric unit consists of one protonated 1,8-bis-(dimethylamino)naphthalene fragment  $[\text{DMANH}]^+$ , one pentachlorophenolate anion  $[\text{PCP}]^-$  and two neutral pentachlorophenol molecules PCP. Fig. 1 gives a view of the asymmetric unit with the adopted numbering scheme and the system of hydrogen bonds. In the structure the  $[\text{DMANH}]^+$  fragment with its  $[\text{N—H}\cdots\text{N}]^+$  intramolecular hydrogen bond is isolated from the cluster consisting of the  $[\text{PCP}]^-$  anion and the two neutral PCP molecules which are linked by a system of two bifurcated hydrogen bonds (Table 3 and Fig. 1). The O—H groups of the two PCP residues each donate an intermolecular hydrogen bond to the phenoxide  $\text{O}^-$  of  $[\text{PCP}]^-$  and within each PCP an intramolecular O—H $\cdots$ Cl interaction is present which constitutes the weak branch of the bifurcated hydrogen-bond interaction. Both four-atom arrangements are planar as indicated by the sum of angles around the H atom, which are  $357(4)$  and  $356(4)^\circ$  for PCP (I) and PCP (II) respectively. Bifurcated interactions of this type have also been observed in the complex  $[\text{4-methylpyridinium}]^+[\text{PCP}]^-$  (Majerz, Malarski & Lis, 1990).

The geometries of  $[\text{PCP}]^-$  and the two PCPs show a good correspondence (Table 2) except for the shortened C—O bond of  $[\text{PCP}]^-$  and its C—C—O angles, which differ by only  $0.6(3)^\circ$ , whereas in the PCPs these angles differ by  $7.3(3)$  and  $8.4(3)^\circ$ . In each PCP the larger C—C—O angle is at the side of the phenolic H atom which in both residues is nearly coplanar with the aromatic ring [deviations  $0.18(3)$  and  $0.20(3)$  Å respectively]. The aromatic rings of  $[\text{PCP}]^-$  and the PCPs are planar with  $\sigma_{\text{plane}}$  values of  $0.02(1)$ ,  $0.02(1)$  and  $0.01(1)$  Å respectively. The average deviation of the Cl and O substituents of  $[\text{PCP}]^-$  and the PCPs amount to  $0.06(3)$ ,  $0.06(3)$  and  $0.05(2)$  Å respectively.

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54599 (50 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0273]

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) with e.s.d.'s in parentheses

$U_{eq}$  is defined as one third of the trace of orthogonalized  $U_{ij}$  tensor. Isotropic thermal parameters  $U_{iso}$  for H atoms.

[DMANH] <sup>+</sup>	x	y	z	$U_{eq}/U_{iso}$
N(1)	0.03384 (18)	0.02774 (13)	0.33387 (10)	0.0121 (6)
H(1)	-0.034 (2)	-0.0202 (16)	0.3373 (13)	0.0239 (17)
N(2)	-0.11475 (18)	-0.08122 (13)	0.36407 (10)	0.0135 (7)
C(1)	0.0438 (2)	0.04964 (15)	0.40401 (12)	0.0137 (7)
C(2)	0.1065 (2)	0.11515 (17)	0.42346 (13)	0.0180 (8)
C(3)	0.1193 (2)	0.13203 (18)	0.49090 (14)	0.0206 (9)
C(4)	0.0736 (2)	0.08134 (17)	0.53678 (13)	0.0200 (9)
C(5)	-0.0365 (2)	-0.04079 (17)	0.56593 (13)	0.0186 (8)
C(6)	-0.0978 (2)	-0.10742 (18)	0.54802 (13)	0.0197 (8)
C(7)	-0.1215 (2)	-0.12209 (16)	0.48102 (13)	0.0165 (8)
C(8)	-0.0812 (2)	-0.07089 (16)	0.43349 (12)	0.0135 (7)
C(9)	-0.0107 (2)	-0.00338 (15)	0.44977 (12)	0.0125 (8)
C(10)	0.0091 (2)	0.01249 (15)	0.51819 (13)	0.0145 (8)
C(11)	-0.0046 (2)	0.09392 (17)	0.29072 (14)	0.0180 (8)
C(12)	0.1432 (3)	-0.01052 (18)	0.30907 (14)	0.0221 (9)
C(13)	-0.0874 (3)	-0.16170 (17)	0.33781 (14)	0.0197 (9)
C(14)	-0.2399 (2)	-0.05945 (19)	0.35412 (14)	0.0202 (9)
[PCP] <sup>-</sup>				
O(1)	0.80086 (14)	0.23628 (10)	0.24335 (8)	0.0141 (5)
C(15)	0.6879 (2)	0.23191 (14)	0.25142 (11)	0.0112 (7)
C(16)	0.6189 (2)	0.29694 (14)	0.27387 (11)	0.0115 (7)
C(17)	0.4977 (2)	0.29378 (15)	0.27991 (11)	0.0115 (7)
C(18)	0.43773 (19)	0.22315 (15)	0.26561 (11)	0.0114 (7)
C(19)	0.5021 (2)	0.15618 (15)	0.24649 (12)	0.0123 (7)
C(20)	0.6230 (2)	0.16110 (14)	0.23859 (11)	0.0115 (7)
Cl(1)	0.69337 (5)	0.38435 (4)	0.29397 (3)	0.0172 (2)
Cl(2)	0.41905 (5)	0.37766 (4)	0.30361 (3)	0.0171 (2)
Cl(3)	0.28591 (5)	0.21900 (4)	0.27157 (3)	0.0194 (2)
Cl(4)	0.43075 (5)	0.06582 (4)	0.23492 (3)	0.0187 (2)
Cl(5)	0.70282 (5)	0.07847 (4)	0.21261 (3)	0.0159 (2)
PCP (I)				
O(2)	0.95446 (16)	0.16925 (11)	0.16125 (9)	0.0159 (6)
H(8)	0.896 (2)	0.1905 (17)	0.1738 (14)	0.0239 (17)
C(21)	0.9695 (2)	0.16582 (15)	0.09597 (12)	0.0135 (7)
C(22)	0.9067 (2)	0.21165 (16)	0.05040 (13)	0.0155 (8)
C(23)	0.9311 (2)	0.20612 (16)	-0.01692 (13)	0.0181 (8)
C(24)	1.0151 (2)	0.15269 (17)	-0.03959 (12)	0.0186 (8)
C(25)	1.0783 (2)	0.10691 (16)	0.00529 (13)	0.0176 (8)
C(26)	1.0578 (2)	0.11481 (15)	0.07222 (12)	0.0153 (7)
Cl(6)	0.80033 (6)	0.27591 (4)	0.07961 (3)	0.0211 (2)
Cl(7)	0.85622 (6)	0.26736 (4)	-0.07149 (3)	0.0257 (2)
Cl(8)	1.04208 (6)	0.14388 (5)	-0.12306 (3)	0.0305 (2)
Cl(9)	1.18137 (6)	0.03852 (4)	-0.02197 (3)	0.0253 (2)
C(10)	1.14147 (6)	0.06238 (4)	0.12842 (3)	0.0231 (2)
PCP (II)				
O(3)	-0.04133 (16)	0.30593 (11)	0.31216 (9)	0.0171 (6)
H(9)	-0.102 (2)	0.2851 (17)	0.2996 (14)	0.0239 (17)
C(27)	-0.0310 (2)	0.32121 (15)	0.37615 (12)	0.0144 (8)
C(28)	0.0501 (2)	0.38059 (15)	0.39502 (12)	0.0145 (8)
C(29)	0.0711 (2)	0.39876 (15)	0.46060 (13)	0.0160 (8)
C(30)	0.0114 (2)	0.35788 (17)	0.51005 (13)	0.0179 (8)
C(31)	-0.0694 (2)	0.29887 (15)	0.49293 (12)	0.0142 (8)
C(32)	-0.0920 (2)	0.28167 (16)	0.42700 (12)	0.0142 (7)
Cl(11)	0.12259 (6)	0.43158 (4)	0.33323 (3)	0.0202 (2)
Cl(12)	0.17220 (6)	0.47200 (4)	0.48044 (3)	0.0245 (2)
Cl(13)	0.03438 (6)	0.38161 (5)	0.59174 (3)	0.0253 (2)
Cl(14)	-0.13929 (6)	0.24470 (4)	0.55370 (3)	0.0219 (2)
Cl(15)	-0.19613 (6)	0.21097 (4)	0.40589 (3)	0.0193 (2)

Table 2. Bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses

[DMANH] <sup>+</sup>			
N(1)—H(1)	1.11 (2)	N(1)—C(1)	1.475 (3)
N(1)—C(11)	1.475 (4)	N(1)—C(12)	1.485 (4)
N(2)—C(8)	1.470 (3)	N(2)—C(13)	1.477 (4)
N(2)—C(14)	1.482 (3)	C(1)—C(2)	1.363 (4)
C(1)—C(9)	1.424 (3)	C(2)—C(3)	1.406 (4)
C(3)—C(4)	1.361 (4)	C(4)—C(10)	1.413 (4)
C(5)—C(6)	1.361 (4)	C(5)—C(10)	1.413 (4)
C(6)—C(7)	1.408 (4)	C(7)—C(8)	1.368 (4)
C(8)—C(9)	1.421 (4)	C(9)—C(10)	1.432 (4)
[PCP] <sup>-</sup>			
O(1)—C(15)	1.296 (3)	C(15)—C(16)	1.414 (3)
C(15)—C(20)	1.416 (3)	C(16)—C(17)	1.384 (3)
C(17)—C(18)	1.391 (3)	C(18)—C(19)	1.390 (3)
C(19)—C(20)	1.386 (3)	Cl(1)—C(16)	1.734 (2)
Cl(2)—C(17)	1.728 (3)	Cl(3)—C(18)	1.731 (2)
Cl(4)—C(19)	1.727 (3)	Cl(5)—C(20)	1.732 (2)
PCP (I)			
O(2)—H(8)	0.79 (2)	O(2)—C(21)	1.338 (3)
C(21)—C(22)	1.396 (4)	C(21)—C(26)	1.401 (3)
C(22)—C(23)	1.398 (4)	C(23)—C(24)	1.384 (4)
C(24)—C(25)	1.389 (4)	C(25)—C(26)	1.385 (4)
Cl(6)—C(22)	1.721 (3)	Cl(7)—C(23)	1.731 (3)
Cl(8)—C(24)	1.729 (3)	Cl(9)—C(25)	1.726 (3)
Cl(10)—C(26)	1.724 (2)		
PCP (II)			
O(3)—H(9)	0.81 (2)	O(3)—C(27)	1.329 (3)
C(27)—C(28)	1.406 (3)	C(27)—C(32)	1.408 (3)
C(28)—C(29)	1.386 (4)	C(29)—C(30)	1.390 (4)
C(30)—C(31)	1.390 (4)	C(31)—C(32)	1.393 (3)
Cl(11)—C(28)	1.725 (3)	Cl(12)—C(29)	1.724 (3)
Cl(13)—C(30)	1.725 (3)	Cl(14)—C(31)	1.723 (3)
Cl(15)—C(32)	1.724 (3)		
[DMANH] <sup>+</sup>			
C(1)—N(1)—C(11)	114.3 (2)	C(6)—C(5)—C(10)	121.2 (2)
C(1)—N(1)—C(12)	111.7 (2)	C(5)—C(6)—C(7)	119.9 (3)
C(11)—N(1)—C(12)	111.6 (2)	C(6)—C(7)—C(8)	120.6 (2)
C(8)—N(2)—C(13)	113.5 (2)	C(7)—C(8)—C(7)	121.1 (2)
C(8)—N(2)—C(14)	110.5 (2)	N(2)—C(8)—C(9)	117.5 (2)
C(13)—N(2)—C(14)	112.0 (2)	C(7)—C(8)—C(9)	121.3 (2)
N(1)—C(1)—C(2)	121.2 (2)	C(1)—C(9)—C(8)	125.8 (2)
N(1)—C(1)—C(9)	116.3 (2)	C(1)—C(9)—C(10)	116.7 (2)
C(2)—C(1)—C(9)	122.4 (2)	C(8)—C(9)—C(10)	117.4 (2)
C(1)—C(2)—C(3)	119.8 (2)	C(4)—C(10)—C(5)	121.2 (2)
C(2)—C(3)—C(4)	120.2 (3)	C(4)—C(10)—C(9)	119.4 (2)
C(3)—C(4)—C(10)	121.3 (2)	C(5)—C(10)—C(9)	119.5 (2)
[PCP] <sup>-</sup>			
O(1)—C(15)—C(16)	123.2 (2)	Cl(3)—C(18)—C(17)	120.5 (2)
O(1)—C(15)—C(20)	122.6 (2)	Cl(3)—C(18)—C(19)	120.8 (2)
C(16)—C(15)—C(20)	114.2 (2)	C(17)—C(18)—C(19)	118.7 (2)
Cl(1)—C(16)—C(15)	116.8 (2)	Cl(4)—C(19)—C(18)	119.5 (2)
Cl(1)—C(16)—C(17)	119.8 (2)	Cl(4)—C(19)—C(20)	120.1 (2)
C(15)—C(16)—C(17)	123.5 (2)	C(18)—C(19)—C(20)	120.4 (2)
Cl(2)—C(17)—C(16)	120.6 (2)	Cl(5)—C(20)—C(15)	116.5 (2)
Cl(2)—C(17)—C(18)	119.3 (2)	Cl(5)—C(20)—C(19)	120.5 (2)
C(16)—C(17)—C(18)	120.1 (2)	C(15)—C(20)—C(19)	123.0 (2)
PCP (I)			
O(2)—C(21)—C(22)	124.6 (2)	Cl(8)—C(24)—C(23)	120.2 (2)
O(2)—C(21)—C(26)	117.3 (2)	Cl(8)—C(24)—C(25)	120.3 (2)
C(22)—C(21)—C(26)	118.0 (2)	C(23)—C(24)—C(25)	119.5 (2)
Cl(6)—C(22)—C(21)	118.1 (2)	Cl(9)—C(25)—C(24)	120.2 (2)
Cl(6)—C(22)—C(23)	121.2 (2)	Cl(9)—C(25)—C(26)	119.5 (2)
C(21)—C(22)—C(23)	120.7 (2)	C(24)—C(25)—C(26)	120.3 (2)
Cl(7)—C(23)—C(22)	119.3 (2)	Cl(10)—C(26)—C(21)	118.4 (2)
Cl(7)—C(23)—C(24)	120.4 (2)	Cl(10)—C(26)—C(25)	120.6 (2)
C(22)—C(23)—C(24)	120.3 (2)	C(21)—C(26)—C(25)	121.1 (2)
PCP (II)			
O(3)—C(27)—C(28)	117.3 (2)	Cl(13)—C(30)—C(29)	120.5 (2)
O(3)—C(27)—C(32)	125.7 (2)	Cl(13)—C(30)—C(31)	120.2 (2)
C(28)—C(27)—C(32)	116.9 (2)	C(29)—C(30)—C(31)	119.5 (2)
Cl(11)—C(28)—C(27)	117.5 (2)	Cl(14)—C(31)—C(30)	119.8 (2)
Cl(11)—C(28)—C(29)	120.6 (2)	Cl(14)—C(31)—C(32)	119.7 (2)
C(27)—C(28)—C(29)	121.9 (2)	C(30)—C(31)—C(32)	120.5 (2)
Cl(12)—C(29)—C(28)	119.6 (2)	Cl(15)—C(32)—C(27)	118.4 (2)
Cl(12)—C(29)—C(30)	120.2 (2)	Cl(15)—C(32)—C(31)	120.4 (2)
C(28)—C(29)—C(30)	120.2 (2)	C(27)—C(32)—C(31)	121.2 (2)

The [DMANH]<sup>+</sup> ring system is moderately planar [ $\sigma_{\text{plane}} = 0.042$  (1) Å] and the N(1) and N(2) atoms are at opposite sides, at 0.19 (1) and 0.25 (1) Å respectively from this plane. This compares well with the deviations of the N atoms of the complex of DMAN and tetrafluoroboric acid, [DMANH]<sup>+</sup>·[TFB]<sup>-</sup>, (0.23 and -0.21 Å) (Woźniak *et al.*, 1990), but is in contrast with [DMANH]<sup>+</sup>·[HSQ]<sup>-</sup> (Kanters *et al.*, 1991a) where the N atoms are coplanar with

the ring plane. The intramolecular  $[N-H\cdots N]^+$  hydrogen bond of the  $[DMANH]^+$  complexes reported to date (Kanters *et al.*, 1991a; Woźniak *et al.*, 1990) leads to decreased  $N\cdots N$  distances [average 2.58 (3), range 2.554 (5)–2.65 (2) Å] compared with the  $N\cdots N$  distance of 2.792 (8) Å of unprotonated DMAN (Einspahr, Robert, Marsh & Roberts, 1973) with the N atoms at opposite sides of the ring at 0.40 Å. The formation of the intramolecular hydrogen bond also has a pronounced effect on the puckering of the naphthalene ring. In unprotonated DMAN ( $\sigma_{\text{plane}} = 0.106$  Å) the puckering is caused by a symmetrical twist about the central C(9)–C(10) bond as follows from the C(1)–C(9)–C(10)–C(4) and C(8)–C(9)–C(10)–C(5) torsion angles which are 8.9 (5) and 10.5 (5)° respectively. In the title compound puckering is much less, the corresponding torsion angles are 4.1 (3) and 3.0 (3)°, in  $[DMANH]^+.[HSQ]^-$  0.6 (2) and 0.3 (2)°, and in  $[DMANH]^+.[TFB]^-$  4.6 (4) and 5.1 (4)°. The intramolecular  $[N-H\cdots N]^+$  hydrogen bond is strong, non-linear and asymmetric with  $N\cdots N$ , N–H and  $N-H\cdots N$  2.555 (3), 1.11 (2) Å and 162 (2)° respectively, and these geometries compare well with those observed in the low-temperature structures of  $[DMANH]^+.[HSQ]^-$  and  $[DMANH]^+.[CAA]^{2-}$ .

It is remarkable that in the other seven reported  $[DMANH]^+$  complexes (Kanters *et al.*, 1991a; Woźniak *et al.*, 1990) which relate to room-temperature structures, the N–H bonds are elongated, ranging from 1.17 to 1.30 Å. This raises the question whether the elongation in the room-temperature structures is the result of progressive disordering, culminating in a formal position of the proton midway between the N atoms with N–H lengths of about one half of the  $N\cdots N$  distance. The

Table 3. *Hydrogen-bond geometry* (Å, °) *with e.s.d.'s in parentheses*

Donor	Acceptor	D...A	D—H	H...A	D—H...A
N(1)—H(1)...	N(2) (x, y, z)	2.555 (3)	1.11 (2)	1.47 (3)	162 (2)
O(2)—H(8)...	O(1) (x, y, z)	2.660 (2)	0.79 (2)	1.94 (3)	151 (3)
O(2)—H(8)...	Cl(6) (x, y, z)	2.997 (2)	0.79 (2)	2.62 (3)	111 (2)
O(3)—H(9)...	O(1) (-1 + x, y, z)	2.553 (2)	0.81 (2)	1.78 (3)	157 (3)
O(3)—H(9)...	Cl(15) (x, y, z)	3.037 (2)	0.81 (2)	2.71 (3)	106 (2)

fact that in  $[DMANH]_2^+.[CAA]^{2-}$ , on which 295 and 150 K analyses were performed (Kanters, Schouten, Duisenberg, Głowiak, Malarski, Sobczyk & Grech, 1991), the N–H distance shows a shortening from 1.14 (3) to 1.07 (3) Å on cooling suggests that this disorder may be dynamic in origin.

The presence of disorder is nicely demonstrated in the low-temperature (100 K) structure of the complex  $[DMANH]_2^+.[\text{squarate}]^{2-}.4H_2O$  (Kanters, Schouten, Kroon & Grech, 1991b). The analysis reveals that the two independent  $[DMANH]^+$  residues have mirror symmetry, with the mirror passing through the central C–C bond and the water molecules and the squarate anion lying in the mirror plane. The symmetry requires the H atom to be located between the N atoms at the mirror plane. However, an electron density difference synthesis, with H omitted from  $F_c$ , showed splitting of the electron density at about 0.35 Å from the mirror plane in both  $[DMANH]^+$  residues and subsequent refinement of the H atoms with 50% occupancies resulted in stable positions with N–H distances of 0.93 (3) Å. This result is in contrast with that observed in the room-temperature structure of  $[DMANH]^+.\text{Br}^-.2H_2O$  (Pyżalska *et al.*, 1983) and the low-temperature structure of  $[DMANH]^+.[\text{OTeF}_5]^-$  (Kellett *et al.*, 1989) where the H atom is reported to be located on the mirror plane of the  $[DMANH]^+$  residue.

The comparison of the low- and room-temperature structures suggests that at low temperature the  $[N-H\cdots N]^+$  hydrogen bond in the absence of symmetry is asymmetric and that in the case of formally symmetrical  $[N\cdots H\cdots N]^+$  bonds the H atom may be either ordered or disordered. The range of elongated N–H bonds commonly observed in room-temperature  $[DMANH]^+$ -containing structures may well reflect various degrees of disordering.

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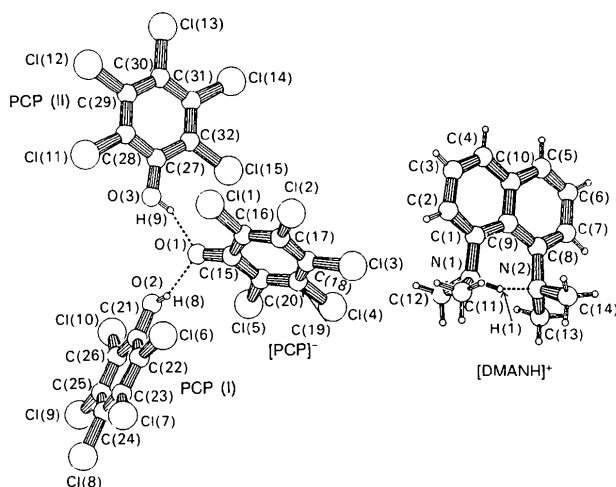


Fig. 1. View of the asymmetric unit with adopted numbering scheme and hydrogen bonds. The residues  $[DMANH]^+$ , PCP (I) and PCP (II) are at  $x, y, z$ ;  $[PCP]^-$  is at  $1 + x, y, z$ .

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## Structures of Colchicine Analogues. V. 2-Methoxy-5-(4-methoxyphenyl)cyclohepta-2,4,6-trien-1-one

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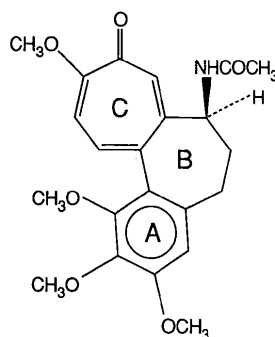
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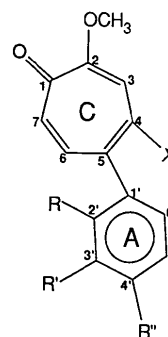
**Abstract.**  $C_{15}H_{14}O_3$ ,  $M_r = 242.3$ , monoclinic,  $Pc$ ,  $a = 13.219$  (1),  $b = 7.072$  (1),  $c = 6.527$  (2) Å,  $\beta = 97.23$  (1)°,  $V = 605.3$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_m$  (floatation) = 1.33 (1),  $D_x = 1.329$  Mg m<sup>-3</sup>,  $\lambda$ (Cu  $K\alpha$ ) = 1.5418 Å,  $\mu$ (Cu  $K\alpha$ ) = 0.66 mm<sup>-1</sup>,  $F(000) = 256$ ,  $T = 291$  (1) K, final  $R = 0.040$  for 905 observed data. The bicyclic molecule adopts a conformation similar to the solid-state conformation of isocolchicine, and the dihedral angle between the planes of the two rings is 41.1 (4)°.

**Introduction.** The alkaloid colchicine (1) is a potent antimitotic agent (Brossi, Yeh, Chrzanowska, Wolff, Hamel, Lin, Quin, Suffness & Silverton, 1988), which exerts its effect by binding to the cytoskeletal protein tubulin. The existence of two partial binding sites on the protein has been established, one for the trimethoxyphenyl *A* ring and one for the troponoid *C* ring. In view of this and the potent antimitotic properties of the *AC*-ring analogues (2) (Fitzgerald, 1976) and (3) (Banwell, Herbert, Buckleton, Clark, Rickard, Lin & Hamel, 1988), comprehensive structure–activity studies of colchicine analogues lacking the central *B* ring could provide important insights into the mode of the colchicine–tubulin interaction. In addition, such systems might represent potentially useful compounds in a therapeutic sense. As part of a continuing conformational study

of colchicine analogues which might have potential as antimitotic agents (Banwell, Gravatt, Buckleton, Clark & Rickard, 1989; Banwell, Collis, Crisp, Lambert, Reum, Scoble, Gable, Mackay & Hamel, 1991), we report here the structure of an *AC*-ring monomethoxyphenyl analogue (4). In earlier studies we reported the structures of the three bicyclic dimethoxyphenyl analogues (5) and (6) (Gable, Mackay, Banwell & Lambert, 1990) and (7) (Banwell *et al.*, 1991).



(1)



- (2)  $R = R' = R'' = OCH_3$ ,  $X = H$   
 (3)  $R = R' = R'' = OCH_3$ ,  $X = Cl$   
 (4)  $R = R' = X = H$ ,  $R'' = OCH_3$   
 (5)  $R = R' = OCH_3$ ,  $R'' = X = H$   
 (6)  $R' = R'' = OCH_3$ ,  $R = X = H$   
 (7)  $R = R'' = OCH_3$ ,  $R' = X = H$