Short Communication

On the Disordered Crystal Structure of Bis(dimethylamino)-heptamethinium Chloride Tetrahydrate at Room Temperature

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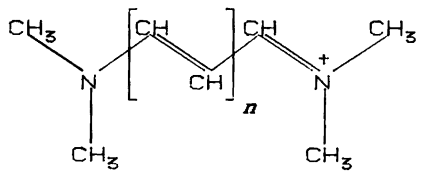
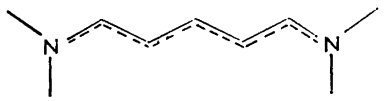
Bis(dimethylamino)tri-, penta- and heptamethinium dyes with various anions have been studied by Dale *et al.*[1]



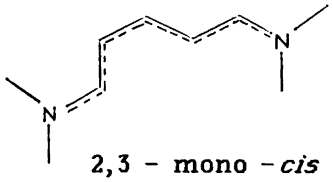
n = 1,2,3

Sterically unhindered *cis* isomers cannot exist for the shortest chain ($n = 1$). There are two possible planar isomers for the bis(dimethylamino)pentamethinium ($n = 2$) cation and four possible planar isomers for the corresponding heptamethinium ($n = 3$) cation. As many as four determinations of the crystal structure of the pentamethinium cation were reported from 1974 to 1977.[2-5] The all-*trans* isomer was found in each of these structures. The present crystal structure investigation was carried out in order to determine which isomeric form is preferred by the heptamethinium cation.

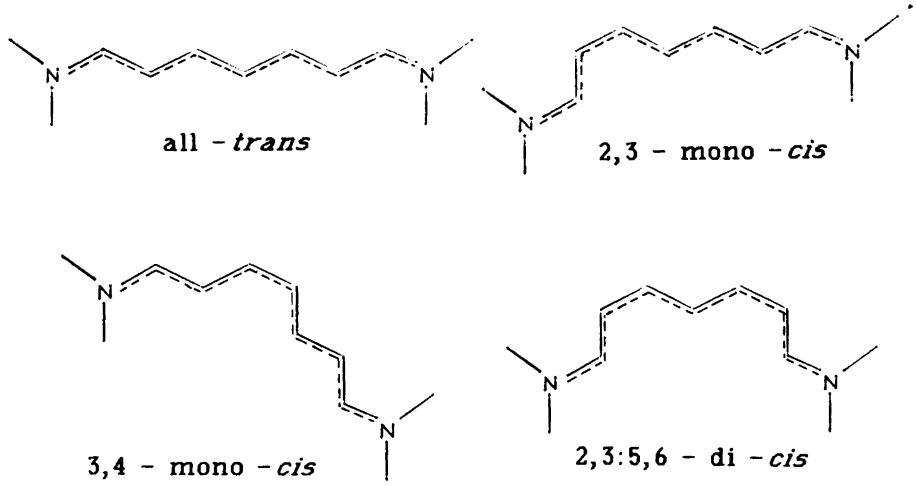


all - *trans*

The crystals of $C_{11}H_{19}N_2^+ \cdot Cl^- \cdot 4H_2O$ are monoclinic with cell dimensions $a = 15.278(4)$, $b = 6.962(2)$ and $c = 9.100(3)$ Å; $\beta = 120.11(2)°$, space group $C2$ and $Z = 2$ ($D_x = 1.13$ gcm^{-3}, $D_m = 1.12$ gcm^{-3}). With $2\theta_{max} = 50°$ and Mo$K\alpha$ radiation, 610 independent reflections [$I > 2.5\sigma(I)$] were recorded on an automatic diffractometer at room temperature. No corrections for absorption or secondary extinction were applied (crystal size 0.3×0.4×0.2 mm). The structure was solved by direct methods[6] and refined by the fullmatrix least-squares technique. $Z = 2$ in space group $C2$ implies that the heptamethinium ion possesses crystallographic two-fold axial symmetry; otherwise, the structure must be disordered. The E-map corresponding to the best figure of merit showed that Cl^- is situated at the two-fold axis of rotation. The map also contained several split peaks for the cation fragment and two additional larger peaks (water molecules) in general positions. The atoms corresponding to the split peaks were given half-weights and refined with isotropic temperature factors. The other atoms were refined with anisotropic thermal parameters, and those of the cation atoms were in turn used to calculate probable positions for "half-atoms".[7] Hydrogen atom positions were partly



2,3 - mono - *cis*



calculated and partly localized in a difference Fourier map and refined with isotropic temperature factors. Weights in least-squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I) = [C_T + (0.02\ C_N)^2]^{\frac{1}{2}}$, where C_T is the total number of counts and C_N the net count. The maximum r.m.s. amplitude of vibration for Cl^- is 0.28 Å, while those for O1 and O2 are as large as 0.41 and 0.40 Å, respectively. The final R-value was 3.3 % (R_w = 3.4 %) for 610 observed reflections. It may be mentioned that attempts to solve (and refine) the structure in space groups *C m* and *C2/m* were unsuccessful.

Final fractional coordinates with estimated standard deviations for the non-hydrogen atoms are listed in Table 1. Bond distances, bond angles and torsion angles with estimated standard deviations may be found in Table 2. Fig. 1 is a perspective drawing showing the disordered heptameth-

Table 1. Final fractional coordinates and equivalent temperature factors with estimated standard deviations for non-hydrogen atoms.

Atom	*x*	*y*	*z*	U_{eq}^a
Cl^-	1.00000	0.03717	1.00000	0.072
O1	0.8456(7)	0.3277(16)	1.0189(14)	0.135
O2	0.8352(7)	−0.2767(16)	1.0052(13)	0.129
C1A	0.9854(4)	0.0303(27)	0.4484(5)	0.047(2)
C2A	0.9277(4)	0.0349(42)	0.5267(8)	0.046(2)
C3A	0.8238(4)	0.0304(41)	0.4501(7)	0.046(1)
C4A	0.7791(4)	0.0330(42)	0.5511(6)	0.046(1)
N1A	0.6825(4)	0.0187(21)	0.5053(7)	0.040(2)
C5A	0.6464(5)	0.0324(41)	0.6215(8)	0.063(2)
C6A	0.6021(5)	0.0422(39)	0.3225(8)	0.061(2)
C7A	1.0885(4)	0.0377(44)	0.5382(8)	0.046(1)
C8A	1.1544(4)	0.0336(41)	0.4738(7)	0.044(1)
C9A	1.2566(4)	0.0350(37)	0.5814(6)	0.047(1)
N2A	1.3289(4)	0.0434(30)	0.5446(7)	0.041(2)
C10A	1.3068(5)	0.0306(42)	0.3642(8)	0.061(2)
C11A	1.4351(5)	0.0123(18)	0.6711(8)	0.063(2)

$^a U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table 2. Bond distances (Å) and angles (°) with estimated standard deviations. The symmetry operators are: ': *x*, 1+*y*, *z*; '': 3/2-*x*, 1/2+*y*, 2-*z*.

Distance		Distance	
C1A–C2A	1.384(8)	C1A–C7A	1.363(8)
C2A–C3A	1.377(8)	C3A–C4A	1.393(8)
C4A–N1A	1.322(8)	N1A–C5A	1.419(9)
N1A–C6A	1.501(9)	C7A–C8A	1.396(8)
C8A–C9A	1.366(7)	C9A–N2A	1.307(8)
N2A–C10A	1.504(9)	N2A–C11A	1.459(9)
Cl^-–O1	3.177(4)	Cl^-–O2	3.352(4)
O1–O2'	2.758(5)	O1–O2''	2.757(5)
Angle		**Angle**	
C2A–C1A–C7A	122.2(5)	C1A–C2A–C3A	127.5(6)
C2A–C3A–C4A	119.2(6)	C3A–C4A–N1A	129.1(6)
C4A–N1A–C5A	123.3(6)	C4A–N1A–C6A	120.3(7)
C5A–N1A–C6A	114.3(6)	C1A–C7A–C8A	127.4(6)
C7A–C8A–C9A	120.3(6)	C8A–C9A–N2A	128.8(6)
C9A–N2A–C10A	121.5(6)	C9A–N2A–C11A	122.6(7)
C10A–N2A–C11A	113.8(6)		

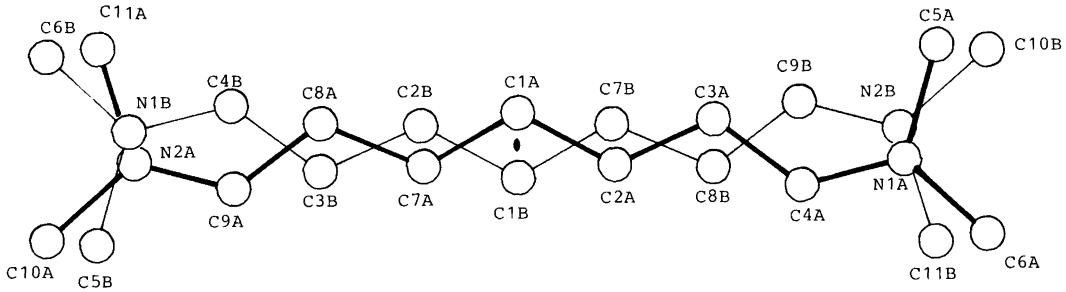


Fig. 1. Perspective drawing of the disordered heptamethinium cation showing the numbering of atoms.

inium cations related by a two-fold axis of symmetry. The numbering of atoms is also indicated. Fig. 2 illustrates the packing of the chromophores. Bond lengths and bond angles are consistent with those observed in the analogous pentamethinium compounds.[2–5] The configuration corresponds to the all-*trans* isomer and is planar to within 0.05 Å for all atoms except C6A and C11A, which are −0.18 and 0.25 Å out of the plane, respectively. A network of bonds is formed between the chloride anions and the water molecules.

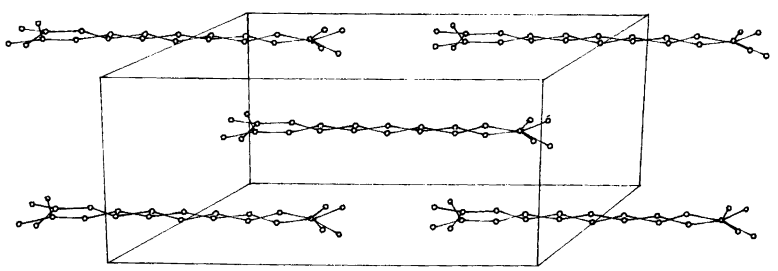


Fig. 2. Perspective drawing showing the packing of the chromophores.

Lists of thermal parameters, hydrogen atom parameters, and observed and calculated structure factors are available from the author on request.

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References

1. Dale, J., Lichtentaler, R. G. and Teien, G. *Acta Chem. Scand., Ser. B 33* (1979) 141.
2. Sieber, K., Kutschabsky, L. and Kulpe, S. *Krist. Techn. 9* (1979) 1101.
3. Ziemer, B. and Kulpe, S. *J. Prakt. Chem. 317* (1975) 185.
4. Selzer, J. O. and Matthews, B. W. *J. Phys. Chem. 80* (1976) 631.
5. Chentli-Benchikha, F., Declercq., J. P., Germain, G. and Van Meerssche, M. *Cryst. Struct. Commun. 6* (1977) 421.
6. Gilmore, C. J. *J. Appl. Crystallogr. 17* (1984) 42.
7. Kartha, G. and Ahmed, F. R. *Acta Crystallogr. 13* (1960) 532.

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