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The Crystal and Molecular Structure of Dipyrido[1,2-a:2',1'-c]pyrazinium Dibromide Monohydrate

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Crystals of dipyrido[1,2-a:2',1'-c]pyrazinium dibromide monohydrate are orthorhombic, space group *Pbca*, with eight formula units of $C_{12}H_{10}N_2^{2+}2Br^-$. H_2O in a unit cell of dimensions a = 17.06, b = 22.50, c = 6.89 Å. The organic cation deviates only slightly from planarity and π -electron delocalization extends over the whole cation. Atomic parameters are based on least-squares refinement using three-dimensional X-ray data. Estimated standard deviations for bond lengths and angles average 0.015 Å and 0.9° respectively. The final value of *R* is 9.4% over 1897 observed structure amplitudes.

Introduction

Dipyrido[1,2-a:2',1'-c]pyrazinium dibromide (I), first reported by Corr & Glover (1965), is closely related to the herbicide diquat (II), and itself possesses herbicidal properties (Black & Summers, 1969). The relationship between stereochemistry and herbicidal activity in bipyridylium salts has been discussed by Boon (1964, 1967) and the crystal structures of diquat dibromide and the inactive tetramethylene analogue (III) have been determined and reported in preliminary form (Derry & Hamor, 1969, 1970). In this paper we describe the crystal structure of (I) as part of our programme of structural investigations on 2,2'-bipyridylium salts.



The crystals of the pyrazinium salt were in the form of thin yellow platelets. Unit-cell dimensions were determined from oscillation and zero-layer Weissenberg photographs taken with the crystal set up about the a and c axes, the a axis being perpendicular to the plane of the platelets.

Experimental

Crystal data

C₁₂H₁₀N₂²⁺2Br⁻.H₂O, F.W. 360·0; Orthorhombic: $a = 17.06 \pm 0.02$, $b = 22.50 \pm 0.02$, $c = 6.89 \pm 0.01$ Å; U = 2644.7Å³; Z = 8; $D_x = 1.81$. Systematic absences: 0kl when k is odd, h0l when l is odd, hk0 when h is odd. Space group Pbca (D_{2h}^{15}) ; λ (Cu K α) = 1.5418Å; $\mu = 85.5$ cm⁻¹.

The intensity data, consisting of the 0kl to 3kl and hk0 to hk5 layers, were recorded on multiple-film equi-inclination Weissenberg photographs and measured with a Joyce-Deeley flying spot integrating microdensitometer. The crystal used had dimensions $0.05 \times 0.1 \times 0.2$ mm. The normal geometric correction factors were applied and corrections for absorption were made using a FORTRAN program made available to us by Dr N. W. Alcock (Alcock, 1969). In all, 1897 independent structure amplitudes were evaluated as above background.

Stucture determination and refinement

The two bromide ions were located from the threedimensional Patterson synthesis. Phase angles, calculated on the basis of the coordinates of the bromide ions, were then used with the observed amplitudes, to evaluate a three-dimensional electron density distribution, and from this the positions of all atoms in the asymmetric unit (except for hydrogen atoms) could be determined. Inclusion of the lighter atoms in the structure factor calculations reduced the conventional discrepancy value R from 40.5% (bromide ions alone) to 26.8%.

Refinement was carried out by the method of least squares. Initially, positional and isotropic thermal parameters were adjusted and R was reduced to 17.3%. Finally, the atoms were allowed to vibrate anisotropically and the least-squares refinement was terminated when the calculated shifts in the parameters were all

Table	1.	Atomic	coordinates	with	estimated	standard	
deviations in parentheses							

Values for the non-hydrogen atoms are multiplied by 10⁴ and for the hydrogen atoms by 10³.

	x/a	y/b	z/c
Br(1)	963 (1)	1759 (1)	9521 (2)
Br(2)	3427 (1)	808 (1)	7735 (2)
C(3)	3621 (7)	-127(4)	2732 (19)
C(4)	4378 (8)	-239(4)	2608 (17)
C(5)	4934 (7)	207 (5)	2493 (16)
C(6)	4698 (6)	796 (4)	2480 (15)
C(7)	3889 (5)	925 (4)	2675 (14)
C(8)	3605 (5)	1519 (4)	2708 (15)
C(9)	4106 (5)	2010 (4)	2693 (18)
C(10)	3777 (7)	2586 (4)	2727 (20)
C(11)	2975 (6)	2661 (4)	2789 (17)
C(12)	2491 (6)	2175 (4)	2823 (16)
C(13)	2292 (6)	1135 (4)	2893 (19)
C(14)	2572 (6)	574 (4)	2853 (17)
N(15)	3357 (5)	462 (3)	2761 (13)
N(16)	2807 (5)	1610 (3)	2781 (13)
O(17)	713 (7)	3220 (5)	9926 (18)
H(C3)	328	- 50	310
H(C4)	460	-70	250
H(C5)	558	10	238
H(C6)	509	117	234
H(C9)	478	195	268
H(C10)	417	298	267
H(C11)	267	312	284
H(C12)	182	223	289
H(C13)	167	122	319
H(C14)	214	22	276

Table 2. Anisotropic thermal parameters (Å²) for the heavier atoms

Temperature factors are in the form $T = \exp \left[-2\pi^2 (U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)\right]$.

All values are multiplied by 104.

U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
701	486	376	-173	7	15
402	257	403	9	2	3
541	159	527	45	- 5	80
564	264	383	8	-21	-8
478	423	272	163	-11	15
327	339	285	46	-93	-110
265	186	239	- 49	46	35
284	160	363	22	- 44	21
279	163	570	-43	-21	-33
452	180	652	14	67	-34
383	285	407	64	18	- 51
323	245	367	47	-16	2
305	320	515	-11	5	28
312	317	395	-143	-67	64
357	77	374	- 56	2	- 58
282	257	226	- 57	-2	54
840	712	509	-119	116	-15
	$U_{11} \\701 \\402 \\541 \\564 \\478 \\327 \\265 \\284 \\279 \\452 \\383 \\323 \\305 \\312 \\357 \\282 \\840 \\$	$\begin{array}{cccc} U_{11} & U_{22} \\ 701 & 486 \\ 402 & 257 \\ 541 & 159 \\ 564 & 264 \\ 478 & 423 \\ 327 & 339 \\ 265 & 186 \\ 284 & 160 \\ 279 & 163 \\ 452 & 180 \\ 383 & 285 \\ 323 & 245 \\ 305 & 320 \\ 312 & 317 \\ 357 & 77 \\ 282 & 257 \\ 840 & 712 \\ \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 3. Molecular dimensions

(a) Bond lengths with estimated standard deviations in parentheses

C(3)-C(4) C(3)-N(15) C(4)-C(5) C(5)-C(6) C(6)-C(7) C(7)-N(15) C(7)-C(8) C(8)-C(9)	1·317 1·401 1·382 1·385 1·417 1·382 1·422 1·397	(18) Å (11) (17) (13) (13) (11) (12) (12)	C(8)—N(C(9)—C(C(10)-C(C(11)-C(C(12)-N(C(13)-N(C(13)-C(C(14)-N(16) 10) 11) 12) 16) 16) 14) 15) 	1.377 1.411 1.379 1.369 1.381 1.385 1.350 1.365	(12) Å (13) (15) (14) (12) (12) (12) (14) (13)
(b) Bond angles N(15)-C(3)-C(4) C(3)-C(4)-C(5) C(4)-C(5)-C(6) C(5)-C(6)-C(7) C(6)-C(7)-C(8) N(15)-C(7)-C(8) C(7)-C(8)-C(9) C(7)-C(8)-N(1) C(9)-C(8)-N(1) C(9)-C(8)-N(1) C(8)-C(9)-C(10)))) 5))) 6) 6) 0)	119.7° 122.6 119.6 118.6 119.2 121.8 118.9 122.3 118.5 118.5 119.2 118.8	C(9)—C(C(10)–C(C(11)–C(N(16)–C(C(13)–C(C(14)–N(C(14)–N(C(13)–N(C(13)–N(C(13)–N(C(12)–N(10)-C(1 11)-C(1 12)-N(1 13)-C(1 14)-N(1 15)-C(3 15)-C(3 15)-C(3 16)-C(1 16)-C(8 16)-C(8	1) 2) 6) 4) 5)))) 2))	120.5° 120.1 119.9 119.7 121.3 120.5 119.4 120.1 117.4 120.9 121.6

Average e.s.d. 0.9°.

Table 4. Hydrogen-bonded and non-bonded distances (Å)

$H_2O\cdots Br^-$ O(17 ⁱ)\cdots Br(1) O(17)\cdots Br(1)	3·19 3·32	$O(17) \cdots Br(1^i)$	3.75
$\begin{array}{c} Cation \cdots Br^- \\ C(7) & \cdots Br(2^{ii}) \\ N(15) & \cdots Br(2) \\ C(11) & \cdots Br(2^{i}) \\ C(13) & \cdots Br(1^{ii}) \\ N(15) & \cdots Br(2^{ii}) \\ C(14) & \cdots Br(2^{iii}) \\ C(7) & \cdots Br(2) \\ C(12) & \cdots Br(1^{ii}) \end{array}$	3.50 3.52 3.53 3.54 3.55 3.55 3.55 3.58 3.58	$\begin{array}{c} C(5) \cdots Br(2^{iv}) \\ C(10) \cdots Br(2^{i}) \\ C(6) \cdots Br(1^{v}) \\ C(14) \cdots Br(2) \\ C(4) \cdots Br(1^{iii}) \\ C(12) \cdots Br(1^{i}) \\ C(9) \cdots Br(1^{v}) \\ C(8) \cdots Br(2^{ii}) \end{array}$	3.61 3.66 3.69 3.70 3.71 3.73 3.75 3.79
Cation \cdots H ₂ O C(6) \cdots O(17 ^{vi}) C(9) \cdots O(17 ^{vi}) Cation \cdots Cation	3·26 3·32	$C(13)\cdots O(17^{i})$ $C(12)\cdots O(17^{i})$	3·36 3·47
$\begin{array}{c} C(10) & \cdots & C(10^{vii}) \\ C(11) & \cdots & C(11^{vii}) \\ C(12) & \cdots & C(11^{vii}) \\ C(11) & \cdots & C(12^{vii}) \\ C(9) & \cdots & C(10^{i}) \end{array}$	3·47 3·52 3·54 3·58 3·58	$\begin{array}{l} C(9) \cdots C(10^{vii}) \\ C(11) \cdots C(10^{vii}) \\ C(12) \cdots C(12^{vii}) \\ C(10) \cdots C(11^{vii}) \end{array}$	3.63 3.71 3.74 3.79

The superscripts refer to the following equivalent positions:

i $x, \frac{1}{2} - y, -\frac{1}{2} + z$	ii x, y, $-1+z$
iii $\frac{1}{2} - x$, $-y$, $-\frac{1}{2} + z$	iv $1 - x$, $-y$, $1 - z$
$v_{1} \frac{1}{2} + x$, y , $1\frac{1}{2} - z$	vi $\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$
vii $x, \frac{1}{2} - y, \frac{1}{2} + z$	

less than one tenth of the corresponding standard deviations, with R=9.4%. Hydrogen atoms were included in the calculations in their theoretical positions, assuming a C-H bond length of 1.08 Å, but their parameters were not refined. The weighting scheme used in the final cycles of least-squares calculations was based on that suggested by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961):

$$\sqrt{w} = (a+b|F_o|+c|F_o|^2)^{-1/2}$$

with a = 10.25, b = -0.067, c = 0.0125, chosen so as to give approximately constant values for the average of $\sum w(|F_o| - |F_c|)^2$ when taken in groups of increasing $|F_o|$ and increasing $\sin \theta/\lambda$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), except for hydrogen atoms, for which those of Stewart, Davidson & Simpson (1965) were used. For N⁺ a composite curve $\frac{1}{3}(2f_N + f_N^{3+})$ was used.

The observed and calculated structure factors are listed in a table available elsewhere (Derry, 1972).*

The final atomic coordinates are given in Table 1 and the thermal parameters are in Table 2. Bond lengths and angles calculated from the coordinates of Table 1 are in Table 3, and non-bonded distances < 3.8Å are in Table 4.

Results and discussion

The crystal structure is illustrated in Fig. 1. It consists of near-planar organic cations stacked along the c axis and interleaved with bromide ions [Br(2)]. The bromide

* Xerox copies of this table may be purchased from the Librarian, The Main Library, University of Birmingham, Birmingham B15 2TT, England.



Fig. 1. The crystal structure as viewed along the c axis.



Fig. 2. Mean dimensions for the dipyrido[1,2-a:2',1'-c]pyrazinium ion.

ions are approximately halfway between successive cations which are virtually perpendicular to the c axis, and separated by the cell translation (6.89Å). The perpendicular from Br(2) to the plane of the cation passes close to the centre of the N(15)-C(7) bond with dis- $Br(2) \cdots N(15) = 3.52$, $Br(2) \cdots C(7) = 3.58$, tances. $Br(2^{ii}) \cdots N(15) = 3.55$ and $Br(2^{ii}) \cdots C(7) = 3.50 \text{ Å}$ (cf. Table 4). A similar stacking arrangement in crystals of N-methylacridinium iodide, which are, however, red in colour, has been correlated with charge transfer from the halide anion to the organic cation (Nakamura, Yasuoka, Kasai, Mikawa & Kakudo, 1970). We defer discussion as to whether the interionic contacts in dipyrido[1,2-a:2',1'-c]pyrazinium dibromide involve any charge transfer, to a later paper.

The crystallographically independent bromide ion Br(1) and the water of crystallization [O(17)] are linked by hydrogen bonds in an infinite chain which runs parallel to the cation $\cdots Br(2)$ stacks and fills the interstices between them. The relevant $Br^- \cdots H_2O$ distances are $Br(1) \cdots O(17^i) = 3 \cdot 19$ and $Br(1) \cdots O(17) = 3 \cdot 32 \text{Å}$, and the donor angle $Br(1) \cdots O(17^i) \cdots Br(1^i)$ is $94 \cdot 6^\circ$.

Consideration of the bond lengths and angles in Table 3 shows that there are no significant differences between pairs of chemically equivalent, but crystallographically independent, lengths or angles. For bonds, on seven degrees of freedom, $\chi^2 = 12.5$ and the organic cation may therefore be considered to be symmetrical about a line through the mid-points of the central bond, C(7)-C(8), and the bridging bond, C(13)-C(14).* Appropriately averaged values for bond lengths and angles are shown in Fig. 2 and these probably represent the most significant dimensions for the cation.

Unfortunately, the accuracy of the analysis is not high, due in large part to the unfavourable shape of of the crystals. Nevertheless, the observed bond lengths can be rationalized to some extent in terms of the five possible non-excited valence bond structures [formulae (I) and (IV), together with the three other canonicals

^{*} Even if the cation is involved in (unsymmetrical) charge transfer interactions with the bromide ions, these would not be expected to lead to measurable changes in the dimensions of the cation (Prout & Murray-Rust, 1969).

derived from (I) by altering the arrangements of double and single bonds in the outer rings].

Thus the carbon-nitrogen bond lengths of 1·365 to 1·40Å are greater than those found in pyridinium derivatives such as pyridoxine hydrochloride (Hanic, 1966), ethionamide hydrochloride (Colleter & Gadret, 1968), diquat dibromide (Derry & Hamor, 1969), 1,1'tetramethylene-2,2'-bipyridylium dibromide (Derry & Hamor, 1970), and paraquat salts with chlorometallate anions (Prout & Murray-Rust, 1969; Russell & Wallwork, 1969), where they range from 1·33 to 1·36Å, but are shorter than the standard C(aromatic)-N single bond length of 1·43Å (Sutton, 1965).

However, the chemically equivalent bonds, C(3)–C(4) at 1.317Å and C(11)–C(12) at 1.369Å are both anomalously short, as is, of course, the average length of 1.34Å. A slight shortening of these bonds would be expected from the contribution of structure (IV), but not to the extent observed.

Valency angles are generally normal. The C–N⁺–C angles within the pyridinium rings are slightly greater than 120° in agreement with previous results (Singh, 1965; Hanic, 1966; Colleter & Gadret, 1968; Derry & Hamor, 1969).

The atomic displacements from the mean plane of the cation are quite small (maximum 0.05Å, root-meansquare deviation 0.02Å) but are, nevertheless, significant, with $\chi^2 = 60.3$ for eleven degrees of freedom. The three rings are each planar to within the limits of experimental error. The two outer rings are, however, displaced slightly in opposite directions from the plane

Table 5. Deviations of atoms from least-squares planes

(a) Plane through whole cation

C(3)	−0·022 Å	C(8)	−0·001 Å	C(13)	-0.003 Å
C(4)	-0.010	C(9)	-0.038	C(14)	-0.004
C(5)	0.017	C(10)	-0.028	N(15)	- 0 ·016
C(6)	0.020	C(11)	0.006	N(16)	0.025
C(7)	-0.006	C(12)	0.028		

(b) Plane through central ring C(7), C(8), N(16), C(13), C(14), N(15)

C(7)	0∙002 Å	C(3)	0∙008 Å	C(9)	—0·052 Å
C(8)	-0.001	C(4)	0.028	C(10)	-0.058
N(16)	0.011	C(5)	0.048	C(11)	-0.030
C(13)	-0.010	C(6)	0.066	C(12)	-0.001
C(14)	0.004			```	
N(15)	0.000				

Equations of planes:

(a) 0.0562X - 0.0009Y + 0.9984Z = 2.2043(b) 0.0525X - 0.0091Y + 0.9986Z = 2.2090

where X, Y, Z, are coordinates, in Å, relative to the cell axes.

of the central ring (Table 5). A similar distortion from planarity in the phenanthrene structure (Trotter, 1963) was attributed to intramolecular overcrowding involving the hydrogen atoms *ortho* to the central bond. A similar effect is probably operative in the dipyrido-[1,2-a:2',1'-c]pyrazinium cation.

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References

- ALCOCK, N. W. (1969). Acta Cryst. A 25, 518.
- BLACK, A. L. & SUMMERS, L. A. (1969). J. Chem. Soc. (C), p. 610.
- BOON, W. R. (1964). Outlook Agric. 4, 163.
- BOON, W. R. (1967). Endeavour, 26, 27.
- BRIMACOMBE, J. S., GENT, P. A. & HAMOR, T. A. (1968). J. Chem. Soc. (B), p. 1566.
- COLLETER, J. C. & GADRET, M. (1968). Acta Cryst. B24, 513.
- CORR, D. H. & GLOVER, E. E. (1965). J. Chem. Soc. p. 5816.
- CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In Computing Methods and the Phase Problem in X-ray Crystal Analysis, p. 32. Oxford: Pergamon Press.
- DERRY, J. E. (1972). Thesis, Univ. of Birmingham.
- DERRY, J. E. & HAMOR, T. A. (1969). Nature, Lond. 221, 464.
- DERRY, J. E. & HAMOR, T. A. (1970). Chem. Commun. p. 1284.
- HANIC, F. (1966). Acta Cryst. 21, 332.
- International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
- Nakamura, N., Yasuoka, N., Kasai, N., Mikawa, H. & Kakudo, M. (1970). *Chem. Commun.* p. 1135.
- PROUT, C. K. & MURRAY-RUST, P. (1969). J. Chem. Soc. (A), p. 1520.
- RUSSELL, J. H. & WALLWORK, S. C. (1969). Acta Cryst. B25, 1691.
- SINGH, C. (1965). Acta Cryst. 19, 861.
- STEWART, R. F., DAVIDSON, F. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175.
- SUTTON, L. E. (1965). Tables of Interatomic Distances and Configuration in Molecules and Ions. London: The Chemical Society.
- TROTTER, J. (1963). Acta Cryst. 16, 605.