

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

BY J. E. DERRY AND T. A. HAMOR

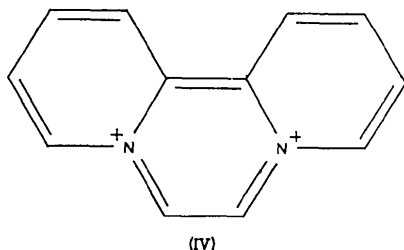
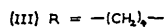
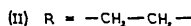
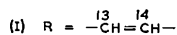
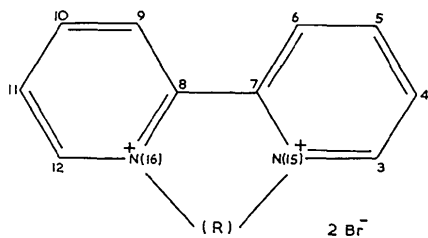
Department of Chemistry, The University, Birmingham B15 2TT, England

(Received 17 September 1971)

Crystals of dipyrido[1,2-*a*:2',1'-*c*]pyrazinium dibromide monohydrate are orthorhombic, space group *Pbca*, with eight formula units of $C_{12}H_{10}N_2^{2+} \cdot 2Br^- \cdot H_2O$ 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 bipyridylum 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'-bipyridylum salts.



Experimental

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.

Crystal data

$C_{12}H_{10}N_2^{2+} \cdot 2Br^- \cdot H_2O$, F.W. 360.0;

Orthorhombic: $a = 17.06 \pm 0.02$, $b = 22.50 \pm 0.02$, $c = 6.89 \pm 0.01$ Å; $U = 2644.7$ Å³; $Z = 8$; $D_x = 1.81$.

Systematic absences: $0kl$ when *k* is odd, $h0l$ when *l* is odd, $hk0$ when *h* is odd.

Space group *Pbca* (D_{2h}^{15});

$\lambda(\text{Cu } K\alpha) = 1.5418$ Å; $\mu = 85.5$ 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.

Structure determination and refinement

The two bromide ions were located from the three-dimensional 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 dis-

crepancy 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 10^4 and for the hydrogen atoms by 10^3 .

	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 (\AA^2) for the heavier atoms*

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

All values are multiplied by 10^4 .

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	701	486	376	-173	7	15
Br(2)	402	257	403	9	2	3
C(3)	541	159	527	45	-5	80
C(4)	564	264	383	8	-21	-8
C(5)	478	423	272	163	-11	15
C(6)	327	339	285	46	-93	-110
C(7)	265	186	239	-49	46	35
C(8)	284	160	363	22	-44	21
C(9)	279	163	570	-43	-21	-33
C(10)	452	180	652	14	67	-34
C(11)	383	285	407	64	18	-51
C(12)	323	245	367	47	-16	2
C(13)	305	320	515	-11	5	28
C(14)	312	317	395	-143	-67	64
N(15)	357	77	374	-56	2	-58
N(16)	282	257	226	-57	-2	54
O(17)	840	712	509	-119	116	-15

Table 3. *Molecular dimensions*

(a) Bond lengths with estimated standard deviations in parentheses

C(3)-C(4)	1.317 (18) \AA	C(8)-N(16)	1.377 (12) \AA
C(3)-N(15)	1.401 (11)	C(9)-C(10)	1.411 (13)
C(4)-C(5)	1.382 (17)	C(10)-C(11)	1.379 (15)
C(5)-C(6)	1.385 (13)	C(11)-C(12)	1.369 (14)
C(6)-C(7)	1.417 (13)	C(12)-N(16)	1.381 (12)
C(7)-N(15)	1.382 (11)	C(13)-N(16)	1.385 (12)
C(7)-C(8)	1.422 (12)	C(13)-C(14)	1.350 (14)
C(8)-C(9)	1.397 (12)	C(14)-N(15)	1.365 (13)

(b) Bond angles

N(15)-C(3)-C(4)	119.7°	C(9)-C(10)-C(11)	120.5°
C(3)-C(4)-C(5)	122.6	C(10)-C(11)-C(12)	120.1
C(4)-C(5)-C(6)	119.6	C(11)-C(12)-N(16)	119.9
C(5)-C(6)-C(7)	118.6	N(16)-C(13)-C(14)	119.7
C(6)-C(7)-N(15)	119.2	C(13)-C(14)-N(15)	121.3
C(6)-C(7)-C(8)	121.8	C(14)-N(15)-C(7)	120.5
N(15)-C(7)-C(8)	118.9	C(14)-N(15)-C(3)	119.4
C(7)-C(8)-C(9)	122.3	C(7)-N(15)-C(3)	120.1
C(7)-C(8)-N(16)	118.5	C(13)-N(16)-C(12)	117.4
C(9)-C(8)-N(16)	119.2	C(13)-N(16)-C(8)	120.9
C(8)-C(9)-C(10)	118.8	C(12)-N(16)-C(8)	121.6

Average e.s.d. 0.9°.

Table 4. *Hydrogen-bonded and non-bonded distances (\AA)*

H ₂ O...Br ⁻			
O(17 ⁱ)...Br(1)	3.19	O(17)...Br(1 ⁱ)	3.75
O(17)...Br(1)	3.32		
Cation...Br ⁻			
C(7)...Br(2 ⁱⁱ)	3.50	C(5)...Br(2 ^{iv})	3.61
N(15)...Br(2)	3.52	C(10)...Br(2 ⁱ)	3.66
C(11)...Br(2 ⁱⁱ)	3.53	C(6)...Br(1 ^v)	3.69
C(13)...Br(1 ⁱⁱ)	3.54	C(14)...Br(2)	3.70
N(15)...Br(2 ⁱⁱⁱ)	3.55	C(4)...Br(1 ⁱⁱⁱ)	3.71
C(14)...Br(2 ⁱⁱⁱ)	3.55	C(12)...Br(1 ⁱ)	3.73
C(7)...Br(2)	3.58	C(9)...Br(1 ^v)	3.75
C(12)...Br(1 ⁱⁱ)	3.58	C(8)...Br(2 ⁱⁱ)	3.79
Cation...H ₂ O			
C(6)...O(17 ^{vi})	3.26	C(13)...O(17 ⁱ)	3.36
C(9)...O(17 ^{vi})	3.32	C(12)...O(17 ⁱ)	3.47
Cation...Cation			
C(10)...C(10 ^{vii})	3.47	C(9)...C(10 ^{vii})	3.63
C(11)...C(11 ^{vii})	3.52	C(11)...C(10 ^{vii})	3.71
C(12)...C(11 ^{vii})	3.54	C(12)...C(12 ^{vii})	3.74
C(11)...C(12 ^{vii})	3.58	C(10)...C(11 ^{vii})	3.79
C(9)...C(10 ⁱ)	3.58		

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	$\frac{1}{2}+x, y, 1\frac{1}{2}-z$	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 \AA, 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, Bu-

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 1.40 Å 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'-bipyridylum dibromide (Derry & Hamor, 1970), and paraquat salts with chlorometallate anions (Prout & Murray-Rust, 1969; Russell & Wallwork, 1969), where they range from 1.33 to 1.36 Å, but are shorter than the standard C(aromatic)–N single bond length of 1.43 Å (Sutton, 1965).

However, the chemically equivalent bonds, C(3)–C(4) at 1.317 Å and C(11)–C(12) at 1.369 Å are both anomalously short, as is, of course, the average length of 1.34 Å. 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 0.05 Å, root-mean-square deviation 0.02 Å) 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)	0.050	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)	–0.007	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.

We thank Dr T. E. Tomlinson and Dr J. A. Farington, of Imperial Chemical Industries Limited, Jealott's Hill Research Station, for supplying the crystals, Professor M. Stacey and Professor J. C. Robb for their interest, and the Science Research Council for financial support. All computations were performed on the Birmingham University KDF9 computer, and we thank the staff of the Computer Centre for their assistance. The major computer programs used in the analysis have been acknowledged elsewhere (Brimacombe, Gent & Hamor, 1968).

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