and six-membered rings, the dimensions of the cation are virtually identical with those found in its $[MCl_4]^{2-}$ salts (M = Fe, Hg) (Rusholme, 1970). As with other 1,2-dithiolium cations, bond lengths and bond angles are indicative of substantial cyclic delocalization in the five-membered ring system.

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The Crystal Structures of 2,2′-Bipyridine.2ICl and 2,2′-Bipyridine.2IBr

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The crystal structures of 2,2′-bipyridine.2ICl and 2,2′-bipyridine.2IBr have been determined from three-dimensional diffractometer data to give $R = 2{\cdot}9$ % and 4·0 % respectively. 2,2′-Bipyridine.2ICl crystallizes in $P2_1/n$ with $a = 11{\cdot}833$ (7), $b = 12{\cdot}427$ (7), $c = 10{\cdot}163$ (5) Å, and $\beta = 101{\cdot}76$ (3)°; $Z = 4$. 2,2′-Bipyridine.2IBr crystallizes in *Pnna*, with $a = 12{\cdot}971$ (4), $b = 11{\cdot}163$ (4), $c = 10{\cdot}387$ (4) Å; $Z = 4$. In the chlorine compound the dihedral angle between the pyridine rings is 88·6°, in the bromine compound 52·9°. A short intramolecular approach of the two iodine atoms in the IBr adduct (4·09 Å) is observed.

Introduction

Several significant differences in the chemical structure of 2,2′-bipyridine.2ICl and 2,2′-bipyridine.2IBr (hereinafter referred to as bipy.2ICl and bipy.2IBr) were inferred from a recent Mössbauer spectroscopic study of ^{129}I (Wynter, Hill, Bledsoe, Shenoy & Ruby, 1969). For example, bipy.2ICl has more π bonding than the IBr adduct. Furthermore, from the larger asymmetry parameter of bipy.2IBr, the authors suggested that bipy.2ICl exists in a *trans* conformation in the solid state, but bipy.2IBr crystallizes in a *cis* conformation. Previously, it had been found that uncomplexed 2,2′-bipyridine crystallizes as a planar molecule with the two nitrogen atoms *trans* to one another (Merritt & Schroeder, 1956). Structural studies have also been done on the ICl and IBr adducts to pyridine (Hassel & Rømming, 1956; Dahl, Hassel & Sky, 1967) showing the N–I–X bonding to be linear. This study was undertaken to compare the detailed geometry of bipy.2ICl, $C_{10}H_8N_2.2ICl$, and bipy.2IBr, $C_{10}H_8N_2.2IBr$.

Experimental

Sample preparation

Both the ICl and IBr adducts are prepared as fine powders by slowly mixing dilute CCl_4 solutions of 2,2′-bipyridine and ICl or IBr (Popov & Pflaum, 1957; Yagi, Popov & Person, 1967). Crystals of both compounds can be grown by sublimation on to a cold finger; bipy.2ICl sublimes at approximately 90°C, bipy.2IBr, 10° lower. Both compounds decompose on standing, bipy.2IBr more rapidly; however, decomposition can be prevented by coating the crystals with a thin layer of halocarbon grease (Kel–F).

Unit cell and space group

Crystallographic data for the two compounds are given in Table 1. Unit cell and space-group data were obtained from Weissenberg and precession photographs and from 12 2θ values measured on a Picker FACS-I diffractometer with a graphite monochromator using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å).

Table 1. *Crystallographic data*

	2,2′-Bipyridine.2ICl	2,2′-Bipyridine.2IBr
System	Monoclinic	Orthorhombic
a	11·833 (7) Å	12·971 (4) Å
b	12·427 (7)	11·163 (4)
c	10·163 (5)	10·387 (4)
β	101·76 (3)°	
Absences	$h0l$, $h+l=2n+1$ $0k0$, $k=2n+1$	$h0l$, $h+l=2n+1$ $hk0$, $h=2n+1$ $0kl$, $k+l=2n+1$
Space group	$P2_1/n$	$Pnna$
Z	4	4
d_x	2·18 g cm^{-3}	2·52 g cm^{-3}
d_m	2·16 (2)	2·49 (2)
μ, Mo $K\alpha$	46·9 cm^{-1}	98·4 cm^{-1}
Crystal size	0·30 × 0·20 × 0·15 mm	0·15 × 0·15 × 0·33 mm

For both compounds systematic extinctions determined the space group uniquely. Densities were measured by flotation in a mixture of CCl_4 and $CHBr_3$.

Intensity data

Three-dimensional intensity data for each crystal were collected with a Picker FACS-I diffractometer with Mo $K\alpha$ radiation and a graphite monochromator.

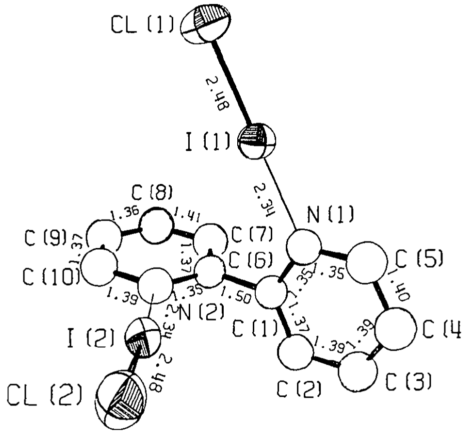

Fig. 1. A molecule of 2,2′-bipyridine.2ICl. The iodine and chlorine atoms are represented by thermal ellipsoids scaled to 50% probability density. The dihedral angle between the two pyridine rings is 88·6° and I(1)···I(2) is 4·34 Å.

Table 2. *Atomic parameters for* 2,2′-*bipyridine*.2ICl *and* 2,2′-*bipyridine*.2IBr

Fractional atomic coordinates (× 10^4) and temperature factor parameters (× 10^4) for the iodine, chlorine, and bromine atoms in the expression $\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. Isotropic temperature parameters for the nitrogen and carbon atoms are listed in Å^2. Standard deviations are given in parentheses.

2,2′-Bipyridine.2ICl

	x	y	z	β_{11}	β_{22}	β_{22}	β_{12}	β_{13}	β_{23}
I(1)	406 (1)	1215 (1)	1670 (1)	86 (1)	70 (1)	103 (1)	−7 (1)	12 (1)	4 (1)
I(2)	685 (1)	4563 (1)	2908 (1)	91 (1)	66 (1)	119 (1)	4 (1)	37 (1)	−1 (1)
Cl(1)	−1335 (2)	181 (2)	1822 (3)	95 (3)	102 (3)	219 (5)	−20 (2)	34 (3)	8 (3)
Cl(2)	−492 (2)	5939 (2)	1483 (3)	125 (3)	90 (2)	181 (4)	30 (2)	55 (3)	26 (3)

	x	y	z	B		x	y	z	B
N(1)	2071 (6)	2178 (6)	1523 (7)	4·22 (15)	N(2)	1683 (6)	3216 (6)	4288 (7)	4·43 (16)
C(1)	2727 (7)	2687 (7)	2583 (8)	3·83 (18)	C(6)	2431 (8)	2512 (7)	3929 (7)	3·84 (18)
C(2)	3640 (8)	3329 (8)	2451 (9)	2·64 (21)	C(7)	2893 (8)	1665 (8)	4719 (10)	5·24 (23)
C(3)	3886 (9)	3462 (8)	1176 (10)	5·31 (23)	C(8)	2568 (9)	1548 (9)	5975 (10)	5·59 (24)
C(4)	3221 (9)	2948 (9)	75 (10)	5·53 (23)	C(9)	1818 (9)	2251 (8)	6349 (10)	5·28 (23)
C(5)	2322 (8)	2279 (8)	289 (10)	5·25 (22)	C(10)	1359 (8)	3079 (8)	5520 (10)	5·08 (22)

2,2′-Bipyridine.2IBr

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	457 (1)	668 (1)	2539 (1)	61 (1)	58 (1)	92 (1)	−2 (1)	8 (1)	0 (1)
Br	−982 (2)	−563 (2)	1454 (2)	75 (2)	12 (2)	165 (3)	−30 (2)	−6 (2)	−18 (3)

	x	y	z	B
N	1803 (9)	1765 (12)	3721 (13)	3·78 (29)
C(1)	2593 (12)	2358 (16)	3215 (15)	3·74 (34)
C(2)	3455 (14)	2692 (18)	3932 (20)	5·70 (49)
C(3)	3457 (14)	2397 (18)	5227 (19)	5·97 (47)
C(4)	2634 (14)	1768 (17)	5768 (18)	5·09 (45)
C(5)	1807 (12)	1460 (16)	4989 (19)	4·67 (42)

θ–2θ scans were used to collect 1302 observed reflections for bipy.2ICl and 555 for bipy.2IBr. A reflection was considered unobserved if the intensity was less than twice its estimated standard deviation.

Structure amplitudes were calculated in the usual way. For both compounds the variance in F^2 was estimated by the expression

$$v(F^2)=\sigma(F^2)^2=(1/\mathrm{Lp})^2\{C+0\cdot825+(t_c/2t_b)^2(B_1+B_2+1\cdot65)+(0\cdot05C)^2+[0\cdot05(B_1+B_2)]^2\}$$

where Lp is the Lorentz–polarization factor, C is the total integrated count obtained in time t_c, and B_1 and B_2 are the two background counts each obtained in time t_b. The intensities were corrected for absorption by means of the *GONO* 9 program (Hamilton, 1956); transmission coefficients for bipy.2ICl ranged from 0·40 to 0·60, and for bipy.2IBr from 0·26 to 0·37.

Structure determination and refinement

Both structures were solved by standard heavy-atom methods and were refined by least-squares methods with the program *BULS*, which is a local variation of the *ORFLS* program (Busing, Martin & Levy, 1962). The function minimized was $\sum w(F_o-F_c)^2$. Weights were taken as $w=4F_o^2/v(F_o^2)$; this is the reciprocal variance in $|F|_o$.

2,2′-*Bipyridine*.2ICl

The two independent iodine atoms and one of the chlorine atoms were located from a three-dimensional Patterson function. The coordinates and isotropic temperature factor parameters of these atoms were refined by two cycles of least-squares adjustment to give $R=19\cdot8\%$, $R_w=29\cdot0\%$ based on observed $|F|$ values. Only reflections with $|F|^2$ values greater than $2\sigma(F^2)$ were included in the refinement. An electron-density difference map clearly showed the remaining chlorine and carbon atoms. Further cycles of refinement with the eventual inclusion of anisotropic thermal parameters for the iodine and chlorine atoms converged to $R=2\cdot9\%$, $R_w=3\cdot5\%$.* The structure was confirmed by a final difference synthesis.

2,2′-*Bipyridine*.2IBr

With four formula units in the space group *Pnna*, the centers of the molecules of bipy.2IBr must lie on either centers of inversion or twofold axes. From a three-dimensional Patterson function the independent iodine and bromine atoms were located about the twofold axes. The coordinates and isotropic thermal parameters of these two atoms were refined by two cycles of least-squares to yield $R=14\cdot9\%$, $R_w=21\cdot7\%$, based on observed $|F|$ values. From a subsequent difference map the remaining carbon and nitrogen atoms were located. Further cycles of refinement, eventually with the inclusion of anisotropic thermal parameters for the iodine and bromine atoms converged to a final $R=4\cdot0\%$, $R_w=4\cdot9\%$.* A final difference map revealed only residual density (1·1 e Å^{-3}) around the iodine atom.

Final positional and thermal parameters for both structures with their estimated standard deviations are listed in Table 2.

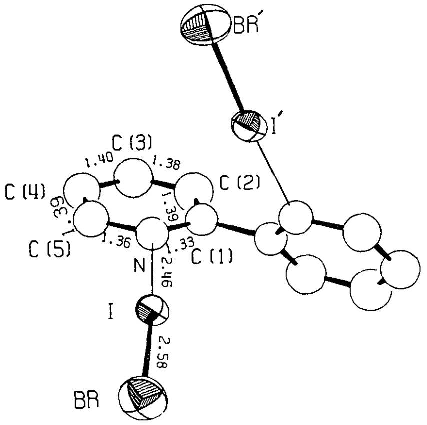

Fig. 2. A molecule of 2,2′-bipyridine.2IBr. The center of the molecule lies on a twofold axis of rotation. The dihedral angle between the two pyridine rings is only 52·9° and the I···I′ separation has become a short 4·09 Å.

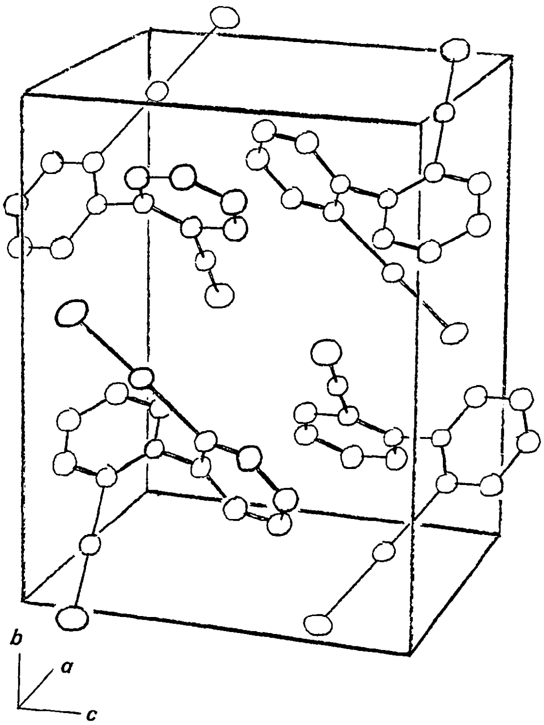

Fig. 3. The unit-cell contents of 2,2′-bipyridine.2ICl. All intermolecular contacts are longer than the van der Waals distances.

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* The final F_o, F_c tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30296 (10 pp). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

The molecules of bipy.2ICl and bipy.2IBr are shown in Figs. 1 and 2, respectively, together with the nomenclature and bond lengths. Packing diagrams are presented in Figs. 3 and 4.

The bond distances and angles in the two compounds are similar to those found in 2,2′-bipyridine (Merritt & Schroeder, 1956), pyridine.ICl (Hassel & Rømming, 1956), pyridine.IBr (Dahl, Hassel & Sky, 1967), and pentamethylenetetrazole.ICl (Baenziger, Nelson, Tulinsky, Bloor & Popov, 1967). Tables 3 and 4 contain the interatomic bond distances and angles of interest for the two compounds.

Table 3. *Bond lengths and angles in* 2,2′-*bipyridine*.2ICl

See Fig. 1 for numbering.

I(1)—Cl(1)	2·479 (4) Å	N(1)—C(1)—C(2)	122·1 (9)°
I(1)—N(1)	2·336 (7)	C(1)—C(2)—C(3)	118·6 (10)
N(1)—C(1)	1·35 (1)	C(2)—C(3)—C(4)	120·2 (10)
C(1)—C(2)	1·37 (1)	C(3)—C(4)—C(5)	118·2 (10)
C(2)—C(3)	1·40 (1)	C(4)—C(5)—N(1)	121·1 (10)
C(3)—C(4)	1·39 (2)	C(5)—N(1)—C(1)	119·8 (8)
C(4)—C(5)	1·40 (1)	N(1)—I(1)—Cl(1)	179·6 (3)
C(5)—N(1)	1·35 (1)	N(2)—C(6)—C(7)	123·1 (9)
C(1)—C(6)	1·50 (1)	C(6)—C(7)—C(8)	117·4 (10)
I(2)—Cl(2)	2·477 (11)	C(7)—C(8)—C(9)	120·1 (11)
N(2)—I(2)	2·344 (7)	C(8)—C(9)—C(10)	120·8 (10)
N(2)—C(6)	1·35 (1)	C(9)—C(10)–N(2)	119·8 (9)
C(6)—C(7)	1·37 (1)	C(10)–N(2)—C(6)	118·8 (9)
C(7)—C(8)	1·41 (1)	N(2)—I(2)—Cl(2)	176·2 (2)
C(8)—C(9)	1·36 (1)		
C(9)—C(10)	1·37 (1)		
C(10)–N(2)	1·39 (1)		
I(1)—I(2)	4·340 (3)		

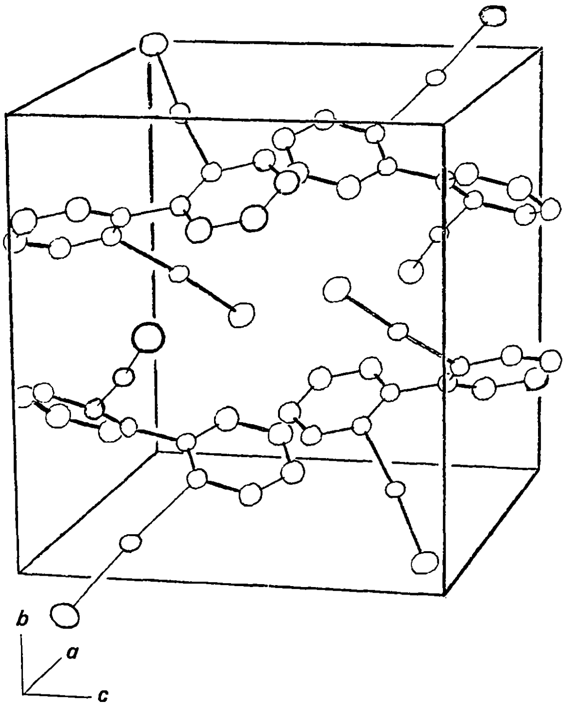

Fig. 4. The unit-cell contents of 2,2′-bipyridine.2IBr. All intermolecular contacts are longer than the van der Waals distances.

Table 4. *Bond lengths and angles in* 2,2′-*bipyridine*.2IBr

See Fig. 2 for numbering.

I—Br	2·577 (2) Å	N—C(1)–C(2)	122·7 (14)°
I—N	2·46 (1)	C(1)–C(2)–C(3)	117·2 (18)
N—C(1)	1·33 (2)	C(2)–C(3)–C(4)	120·7 (19)
C(1)–C(2)	1·40 (2)	C(3)–C(4)–C(5)	118·7 (18)
C(2)–C(3)	1·38 (3)	C(4)–C(5)–N	120·4 (16)
C(3)–C(4)	1·40 (2)	C(5)–N—C(1)	120·3 (41)
C(4)–C(5)	1·39 (2)	N—I—Br	175·9 (3)
C(5)–N	1·36 (2)		
C(1)–C(1′)	1·52 (3)		
I····I′	4·091 (3)		

The N–I–Cl and N–I–Br groups are most readily described as three-center four-electron bonds, containing one pair of bonding and one pair of nonbonding electrons (Rundle, 1962). This three-center four-electron bonding also occurs, for example, in α- and β-ICl (Boswijk, van der Heide, Vos & Wiebenga, 1956; Carpenter & Richards, 1962), in IBr (Swink & Carpenter, 1968), and in the ICl_2^- and IBr_2^- anions (Soled & Carpenter, 1973 *a*, *b*). When atoms X–Y–Z are linked by a three-center four-electron bond, bonds X–Y and Y–Z are weaker and longer than normal electron-pair bonds. If the bonding electron density shifts toward atom X, bond X–Y becomes weaker and longer, whereas bond Y–Z becomes stronger and shorter. In bipy.2ICl the N–I bond length 2·34 Å is 0·31 Å longer than a nominal single bond, and the I–Cl bond length 2·48 Å is 0·16 Å longer than a nominal single bond. [Nominal bond lengths are sums of Pauling's (1960) single-bond covalent radii]. In bipy.2IBr the N–I bond length 2·46 Å is 0·43 Å longer than a single bond, and the I–Br bond length 2·58 Å is 0·11 Å longer than a single bond. This indicates some shift, relative to the ICl adduct, of bonding electrons toward the nitrogen atom, as is consistent with the electronegativity of nitrogen being greater than that of bromine.

The individual pyridine rings of both bipy.2ICl and bipy.2IBr are nearly planar. Least-squares planes through the pyridine rings of both complexes, together with the deviations of all the atoms from these planes, can be found in Table 5. The iodine atoms in bipy.2ICl are 0·3 Å closer to the ring plane than the iodine atoms in bipy.2IBr. This is consistent with Mössbauer measurements, which indicate a higher percentage of π-bond character for the iodine atoms in the ICl adduct (7% *vs.* 4%). Furthermore, in the ICl adduct the iodine atoms are twisted out of the plane of the ring atoms toward one another, whereas in the IBr adduct, the iodine atoms are twisted away from one another.

Unlike 2,2′-bipyridine (Merritt & Schroeder, 1956) or biphenyl (Trotter, 1961; Hargreaves & Rizvi, 1962), which are both planar in the solid state, the pyridine rings in both bipy.2ICl and bipy.2IBr are significantly twisted with respect to one another. Wynter *et al.* (1969) suggested that the asymmetry parameter derived

Table 5. *Least-squares planes in* 2,2′-*bipyridine*.2ICl *and* 2,2′-*bipyridine*.2IBr

2,2′-Bipyridine.2IBr		2,2′-Bipyridine.2ICl			
Plane through, N, C(1)–C(5)		Plane through N(1), C(1)–C(5)		Plane through N(2), C(6)–C(10)	
$-5\cdot776x+9\cdot680y+2\cdot319z=1\cdot529$		$-7\cdot029x+9\cdot784y-0\cdot411z=0\cdot6049$		$8\cdot170x+7\cdot219y+2\cdot858z=4\cdot920$	
Distances of atoms from this plane		Distances of atoms from these planes			
N	0·0016 Å	N(1)	0·0079 Å	N(2)	0·0022 Å
C(1)	0·0014	C(1)	0·0010	C(6)	0·0019
C(2)	−0·0069	C(2)	−0·0072	C(7)	−0·0066
C(3)	0·0067	C(3)	0·0021	C(8)	0·0033
C(4)	−0·0020	C(4)	0·013	C(9)	0·0050
C(5)	−0·0020	C(5)	−0·019	C(10)	−0·0092
r.m.s. deviation =0·0017 Å		r.m.s. deviation =0·0042 Å		r.m.s. deviation =0·0022 Å	
I	−0·56	I(1)	0·23	I(1)	−0·24
Br	−1·17	Cl(1)	0·45	Cl(2)	−0·61

from Mössbauer spectroscopic measurements indicates that bipy.2ICl exists in a *trans* conformation and bipy.2IBr in a *cis* conformation. However, these conformations are sterically impossible in these compounds. A *cis* conformation would place the terminal halogen atoms in extremely close proximity, while in a *trans* conformation each iodine atom and its nearest carbon (and hydrogen) atom on the attached ring would be unreasonably close. (For example, in the case of an exactly *trans* bipy.2IX compound with all ring C–C bond distances 1·39 Å and with an N–I separation of 2·40 Å, the I···C separation would only be 2·67 Å.)

Indeed, in bipy.2ICl the best least-squares planes through the two rings are at 88·6° from the *cis* conformation, and there are no conspicuously short intra- or intermolecular distances. However, the intramolecular iodine–iodine distance of 4·34 Å is just the normal van der Waals separation. In bipy.2IBr, the twist from the *cis* conformation is only 52·9°, and the intramolecular iodine–iodine separation is only 4·09 Å. It appears, then, that in both cases the two iodine atoms are weakly drawn together with a resultant decrease in the dihedral angle between the two pyridine rings. Whether the greater effect in the IBr adduct arises from intrinsic factors or from extrinsic packing considerations is not obvious. This type of interaction also occurs in $KICl_2$ (Soled & Carpenter, 1973*a*) which has pairs of parallel ICl_2^- ions separated by only 4·15 Å.

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