Atom	Attached to	x/a	y/b	z/c
H(1)...	C(3)	0·518	0·067	0·121
H(2)...	C(4)	0·811	0·169	0·352
H(3)...	C(5)	0·861	0·328	0·660
H(4)...	C(6)	0·614	0·379	0·764
H(5)...	C(8)	0·299	0·344	0·722
H(6)...	C(8)	0·233	0·233	0·685
H(7)...	O(1)	0·092	−0·030	−0·088
H(8)...	O(3)	−0·059	0·534	0·167

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The Crystal Structure of N,N'-Dibenzyl-4,4'-bipyridylium diiodide

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$(C_6H_5.CH_2.NC_5H_4.C_5H_4N.CH_2.C_6H_5)^{2+}$ $2I^-$ forms red monoclinic crystals, space group $P2_1/c$, and each unit cell of dimensions $a = 7·009$, $b = 12·99$, $c = 12·74$ Å, $\beta = 90·2°$ contains two bipyridylium ions and four iodide ions. Although the iodide ion does not lie directly over the pyridylium ring, close interatomic approaches indicate that charge transfer from the iodide ion to the bipyridylium ion occurs.

Introduction

The crystal structures of a series of quaternary salts of N,N'-substituted-4,4'-bipyridyls have been determined as part of a programme aimed at investigating possible interactions between the anion and cation in relation to observed properties of the compounds. The first of these papers (Russell & Wallwork, 1969) reported the structure of the dimethyl substituted tetrachlorocuprate and a future paper will report the structures of the dimethyl substituted dichloride, dibromide and diiodide. This paper describes the crystal structure of N,N'-dibenzyl-4,4'-bipyridylium diiodide.

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Bipyridylium salts possess a number of interesting properties, one of which has enabled them to find commercial application as herbicides (Boon, 1964). Some have also been shown to be charge transfer complexes, (Macfarlane & Williams, 1969) as exhibited by their spectra. It is hoped that the present investigations will shed further light on the nature of the charge transfer interactions by studying the relative dispositions of the ions; this aspect will be discussed in a future paper.

Experimental

The material, in the form of red crystals suitable for X-ray photography, was supplied by the Mond Division of Imperial Chemical Industries Ltd. Oscillation and equi-inclination Weissenberg photographs were

Table 1. *Analysis of agreement between* F_o *and final* F_c (*both on* 50 *times absolute scale*)

$|F_o|$ range	No. of reflexion	$\sum ||F_o| - |F_c||$	R	Av. $\sum w(|F_o| - |F_c|)^2 10^{-3}$
0–999	1057	112402	0·185	32·7
1000–1999	412	47058	0·081	24·3
2000–2999	146	26262	0·074	10·1
3000–3999	86	24367	0·082	17·9
4000–4999	43	13084	0·068	7·4
5000–5999	24	13396	0·103	49·9
6000–7999	21	8813	0·060	6·3
8000–9999	2	1358	0·077	11·5
>9999	3	2999	0·094	16·7

taken with the crystals rotating about all three crystallographic axes, using Cu $K\alpha$ radiation ($\lambda = 1\cdot542$ Å). Unit-cell dimensions, as calculated from these photographs, were refined using a linear diffractometer (Arndt & Phillips, 1961) which was also used to collect intensity data for the $0kl$ to $9kl$ reciprocal lattice levels, using Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å). The intensities were corrected for Lorentz and polarization factors but not for absorption or extinction.

Determination and refinement of the structure

Crystal data

$(C_6H_5.CH_2.NC_5H_4.C_5H_4N.CH_2.C_6H_5)^{2+}2I^-$,
M.W. 591·8, Monoclinic.
$a = 7\cdot009 \pm 0\cdot001$, $b = 12\cdot99 \pm 0\cdot01$, $c = 12\cdot74 \pm 0\cdot01$ Å,
$\beta = 90\cdot2 \pm 0\cdot2°$,
$U = 1160$ Å^3, $D_m = 1\cdot70$ g.cm^{-3}, $Z = 2$, $D_c = 1\cdot70$ g.cm^{-3},
$F(000) = 572$.
Mo $K\alpha$ ($\lambda = 0\cdot7107$ Å), $\mu = 28$ cm^{-1}.
Absent spectra, $h0l$ when l is odd, $0k0$ when k is odd.
Space group $P2_1/c$ (No. 14).

Examination of two-dimensional Patterson syntheses in the $hk0$ and $0kl$ projections revealed the location of the single iodide ion in the asymmetric unit. The coordinates of the iodide ion were employed in structure factor calculations for each of the two projections and, using the calculated phases and observed amplitudes,

Fourier syntheses were computed, from which the approximate locations of the atoms of the bipyridylium ion were located. Successive Fourier syntheses and structure factor calculations refined the atomic locations to give residuals, $R = \sum||F_o| - |F_c|/\sum|F_o|$, of 0·20 and 0·33 for the $0kl$ and $hk0$ projections respectively.

Further refinement was carried out using three-dimensional data, by the block-diagonal, least-squares method with the aid of a program written by R. D. Diamand. The weighting scheme employed was $\sqrt{w} = 1$ if $|F_o| < F^*$, otherwise $\sqrt{w} = F^*/|F_o|$, with F^* adjusted to give approximately equal values of $\sum w(|F_o| - |F_c|)^2$ for all ranges of $|F_o|$. The scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for all atoms. Four cycles of isotropic least-squares refinement reduced the residual to 0·24. This was followed by five cycles of anisotropic refinement, as a result of which the residual converged to its final value of 0·106 for 1794 reflexions. Further refinement was not considered worth while in view of the extent to which the heavy iodide ion was dominating the values of the structure factors. The observed structure factors are compared with the values calculated from the final set of atomic parameters in a table available elsewhere (Russell, 1967).† An analysis of the comparison is given in Table 1.

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† Copies of this Table may be purchased from the Science Library, The University, Nottingham, England.
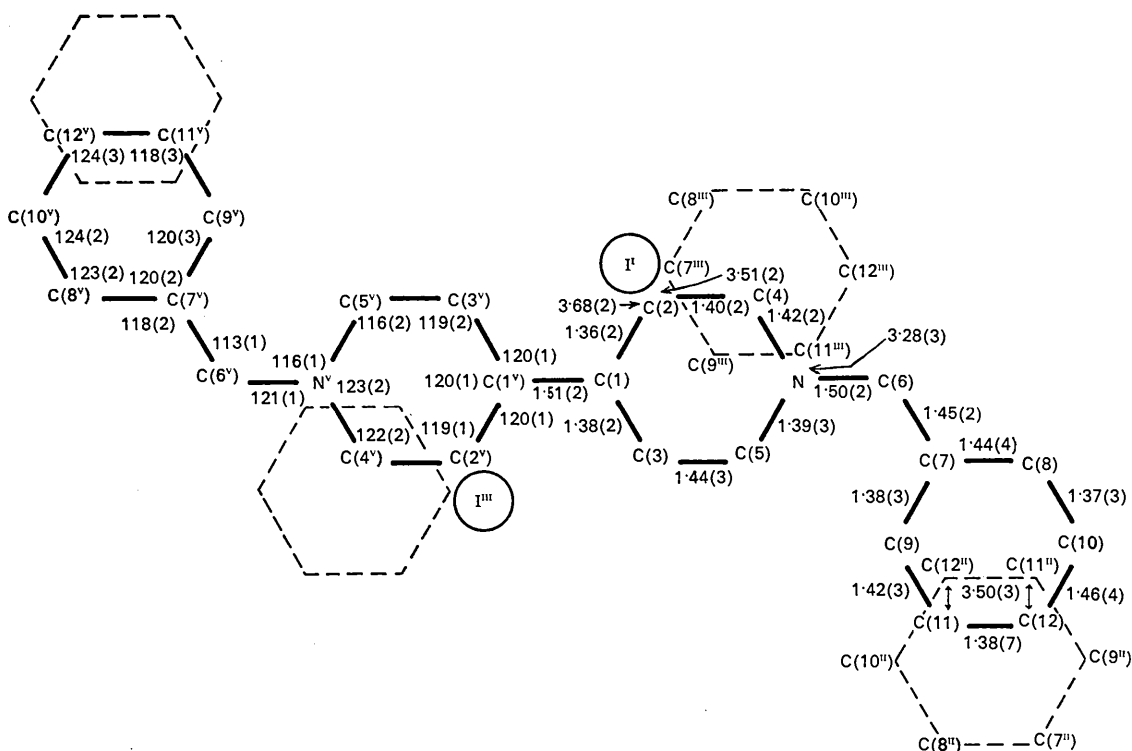

Fig. 1. Bond lengths (Å) and angles (°) with standard deviations in parentheses. The overlap with the nearest halogen ions and benzyl rings of adjacent molecules is also shown.

Table 2. *Final fractional atomic coordinates and anisotropic thermal parameters*

Standard deviations in parentheses; B_{ij} values are coefficients in the temperature factor expression

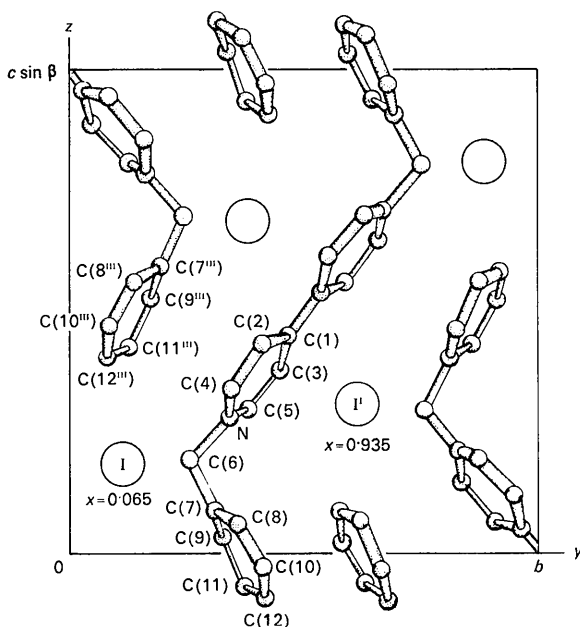$$\exp\left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\right].$$

Fractional coordinates and thermal parameters are multiplied by 10^4. The units of mean σ are $\times 10^3$.

	x/a	y/b	z/c	Mean σ ($\text{Å} \times 10^3$)	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	653·3 (1·4)	1170·8 (1·1)	1916·3 (1·1)	1	179 (8)	88 (3)	101 (3)	−1 (2)	−23 (3)	−55 (2)
N	5518 (16)	3291 (10)	2914 (9)	12	131 (25)	51 (8)	51 (8)	40 (22)	−2 (21)	7 (12)
C(1)	5084 (18)	4626 (11)	4550 (11)	17	125 (26)	46 (9)	42 (8)	7 (23)	4 (22)	5 (13)
C(2)	6723 (24)	4092 (12)	4401 (13)	16	195 (35)	41 (9)	70 (12)	51 (27)	18 (31)	−28 (16)
C(3)	3563 (32)	4474 (17)	3882 (13)	20	364 (57)	93 (16)	43 (10)	187 (50)	−54 (38)	−37 (20)
C(4)	6849 (25)	3408 (12)	3551 (14)	17	216 (38)	44 (10)	82 (13)	30 (30)	51 (35)	−32 (18)
C(5)	3737 (49)	3737 (15)	3044 (15)	24	640 (94)	50 (12)	59 (13)	89 (49)	−139 (17)	−25 (19)
C(6)	5705 (21)	2551 (12)	2013 (12)	15	176 (32)	43 (9)	55 (10)	−1 (26)	−38 (27)	−1 (14)
C(7)	5838 (23)	3097 (13)	941 (13)	16	178 (10)	56 (10)	57 (11)	59 (29)	29 (28)	−25 (5)
C(8)	7641 (57)	3530 (16)	634 (16)	27	853 (136)	55 (12)	56 (14)	32 (69)	160 (70)	−1 (21)
C(9)	4259 (45)	3217 (15)	309 (15)	23	662 (99)	50 (12)	57 (13)	135 (54)	−110 (54)	−22 (19)
C(10)	7894 (50)	4054 (15)	−286 (16)	25	777 (120)	58 (12)	45 (11)	−27 (62)	82 (58)	−74 (63)
C(11)	4439 (94)	3729 (20)	−670 (19)	39	1750 (310)	83 (19)	51 (15)	446 (125)	−96(107)	−66 (26)
C(12)	6197 (49)	4120 (15)	−944 (19)	26	693 (110)	41 (11)	89 (17)	57 (55)	253 (72)	−29 (22)

The final positional and thermal atomic parameters, together with their standard deviations, obtained by inversion of the least-squares normal-equations matrix, are summarized in Table 2. Fig. 1 shows the bond lengths and interbond angles, together with their standard deviations. Fig. 2 shows the structure projected along the a axis. Table 3 gives the close interionic approaches and some of these are illustrated in Fig. 1.

Description of the structure and discussion

In view of the rather large standard deviations of the coordinates of all atoms except iodine a detailed discussion of the dimensions of the dibenzylbipyridylium ion is not possible. They are, however, all consistent

within the rather large experimental error (e.s.d. for bond lengths ~0·03 Å and for bond angles ~2°) with expected values.

Table 3. *Close interionic approaches*

Bipyridylium to I^- less than 3·9 Å

C(2)...I^I	3·68 (2) Å
C(3)...I^{IV}	3·82 (2)

Bipyridylium to bipyridylium less than 3·6 Å

N.....C(11^{III})	3·28 (3)
N.....C(12^{III})	3·49 (3)
C(2)...C(7^{III})	3·51 (2)
C(4)...C(9^{III})	3·58 (3)
C(4)...C(11^{III})	3·40 (4)
C(4)...C(12^{III})	3·38 (3)
C(6)...C(11^{III})	3·50 (3)
C(6)...C(12^{III})	3·41 (3)
C(9)...C(12^{II})	3·57 (3)
C(10)..C(11^{II})	3·53 (5)
C(11)..C(12^{II})	3·50 (3)

Superscripts denote equivalent positions as follows:

none	x y, z
I	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
II	$1-x, 1-y, \bar{z}$
III	$x, \frac{1}{2}-y, \frac{1}{2}+z$
IV	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$

The crystal structure consists of alternate layers of dibenzylpyridylium ions and iodide ions parallel to the (100) plane and separated by $a/2$, *i.e.* the mean plane through a layer of iodide ions is at $x=0$ and the bipyridylium ions are centred at $\frac{1}{2},0,0$ and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. The N–N axis of each bipyridylium moiety makes an angle of about 6° with the (100) plane and 50° with the (001) plane. The C(6)–C(12) axis of each benzyl group makes an angle of $4\frac{1}{2}°$ with (100) and 61° with (001). The bipyridylium group and the benzyl group are each planar, within experimental error and they make dihedral angles of 71° and 76° respectively with the (100) plane, and 108° with each other within the same molecule.

Fig. 2. View of the crystal structure along the a axis.

These orientations are such as to prevent clashes with iodide ions in the adjacent layers.

As may be seen from Fig. 2, the structure contains groups of four aromatic rings stacked with one pair exactly parallel to each other (benzyl groups) and the other two (pyridine rings) almost parallel to the first pair. The rings of the centrosymmetrically related pair of benzyl groups have a perpendicular separation of 3·43 Å and the closest approach between a benzyl group and a pyridine ring is 3·28 Å from N to C(11^{III}). The latter is rather small for a van der Waals separation and probably indicates difficulty in packing rather awkwardly shaped molecules. There is evidence for charge-transfer interaction between the iodide ion and the pyridylium ring in the close approaches $I^{I}\cdots C(2) = 3\cdot68$ Å and $I^{IV}\cdots C(3) = 3\cdot82$ Å and this will be discussed further in comparison with other quaternary bipyridylium salts in a later paper. The lack of $I^{I}\cdots N$ interaction and the close approach $N\cdots C(11)$ probably result from a compromise between charge-transfer and packing requirements.

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Structure Cristalline du Composé d'Addition Iodure de Lithium, Triéthylènediamine LiI.3en

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Crystals of LiI.3en are trigonal, space group $P\bar{3}1c$ with two formula units in the cell. The cell parameters are $a = 9\cdot13 \pm 0\cdot03$, $c = 9\cdot62 \pm 0\cdot03$ Å. Iodine has been located by interpretation of the Patterson function and carbon and nitrogen by three-dimensional difference-synthesis calculations. The structure has been refined by least-squares methods. The lithium and iodine ions occupy the centres of deformed octahedra of nitrogen atoms. The en group is present in *cis* conformation.

Introduction

Dans le cadre des études des complexes formés par les halogénures de lithium et l'éthylènediamine, nous avons précédemment étudié les structures des composés d'addition LiCl.2en (Jamet-Delcroix, 1967) et LiBr.2en. La détermination de la structure du composé LiI.3en fera l'objet de cet exposé.

Isbin & Kobe (1945) ont signalé l'existence de ce solvate, dont nous avons préparé les cristaux en dissolvant à chaud une mole d'iodure de lithium anhydre dans trois moles d'éthylènediamine. Les cristaux obtenus par refroidissement se présentent sous forme d'aiguilles cylindriques (0,6 mm de diamètre, 2,5 mm de longueur) très fragiles, hygroscopiques et efflorescentes. En plaçant des cristaux dans un capillaire plongeant dans un bain d'huile et en élevant la tempé-

rature, nous avons pu déterminer qu'ils se décomposent vers 45°C. Une analyse gravimétrique par la méthode de Volhard nous a permis de vérifier leur composition chimique. Toutes les manipulations ont été faites sous atmosphère anhydre dans 'une boîte à gants' car sel et solvant sont très hygroscopiques.

Etude cristallographique préliminaire

Les cristaux enrobés d'huile de vaseline ont été engagés dans des tubes capillaires en verre de Lindemann suivant leur direction d'allongement (c). Les paramètres de la maille ont été déterminés à partir des diagrammes de cristal tournant et de Weissenberg enregistrés par rotation autour de c et des diagrammes de précession relatifs au plan a^*c^*. Les paramètres de la maille hexagonale valent: