The Crystal Structure of the 1:1 Complex between N,N'-Dimethyl-4,4'-bipyridylium Diiodide and Quinol

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The complex is monoclinic, space group $P2_1/c$, with $a=6\cdot817$ (1), $b=7\cdot897$ (1), $c=19\cdot351$ (2) Å, $\beta=102\cdot7$ (1)°, $Z=2$. The structure was solved by the heavy-atom method and refined by block-diagonal, least-squares calculations to a final R of $0\cdot036$ for 2204 reflexions. Each quinol molecule is hydrogen bonded to two I^- ions with $O\cdots I^-$ distances $3\cdot457$ (3) Å, and each I^- is $0\cdot68$ Å out of the quinol plane. Such centrosymmetric quinol.$2I^-$ units are stacked alternately with centrosymmetric bipyridylium ions in infinite columns along **b**. The tilt of these units is such that each pyridine ring has a quinol molecule lying over or under it on one side (with a dihedral angle between the two rings of $3\cdot4°$ and an average perpendicular separation of $3\cdot38$ Å) and an I^- ion on the other side (perpendicular distance from the ring $3\cdot73$ Å) almost directly above or below the N atom at a distance of $3\cdot736$ (3) Å. This arrangement is indicative of charge-transfer interaction between both quinol and I^- as donors and the bipyridylium ion as acceptor.

Introduction

Soon after the herbicidal properties of bipyridylium salts were first recognized (Boon, 1964), their ability to form complexes attracted attention. It was also found that there is charge-transfer interaction between the oppositely-charged ions in the salts themselves (Macfarlane & Williams, 1969) and that this is associated with close approaches in their crystal structures (Russell & Wallwork, 1972). The question therefore arises whether the complexes are held together by charge-transfer forces and, if so, whether this inhibits the charge-transfer interaction between anion and cation. A further point of interest in some complexes is the possibility of hydrogen bonding and the effect that this might have on the charge-transfer interaction. This paper reports the structure determination of the 1:1 complex formed between the diiodide and quinol where both charge-transfer interaction (quinol acting as a donor) and hydrogen bonding might occur.

Experimental

Crystals of the complex were kindly supplied by Imperial Chemical Industries Ltd., Agricultural Division. They were in the form of red-brown laths elongated along **a**, the main face being usually (001). The crystals exhibited pleochroism, the colour of thin crystals being red when the plane of polarized light was parallel to **b** and yellow when parallel to **a**. Charge-transfer complexes are usually pleochroic, exhibiting the deepest colour when the electric vector is parallel to the stack of alternate donor and acceptor molecules. If this is the origin of the pleochroism in this complex, it suggests stacking along **b**.

A crystal, $0\cdot54\times0\cdot28\times0\cdot26$ mm, was mounted on a goniometer head and the space group and approximate cell dimensions were found from oscillation and Weissenberg photographs. The cell dimensions were refined on a Hilger and Watts, computer-controlled, four-circle diffractometer and intensities within the range $1°<\theta\le30°$ were collected on the diffractometer with Mo $K\alpha$ radiation, a $\theta/2\theta$ scan and a scintillation counter. 2640 reflexions were measured, of which 2204 were regarded as observed with $I>3\sigma(I)$. The intensities were corrected for Lorentz and polarization factors but not for absorption. The density was determined by flotation in mixtures of chloroform and methyl iodide.

Crystal data

$[H_3C-NC_5H_4-C_5H_4N-CH_3]^{2+}2I^-\cdot HO-C_6H_4-OH$,
$M_r=550\cdot2$. Monoclinic, $a=6\cdot817$ (1), $b=7\cdot897$ (1), $c=19\cdot351$ (2) Å, $\beta=102\cdot7$ (1)°; $U=1016\cdot1$ Å^3, $D_m=1\cdot80$ (2), $Z=2$, $D_c=1\cdot797$ g cm^{-3}; $F(000)=528$, Mo $K\alpha$ $(\lambda=0\cdot71069$ Å), $\mu=31\cdot4$ cm^{-1}. Space group $P2_1/c$ from systematic absences.

Structure determination and refinement

The $I\cdots I$ vectors were readily recognized in a Patterson synthesis and structure factors calculated for the I position so derived. All the non-hydrogen atoms in the structure appeared as peaks on a subsequent difference map. Their positions, and that of the I^- ion, were refined by block-diagonal, least-squares calculations with all the observed structure factors. The thermal parameters were refined at first isotropically and then anisotropically. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962), apart from those for I^- which were from Cromer & Waber (1965). All H atoms were located by a
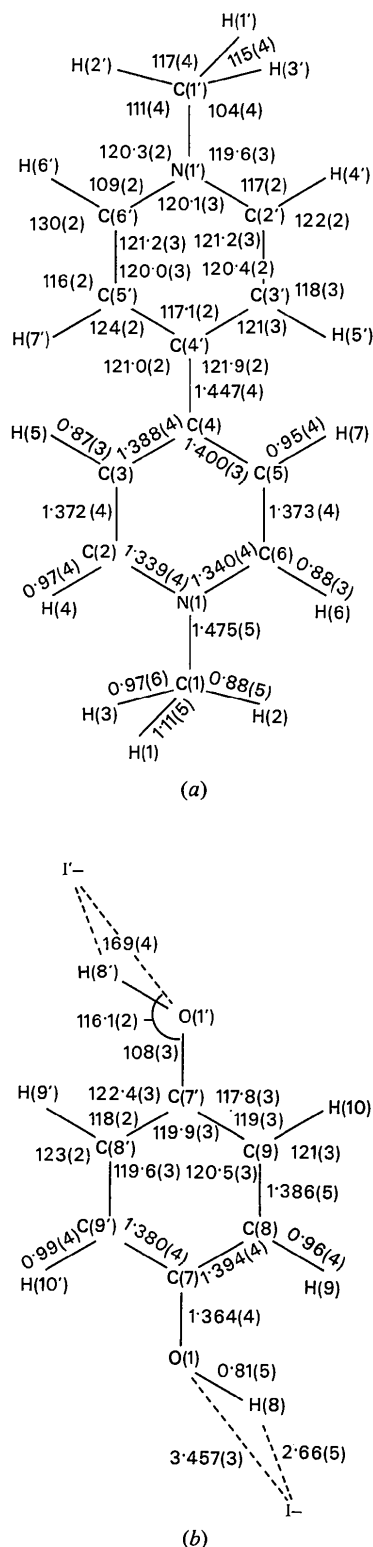
(a)

(b)

Fig. 1. Bond lengths (Å) and angles (°) for (a) the bipyridylium ion and (b) the quinol molecule and the hydrogen bond. Angles not shown are: N(1)C(1)H(1) = 103 (3)°, H(2)C(1)H(3) = 106 (4)°.

difference synthesis and were included with isotropic temperature factors. In the later cycles the weighting scheme was $w = 1/\{1 + [(F_o - B)/A]^2\}$, with $A = 20$, $B = 7$ and F_o on absolute scale, and 28 reflexions having $w\Delta F > 2\cdot0$ were omitted. R fell to the final value 0·036 for 2204 reflexions.

The computer programs used were the X-RAY system edited by J. M. Stewart, F. A. Kundell & J. C. Baldwin and the *MANTAP*, *DRAWCELL* and *MOL-PLOT* programs written by T. J. King of Nottingham University.

The final atomic coordinates and thermal parameters are listed in Table 1. The bond lengths and angles are shown in Fig. 1 and details of least-squares planes calculated for the two molecules are given in Table 2.*

Description and discussion of the structure

The structure is seen in projection along **a** in Fig. 2. Since $Z = 2$ both the bipyridylium ions and the quinol molecules lie on centres of symmetry. In doing so, they are arranged alternately in infinite columns along **b** with their centres at 0,0,0 and 0,$\frac{1}{2}$,0, *etc*. The molecules are not perpendicular to **b** but tilted so that the quinol molecule at 0,$\frac{1}{2}$,0 lies under the right-hand ring of the bipyridylium ion at 0,0,0 and above the left-hand ring of the bipyridylium ion at 0,1,0 with an average perpendicular separation from each of 3·38 Å. There is a dihedral angle of 3·85° between alternate molecules and they do not have their aromatic rings in the same orientation round **b**, so the separation quoted is the average over the region of overlap. The mode of over-lap is illustrated in Fig. 3 where the quinol molecule and one of the adjacent I⁻ ions are projected onto the plane of the bipyridylium ion. The I⁻ ion is hydrogen bonded to the OH group of the quinol molecule with an O···I⁻ distance of 3·457 (3), H···I⁻ = 2·66 (5) Å and an O–H···I⁻ angle of 169 (4)°. A similarly related I⁻ ion is hydrogen bonded to the other OH group of the quinol molecule. The arrangement of the quin-ol.2I⁻ group so formed is such that one I⁻ is above the right-hand N atom of the bipyridylium ion centred at 0,1,0 and the other I⁻ is below the left-hand N atom of the bipyridylium ion centred at 0,0,0. Each I⁻ is 0·68 Å out of the quinol plane in a direction away from the nearest bipyridylium ion so that its perpendic-ular distance from that ion is 3·71 and its distance from the N atom is 3·736 (2) Å. Neither the bipyridyl-ium ion nor the quinol molecule has an exactly planar skeleton (Table 2). The methyl C atom is 0·05 Å out of the plane of the pyridine ring in a direction away from the nearest quinol molecule but towards the I⁻ ion which overlaps the adjacent N atom. The quinol

Table 1. *Final fractional atomic coordinates and thermal parameters* (all $\times 10^4$ for C, O, N and I⁻ and $\times 10^3$ for H)

U is the mean square amplitude of vibration in Å² and the anisotropic temperature factors are given by:
$$\exp\left[-2\pi^2(h^2 U_{11}a^{*2} + k^2 U_{22}b^{*2} + l^2 U_{33}c^{*2} + hk\,U_{12}a^*b^* + hl U_{13}a^*c^* + kl U_{23}b^*c^*)\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	8036 (6)	2751 (5)	2063 (2)	721 (22)	673 (20)	515 (17)	85 (17)	160 (16)	−146 (15)
C(2)	7399 (4)	2021 (4)	813 (2)	389 (13)	594 (17)	470 (14)	85 (12)	44 (11)	−10 (12)
C(3)	7891 (4)	1259 (4)	236 (1)	359(12)	595 (16)	381 (12)	60 (12)	−3 (9)	7 (11)
C(4)	9707 (4)	409 (3)	305 (1)	337 (11)	389 (11)	356 (11)	0 (9)	17 (9)	45 (9)
C(5)	10979 (4)	371 (4)	980 (1)	427 (13)	547 (15)	368 (12)	110 (12)	−12 (10)	25 (11)
C(6)	10416 (4)	1164 (4)	1537 (1)	486 (14)	520 (15)	375 (12)	45 (12)	2 (11)	17 (11)
C(7)	1679 (4)	931 (4)	4938 (2)	429 (13)	461 (14)	540 (15)	−12 (11)	20 (11)	−63 (12)
C(8)	82 (5)	732 (4)	4354 (2)	489 (14)	477 (14)	495 (14)	13 (12)	9 (12)	−18 (12)
C(9)	−1589 (4)	−198 (4)	4423 (2)	439 (14)	519 (15)	488 (14)	3 (12)	−44 (11)	−44 (12)
O(1)	3329 (4)	1885 (4)	4911 (2)	561 (14)	925 (20)	641 (15)	−255 (13)	−12 (12)	33 (13)
N(1)	8650 (4)	1972 (3)	1451 (1)	478 (12)	437 (11)	400 (11)	−1 (9)	83 (9)	2 (9)
I⁻	3929·0 (3)	2959·7 (3)	3238·0 (1)	460 (1)	646 (1)	568 (1)	−55 (1)	75 (1)	−109 (1)

	x	y	z	U			x	y	z	U
H(1)	690 (8)	186 (6)	218 (3)	60 (15)		H(6)	1105 (5)	123 (5)	198 (2)	25 (8)
H(2)	908 (7)	295 (6)	241 (3)	50 (13)		H(7)	1227 (6)	−16 (5)	109 (2)	32 (9)
H(3)	751 (9)	385 (8)	189 (3)	82 (18)		H(8)	329 (7)	211 (5)	450 (3)	46 (13)
H(4)	615 (6)	264 (5)	78 (2)	37 (10)		H(9)	16 (6)	130 (5)	392 (2)	33 (9)
H(5)	706 (5)	135 (5)	−17 (2)	25 (8)		H(10)	−274 (6)	−35 (6)	402 (2)	44 (11)

Table 2. *Details of molecular planes* (distances in Å)

Each plane, except plane (4), was defined by the atoms listed plus the atoms related to these through the molecular centre of symmetry.

Atoms defining the plane	Distance out of plane	Atoms not defining the plane	Distance out of plane
Plane 1: $3·446x + 6·494y − 7·082z − 6·693 = 0$			
C(7)	0·018	H(8)	0·120
C(8)	0·010	H(9)	−0·027
C(9)	−0·011	H(10)	−0·022
O(1)	−0·014	I⁻	0·680
Plane 2: $3·368x + 6·551y − 7·016z − 6·644 = 0$			
C(7)	−0·001	H(8)	0·078
C(8)	0·001	H(9)	−0·042
C(9)	−0·001	H(10)	−0·005
		O(1)	−0·052
		I⁻	0·621
Plane 3: $3·332x + 6·703y − 5·889z − 3·332 = 0$			
C(1)	−0·025	H(1)	−1·070
C(2)	0·010	H(2)	0·251
C(3)	0·002	H(3)	0·639
C(4)	−0·003	H(4)	0·024
C(5)	−0·002	H(5)	0·023
C(6)	0·014	H(6)	0·008
N(1)	0·017	H(7)	0·009
		I⁻	−3·714
Plane 4: $3·356x + 6·675y − 6·018z − 3·345 = 0$			
C(2)	−0·002	H(1)	−1·100
C(3)	0·001	H(2)	0·220
C(4)	0·002	H(3)	0·608
C(5)	−0·003	H(4)	0·008
C(6)	0·002	H(5)	0·025
N(1)	0·000	H(6)	−0·008
		H(7)	0·011
		C(1)	−0·054
		I⁻	−3·730

Dihedral angles between planes (°)

	1	2	3
2	0·78		
3	3·85	3·54	
4	3·42	3·14	0·45

O atoms are each 0·05 Å out of the plane of the aromatic ring towards the overlapping bipyridylium ions. The dihedral angle between the two overlapping rings is 3·14° so as to reduce the distance between C(4) and C(7) to 3·329 (4) but to increase the distance between C(2) and C(8') to 3·447 (4) Å.
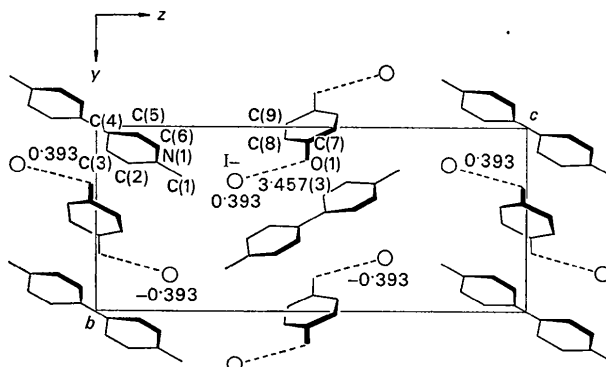

Fig. 2. Projection of the structure along *a* showing the OH···I⁻ hydrogen bonds (length in Å) and the *x* coordinates of the I⁻ ions.
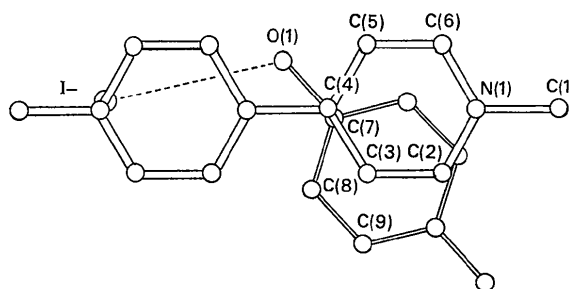

Fig. 3. A quinol molecule and one of its hydrogen-bonded I⁻ ions projected onto the plane of the adjacent bipyridylium ion.

The stacking of approximately parallel alternate donor and acceptor molecules is typical of aromatic charge-transfer complexes (Wallwork, 1961); thus the existence of this arrangement in the present complex suggests that there is charge-transfer interaction between quinol as donor and bipyridylium as acceptor. The relative orientation of these two moieties is not particularly favourable for overlap of molecular orbitals in this interaction but it probably results from a tendency for the hydrogen-bonded I^- ion to approach as closely as possible the N atom of the bipyridylium ion. This close approach may be due merely to electrostatic interaction between the negative and positive ions but it may be indicative of further charge-transfer interaction with I^- acting as a second donor. Whether quinol molecules or I^- ions or both act as donors, the charge-transfer interaction in the stack as a whole is parallel to **b** in agreement with the indications from the pleochroism. The stacks are held together by van der Waals forces.

In an attempt to obtain further information on the charge-transfer interaction, the solid-state electronic spectrum of the complex has been recorded with the KBr disc technique, and compared with the spectrum of bipyridylium diiodide. The complex exhibits broad bands with maxima at about 35500 and 25000 cm^{-1}, of which the latter is almost certainly a charge-transfer band, whereas the diiodide has maxima at about 37500, 33500, and 20500 cm^{-1}, the last being again a charge-transfer band. The difference in the positions of the charge-transfer bands is presumably due partly to the different type of interaction of I^- with the bipyridylium ion and partly to the addition of charge-transfer effects from the quinol molecule (possibly giving a further, unresolved band). In the simple salt the I^- ion lies above a point outside the pyridine ring between the N atom and an adjacent C atom, with contact distances $I^- \cdots N = 3\cdot84$ and $I^- \cdots C = 3\cdot67$ Å.

The dimensions of the bipyridylium ion, Fig. 1(a), are in good agreement with the dimensions found in dimethylbipyridylium dibromide and diiodide (Russell & Wallwork, 1972), in the tetrachlorocuprate (Rus-

sell & Wallwork, 1969), and in the TCNQ complex salts of dibenzylbipyridylium (Sundaresan & Wallwork, 1972), diethylbipyridylium (Ashwell, Eley, Wallwork & Willis, 1975a) and dipropylbipyridylium (Ashwell, Eley, Wallwork & Willis 1975b). The dimensions of the quinol molecule, Fig. 1(b), are also in agreement with previous determinations (Mahmoud & Wallwork, 1975, and references therein) except that the C–O bond of $1\cdot364$ (4) Å is slightly but significantly shorter than usual.

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