

ouverture du cycle dans le cas de l'iminodibenzyle affecte en l'accentuant l'angle de torsion τ_3 propre au pont $-\text{CH}_2-\text{CH}_2-$ (Tableau 5).

Empilement moléculaire

Une vue stéréoscopique (Fig. 2) permet d'observer l'empilement moléculaire dans la maille cristalline.

Un calcul de distances interatomiques entre les molécules du cristal indique que les contacts intramoléculaires sont du type van der Waals.

Nous tenons à remercier Monsieur J. P. Astier pour l'enregistrement des intensités diffractées qui a été effectué au Centre de Recherche sur les Mécanismes de la Croissance Cristalline, Université à Marseille.

Références

DENNE, W. A. & MACKAY M. F. (1970). *Tetrahedron*, **26**, 4435–4442.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MALRIEU, J. P. & PULLMAN, B. (1964). *Theor. Chim. Acta*, **2**, 293–301.

PAULUS, E. F. (1978). *Acta Cryst.* **B34**, 1942–1947.

POST, M. L. & HORN, A. S. (1977). *Acta Cryst.* **B33**, 2590–2595.

POST, M. L., KENNARD, O. & HORN, A. S. (1975). *Acta Cryst.* **B31**, 1008–1013.

REBOUL, J. P. & CRISTAU, B. (1977). *Eur. J. Med. Chem. Chim. Ther.* **12**, 71–79.

REBOUL, J. P. & CRISTAU, B. (1978). *J. Chim. Phys. Phys. Chim. Biol.* **75**, 1110–1118.

REBOUL, J. P., CRISTAU, B., ESTIENNE, J. & ASTIER, J. P. (1980). *Acta Cryst.* **B36**, 2108–2112.

REBOUL, J. P., CRISTAU, B., SOYFER, J. C. & ESTIENNE, J. (1980). *Acta Cryst.* **B36**, 2683–2688.

SHELDRIK, G. M. (1976). *SHELX*. Programme pour la détermination de structures cristallines. Univ. de Cambridge, England.

Acta Cryst. (1981). **B37**, 398–401

The Structure of the Tetrahydrated 1:1 Complex between 1,1'-Dimethyl-4,4'-bipyridylium Dichloride and Hydroquinone

BY M. M. MAHMOUD* AND S. C. WALLWORK

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, England

(Received 7 July 1980; accepted 27 October 1980)

Abstract

The complex, $\text{C}_{12}\text{H}_{14}\text{N}_2^{2+} \cdot \text{C}_6\text{H}_6\text{O}_2 \cdot 2\text{Cl}^- \cdot 4\text{H}_2\text{O}$, $M_r = 439.3$, is monoclinic, space group $P2_1/n$, with $a = 6.631$ (1), $b = 24.394$ (4), $c = 7.124$ (1) Å, $\beta = 103.63$ (1)°, $U = 1119.9$ (2) Å³, $Z = 2$, $F(000) = 464$. Final $R = 0.044$ for 1619 reflections. Hydroquinone molecules and dimethylbipyridylium ions are stacked alternately in infinite columns along c with an average perpendicular separation of 3.30 Å, suggesting charge-transfer interaction. Unlike the I^- in the corresponding diiodide complex, the Cl^- ions do not appear to take part in further charge-transfer interactions. They are, however, involved together with the water molecules in forming sheets parallel to (010) of alternately left- and right-handed, hydrogen-bonded spirals parallel to c .

* Present address: Physics Department, University of Sulaimaniyah, Sulaimaniyah, Iraq.

The hydroquinone molecules are also hydrogen bonded to water molecules in these spirals.

Experimental

Crystals suitable for X-ray study, in the form of dark-red laths, were obtained by recrystallizing a crude sample of the complex from water. The space group and approximate cell dimensions were obtained from oscillation and Weissenberg photographs with Cu $K\alpha$ radiation. The cell dimensions were refined and intensities measured on a Hilger & Watts computer-controlled four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å, $\mu = 0.328$ mm⁻¹), a scintillation counter and a $\theta/2\theta$ scan. Of the 1978 reflections with $\theta \leq 25^\circ$, 1619 had $I > 3\sigma(I)$ and were used in the structure analysis. They were corrected for Lorentz and polarization effects but not for absorption.

The density of the crystals was measured by flotation in mixtures of xylene and inhibisol [$D_m = 1.31(1)$, $D_c = 1.303 \text{ Mg m}^{-3}$].

Structure determination and refinement

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and 200 reflexions with $E \geq 1.40$. Application of the \sum_1 relationship gave positive signs to two reflexions and the origin was defined by giving positive signs to three further reflexions. Four reflexions were used in the starting set to be given all combinations of positive and negative signs. An E map based on the set of signs so derived with the highest figure of merit gave the positions of all non-hydrogen atoms. A structure factor calculation based on these positions and an overall isotropic temperature factor $B = 4.0 \text{ \AA}^2$ gave $R = 0.290$.

The positions and thermal parameters (at first isotropic and later anisotropic) for all the non-hydrogen atoms were refined by full-matrix least squares to $R = 0.075$. All the H atoms were located in a difference map and were included in further refinement with isotropic thermal parameters. For the last

Table 1. Final fractional atomic coordinates and isotropic thermal parameters

$$\text{Temperature factor} = \exp[-8\pi^2 U(\sin \theta/\lambda)^2];$$

$$U_{\text{eq}}(\text{non-H atoms}) = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq} or U_{iso} (10^{-3} \AA^2)
C(1)	0.6905 (3)	0.98002 (9)	0.6045 (3)	4.73 (6)
C(2)	0.5153 (3)	0.94646 (8)	0.5657 (3)	4.66 (6)
C(3)	0.3281 (3)	0.96647 (8)	0.4629 (3)	4.85 (6)
C(4)	0.4044 (4)	0.19372 (10)	0.7708 (4)	6.23 (8)
C(5)	0.2711 (3)	0.10146 (9)	0.8045 (3)	5.23 (7)
C(6)	0.2938 (3)	0.04829 (9)	0.8654 (3)	4.96 (7)
C(7)	0.4848 (3)	0.02882 (8)	0.9665 (3)	3.97 (6)
C(8)	0.6493 (3)	0.06595 (9)	1.0017 (3)	5.14 (7)
C(9)	0.6199 (3)	0.11899 (9)	0.9379 (3)	5.22 (7)
N(1)	0.4327 (3)	0.13625 (7)	0.8403 (2)	4.53 (5)
O(1)	0.8785 (2)	0.96274 (7)	0.7101 (3)	6.85 (6)
O(2)	0.0670 (3)	0.14473 (8)	0.2222 (3)	7.65 (7)
O(3)	0.0824 (4)	0.70459 (11)	0.2575 (4)	9.56 (10)
Cl(1)	0.33721 (9)	0.32089 (2)	0.04379 (11)	6.69 (2)
H(1)	0.879 (5)	0.932 (1)	0.724 (5)	6.2 (10)
H(2)	0.528 (4)	0.912 (1)	0.608 (3)	2.7 (6)
H(3)	0.213 (4)	0.945 (1)	0.435 (3)	3.0 (6)
H(4)	0.006 (6)	0.157 (2)	0.312 (5)	7.0 (10)
H(5)	0.162 (5)	0.162 (1)	0.236 (4)	5.0 (8)
H(6)	0.409 (7)	0.194 (2)	0.640 (7)	10.9 (15)
H(7)	0.301 (7)	0.204 (2)	0.819 (6)	10.0 (14)
H(8)	0.494 (8)	0.216 (2)	0.847 (7)	11.4 (16)
H(9)	0.152 (4)	0.115 (1)	0.747 (4)	4.9 (8)
H(10)	0.171 (4)	0.025 (1)	0.829 (4)	3.5 (6)
H(11)	0.786 (4)	0.057 (1)	1.071 (4)	4.2 (7)
H(12)	0.732 (4)	0.147 (1)	0.956 (4)	4.1 (7)
H(13)	-0.051 (6)	0.703 (1)	0.178 (5)	7.3 (10)
H(14)	0.112 (3)	0.731 (1)	0.185 (3)	0.1 (5)

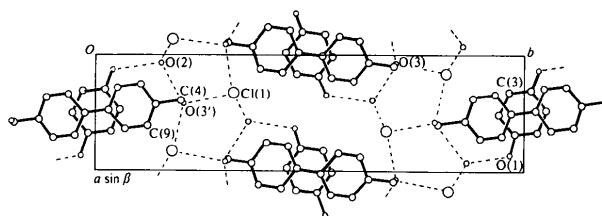


Fig. 1. The structure projected along c . H atoms are omitted. Broken lines represent hydrogen bonds.

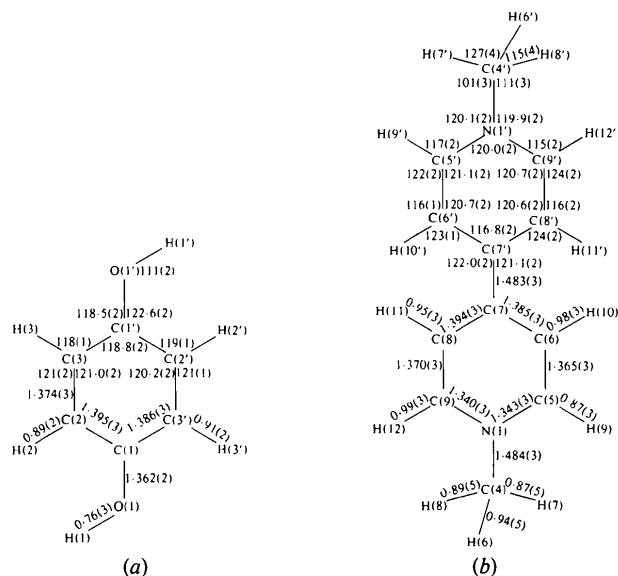


Fig. 2. Bond lengths (\AA) and angles ($^\circ$) for (a) the hydroquinone molecule and (b) the dimethylbipyridylum ion. Angles not shown: $\text{N}(1)\text{C}(4)\text{H}(6) = 108(3)$, $\text{H}(7)\text{C}(4)\text{H}(8) = 93(4)^\circ$.

few cycles a weighting scheme $1/w = 1 + [(|F_o| - B)/A]^2$ was used with $A = 7.0$, $B = 3.0$ and $|F_o|$ on the absolute scale. The refinement converged at $R = 0.044$ for 1619 reflexions. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The programs used were those of the XRAY system (Stewart, Kundell & Baldwin, 1970).

The final atomic coordinates are listed in Table 1.* The structure is illustrated in Fig. 1 and bond lengths and angles are shown in Fig. 2.

Description and discussion of the structure

The dimethylbipyridylum (paraquat) ions lie across centres of symmetry at $\frac{1}{2}00$ and $0\frac{1}{2}0$ and these and the hydroquinone molecules, which lie across centres of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35653 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

symmetry at $\frac{1}{2}0\frac{1}{2}$ and $0\frac{1}{2}0$, form infinite stacks of alternate species. They are almost parallel to each other (dihedral angle 2.4°) and are tilted from the position where they would be perpendicular to the stacking (c) axis so that the average perpendicular separation is reduced to 3.30 Å. Such arrangements and separations are typical of the alternation of donors and acceptors in charge-transfer complexes (Wallwork, 1961). This, together with the deep colour, suggests that this complex is of the charge-transfer type with hydroquinone as the donor and the paraquat ion as the acceptor of electrons. The electronic spectrum of the solid complex (in a KBr disc) shows a band, additional to those of the components, at $22\,000\text{ cm}^{-1}$ which must be a charge-transfer band. The related complex between hydroquinone and paraquat diiodide has similarly been interpreted as a charge-transfer complex (Mahmoud & Wallwork, 1976) with an additional band at $25\,000\text{ cm}^{-1}$. In that complex it was considered possible that the I^- ion was also acting as a charge-transfer donor to the paraquat because of its location over the paraquat N atom. In the present complex it is unlikely that the Cl^- ion is taking part in the charge-transfer interaction because it has no special relationship to the paraquat plane. The projection of the nearest Cl^- ions and the hydroquinone and water molecules on to the plane of the paraquat ion is shown in Fig. 3. The type of overlap between hydroquinone and the paraquat ion, with bonds centrally over rings, is fairly common in charge-transfer complexes. This type of overlap cannot quite be achieved in the iodide complex, because of the necessity of the hydroquinone to form hydrogen bonds with the I^- ion, which also has a specific location with respect to the same paraquat ion.

The other type of interaction which plays an important part in this structure is hydrogen bonding (Fig. 4) involving the Cl^- ions and the water molecules. This takes the form of sheets parallel to (010) of alternate, oppositely rotating spirals, both with axes parallel to z . One of these spirals consists of $Cl(1) \cdots O(3') = 3.159(3)$, $O(3') \cdots O(2) = 2.720(3)$, $O(2) \cdots Cl(1'') = 3.150(2)$, $Cl(1'') \cdots O(3''') = 3.159(3)$, $O(3''') \cdots Cl(1''') = 3.150(2)$ Å where

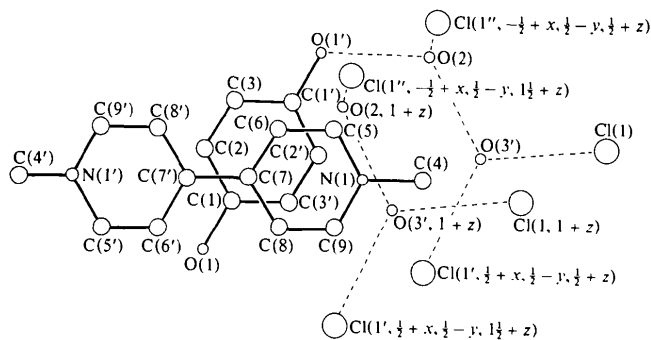


Fig. 3. Projection of the nearest Cl^- ions and hydroquinone and water molecules on to the plane of the dimethylbipyridylum ion.

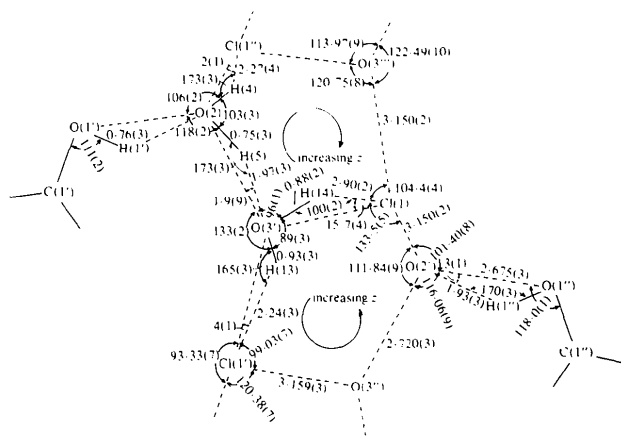


Fig. 4. Details of the hydrogen-bonding geometry (lengths in Å and angles in degrees).

$Cl(1''')$ is one unit cell along z above $Cl(1)$. The other spiral is glide-plane-related to the first and shares the hydrogen bond $Cl(1) \cdots O(3')$ with it and $Cl(1') \cdots O(3'')$ with the next spiral of the first type, translated along a and c from the original one. These spirals are also hydrogen bonded to the parallel sheets of charge-transfer-bonded moieties by $O(1')-H \cdots O(2) = 2.675(3)$ Å from hydroquinone. All the hydrogen-bond distances are normal (Wallwork, 1962), though the $OH \cdots OH_2$ distance from hydroquinone is appreciably shorter than the $HOH \cdots OH_2$ distance between water molecules.

The dimensions of the paraquat ion and the hydroquinone molecule agree well with corresponding dimensions in the paraquat diiodide-hydroquinone complex (Mahmoud & Wallwork, 1976) apart from the central C-C bond of paraquat, which is significantly longer, and the C-C bond parallel to the long axis of the hydroquinone molecule, which is possibly shorter, in the current structure. The paraquat ion is planar, apart from the methyl group, the C atom of which is 0.011 Å out of the mean plane of the ion. The hydroquinone molecule is slightly non-planar with the O atom 0.029 Å out of the plane of the ring, surprisingly towards the nearest non-bonded contacting atom in the same stack [C(6) of the paraquat ion below at 3.486 Å] and away from the water molecule to which it is hydrogen bonded (though this is only 0.496 Å out of the hydroquinone plane).

We thank Imperial Chemical Industries, Agricultural Division, for supplying the complex, the Ministry of Higher Education and Scientific Research of Iraq for a maintenance grant (to MMM), the Science Research Council for contributing to the cost of the diffractometer, Professor T. J. King for assistance with the diffractometry and computing, the Director of the Cripps Computing Centre of Nottingham University

for computing facilities, and the authors of the computer programs used.

References

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

MAHMOUD, M. M. & WALLWORK, S. C. (1976). *Acta Cryst.* B32, 440–443.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

WALLWORK, S. C. (1961). *J. Chem. Soc.* pp. 494–499.

WALLWORK, S. C. (1962). *Acta Cryst.* 15, 758–759.

Acta Cryst. (1981). B37, 401–406

X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems.

XI. The Structure of 9*H*-Cyclohepta[2,1-*b*:4,5-*b'*]dithiophen-4-ylum Perchlorate at 173 K

BY JAN-ERIK ANDERSSON

Division of Inorganic Chemistry 2, Chemical Center, University of Lund, PO Box 740, S-220 07 Lund 7, Sweden

(Received 14 July 1980; accepted 9 October 1980)

Abstract

$C_{11}H_7S_2^+ \cdot ClO_4^-$ is monoclinic, space group $P2_1/c$, with $a = 10.4615$ (18), $b = 25.7202$ (26), $c = 26.8840$ (23) Å, $\beta = 94.657$ (10)° at 173 K, and $Z = 24$. The structure was refined to an R of 0.12 for 3794 non-zero counter reflexions at 173 K. The cations are approximately planar. Aromatic character is indicated by the relatively uniform C–C lengths. The S–C bonds are equal. The structure is built up of columns of cations with the anions in between. There is orientational disorder, and diffuse scattering is observed in Weissenberg photographs. A comparison with another phase of the same compound and a similar compound is made.

Introduction

The title compound is composed of cycloheptadithiophenylum cations and ClO_4^- anions ($G \cdot ClO_4^-$, Fig. 1); it has two modifications. Aurivillius (1974) determined the crystal structure of the phase with a small unit cell (phase I, G I) and found the cation to be approximately planar. The present crystal structure is that of another phase with a large unit cell (phase II, G II). The structure of a corresponding compound, 4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-ylum tetrafluoroborate (E), has been determined and its molecular structure related to a series of similar compounds (Andersson,

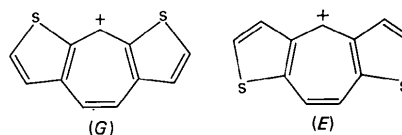


Fig. 1. Schematic drawings of molecules G (9*H*-cyclohepta[2,1-*b*:4,5-*b'*]dithiophen-4-ylum perchlorate), and E (4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-ylum tetrafluoroborate).

1979). The cation G has an even higher degree of aromaticity than E (Yom-Tov, 1972).

The packing of the present compound has been studied, and compared between the two phases and the corresponding compound mentioned above. The structure was determined at 173 K.

Experimental

Crystals were formed when a saturated solution of $G \cdot ClO_4^-$ in boiling acetonitrile was cooled to room temperature. By cooling in air, plate-like crystals (phase I) were formed and, by using ice-water, needles (phase II) were obtained.

It was possible to transform phase II to phase I by heating to 458 K for some days, or by shaking the crystals in their saturated solution at room temperature, but not the reverse. When a single crystal of II was transformed to I, it retained its habit, but the