

Fig. 4. The molecules in the crystal. (a) The molecular chain projected along *a*. (b) The molecular chain projected along *b*. (c) The packing of the molecule in the crystal projected along *c*.

The two molecules *A* and *B* are different in the shape of the *ansa* chain. For molecule *A*, the torsion angles C(4)–C(5)–C(6)–C(7), and C(5)–C(6)–C(7)–S(8) are *trans*, and the atoms from C(4) to S(8) make an approximately linear chain, while for molecule *B*, the *trans* conformations appear at C(3)–C(4) and C(4)–C(5), and the atoms from S(2) to C(6) make an approximately linear chain (Fig. 2*b*). These two conformations of the *ansa* chain are approximately mirror related to each other, with respect to the plane perpendicular to the pyridine plane, and may have similar conformational energies.

The hydrogen atoms attached to O(14) and O(16) are not well resolved, but judging from the O...O distances (2.622 and 2.658 Å for molecules *A* and *B*, respectively), an intramolecular hydrogen bond is

assumed to exist between O(14) and O(16). The two molecules are connected by an intermolecular hydrogen bond between O(16) of molecule *A* and N(2) of molecule *B* and *vice versa*, thus forming a long chain of the molecules along the *c* axis (Fig. 4*a,b*).

The calculations were performed on the FACOM 230-75 computer of this Institute using the UNICS III program system (Sakurai & Kobayashi, 1979).

The research was supported, in part, by a Scientific Grant from the Ministry of Education.

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Mixed-Stack Complexes of Tetrathiafulvalene. The Structures of the Charge-Transfer Complexes of TTF with Chloranil and Fluoranil

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(Received 15 March 1979; accepted 16 July 1979)

Abstract

The structures of the 1:1 charge-transfer complexes of tetrathiafulvalene (TTF) with chloranil and fluoranil have been determined. The two materials are not isomorphous. TTF–chloranil, C₆H₄S₄·C₆Cl₄O₂,

crystallizes in *P2₁/n* with *a* = 7.411 (1), *b* = 7.621 (2), *c* = 14.571 (3) Å, β = 99.20 (1)°, and *Z* = 2. TTF–fluoranil, C₆H₄S₄·C₆F₄O₂, crystallizes in *P1* with *a* = 7.298 (2), *b* = 7.357 (3), *c* = 7.045 (2) Å, α = 93.07 (1), β = 102.31 (1), γ = 106.12 (1)°, and *Z* = 1. In both structures the molecules stack in columns of

0567-7408/79/122988-08\$01.00

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alternating donor and acceptor molecules, the first such structures reported for TTF. The main difference in the two structures is in the overlap between donor and acceptor. This difference and the alternate stacking mode are discussed in terms of steric interactions and orbital overlap. Structural and optical evidence indicate that the degree of charge transfer is small in both structures.

Introduction

Since the discovery of the dramatic electrical properties of TTF-TCNQ (Ferraris, Cowan, Walatka & Perlstein, 1973; Coleman, Cohen, Sandman, Yamagishi, Garito & Heeger, 1973), a vast amount of research has been carried out in an attempt to understand those properties and to define the parameters necessary to achieve them in new systems. Although much effort has been expended trying to increase the number and types of organic molecules that yield highly conducting charge-transfer complexes, success has been minimal, limited essentially to derivatives of TTF-TCNQ. In fact, until now all highly conducting materials that contain both an organic donor and an organic acceptor in a 1:1 ratio contain TCNQ or a TCNQ-like molecule as the acceptor.

In order for an organic charge-transfer complex to exhibit high electrical conductivity, there are two essential requirements that must be met. They are (1) that the molecules crystallize in separate (segregated) stacks of donors and acceptors, as opposed to the arrangement of alternating donors and acceptors usually found for charge-transfer compounds, and (2) that the charge transfer from donor to acceptor be incomplete. We have embarked on a program to systematically define the properties that a given pair of molecules must possess such that, when reacted together, both the requirements of segregated-stack formation and partial charge transfer are met, and a highly conducting complex results. For reasons based on electrochemical and orbital-symmetry considerations, we have chosen the TTF family of donors and the tetrahalo-*p*-benzoquinone family of acceptors as having just such a suitable match of properties (Torrance, Mayerle, Lee & Bechgaard, 1979).

We have found that reaction of TTF and its derivatives with the tetrahalo-*p*-benzoquinones yields a complex system of charge-transfer compounds. Nearly every pair of donor and acceptor crystallizes in two different phases, each with 1:1 stoichiometry. As a further complication, substitution of one halogen atom for another in the acceptor molecule generally does not yield isomorphous compounds. However, as we had anticipated, several of these phases contain segregated stacks of donors and acceptors for which the charge transfer is incomplete. These materials are highly

conducting. For example, tetramethyl-TTF-chloranil exhibits a room-temperature pellet electrical conductivity of $2 \times 10^3 \Omega^{-1} \text{ m}^{-1}$ (Torrance, Mayerle, Lee & Bechgaard, 1979) compared to a value of $7 \times 10^3 \Omega^{-1} \text{ m}^{-1}$ for TTF-TCNQ. However, the constituents of some of these highly conducting materials also crystallize in a second phase which is electrically insulating. The structures of two of these latter compounds, TTF-chloranil (hereafter TTF-Chl) and TTF-fluoranil (hereafter TTF-Flr), were determined as part of an investigation to discover why, under certain conditions, the guidelines we use to design organic conductors are not successful for some of the members of the TTF-tetrahalobenzoquinone system.

Experimental

TTF-Flr was prepared by the reaction of stoichiometric quantities of the constituent molecules in acetonitrile. Cooling of the reaction solution led to the crystallization of the product. A platelet measuring $0.16 \times 0.20 \times 0.33 \text{ mm}$ perpendicular to the (010), (100), and (001) faces, respectively, was used for data collection. The crystal was mounted on the end of a glass fiber and transferred to an Enraf-Nonius CAD-4 automatic diffractometer where, following machine location and centering of seven reflections, a preliminary unit cell and orientation matrix were computed. Subsequent to this, 12 reflections ($2\theta > 26^\circ$) were computer-centered and the initial cell constants refined to those given in Table 1, based on Ni-filtered Cu $K\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$).

Several open-counter ω scans gave peak widths at half-height of $0.15\text{--}0.20^\circ$. Data ($\pm h, \pm k, l$) were collected by the θ - 2θ -scan method using Ni-filtered Cu $K\alpha$ radiation to $\theta = 75^\circ$. The scan range was computed according to the formula $\Delta\theta = (0.9 + 0.2 \tan \theta)^\circ$ and

Table 1. *Crystal data*

TTF-Flr	
Molecular formula: $\text{C}_6\text{H}_4\text{S}_4 \cdot \text{C}_6\text{F}_4\text{O}_2$, $M_r = 384.39$	
Triclinic, space group $P1$	
$a = 7.298$ (2) \AA	$Z = 1$
$b = 7.357$ (3)	$D_c = 1.81 \text{ Mg m}^{-3}$
$c = 7.045$ (2)	$D_x = 1.78$ (2)
$\alpha = 93.07$ (1) $^\circ$	
$\beta = 102.31$ (1)	
$\gamma = 106.12$ (1)	
TTF-Chl	
Molecular formula: $\text{C}_6\text{H}_4\text{S}_4 \cdot \text{C}_6\text{Cl}_4\text{O}_2$, $M_r = 450.19$	
Monoclinic, space group $P2_1/n$	
$a = 7.411$ (1) \AA	$Z = 2$
$b = 7.621$ (2)	$D_c = 1.84 \text{ Mg m}^{-3}$
$c = 14.571$ (3)	$D_x = 1.83$ (2)
$\beta = 99.20$ (1) $^\circ$	

was extended by 25% on each end of the scan range for background measurement. The scan rate, based on a fast prescan, was computed such that 10^4 counts were to be obtained, if possible, in a maximum allowed time of 90 s for each reflection. An aperture with a height of 4 mm and a variable width of $(4.0 + 0.87 \tan \theta)$ mm was placed in front of the scintillation counter at a distance of 173 mm from the crystal. The intensities of three standard reflections, measured after every 50 reflections, varied by 2% about their mean during the course of data collection. A total of 1433 reflections were collected, of which 1324 were unique. The 109 reflections that were collected twice each were averaged, giving an averaging residual $(= \sum |F_i^2 - \bar{F}_i^2| / \sum \bar{F}_i^2)$ of 0.027. Of the 1324 unique reflections, 1242 were judged to be observed by the criterion $F_o^2 > 3\sigma(F_o^2)$. The data were corrected for Lp and absorption effects. The transmission coefficients ranged between 0.18 and 0.48 based on a linear transmission coefficient of 6.453 mm^{-1} .

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) using 300 reflections for which $E > 1.2$. The intensity statistics indicated the structure to be centrosymmetric. An *E* map computed with the phases obtained from the set with the highest combined figure of merit revealed all the non-hydrogen atoms. With these included the structure was refined, using isotropic temperature factors, to an *R* value of 0.123. From this point, refinement was continued with anisotropic thermal parameters and converged at $R = 0.035$. A difference Fourier map clearly revealed the positions of the H atoms. These were included in the subsequent refinement, which converged at $R = 0.031$ and $R_w = 0.046$, based on 106 variables and 1242 observations and using as weights $w = 4F_o^2/\sigma^2(F_o^2)$. The error in an observation of unit weight was computed to be 1.57. The H positions, but not the isotropic temperature factors ($B = 5.0 \text{ \AA}^2$), were varied. The C–H distances were 0.84 (4) and 1.02 (3) Å. During

the last refinement cycle, no parameter changed by more than 0.01 of its standard deviation. The neutral scattering factors of the non-H atoms were taken from *International Tables for X-ray Crystallography* (1974, pp. 72–98), as were the corrections for anomalous dispersion applied to the scattering factors of S (*International Tables*, 1974, pp. 149–150). The scattering factors of H were those of Stewart, Davidson & Simpson (1965). The final atomic positional parameters are listed in Table 2.*

TTF–Chl was also prepared by the reaction of stoichiometric quantities of the two molecules in acetonitrile. The crystal used for data collection was a five-sided needle bounded by the faces (001), (00 $\bar{1}$), (0 $\bar{1}$ 1), (01 $\bar{1}$), and (0 $\bar{1}$ 1). The ends of the needle were bounded by the (100) faces. The average dimensions were 0.1 mm thick and 0.45 mm long. Auto-indexing of 11 reflections found and centered automatically gave a preliminary unit cell and orientation matrix. Least-squares refinement of the setting angles of 12 reflections ($2\theta > 66^\circ$) led to the unit-cell constants, based on Ni-filtered Cu $K\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$), listed in Table 1.

Unless stated otherwise, the data-collection parameters were identical to those of TTF–Flr. Data ($h, k, \pm l$) were collected to $\theta = 30^\circ$ using graphite-monochromatized Mo $K\alpha$ radiation. The scan range was taken as $\Delta\theta = (0.85 + 0.35 \tan \theta)^\circ$. The aperture width was set to $(3.5 + 0.87 \tan \theta)$ mm. The intensities of three standard reflections, measured after every 50 reflections, decreased by 4% over the course of data collection. The data were corrected for this. A total of 1559 reflections were collected. Of these, 1221 satisfied the condition $F_o^2 > 3\sigma(F_o^2)$ and were used during the ensuing refinement. The data were corrected for Lp effects as well as absorption ($\mu = 1.22 \text{ mm}^{-1}$).

Analysis of the systematic absences, $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, indicated the space group to be $P2_1/n$. The structure was solved by the Patterson method, from which the positions of the Cl atoms were located. The usual refinement and difference Fourier methods revealed the remainder of the structure. Refinement of the position and isotropic thermal parameters of all the non-H atoms converged at $R = 0.087$. Continued refinement employing anisotropic thermal parameters converged at $R = 0.037$ and $R_w = 0.053$. A subsequent difference map clearly revealed the positions of the H atoms. These were included in the refinement with varying positional parameters but a fixed isotropic temperature factor of 4.0 \AA^2 . The C–H distances were computed to be a rather short 0.82 (3)

Table 2. Final atomic positional parameters ($\times 10^4$) for TTF–Flr

Standard deviations are in parentheses.

	x	y	z
S(1)	92 (1)	2845 (1)	6181 (1)
S(2)	3212 (1)	1093 (1)	5928 (1)
F(1)	7088 (2)	1657 (2)	11 (2)
F(2)	6156 (2)	–2062 (2)	–1485 (2)
O	897 (3)	3604 (2)	1593 (2)
C(1)	2514 (4)	4251 (3)	7041 (4)
C(2)	694 (3)	824 (2)	5436 (3)
C(3)	3901 (4)	3472 (3)	6917 (4)
C(4)	491 (3)	1980 (3)	835 (3)
C(B)	8459 (3)	800 (3)	–26 (3)
C(C)	8009 (3)	–1016 (3)	–749 (3)
H(1)	2480 (41)	5569 (40)	7524 (41)
H(2)	5126 (46)	3871 (42)	7266 (41)

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34686 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Final atomic positional parameters ($\times 10^4$) for TTF-Chl

Standard deviations are in parentheses.

	x	y	z
S(1)	3866 (1)	2380 (1)	148 (1)
S(2)	4399 (1)	4451 (1)	-1494 (1)
Cl(1)	4108 (1)	447 (1)	2839 (1)
Cl(2)	3338 (1)	3540 (1)	4175 (1)
O	5821 (3)	-2542 (3)	3879 (1)
C(1)	3131 (5)	1480 (4)	-941 (2)
C(2)	4633 (4)	4340 (4)	-280 (2)
C(3)	3365 (5)	2403 (5)	-1674 (2)
C(A)	5413 (4)	-1411 (4)	4389 (2)
C(B)	4564 (4)	271 (4)	4019 (2)
C(C)	4224 (4)	1570 (4)	4585 (2)
H(1)	2603 (47)	526 (44)	-986 (23)
H(2)	3142 (43)	2069 (45)	-2264 (22)

and 0.87 (3) Å. Refinement converged at $R = 0.031$ and $R_w = 0.040$, based on 100 variables and 1221 observations. During the last refinement cycle no parameter changed by more than 0.01 that of its standard deviation. The error in an observation of unit weight was computed to be 1.08. Corrections for anomalous dispersion were applied to the scattering factors of S and Cl. The final atomic positional parameters are listed in Table 3.* Computer programs used have been described previously (Mayerle, 1977).

Results and discussion

One of the primary objectives in our research program is to select pairs of molecules that will crystallize in segregated stacks of donors and acceptors as well as exhibit incomplete charge transfer between the two species, conditions that must be fulfilled for high conductivity to result. The program has been undertaken to test and refine our ideas as to what factors are important in designing organic conductors (Torrance, 1979*a,b*). Since the donors and acceptors are chosen on the basis of electrochemical and orbital-symmetry arguments to have physical properties that satisfy our synthetic guidelines, the structures reported here are of interest precisely because they are not the expected result. Since optical evidence indicated that segregated-stack formation had not occurred in these materials, their structures were of importance insofar as they would reveal how orbital-symmetry considerations, if important, were circumvented. Of additional interest is the fact that these compounds are, to our knowledge, the only well characterized examples of TTF-containing complexes in which the TTF molecules do not stack on top of each other, *i.e.* these are the first examples of alternate stacking in TTF complexes. They

are also of interest in that they are two uncommon cases of a given pair of donor and acceptor crystallizing in both segregated and alternate stacking phases. Although polymorphism is quite common in weak charge-transfer compounds (Herbstein, 1971), most of the phases exhibit alternate stacking. In the polymorphs of TTF-Flr and TTF-Chl, the charge transfer in the alternate-stack phases is weak, whereas in the case of the segregated-stack phases, the constituents are largely ionic.

The packing modes of TTF-Flr and TTF-Chl are shown stereoscopically in Figs. 1 and 2, respectively. Although not isomorphous, both consist of stacks of alternating donor and acceptor molecules, a packing motif common to the vast majority of organic charge-transfer complexes. In TTF-Flr, the molecules stack along the c axis, with an average intrastack interplanar spacing between donors and acceptors of 3.38 Å. This is, however, not uniform; the donor and acceptor planes form a dihedral angle with each other of 4.2°. In addition, the perpendicular to the donor plane lies at an angle of 17.7° to the c axis. In TTF-Chl the donor and acceptor molecules pack alternately along the crystallographic a axis. The mean interplanar spacing between donor and acceptor is 3.39 Å, essentially identical to the corresponding distance in TTF-Flr. If we consider the difference in size between F and Cl, this result is somewhat surprising. However, as can be seen in Fig. 3, the F atoms in TTF-Flr lie more nearly over the S atoms than do the Cl atoms in TTF-Chl, the relevant S-halogen distances being 3.345 and 3.771 Å for

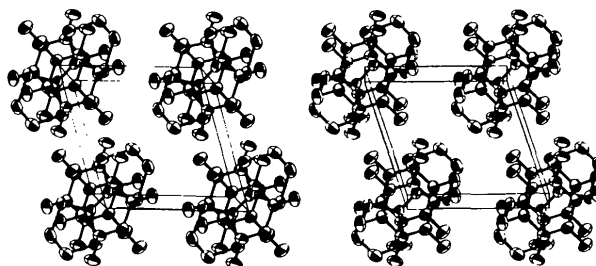


Fig. 1. Stereographic view of the molecular packing in TTF-Flr. The origin of the cell is at the lower-left front corner. The a axis runs vertically from bottom to top, b horizontally from left to right, and c completes the right-handed coordinate system.

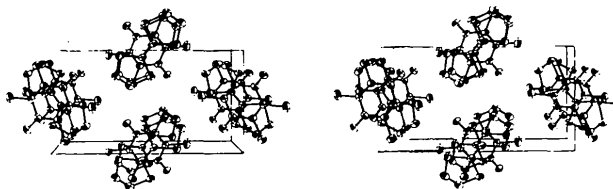


Fig. 2. Stereographic view of the molecular packing in TTF-Chl. The origin of the cell is at the lower-left front corner. The b axis runs vertically from bottom to top, c horizontally from left to right, and a completes the right-handed coordinate system.

* See preceding footnote.

TTF-Flr and TTF-Chl, respectively. In fact, in TTF-Chl the Cl and S atoms are staggered relative to each other, thereby allowing a close approach of donor and acceptor. The dihedral angle between the TTF and chloranil planes is 3.0° . The angle between the perpendicular to the donor plane and the stacking axis is 24.6° . Thus, the stacks in TTF-Chl are tilted slightly more steeply than they are in the fluoranil analog.

Since we had specific ideas about how these molecules would pack, one of the most important aspects of this work was the determination of the relative orientation of the donors and acceptors within a stack. Briefly, our argument (Mayerle, Torrance, Crowley, Lee & Metzger, 1979) is that if the relevant frontier orbitals of the constituent molecules (the HOMO of the donor and the LUMO of the acceptor) have opposite symmetry, with respect to inversion for example, then eclipsed overlap of donor and acceptor would give zero charge-transfer stabilization and should not occur. Some stabilization could be achieved, however, by slippage or rotation of the donor and acceptor relative to each other. If the resulting orbital overlap was poor and, consequently, the charge-transfer stabilization was sufficiently weak, then segregated-stack formation might occur by default. This argument, together with electrochemical considerations, led to our selecting the charge-transfer compounds of TTF with the tetrahalo-*p*-benzoquinones as compounds for study. In fact, most of the

compounds in this class have been found to have segregated stacks of donors and acceptors (Torrance, Mayerle, Lee & Bechgaard, 1979), consistent with the above argument. The phases of TTF-Flr and TTF-Chl discussed here, however, have mixed stacks. It is of interest, therefore, to examine the relative donor-acceptor orientation in order to gain some understanding of this stacking mode in view of the above orbital-symmetry guideline.

The overlap between donor and acceptor, depicted by the projection of the acceptor molecule onto the TTF plane, is shown in Fig. 3 for both complexes. The relative orientations of donors to acceptors are quite different. In both structures, the overlap is far from eclipsed, with extensive rotation and sideways displacement being the case. Since fluoranil is, for the purpose of discussing non-bonded interactions, essentially sixfold symmetric (the C=O bond length is 1.21 \AA compared to 1.33 \AA for the C-F bond), it can take up almost any orientation about its center without severely disrupting its surroundings. Hence, the rotational position it does assume is probably, to a large extent, determined by maximum orbital overlap between itself and TTF, as in other donor-acceptor complexes (Mayoh & Prout, 1972).

The donor-acceptor overlap in TTF-Chl is quite different from that in TTF-Flr, Fig. 3. Because chloranil is significantly longer perpendicular to the O-O axis than parallel to it (the C=O bond length is 1.21 \AA compared to 1.70 \AA for the C-Cl bond), the best stereochemical overlap would be achieved if it aligned itself with TTF such that the O-O axis is nearly perpendicular to the long axis of the TTF molecule. As can be seen in Fig. 3(b), such is largely the case. In TTF-Flr, on the other hand, the O-O axis is much more nearly parallel to the long TTF molecular dimension. Apparently, if both donor and acceptor have a long molecular axis, they tend to line up. This pair of complexes taken together is an instructive example of the orbital overlap seeming to determine the relative orientations in one case (TTF-Flr), but yielding to large steric interactions in the other (TTF-Chl). Actually, a careful look at the resulting overlap in TTF-Chl suggests that the $\sim 60^\circ$ rotation the chloranil molecule undergoes relative to the fluoranil molecule in TTF-Flr should not seriously disrupt the net stability gained by the charge-transfer interaction. In the absence of detailed MO calculations this is, of course, quite speculative.

The second guideline we used in selecting this family of materials was their electrochemical redox properties. In order to achieve metallic behavior, it is necessary to have incomplete transfer of charge from donor to acceptor. This is accomplished by selecting donor-acceptor pairs whose redox potentials are between those which would give a neutral solid and those which would result in an ionic solid (Wheland, 1976;

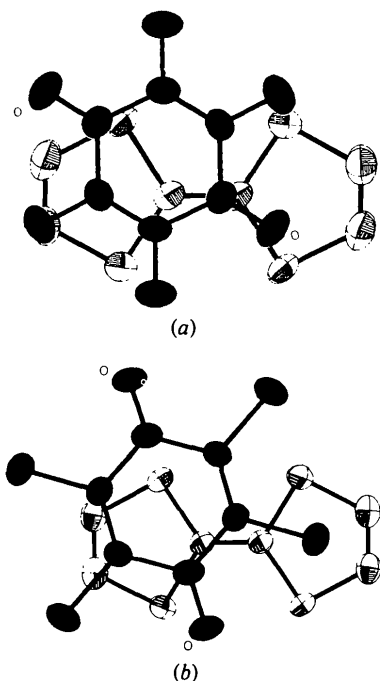


Fig. 3. (a) Projection of the fluoranil moiety onto the plane of the TTF moiety in TTF-Flr. (b) Projection of the chloranil moiety onto the plane of the TTF moiety in TTF-Chl.

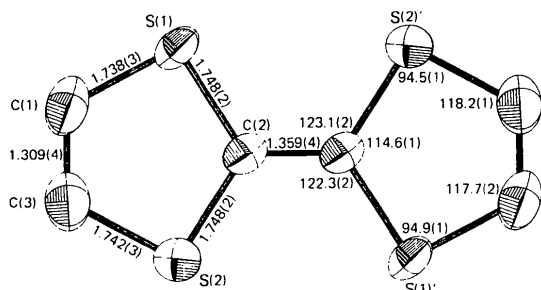


Fig. 4. The numbering scheme and the molecular geometry of the TTF moiety in TTF-Flr. The 50% probability ellipsoids are depicted.

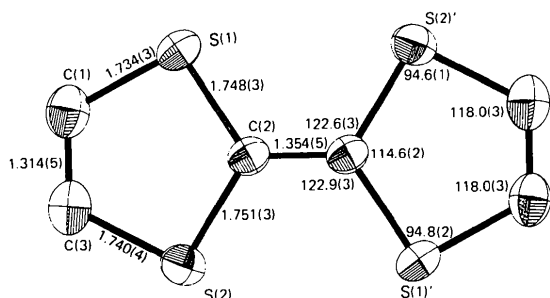


Fig. 5. The numbering scheme and the molecular geometry of the TTF moiety in TTF-Chl. The 50% probability ellipsoids are depicted.

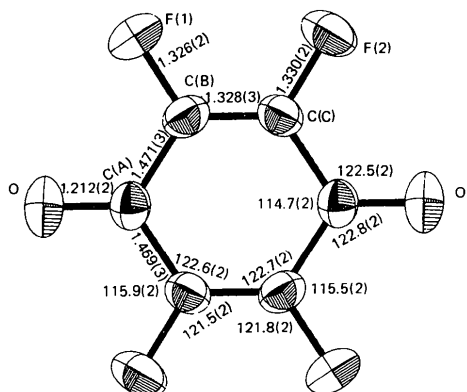


Fig. 6. The numbering scheme and the molecular geometry of the fluoranil moiety in TTF-Flr. The 50% probability ellipsoids are shown.

Torrance, 1979a). Although the redox properties of TTF and the tetrahalo-*p*-benzoquinones indicate that the transfer of charge in the resulting compounds would be significant, the circumvention of the orbital overlap argument could be more easily rationalized if these solids were neutral since, under such conditions, only mixed stacks are stabilized by charge-transfer interactions. It was therefore of interest to determine the degree of charge transfer in TTF-Chl and TTF-Flr. By

comparing various geometric parameters that depend on the state of ionization of the constituent molecules to parameters in the same molecules in known oxidation states, one can sometimes obtain an estimate of this quantity. As we shall see, the structural evidence suggests that the degree of charge transfer is small, in agreement with our optical evidence, which indicates at least in the case of TTF-Chl, that the molecules in both complexes are neutral.

Figs. 4 and 5 show the thermal ellipsoids as well as the bond lengths and angles of the TTF moiety in TTF-Flr and TTF-Chl, respectively. The same information is portrayed for the fluoranil and chloranil molecules in these complexes in Figs. 6 and 7. Table 4 lists the bond lengths of the TTF moiety in various complexes. The bond apparently most sensitive to the degree of charge transfer is the ring double bond (*d* in Table 4). This length is 1.309 (4) Å in the fluoranil complex and 1.314 (5) Å in the chloranil complex, compared to a value of 1.314 (3) in neutral TTF (Cooper, Kenny, Edmonds, Nagel, Wudl & Coppens, 1971). Since this bond length seems to increase rapidly with charge transfer, being 1.323 (4) and 1.336 Å in TTF-TCNQ (Kistenmacher, Phillips & Cowan, 1974) and TTF-I_{0.71} (Johnson & Watson, 1976), respectively, these values seem to indicate only a slight degree of ionicity in these phases of TTF-Flr and TTF-Chl.

The geometrical parameters of the acceptors are also quite close to those of the neutral molecules. Thus, the chloranil C=O and C=C bond lengths of 1.207 (3) and 1.338 (4) Å in TTF-Chl are virtually identical to the values of 1.211 (2) and 1.344 (2) Å found for neutral chloranil at 110 K (Van Weperen & Visser, 1972). They are also quite similar to the less precise room-temperature values (Chu, Jeffrey & Sakurai, 1962). The C=O bond length of 1.212 (2) Å found in the fluoranil molecule in TTF-Flr is quite close to the value of 1.206 (7) found in the neutral molecule (Meresse,

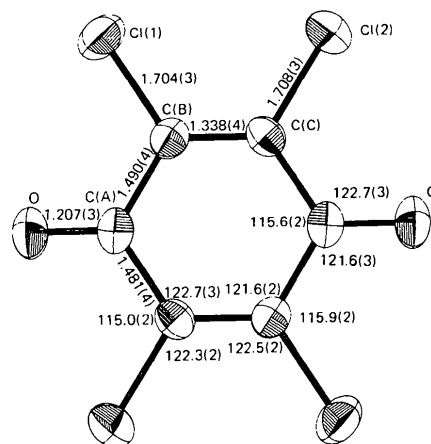
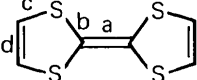


Fig. 7. The numbering scheme and the molecular geometry of the chloranil moiety in TTF-Chl. The 50% probability ellipsoids are shown.

Table 4. A compilation of the bond lengths (in Å) of TTF at various levels of oxidation



	TTF ⁰ 1	TTF-I _{0.71} 2	TTF-TCNQ 3	TTF-TCNQ(Et ₂) 4	TTF-Flr 5	TTF-Chl 5
a	1.349 (3)	1.350	1.369 (3)	1.367 (5)	1.359 (4)	1.354 (5)
b	1.757 (2)	1.732	1.744 (3)	1.754 (3) 1.745 (3)	1.748 (2)	1.748 (3) 1.751 (3)
c	1.731 (3)	1.721	1.733 (3) 1.740 (3)	1.707 (3) 1.733 (3)	1.738 (3) 1.742 (3)	1.734 (3) 1.740 (4)
d	1.314 (3)	1.336	1.323 (3)	1.323 (4)	1.309 (4)	1.314 (5)

References: (1) Cooper *et al.* (1971). (2) Johnson & Watson (1976). Standard deviations not given. (3) Kistenmacher *et al.* (1974). (4) Schultz, Stucky, Craven, Schaffman & Salamon (1976). (5) This work.

Courseille & Chanh, 1974), whereas the C=C length of 1.328 (3) Å in the complexed molecule is somewhat larger than that of 1.305 (5) Å in the uncomplexed species. The C=O and C=C lengths in the ionic salt K-chloranil are 1.31 (16) and 1.35 (22) Å, respectively (Konno, Kobayashi, Marumo & Saito, 1973). Unfortunately, these values are too imprecise to be used for comparative purposes insofar as the extent of charge transfer is concerned. It should be pointed out that the donor-acceptor spacing of 3.38 Å in TTF-Flr and 3.39 Å in TTF-Chl also suggests weak charge-transfer interactions.

Further evidence for the degree of charge transfer can be readily obtained from optical measurements. The absorption spectrum of a powdered sample of TTF-Chl dispersed in KBr is compared in Fig. 8 with the solution spectra of TTF and chloranil in acetonitrile. The spectrum of TTF-Chl is reasonably well represented by the sum of the spectra of the neutral molecules and a charge-transfer band, centered at 5700 cm⁻¹. If this phase of TTF-Chl were ionic, there would be a strong absorption peak near 17 000 cm⁻¹, characteristic of the TTF⁺ radical cation. TTF-Flr appears to react with or decompose in the KBr matrix, making it impossible to obtain a reliable spectrum. However, the lime-green color of TTF-Flr is quite similar to that of TTF-Chl and we can conclude that both are weak charge-transfer complexes, composed of nominally neutral molecules.

The TTF family of donors and the tetrahalo-*p*-benzoquinone family of acceptors were originally chosen in the hope that their charge-transfer complexes would crystallize in segregated stacks of donors and acceptors. In fact, most of these compounds do exhibit such stacking, but some of them, including the two described in this paper, crystallize in stacks of alternating donor and acceptor molecules. We believe that the structural determinations of TTF-Flr and TTF-Chl provide some insight into formation of mixed

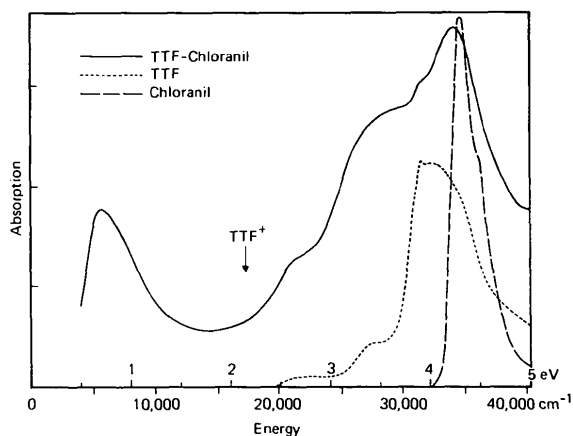


Fig. 8. The electronic spectrum of TTF-Chl, compared with the solution spectra of the neutral constituents.

stacks in these cases. Our frontier orbital guidelines predicted that the opposite orbital symmetries of the donor and acceptor would prohibit eclipsed donor-acceptor overlap. If no other significant donor-acceptor overlap could be obtained, segregated-stack formation might have occurred by default. In fact, by rotation and displacement, the molecules in both cases were able to find a non-eclipsed configuration in which some net positive orbital overlap was achieved. Another important factor is that the redox properties of these two types of molecules suggest that their charge-transfer complexes will verge on the border between neutral and ionic. For this reason, some of the complexes might be expected to be neutral solids. Since the charge-transfer stabilization for neutral molecules in segregated stacks is very weak, any such solid will have mixed stacks. We suggest that these two factors are largely responsible for the mixed-stack complexes of TTF with fluoranil and chloranil reported here.

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The Crystal Structures of a Pentacoordinate Phosphorus Compound: 3,4,8,9-Dibenzo-5,7-dimethyl-1-phenyl-2,6,10,11-tetraoxa-1-phosphatricyclo[5.3.1.0^{1,5}]undecane and its Hydrolysis Product: [1-Hydroxy-1-(2-hydroxyphenyl)ethyl]phenylphosphinic acid

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(Received 13 June 1979; accepted 25 July 1979)

Abstract

Reaction of PhPCl_2 with $o\text{-HOC}_6\text{H}_4\text{COCH}_3$ gives an unusual tricyclic tetraoxaphosphaundecane. Crystals of this compound are monoclinic, $P2_1/c$, with $a = 13.874$ (7), $b = 7.924$ (4), $c = 16.572$ (8) Å, $\beta = 94.5$ (2)°, $Z = 4$. The geometry around the P atom is distorted trigonal bipyramidal, with the two five-membered rings and one six-membered ring all in apical-equatorial positions. It is postulated that permutational isomerization in solution is unlikely for this compound partly because of its molecular rigidity. Crystals of the disubstituted phosphinic acid formed as its hydrolysis product are monoclinic, $P2_1/n$, with $a = 13.886$ (7), $b = 7.378$ (4), $c = 15.280$ (8) Å, $\beta = 116.9$ (2)°, $Z = 4$. The P atom has the expected tetrahedral environment. $\text{O}\cdots\text{O}$ close contacts < 2.76 Å indicate hydrogen bonding which extends throughout the lattice.

Introduction

The synthesis of $\text{PhP}(\text{OC}_6\text{H}_4\text{COCH}_3)_2$ by the reaction of PhPCl_2 with $o\text{-HOC}_6\text{H}_4\text{COCH}_3$ in the presence of triethylamine was attempted as part of a general study of the influence of transition metals on the photochemistry of organic molecules. The resulting solid (I) is an unusual tricyclic tetraoxaphosphaundecane. On recrystallization from wet acetone, (I) underwent hydrolysis to yield the substituted phosphinic acid (II). The structures of these compounds could not be readily ascertained by spectroscopic techniques and were thus solved by X-ray methods.

Experimental

12.62 g (0.1 mol) $o\text{-HOC}_6\text{H}_4\text{OCH}_3$ in 70 ml benzene was added dropwise at 273 K to a solution of 10.12 g