Charge-Transfer Complex of 2,2′,5,5′-Tetrathiafulvalene and p-Benzoquinone

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Abstract. The charge-transfer complex of 2,2′,5,5′-tetrathiafulvalene (TTF) and p-benzoquinone, $C_6H_4S_4.C_6H_4O_2$, $M_r = 312.44$, monoclinic, $P2_1/n$, $a = 6.385$ (6), $b = 15.49$ (1), $c = 6.935$ (7) Å, $\beta = 104.76$ (7)°, $V = 663$ (1) Å^3, $Z = 2$, $D_x = 1.565$ (3) g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 6.8$ cm^{-1}, $F(000) = 320$, $T = 300$ K, $R = 0.029$, $wR = 0.036$ for 1292 unique reflections with $|F_o| > 3\sigma(F_o)$. TTF and benzoquinone unexpectedly form a mixed-stack complex despite incompatible orbital overlap.

Introduction. Tetrathiafulvalene (TTF) is a well known electron-donor molecule used in the synthesis of organic conductors (Conwell, 1988). TTF is particularly suited to this purpose because its complexes tend to crystallize with segregated stacks, a necessary structural requirement that may lead to electrical conduction in organic crystals. TTF–benzoquinone (1), Fig. 1, is unusual because it crystallizes having mixed stacks.

Frontier orbital theory predicts that quinone compounds should favor segregated stacks when complexed with TTF because the LUMO orbitals of a quinone compound lack the inversion symmetry of the TTF HOMO orbitals (Torrance, Mayerle, Lee & Bechgaard, 1979). Mayerle and co-workers (Mayerle, Torrance & Crowley, 1979) crystallized both fluoranil (2,3,5,6-tetrafluoro-1,4-benzoquinone) and chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) with TTF, expecting TTF–fluoranil (2) and TTF–chloranil (3), Fig. 1, to crystallize in segregated stacks as a result of the mismatched orbital inversion symmetry of the components. Charge-transfer complexes (2) and (3), like (1), were found to crystallize having mixed stacks. However, (2) and (3) also form conductive charge-transfer complexes that presumably have crystallized having segregated stack structures (Torrance *et al.*, 1979).

Experimental. Deep green highly reflective crystals of (1) were grown from an equimolar solution of the two materials in ethyl acetate at room temperature.

Crystals of (1) melt at 345–347 K and convert to a yellow compound within days if left at room temperature. A crystal of dimensions $0.1 \times 0.1 \times 0.2$ mm was used for data collection on a Nicolet $P2_1$ diffractometer. Unit-cell dimensions derived from a least-squares refinement based on the setting angles of 19 reflections ($10 < 2\theta < 18°$). Intensity data were collected using the θ–2θ scan technique with mono-chromated Mo $K\alpha$ radiation and variable scan speeds of 2 to 12° min^{-1} to $\sin\theta/\lambda = 0.70$, $-2 \le h \le 8$, $-21 \le k \le 21$, $-9 \le l \le 9$. Three standard reflections measured every 100 reflections showed <2% intensity variation. No absorption correction was made. Averaging of the 3880 intensities [$R_{int}(F_o) = 0.029$] and removal of the systematic absences ($0k0$: $k = 2n + 1$; $h0l$: $h + l = 2n + 1$) gave 1516 independent reflections. The structure was solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms were included at calculated positions with $B_{iso} = 5.0$ Å^2. All non-H atoms were refined by use of anisotropic thermal parameters. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ and $\sigma(F_o) = [\sigma^2(F_o^2) + 0.02F_o^2)^2]^{1/2}/2F_o$, with the value of $\sigma(F_o^2)$ based on counting statistics, $\Delta/\sigma \le 0.05$ in the final least-squares cycle. Final agreement factors were $R(F_o) = 0.029$, $wR(F_o) = 0.036$ and $S = 1.29$ for 82 variable parameters and 1292 data with $|F_o| > \sigma(F_o)$. The largest difference from zero on the final difference map was ± 0.4 e Å^{-3}. Atomic scattering factors including anomalous-scattering contributions were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were done
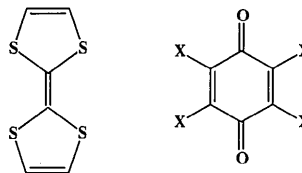

Fig. 1. The general formula for TTF–acceptor charge-transfer complexes referred to in the text. The complexes include: TTF–benzoquinone, (1), $X = H$; TTF–fluoranil, (2), $X = F$; TTF–choranil, (3), $X = Cl$.

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by use of a local modification of the *UCLA Crystallographic Package* (Strouse, 1978).*

Discussion. The atom labeling scheme for (1) is given in Fig. 2; Table 1 contains the final atomic positional parameters. A stereoview of (1), Fig. 3, shows that TTF and benzoquinone pack alternately along the crystallographic c axis. The dihedral angle between the planes of the TTF and benzoquinone molecules is $4.0°$ and the spacing between these molecules is approximately $c/2$. The inversion centers of TTF and benzoquinone are on a line parallel with the c axis so the molecules are eclipsed.

Bond distances and angles are collected in Table 2. The length of the alkene bond in TTF has been correlated to the degree of charge transfer in TTF complexes (Yakushi, Nishimura, Sugano, Kuroda & Ikemoto, 1980). The C(1)—C(1') bond length in (1), 1.345 (3) Å, is identical to the alkene bond length in

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* Lists of structure factors, anisotropic thermal parameters and calculated H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53383 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
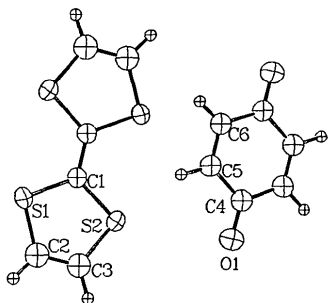

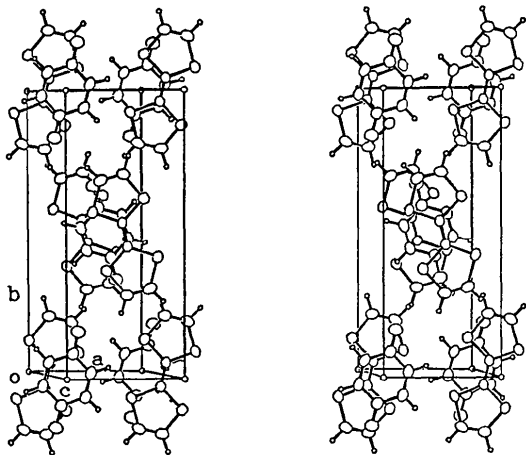Fig. 2. *ORTEP* (Johnson, 1965) drawing of TTF–benzoquinone (1) with the atomic numbering system.

Fig. 3. Stereodrawing of the crystal structure of (1) viewed down c.

Table 1. *Non-H-atom parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	U_{eq} (Å² × 10⁴)
S1	−0.29435 (6)	0.07946 (3)	0.44273 (7)	449 (2)
S2	0.16950 (6)	0.12509 (2)	0.52870 (7)	471 (2)
C1	−0.0253 (2)	0.04223 (9)	0.4939 (2)	358 (5)
C2	−0.2264 (3)	0.18785 (11)	0.4502 (3)	531 (6)
C3	−0.0186 (3)	0.20832 (11)	0.4869 (3)	544 (6)
O1	0.8909 (2)	0.16543 (8)	0.9709 (2)	640 (5)
C4	0.9410 (3)	0.08923 (11)	0.9840 (2)	449 (5)
C5	0.7755 (3)	0.02065 (11)	0.9431 (3)	468 (6)
C6	1.1699 (3)	0.06172 (11)	1.0411 (3)	467 (6)

The complete temperature factor is $\exp(-8\pi^2 U_{eq}\sin^2\theta/\lambda^2)$, where
$$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

Table 2. *Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses*

S1—C1	1.761 (2)	C1—C1'	1.345 (3)
S2—C3	1.736 (2)	C4—C5	1.474 (2)
O1—C4	1.220 (2)	S2—C1	1.760 (2)
C5—C6	1.320 (3)	C2—C3	1.324 (3)
S1—C2	1.731 (2)	C4—C6	1.476 (3)

C2—S1—C1	95.04 (9)	C3—S2—C1	94.81 (11)
C1'—C1—S2	123.4 (2)	C1'—C1—S1	122.56 (15)
S2—C1—S1	114.06 (10)	C3—C2—S1	117.94 (13)
C2—C3—S2	118.14 (15)	O1—C4—C5	121.4 (2)
O1—C4—C6	121.5 (2)	C5—C4—C6	117.1 (2)
C6—C5—C4	121.2 (2)	C5—C6—C4	121.64 (15)

neutral TTF, indicating that there is near zero charge transfer between TTF and benzoquinone in (1).

The IR spectrum of a nujol mull of crystalline (1) indicates there is a small degree of charge transfer between TTF and benzoquinone in (1). The position of the ν_{16} peak, representing a C—S stretching mode in TTF, is sensitive to the ionization state of TTF (Inoue, Inoue, Fernando & Nebesny, 1986). The position of ν_{16} in a spectrum of (1) is $798\,cm^{-1}$, indicating the mean charge on TTF to be $+0.1$.

The eclipsed mixed-stack structure of (1) is unexpected because the HOMO's of the donor molecule and the LUMO's of the acceptor molecule have opposite inversion symmetry, a condition that should inhibit good donor–acceptor overlap. Although (2) and (3) crystallize in mixed stacks, the long axes of the component molecules are rotated out of alignment and the planes of the components are staggered, preventing the planes from being eclipsed (Mayerle *et al.*, 1979). The staggered arrangement of molecules in (2) and (3) is thought to allow more favorable orbital overlap than the eclipsed arrangement, leading to a greater degree of charge transfer between components. The structure of (1) demonstrates that molecules with opposite inversion symmetry can crystallize with eclipsed mixed-stack structures in charge-transfer complexes.

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Solid-State Stereochemistry of Diels–Alder Adducts between a Bicyclic Cyclohexadienone Derivative and α-Acyloxyacrylonitrile

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Abstract. λ(Cu $K\overline{\alpha}$) = 1·54056 Å, T = 298 K. (4a): rel-(1S,7S,9S,11R)-11-Cyano-1-methyl-8-oxo-9,9-(oxoethylenedioxy)tricyclo[5.2.2.0²,⁶]undec-2(6)-en-11-yl acetate, $C_{17}H_{17}NO_6$, M_r = 331·32, monoclinic, $P2_1/a$, a = 9·3791 (5), b = 14·8506 (15), c = 12·7209 (15) Å, β = 110·188 (7)°, V = 1663·0 (3) Å³, Z = 4, D_x = 1·323 Mg m⁻³, μ = 0·81 mm⁻¹, $F(000)$ = 695·91, $R(F)$ = 0·079, wR = 0·045, S = 4·35 for 2127 significant reflections. (4b): rel-(1S,7S,9S,11R)-11-Cyano-1-methyl-8-oxo-9,9-(oxoethylenedioxy)tricyclo[5.2.2.0²,⁶]undec-2(6)-en-11-yl 3,3-ethylenedioxybutanoate, $C_{21}H_{23}NO_8$, M_r = 417·41, orthorhombic, $P2_1nb$, a = 8·5159 (3), b = 10·3035 (3), c = 23·1263 (8) Å, V = 2029·18 (12) Å³, Z = 4, D_x = 1·366 Mg m⁻³, μ = 0·85 mm⁻¹, $F(000)$ = 879·89, $R(F)$ = 0·038, wR = 0·027, S = 1·709 for 2039 significant reflections. (5a): rel-(1S,7S,9R,11R)-11-Cyano-1-methyl-8-oxo-9,9-(oxoethylenedioxy)tricyclo[5.2.2.0²,⁶]undec-2(6)-en-11-yl acetate, $C_{17}H_{17}NO_6$, M_r = 331·32, triclinic, $P\overline{1}$, a = 8·3623 (8), b = 9·0673 (6), c = 11·4951 (10) Å, α = 102·982 (8), β = 95·983 (6), γ = 106·828 (5)°, V = 799·45 (6) Å³, Z = 2, D_x = 1·376 Mg m⁻³, μ = 0·84 mm⁻¹, $F(000)$ = 347·95, $R(F)$ = 0·039, wR = 0·030, S = 3·75 for 2685 significant reflections. (5b): rel-(1S,7S,9R,11R)-11-Cyano-1-methyl-8-oxo-9,9-(oxoethylenedioxy)tricyclo[5.2.2.0²,⁶]undec-2(6)-en-11-yl 3,3-ethylenedioxybutanoate, $C_{21}H_{23}NO_8$, M_r = 417·41, monoclinic, A2/n, a = 17·8531 (5), b = 11·2599 (3), c = 20·7317 (7) Å, β = 104·593 (3)°, V = 4033·13 (8) Å³, Z = 8, D_x = 1·375 Mg m⁻³, μ = 0·85 mm⁻¹, $F(000)$ = 1759·77, $R(F)$ = 0·042, wR = 0·024, S = 1·27 for 2803 significant reflections. The crystal structures of the two pairs of Diels–Alder adducts reveal the stereochemistry of the spirolactonic ring and the cyanoester moiety. In the four molecules the cyano groups are cis to the cyclopentene bridge. The high values of $R(F)$ (0·079) and S (4·35) for (4a) reflect the poor quality of the crystals. This spatial arrangement is compatible with the classical endo approach of the reagents.

Introduction. In the course of the total synthesis of ryanodol (1) (Deslongchamps, Bélanger, Berney, Borschberg, Brousseau, Doutheau, Durand, Katayama, Lapalme, Leturc, Liao, Maclachlan, Maffrand, Marazza, Martino, Moreau, Ruest, St-Laurent, Saintonge & Soucy, 1990), the Diels–Alder reactions between spirolactone dienone (2) and dienophiles (3a) and (3b) were investigated. Fol-