Crystal Structure of a Complex of *peri*-Xanthenoxanthene (PXX) with Tetracyanoquinodimethane (TCNQ)

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The crystal structure of a 1:1 complex of *peri*-xanthenoxanthene (PXX) with tetracyanoquinodimethane (TCNQ), $C_{20}H_{10}O_2 \cdot C_{12}H_4N_4$, has been determined from single-crystal X-ray diffraction studies. The crystals are triclinic, $P\bar{1}$, $Z = 1$, with the unit cell dimensions $a = 6.645(1)$, $b = 8.434(4)$, $c = 11.145(5)$ Å, $\alpha = 68.00(4)$, $\beta = 76.39(5)$ and $\gamma = 84.43(5)°$. The structure (including H-atoms) was refined from all data, giving final $R(F) = 0.052$ for the 1452 reflections with $I > 2\sigma(I)$ and $R_w(F^2) = 0.184$ for all data. The two molecules are situated on inversion centres and close to planar, with their least-squares planes almost parallel. The PXX and TCNQ molecules stack alternately along a, with an interplanar distance of ca. 3.3 Å. Extraordinary interaction between the stacks is present only as short C–H⋯O and C–H⋯N contacts. Empirical estimates of the charge transfer from bond lengths in TCNQ indicate little or zero charge transfer, suggesting very low conductivity.

Several organic conductors have been prepared using chalcogen-substituted organic heterocyclic molecules; a well known example is the tetrathiafulvalene (TTF) molecule. However, the hitherto most extensively studied donors contained heavy hetero atoms such as sulfur or selenium, and relatively little is known of charge transfer complexes or radical salts with oxygen substituted donors. In the search for new organic conducting materials the study of new π-electron donor molecules is important, and thus it is considered of value to extend the knowledge of donors with oxygen as heteroatom. This work is part of the continuing search for new materials with potential use as organic conductors. In the series of oxygen-containing compounds we have recently reported three dioxapyrene (DOP) compounds: a charge-transfer complex of diethyldimethyldioxapyrene with tetracyanoquinodimethane (TCNQ)[1] and two radical salts of tetramethyldioxapyrene with BF_4^- and PF_6^-, respectively.[2] Here we report the crystal structure of a complex of *peri*-xanthenoxanthene (PXX) **1** with TCNQ. The *peri*-xanthenoxanthene molecule has been known since early this century, and the existence of an iodide salt has been shown by Ref. 3. However, no crystal structures of charge-transfer complexes or radical salts with PXX as donor have been published previously.

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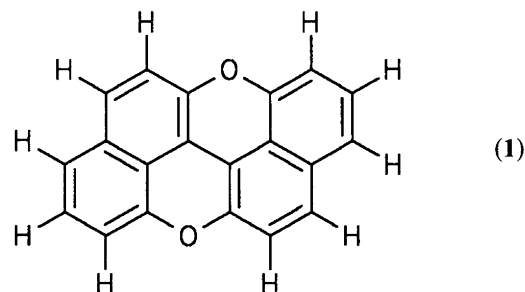
Experimental

Peri-xanthenoxanthene (PXX) was prepared using the method described in Ref. 4. Recrystallisation from a solution of PXX and TCNQ in dimethylformamide gave black prismatic crystals (elongated in the *a*-direction) of the PXX-TCNQ complex. Preliminary experiments using photographic techniques were used to select a crystal of suitable quality for data collection. The unit cell dimensions were derived from 25 reflections, using four settings of each to minimize zero point errors. X-Ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer, using graphite monochromatised Mo*K*α radiation. The data were corrected for Lorentz and polarisation effects, but absorption effects were ignored

Table 1. Crystal data and experimental conditions during data collection and refinement.

Formula	$C_{20}H_{10}O_2 \cdot C_{12}H_4N_4$
Formula weight	486.5
Space group	$P\bar{1}$
Unit cell	$a = 6.645(1)$, $b = 8.434(4)$, $c = 11.145(5)$ Å,
	$\alpha = 68.00(4)$, $\beta = 76.39(5)$, $\gamma = 84.43(5)°$
Formula units per unit cell	1
Unit cell volume/Å^3	562.9(1)
Calculated density/g cm^{-3}	1.4352(4)
$F(000)$	250
Radiation	Mo$K\alpha$
Wavelength/Å	0.71073
Linear absorption coefficient/cm^{-1}	0.86
Temperature/K	293
Crystal shape	Prismatic
Crystal size/mm	$0.05 \times 0.13 \times 0.30$
Determination of unit cell:	
No. of reflections used	25
θ-range/°	5.2–19.9
Intensity data collection:	
Maximum $\sin(\theta)/\lambda/Å^{-1}$	0.81
Range of h, k and l	0 to 10; -13 to 13; -17 to 17
Standard reflections	$\bar{1}\bar{1}4$ $1\bar{2}\bar{1}$ $\bar{2}00$
Intensity instability	Insignificant
No. of collected reflections	5578
No. of unique reflections	4935, of which one was suppressed
$R(\text{int})$	0.041
Absorption correction	None
Structure refinement:	
Minimization of	Sum of $w(F_0^2 - F_c^2)^2$
Weighting scheme	$(\sigma_1^2 + (0.0844P)^2)^{-1}$,
	where $P = \frac{1}{3}[\max(F_0^2, 0) + 2F_c^2]$
No. of refined parameters	200
Final $R(F)$ for 1452 reflections with $I > 2\sigma(I)$	0.052
Final $R_w(F^2)$ for all data	0.184
Max. Δ/σ	0.001
Min. and max. $\Delta\rho/e$ Å^{-3}	-0.25 and 0.38

Table 2. Fractional coordinates and equivalent isotropic atomic displacement parameters (Å^2) for PXX-TCNQ.

Atom	x	y	z	U_{iso}^a
O	0.0639(2)	−0.2382(2)	−0.0903(1)	0.0396(3)
C(1)	−0.0969(3)	0.0857(2)	0.1998(2)	0.0341(4)
C(2)	−0.1587(4)	0.0938(3)	0.3229(2)	0.0470(5)
C(3)	−0.1911(4)	−0.0594(3)	0.4329(2)	0.0522(6)
C(4)	−0.1644(3)	−0.2151(3)	0.4216(2)	0.0465(5)
C(5)	−0.1023(3)	−0.2277(2)	0.2951(2)	0.0355(4)
C(6)	−0.0746(3)	−0.3820(3)	0.2698(2)	0.0406(5)
C(7)	−0.0190(3)	0.3860(2)	0.1451(1)	0.0391(4)
C(8)	0.0105(3)	−0.2325(2)	0.0356(2)	0.0317(4)
C(9)	−0.0139(3)	−0.0793(2)	0.0547(2)	0.0286(4)
C(10)	−0.0700(3)	−0.0736(2)	0.1832(2)	0.0295(4)
N(1)	0.4598(3)	−0.5992(3)	0.2021(2)	0.0614(6)
N(2)	0.3417(3)	−0.3025(3)	0.4595(2)	0.0558(5)
C(11)	0.5205(3)	−0.1560(2)	−0.0199(2)	0.0347(4)
C(12)	0.4695(3)	−0.1539(2)	0.1128(2)	0.0319(4)
C(13)	0.4511(3)	0.0103(2)	0.1263(2)	0.0336(4)
C(14)	0.4385(3)	−0.3037(2)	0.2220(2)	0.0352(4)
C(15)	0.4528(3)	−0.4680(3)	0.2105(2)	0.0415(5)
C(16)	0.3860(3)	−0.3035(3)	0.3541(3)	0.0391(4)
H(2)	−0.176(4)	0.204(3)	0.330(2)	0.063(7)
H(3)	−0.230(4)	−0.048(3)	0.515(3)	0.077(8)
H(4)	−0.184(4)	−0.318(3)	0.496(2)	0.055(7)
H(6)	−0.092(3)	−0.484(3)	0.343(2)	0.056(6)
H(7)	−0.004(3)	−0.493(3)	0.129(2)	0.045(6)
H(11)	0.537(3)	−0.271(3)	−0.030(2)	0.040(5)
H(13)	0.421(3)	0.015(3)	0.212(2)	0.044(6)

$^a U_{iso}$ has estimated as $\frac{1}{3}\sum_i \sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$ for the non-hydrogen atoms.

atoms were taken from Ref. 6. The program used for the refinement was SHELXL-93.[7] This program refines on F^2 using all data, which is the cause of the somewhat high R_w-value of 0.184; the conventional R-value calculated from the 1452 most significant reflections is 0.052. The resulting coordinates and equivalent isotropic displacement parameters are given in Table 2. Lists of anisotropic displacement parameters and structure factor tables are available from the authors upon request. Additional programs used were ORTEP-II[8] for the crystal structure illustrations and PLATON[9] for geometric calculations.

Discussion

The PXX and TCNQ molecules are both situated on inversion centres. Furthermore they are nearly planar, with their least-squares planes almost coplanar. A projection of the structure on the common least-squares plane is seen in Fig. 1, which also shows the atomic numbering scheme used. In the a-direction the molecules stack alternately, with the stacking distance $ca.$ 3.3 Å, $cf.$ Fig. 2. The stacking distance is less than the sum of the van der Waals radii for two carbon atoms (3.40–3.54 Å, largest for purely aromatic carbons),[10] and significant overlap of the π-electrons of the molecules could be expected. Atomic distances and angles are listed in Table 3. The PXX molecule has been little studied: only one crystal structure has been published previously: tetra-*tert*-butyl-*peri*-xanthenoxanthene.[11] All C–C bond lengths of the PXX molecule are in the range 1.36–1.43 Å, *i.e.* not deviating very much from the expected aromatic C–C bond length of 1.40 Å. This suggests a significant charge delocalisation throughout the molecule, including the central C(9)–C(9) bond, which was also seen in Ref. 11. However, in dioxapyrene and dithiapyrene structures it has been observed that the C–C bond lengths in the oxygen- or sulfur-containing ring may deviate significantly in some cases, but not in all (*cf.* Ref. 2). Thus it may very well be that the charge delocalisation of PXX is similarly dependent on the environment. The TCNQ molecular geometry is in accordance with what is generally observed. Interaction between the molecules may be present in form of weak C–H···O or C–H···N contacts. The existence and significance of such contacts has been argued by *e.g.* Refs. 12 and 13. The evaluation of possible short con-

Fig. 1. Projection of the structure on the least-squares plane for the two molecules, showing the atomic numbering scheme and short C–H···X contacts (broken lines). The *b*-axis is vertical. The atomic displacement ellipsoids are scaled to 50% probability; the hydrogen atoms are spheres of arbitrary radius.

considering the low absorption coefficient (0.86 cm⁻¹). Further details on crystal data and experimental conditions are summarized in Table 1. The crystal structure was solved using direct methods for locating all non-hydrogen atoms (SHELXS-86),[5] and subsequently locating the hydrogen atoms from difference density maps. In the final cycles of refinement the displacement parameters were anisotropic for the C, O and N atoms, and isotropic for the H atoms. All atoms, including hydrogens, were refined unrestrained. Atomic scattering factors for neutral
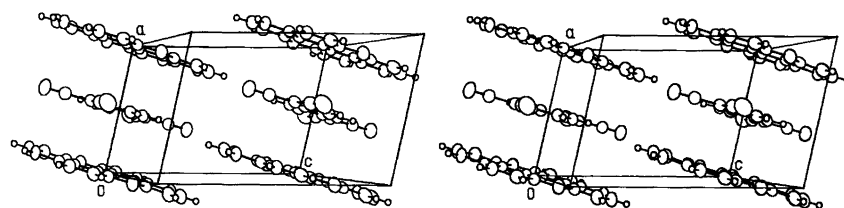

Fig. 2. View of the unit cell showing the stacks of alternating PXX and TCNQ molecules. Atomic displacement ellipsoids are as in Fig. 1.

Table 3. Bond lengths (in Å) and angles (in °) for PXX–TCNQ.

O–C(1)ᵃ	1.394(2)	N(1)–C(15)	1.140(3)
O–C(8)	1.382(2)	N(2)–C(16)	1.146(2)
C(1)–C(2)	1.362(3)	C(11)–C(12)	1.443(2)
C(1)–C(10)	1.412(3)	C(11)–C(13)ᵇ	1.342(3)
C(2)–C(3)	1.401(3)	C(12)–C(13)	1.439(3)
C(3)–C(4)	1.357(3)	C(12)–C(14)	1.378(3)
C(4)–C(5)	1.414(3)	C(14)–C(15)	1.432(3)
C(15)–C(6)	1.418(3)	C(14)–C(16)	1.432(3)
C(5)–C(10)	1.416(3)	C(2)–H(2)	0.96(2)
C(6)–C(7)	1.365(3)	C(3)–H(3)	0.93(3)
C(7)–C(8)	1.399(3)	C(4)–H(4)	0.95(2)
C(8)–C(9)	1.375(2)	C(6)–H(6)	0.93(2)
C(9)–C(9)ᵃ	1.426(3)	C(7)–H(7)	0.98(2)
C(9)–C(10)	1.410(2)	C(11)–H(11)	1.01(2)
		C(13)–H(13)	0.94(2)
C(1)ᵃ–O–C(8)	119.3(2)	C(11)–C(12)–C(13)	117.5(2)
Oᵃ–C(1)–C(2)	118.5(2)	C(11–C(12)–C(14)	121.1(2)
Oᵃ–C(1)–C(10)	120.7(2)	C(13)–C(12)–C(14)	121.5(2)
C(2)–C(1)–C(10)	120.8(2)	C(12)–C(13)–C(11)ᵇ	121.4(2)
C(1)–C(2)–C(3)	118.6(2)	C(12)–C(14)–C(15)	122.3(2)
C(2)–C(3)–C(4)	122.6(2)	C(12)–C(14)–C(16)	121.7(2)
C(3)–C(4)–C(5)	120.1(2)	C(15)–C(14)–C(16)	116.0(2)
C(4)–C(5)–C(6)	125.6(2)	N(1)–C(15)–C(14)	178.6(2)
C(4)–C(5)–C(10)	117.7(2)	N(2)–C(16)–C(14)	179.2(2)
C(6)–C(5)–C(10)	116.7(2)	C(1)–C(2)–H(2)	118(1)
C(5)–C(6)–C(7)	123.0(2)	C(3)–C(2)–H(2)	123(1)
C(6)–C(7)–C(8)	119.5(2)	C(2)–C(3)–H(3)	116(2)
O–C(8)–C(9)	121.3(2)	C(4)–C(3)–H(3)	122(2)
O–C(8)–C(7)	119.0(2)	C(3)–C(4)–H(4)	122(1)
C(9)–C(8)–C(7)	119.8(2)	C(5)–C(4)–H(4)	118(1)
C(8)–C(9)–C(9)ᵃ	121.1(2)	C(5)–C(6)–H(6)	117(1)
C(8)–C(9)–C(10)	121.2(2)	C(7)–C(6)–H(6)	120(1)
C(9)ᵃ–C(9)–C(10)	117.7(2)	C(6)–C(7)–H(7)	122(1)
C(1)–C(10)–C(5)	120.2(2)	H(7)–C(7)–C(8)	118(1)
C(1)–C(10)–C(9)	119.2(2)	C(12)–C(11)–H(11)	118(1)
C(5)–C(10)–C(9)	119.8(2)	H(11)–C(11)–C(13)ᵇ	121(1)
C(12)–C(11)–C(13)ᵇ	121.2(2)	C(12)–C(13)–H(13)	119(2)
		H(13)–C(13)–C(11)ᵇ	119(2)

Symmetry operations: ᵃ −x, −y, −z · ᵇ1−x, −y, −z.

tacts is, however, very dependent on the choice of van der Waals radius for hydrogen, which may depend on the nature of the C–H bond.[10,12] Here we have chosen the value 1.2 Å as the van der Waals radius of hydrogen. Analysis using these values reveals three contacts with H···O or H···N distances less than the sum of the van der Waals radii in the present structure, cf. Table 4 and Fig. 1. The shortest of the contacts is between symmetry-related TCNQ molecules, forming a chain of TCNQ molecules in the b-direction. The second contact connects the PXX and TCNQ molecules. Finally, the third contact (which is the longest, but also less bent) is between PXX molecules forming a chain of PXX molecules. These

Table 4. Distances (in Å) and angles (in °) for possible C–H···X interactions.

	C···X	H···X	C–H···X
C(6)–H(6)···N(2)	3.423(4)	2.56(2)	148(2)
C(7)–H(7)···O	3.497(3)	2.54(2)	165(2)
C(11)–H(11)···N(1)	3.372(3)	2.54(2)	140(1)

contacts, shown in Fig. 1 with broken lines, are thus possibly a relevant factor in forming the layers. The charge transfer between the molecules is expected to be low owing to the mixed stacking of the PXX and TCNQ molecules. The geometry of the TCNQ molecule is dependent on the amount of charge transfer, and a number of attempts to relate the charge transfer to the bond lengths have been published.[14–17] Estimates of the charge transfer using these methods gives $-0.07e$,[14] $-0.08e$,[15] $-0.12e$,[16] $-0.16(13)e$[17] and $-0.19(5)e$.[17] The spread in the values and the standard deviations on the last two values indicate that the charge transfer is small and hardly significant. Thus, as a consequence the conductivity is expected to be low.

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