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CRYSTAL STRUCTURES OF MOLECULAR COMPLEXES OF 2-CHLORO-11,11,12,12-TETRACYANOANTHRAQUINODIMETHANE WITH BENZENE (1:1) AND PYRENE(2:1)

A NOVEL TYPE OF CHARGE TRANSFER COMPLEXES

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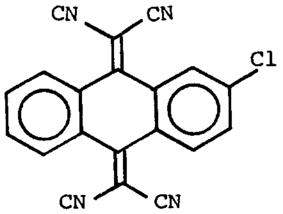
Abstract: X-Ray crystal studies of the titled molecular complexes have revealed the arrangement of parallel overlap between one of the benzene rings of the heavily deformed TCNAQ moiety and donor benzene and pyrene molecules, presumably attributable to the complex formation with weak charge transfer interactions.

Many attempts to prepare molecular complexes of 11,11,12,12-tetracyanoanthraquinodimethane (TCNAQ) with donors have been so far insuccessful and thus the general view has been supported that planarity of species is necessary for this type of complexation.1),2) However we have, recently, found that its derivatives easily form stable molecular complexes with various kinds of donors.3),4) These complexes have been shown to exhibit a weak π-π^* charge transfer interaction, although they are insulators without electrical conductivity. In order to know the crystal structures, the X-ray analyses of two complexes of 2-chloro-TCNAQ with benzene (1:1), (I) and pyrene (2:1), (II) have been carried out.5)

We wish to report here a novel type of charge transfer interaction along with the heavily deformed Cl-TCNAQ molecular structure.



Cl-TCNAQ

(I) Benzene (1:1) Complex

(II) Pyrene (2:1) Complex

Fig. 1 and Fig. 3 show the crystal structures of (I) and (II) viewed along a axis. The TCNAQ moieties of (I) and (II) have essentially the same structure of a well-known butterfly form.6),7) The structure shows no deviation from the ideal symmetry of the TCNAQ molecule, indicating no steric effect of chlorine atom in 2-position. The central ring is bent into a deep boat form with the dihedral angle of 140° between the two benzene rings.7) According to this non-planarity, the bond lengths around the central ring, av. 1.344 Å for exo-methylene double bonds and av. 1.480 Å for C-C single bonds, seem to show little π-delocalization effect.

The crystal structure of (I) showed that benzene and Cl-TCNAQ molecules form stacks of A-D-A'-D' along [101] projection by the operation of n-glide symmetry. There are two modes of molecular contact such as A-D and A'-D (see Fig.1). The former, in which benzene molecule gets into the deep boat central ring, contains some short atom contacts between benzene and dicyanomethylene groups (see Fig. 2a). However, they are not situated in the direct overlapping. The more important finding may be the fact that in the latter, the benzene molecule is arranged in the almost parallel overlap to one benzene ring of Cl-TCNAQ molecule. The interplanar distance of 3.75 Å is somewhat longer than those for TCNQ complexes (3.41-3.56 Å)8) and comparable to complex of pyrene and 2,4,6-trinitroanisole (3.79 Å).9) The two benzene rings are rotated by the angle of 27° from the superimposable overlap (see Fig. 2b). A similar orientation is found in TCNQ-anthracene complex.8)

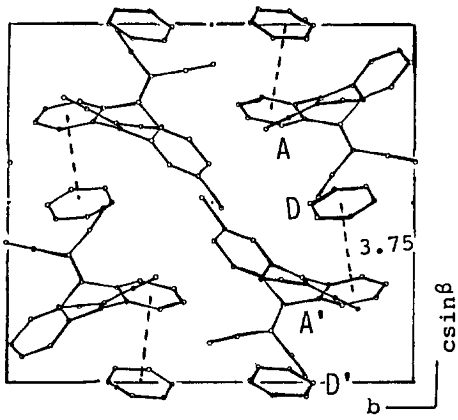


Fig. 1

Fig.1 Crystal packing of (I) viewed along a axis.

Fig.2 Molecular overlappings of A-D (Fig.2a) and A'-D (Fig.2b) viewed along the direction perpendicular to benzene molecule.

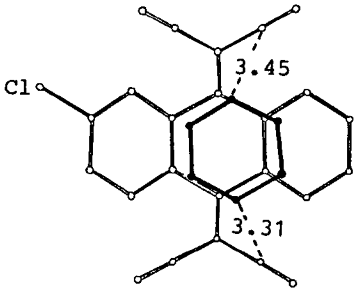


Fig.2a

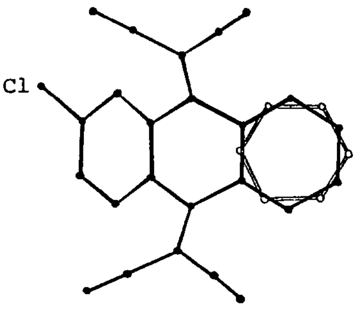


Fig.2b

On the other hand, the crystal structure of (II) is made up of isolated A-D-A' complexes in which pyrene is held between two Cl-TCNAQ molecules through a center of symmetry. Importantly, the overlap is similar to the case of (I), though it is observed in the different benzene ring with the disordered chlorine atom. The two planes are not strictly parallel but incline by 9.1°, and the distance between the midpoints of the benzene ring and pyrene molecule is 3.59 Å (see Fig. 4a). The mode of overlapping is shown in Fig. 4b viewed perpendicular to the chlorine-bearing benzene ring.

In conclusion, the crystal structures have showed that the complexes form neither the segregated stacks of acceptors and donors such as TCNQ-TTF,[10)] nor the alternately overlapped stacks as found in the usual charge transfer complexes. The complexes exist as the isolated units of A-D (1:1) in (I) and A-D-A' (2:1) in (II). It is, however, apparent that the complexes are stabilized by the weak π-π^* charge transfer interaction induced by the parallel overlap between donors and the planar aromatic parts in the heavily deformed acceptors.

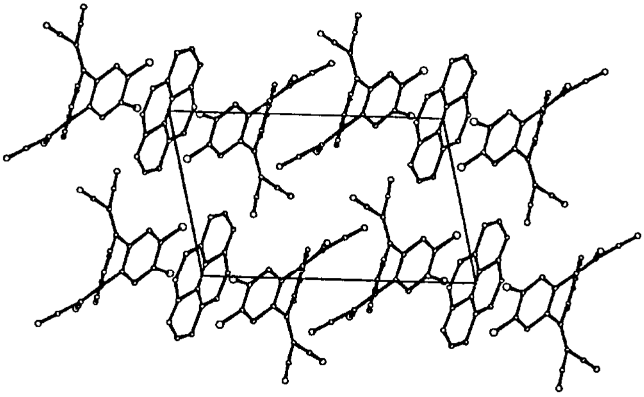


Fig. 3

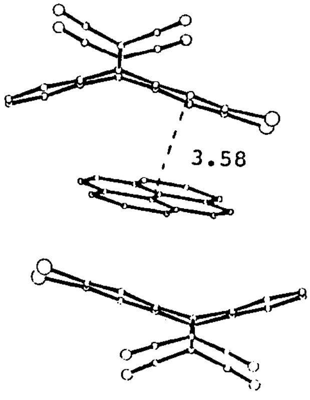


Fig. 4a

Fig.3 Crystal packing of (II) viewed along a axis.

Fig.4a Molecular arrangement (side view).

Fig.4b Molecular overlapping viewed along the direction perpendicular to the plane of chlorine-bearing benzene ring of Cl-TCNAQ.

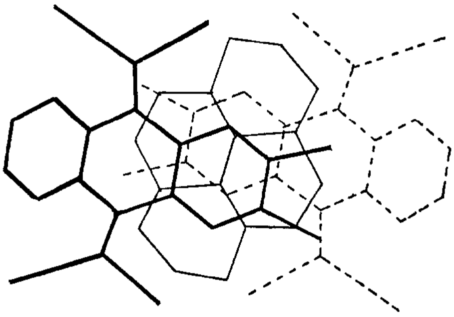


Fig. 4b

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5) Crystal data of (I): size=0.20x0.25x0.25 mm, $C_{20}N_4H_7Cl.C_6H_6$, cell dimensions; a=9.052(2), b=16.300(3), c=14.429(3) Å, β=96.13(2)° ; space group= $P2_1/c$ (Z=4). Dcalcd.=1.18 g/cm^3. The intensity data were measured on a Rigaku four-circle diffractometer (AFC-5) using Mo-Kα radiation and solved successfully by introducing some non-automatic input parameters in MULTAN81 program. The block-diagonal least-squares refinement with finally all hydrogen atoms which were calculated geometrically and then verified from difference Fourier map, converged to give an R factor of 0.090 (Rw=0.085) for the 2805 reflections with $Fo>3\sigma(Fo)$ of a total of 4179 measured reflections within 2θ=50°. Crystal data of (II): size=0.20x0.35x0.50mm, $C_{20}N_4H_7.1/2(C_{16}H_{10})$, cell dimension; a=10.172(2), b=13.798(3), c=9.302(2) α=92.56(2), β=117.24(2), γ=108.80(2)° ;space group P_1 (Z=2). The intensity data were measured by a Syntex R3 diffractometer using graphite monochromated Mo-Kα radiation and the structure was solved by the direct method program MULTAN78. The structure of 2-chloro-TCNAQ was disordered due to the transposition of the chlorine atom in such a way that the chlorine attached also on C_3 of TCNAQ nuclei so as to have m symmetry within the molecule. Refinement of the structure by the block-diagonal least-squares method gave an R factor of 0.099 (Rw=0.100) for 2745 reflections with $Fo> 3\sigma(Fo)$ of a total of 4916 measured reflections within 2θ<55° . All calculations were performed using UNICS3 system written by T. Sakurai and K. Kobayashi [Rep. Inst. Phys & Chem. Res., 55, 69 (1979)].

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