

CHARGE-TRANSFER COMPLEXES FORMATION BETWEEN 1,4-DIACETOXYNAPHTHALENE DERIVATIVES

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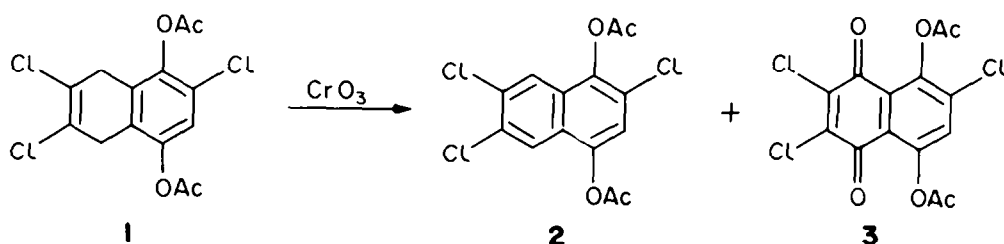
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Abstract—2, 6, 7-Trichloro-1, 4-diacetoxynaphthalene **2**, forms a charge-transfer complex (**A**) with itself; moreover it participates in a molecular sandwich (**B**) between two molecules of 2, 3, 6-trichloronaphthazarin diacetate **3**. Complexes **A** and **B** has been isolated and analyzed by UV and ¹H-NMR. The crystal structure of complex **A** has been determined by X-ray diffraction techniques.

RESULTS AND DISCUSSION

According to the procedure previously described¹ for the preparation of naphthazarin diacetates, chromic acid oxidation of the 2, 6, 7-trichloro-1, 4-diacetoxy-5, 8-dihydronaphthalene **1**, leads to a mixture of 2, 6, 7-trichloro-1, 4-diacetoxynaphthalene, **2**, and 2, 3, 6-trichloronaphthazarin diacetate, **3**. Trichloro derivative **1** was obtained by Diels Alder reaction of 2, 3-dichloro-1, 3-butadiene and chloro-*p*-benzoquinone and subsequent acetylation of the adduct.² The reaction is shown in the following Scheme:



TLC of the crude mixture enables the isolation of two charge-transfer complexes **A** (C₂₈H₁₈O₈Cl₆) and **B** (C₄₂H₂₃O₁₆Cl₆). The first compound, crystallized from carbon tetrachloride as orange-yellow prisms, m.p. 187–188°. The ¹H-NMR spectrum of this compound, shown the different signals in the aromatic region, δ 7.93 and 7.85 for the C₅ and C₈ protons, 7.38 for the C₃ proton, and 2.45 and 2.40 ppm for the Me of the acetoxy groups.

The UV-visible spectral data in CCl₄, give an absorption band at 460 nm, ε = 1200 l.mol⁻¹. cm⁻¹.

The **B** compound was isolated as minor component, as a brown-orange crystalline substance m.p. 120–121° (dec). Elemental and ¹H-NMR analysis, showed, that **B** is a molecular complex composed of two molecules of 2, 3, 6-trichloronaphthazarin diacetate and one molecule of the 2, 6, 7-trichloro-1, 4-diacetoxynaphthalene.

The ¹H-NMR shows several signals, at 7.88, 7.82, 7.40–7.36 in a ratio 1:1:3 and also at 2.45–2.42 and 2.38–2.36 as double signals of the acetoxy groups on

naphthazarin and naphthalene nucleus respectively, in a ratio of 2:1.

The UV spectrum gives three absorption bands in the visible region at 465, 445 and 438 nm in CCl₄ solvent with ε = 46.000, 52.000 and 40.000 l.mol⁻¹ cm⁻¹ respectively.

To confirm the molecular composition of **B**, a sample of the complex was treated with 0.1 M Na₂CO₃. After stirring, the solid residue was filtered off, solved in methylene chloride and crystallized, yielding **A** previously analyzed. The 2, 3, 6-trichloronaphthazarin, was extracted with methylene chloride from the aqueous basic

solution, after a treatment with hydrochloric acid. The naphthazarin is a red crystalline compound, m.p. 168–170° (dec), which has a simple ¹H-NMR spectrum that shows a signal at 7.40 and a double signal at 12.35 and 12.75 ppm of the OH protons. This compound was identical in spectral and physical data to an authentic sample obtained by an independent route.

The crystal structure of **A** has been determined by X-ray diffraction methods to verify the presence of the charge-transfer complex.

Molecular X-ray numbering, bond distances and angles, are shown in Fig. 1. Bond lengths shown in partial localization of the double bond character on the C atoms situated in the extreme positions of the aromatic nucleus, C(4)–C(5) and C(4')–C(5') of 1.377(7) Å and C(1)–C(2) and C(1')–C(2') of 1.354(7) Å, whilst a significant single bond character is present in the C(3)–C(3') of 1.422(7) Å and C(3)–C(4) and C(3')–C(4') of 1.431(7) Å and C(2)–C(3) and C(2')–C(3') of 1.417(7) Å distances. However a shortening

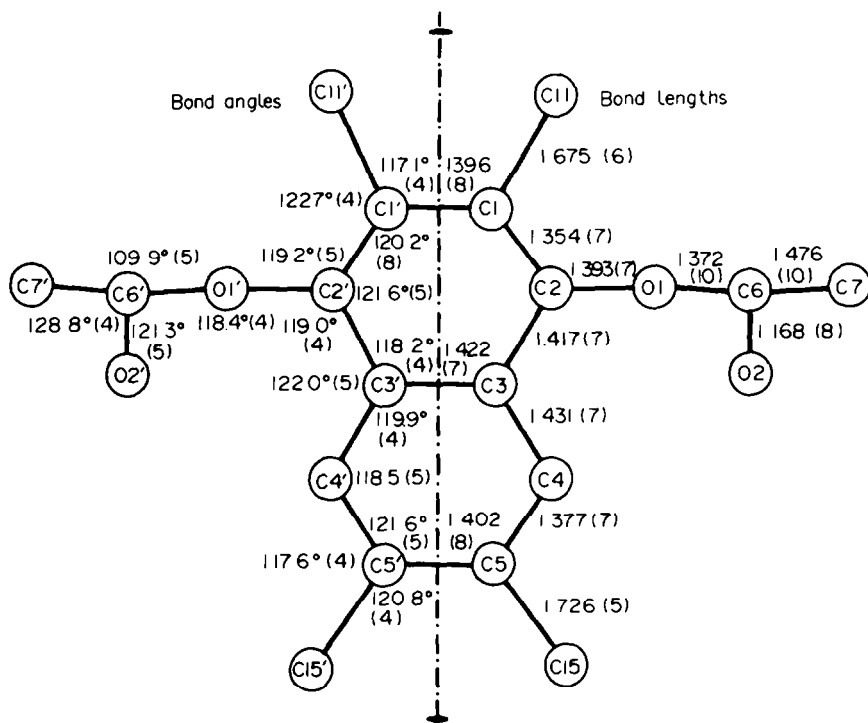


Fig. 1. Molecular structure of the A compound: (a) bond angles and (b) bond lengths.

of the C–Cl bond lengths is observed, being the shortest the C(1)–Cl(1) and C(1')–Cl(1') of 1.675(6) Å in which the disordered Cl(1) atoms are implicated. These facts show a possible electronic effect of charge donation characteristics of a molecular complex of the charge-transfer between the two naphthalene rings (Fig. 2a). Effectively, the mean interplanar spacing between the two nucleus is 3.44 Å, Fig. 2b. It means that the interaction between the donor and acceptor zones of the molecules must be important. The acceptor zone in the 2, 6, 7-trichloro-1,4-diacetoxynaphthalene should be located on the part of the benzenoid ring where the acetoxy groups are substituted, whilst the donor zone should be on the opposite benzenoid ring of the naphthalene nucleus. Thus, the centroid of the electron acceptor zone of one naphthalene nucleus, projected on the donor zone of the other naphthalene nucleus is approximate closely to the naphthalene C(3)–C(3') bond.

EXPERIMENTAL

Diacetate of the adduct **1** and their chromic acid oxidation were prepared according to the known procedures.^{1,2}

The identity of the compounds were established from chemical analysis and ¹H-NMR spectroscopy. All described compounds gave satisfactory elemental analysis. The UV-visible spectra were recorded on a Perkin Elmer 124 Spectrophotometer and ¹H-NMR was obtained by a Hitachi Perkin Elmer R-24A, 60 MHz spectrometer.

Crystals of **2** (C₁₄H₆O₄Cl₃) are monoclinic, space group C2/c with *a* = 12.812(2), *b* = 17.717(4), *c* = 7.522(1) Å, β = 118.76(2)°, *V* = 1496.67(2) Å³, *D*_c = 1.542(3) g cm⁻³ and *Z* = 4, *F*(000) = 704, μ(MoKα₁) = 0.623 mm⁻¹.

The space group and preliminary cell parameters were determined photographically (CuKα, radiation). Intensity data were collected on a Philips automatic 1100 diffractometer (graphite

monochromated MoK_α radiation, ω/2θ scan mode). Of the 2323 independent reflections in the scan range, 4 < 2θ < 70, 1196 with *I* > 2σ(*I*) were considered to be observed.

The data were corrected for Lorentz and polarization factors,

Table 1. Fractional coordinates (× 10⁴) for non-hydrogen atoms and (× 10³) for hydrogen atoms, with estimated standard deviations in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C1 1	6197(2)	2573(2)	2719(4)
C1 5	6322(2)	6978(1)	2849(2)
O 1	7206(3)	4062(2)	2660(4)
O 2	8207(3)	4221(3)	5990(5)
C 1	5566(4)	3415(3)	2581(7)
C 2	6120(4)	4075(3)	2664(6)
C 3	5579(4)	4780(3)	2594(5)
C 4	6164(4)	5480(3)	2707(6)
C 5	5577(4)	6142(3)	2619(6)
C 6	8233(4)	4107(3)	4403(7)
C 7	9278(5)	4029(4)	4163(9)
H 1	585	300	274
H 4	712	555	315
H 71	930	438	332
H 72	931	356	361
H 73	990	402	520

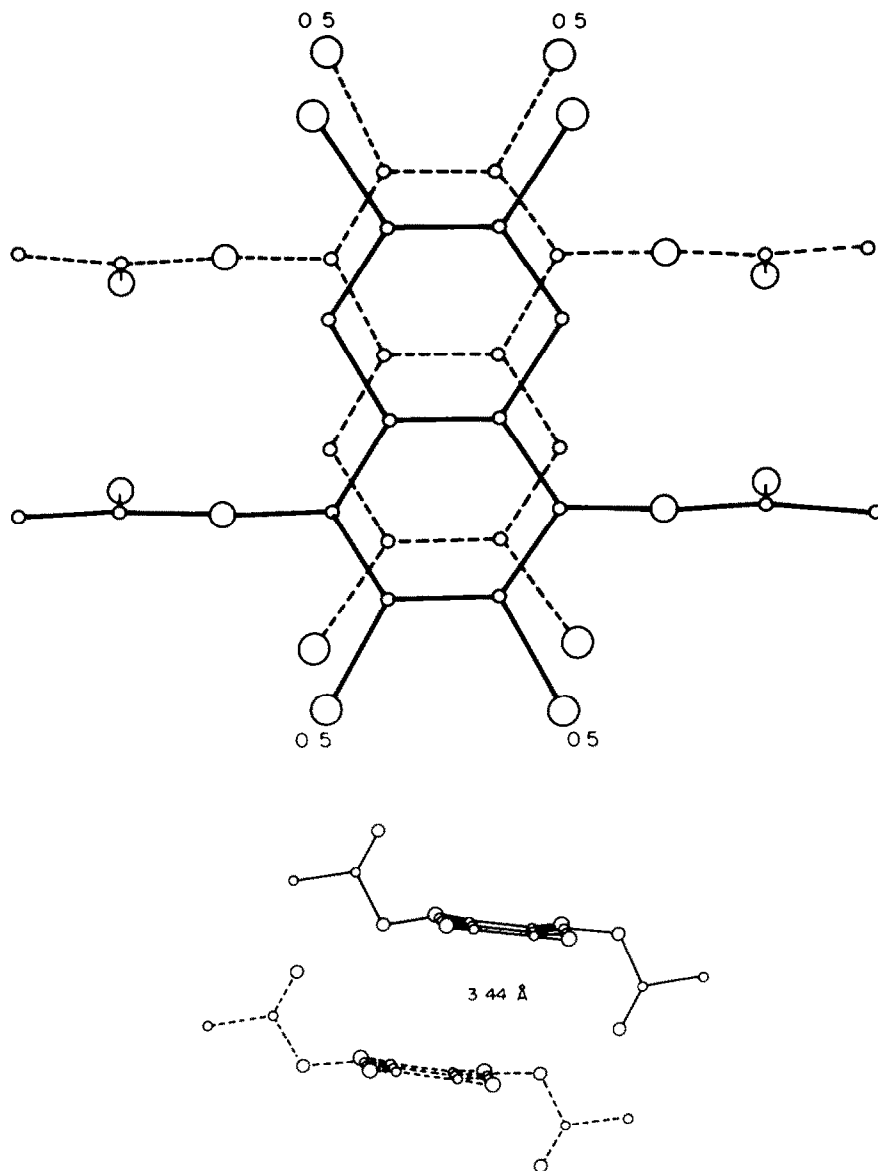


Fig. 2. (a) Overlap diagram of the molecule and (b) interplanar distance.

but no absorption corrections were applied. The structure was solved by direct methods³ and Fourier synthesis.

As $Z = 4$, the molecule must occupy a special position, which may be at a two-fold axis or a center of symmetry, the first position was chosen since the molecule has a two-fold axis, excepting for the Cl(1) and H(1) atoms. As there are three Cl atoms and 9 H it was supposed that the Cl(1) and H(1) were disordered at 50%. Electron density and difference synthesis maps were consistent with this hypothesis.

The structure was refined by full-matrix least-squares first with isotropic and finally with anisotropic temperature factors. All the H atoms with the exception of the half populated H(1) were determined in a difference synthesis. The H(1) was located in the ideal position. All H atoms were included in subsequent refinements but they were kept fixed.

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