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X-Ray Diffraction Analysis of Charge-Transfer Complex Dyes of Ethylcarbazole and Dicyanonaphthoquinones

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ABSTRACT

The crystal structure of the intermolecular charge-transfer (CT) complex dyes of ethylcarbazole and dicyanonaphthoquinone derivatives was determined by X-ray diffraction analysis. In the crystal, donor and acceptor molecules are stacked alternatively, i.e. each donor has two adjacent acceptor partners and each acceptor has two adjacent donor partners. The component molecules are stacked on top of each other to form a column, and the columns are assembled in the closest packing manner with the usual van der Waals contact between them. More than two kinds of overlap schemes between donor and acceptor molecules were observed by X-ray diffraction analysis.

1 INTRODUCTION

There is interest in the development of new special dyes for electro-optical application.[1] In previous studies, intermolecular charge-transfer (CT) complex dyes of carbazole–naphthoquinone were prepared and their

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Dyes and Pigments 0143-7208/91/$03·50

properties reported.[2,3] These CT complex dyes showed a 1:1 stoichiometry in methylene chloride solution. In general, the properties of intermolecular CT complex dyes such as electrical conductivity and photoconductivity are largely affected by the stereochemical configurations in the solid state. There is a major difference between the structures in the solid state and in solution, although a given complex may have the same stoichiometry of a 1:1 molar ratio in both phases. The complex will probably exist as discrete pairs containing single donor and acceptor molecules in solution, while in the solid phase the structures usually consist of infinite stacks of alternate donor and acceptor molecules. Thus, it is important to study the solid-phase structure in relation to the structures and characteristics of the CT complex.

In this present study, the solid-phase structure of two intermolecular CT complex dyes was determined by means of X-ray diffraction analysis. One complex was that from ethylcarbazole (**1**) and 5-nitro-2,3-dicyanonaphthoquinone (**2**) (complex **I**), and the other from **1** and 2,3-dicyanonaphthoquinone (**3**) (complex **II**).

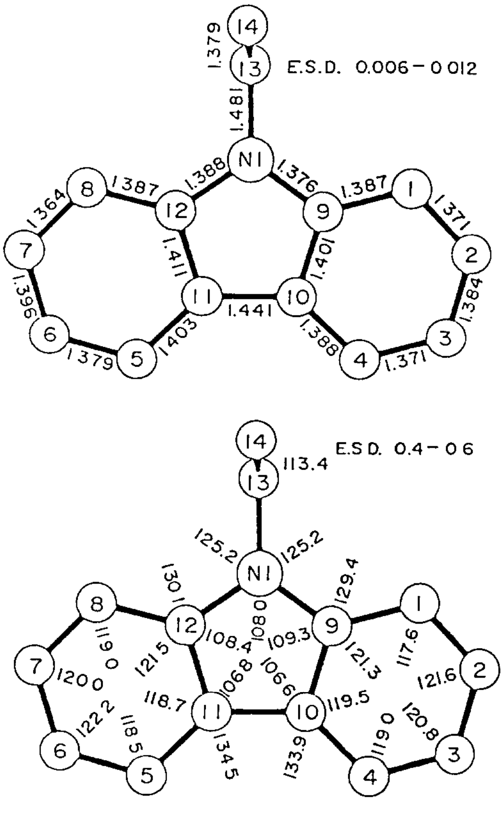


Fig. 1. Interatomic distances (in Å) and bond angles (in degrees) of *N*-ethylcarbazole, **1**.

2 RESULTS AND DISCUSSION

2.1 The CT complex of ethylcarbazole (1)–5-nitro-2,3-dicyanonaphthoquinone (2) (complex I)

The crystal structure of complex **I** has been briefly reported by us.[4] The bond distances and the bond angles of **1** in complex **I** are shown in Fig. 1. The carbazole ring is in the same plane, while the C–Me bond of the *N*-ethyl group protrudes from the carbazole plane with a bond angle of 113·4°. Its bond length (1·379 Å) is much shorter than that for a normal sp^3 hybridized C–C bond.

The bond distances and the bond angles of **2** in complex **I** are shown in Fig. 2. All atoms of the naphthoquinone ring in **2** are arranged in the same plane, but the 5-nitro group is almost perpendicular to the naphthoquinone

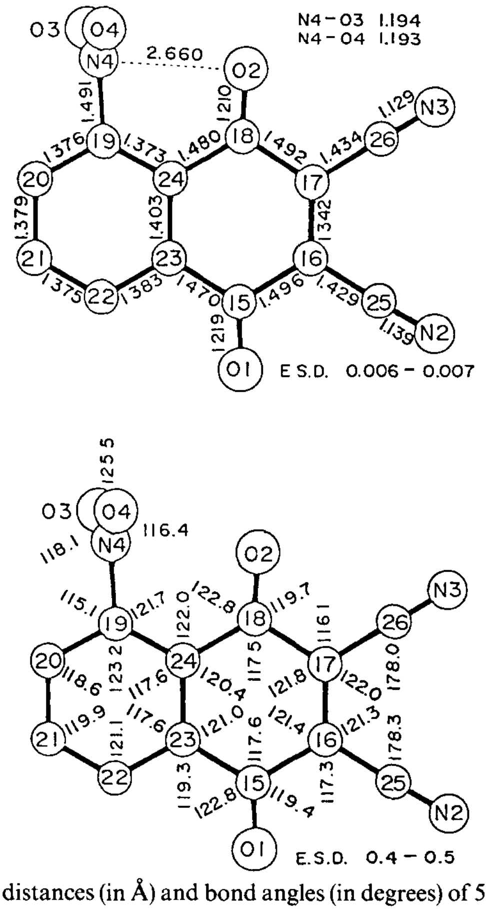


Fig. 2. Interatomic distances (in Å) and bond angles (in degrees) of 5-nitro-2,3-dicyano-1,4-naphthoquinone, **2**.

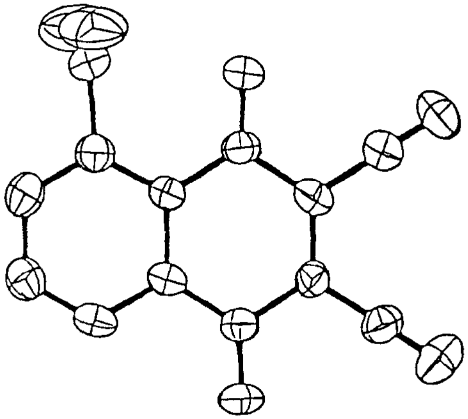
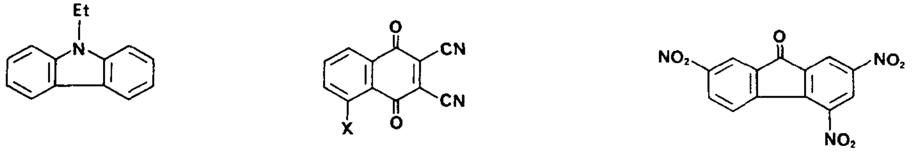


Fig. 3. The thermal ellipsoids of 5-nitro-2,3-dicyano-1,4-naphthoquinone, **2**.

plane. The angle between the naphthoquinone plane and the nitro plane was found to be 83·5°. The nitro group is believed to be in the same plane as the naphthoquinine moiety in solution and the observations in crystals are interesting and valuable in evaluating the characteristics of the CT complex dye. The distance between O(2) and N(4) is 2·66 Å and is shorter than the sum of their van der Waals radii, suggesting that a strong steric repulsion exists between them. If the nitro group was sited in the same plane as the naphthoquinone, a stronger steric repulsion would be operative, resulting in the nitro group rotating to be perpendicular to the naphthoquinone plane. The bond angle of N(4)–C(19)–C(24) (121·7°) is a little larger than that of N(4)–C(19)–C(20) (115·1°). Although the difference is small, this is important evidence for steric hindrance. The quite large thermal ellipsoids of the nitro moiety produced by the steric hindrance are shown in Fig. 3.

In contrast, the nitro groups of 2,4,7-trinitrofluoroenone (**4**) have coplanar geometry to the π-plane of the fluorenone skeleton, with the exception of the 4-NO_2 group which is more crowded than the others.[5] The geometry of the nitro groups is governed by steric factors and the substitution of nitro groups at the 2,4,7-positions of fluorenone are considered to be more effective than that of **2**.

The crystal data of the complex **I** are summarized in Table 1. Some of the molecular arrangements have been reported previously.[4] The crystals of



1

2, X=NO_2
3, X=H

4

Scheme 1

TABLE 1
Crystal Data of the CT Complexes I and II

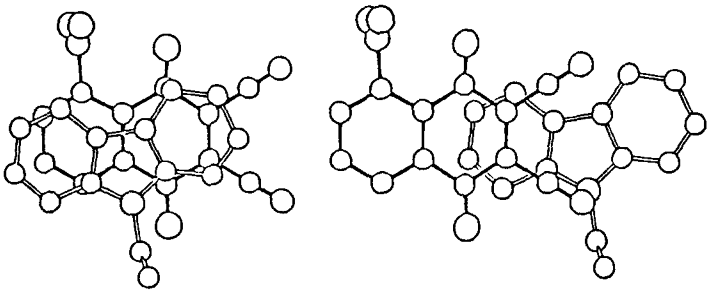
	Complex I	*Complex II*
Formula	$C_{14}H_{13}N.C_{12}H_3N_3O_4$	$C_{14}H_{13}N.C_{12}H_4N_2O_2$
Formula weight	448·43 (3)	403·44 (3)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$\bar{P}_1$
Cell dimensions		
a, Å	8·240 (1)	14·199 (2)
b, Å	16·576 (4)	15·688 (2)
c, Å	15·735 (4)	10·065 (1)
α, deg.	—	103·29 (1)
β, deg.	97·19 (8)	95·59 (1)
γ, deg.	—	105·76 (1)
U, Å^3	2 131·8 (8)	2 069·0 (5)
Z	4	4
D_x, g cm^{-3}	1·397 2 (4)	1·295 2 (3)
D_m^*, g cm^{-3}	1·391	1·100
μ(Mo-Kα), cm^{-1}	1·04	0·906

[a] By flotation method.

complex **I** belong to the monoclinic space group $P2_1/n$ with four pairs of **1** and **2** residues in the unit cell dimensions, $a = 8{\cdot}240(1)$ Å, $b = 16{\cdot}576(4)$ Å, $c = 15{\cdot}735(4)$ Å and $\beta = 97{\cdot}19(8)$ Å. The X-ray study verified the 1:1 composition in the complex. The component molecules are stacked on top of each other to form a column along the *a*-axis. These columns are assembled in the closest packing manner with the usual van der Waals contact between them. In the column, the molecular planes are almost parallel to each other (within 1·3°). There are two kinds of overlap patterns of the donor and acceptor molecules, as illustrated in Fig. 4, one being more overlapped than the other. In each case, the molecules stack in such a way as to avoid the steric hindrance between the *N*-ethyl and the nitro group. The interplanar separations of 3·31 Å and 3·28 Å are lower than the normal van der Waals separation of 3·4–3·6 Å between aromatic rings, but are larger than that of the quinhydrone (3·16 Å) between quinone and hydroquinone. The view along the *c*-axis of complex **I** is shown in Fig. 5; the packing modes in the column are well represented.

2.2 The CT complex ethylcarbazole 1 and 2,3-dicyanonaphthoquinone 3 (complex II)

The crystal structure of **1** in the complex **II** is the same as that in the complex **I**. The bond distances and the bond angles of **3** in complex **II** are shown in Fig. 6.



(more overlap) (less overlap)

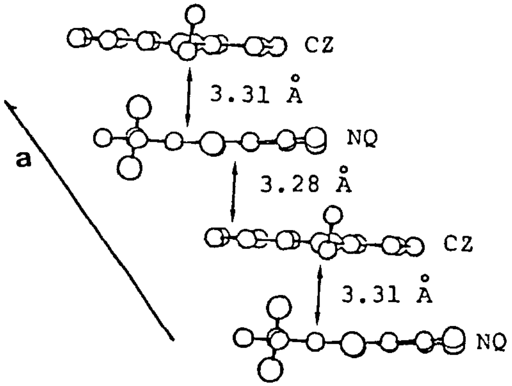


Fig. 4. Two kinds of overlaps between **1** and **2** viewed perpendicular to the molecular plane, and alternate stacking modes of **1** and **2** along the *a*-axis, the interplanar separations being given.

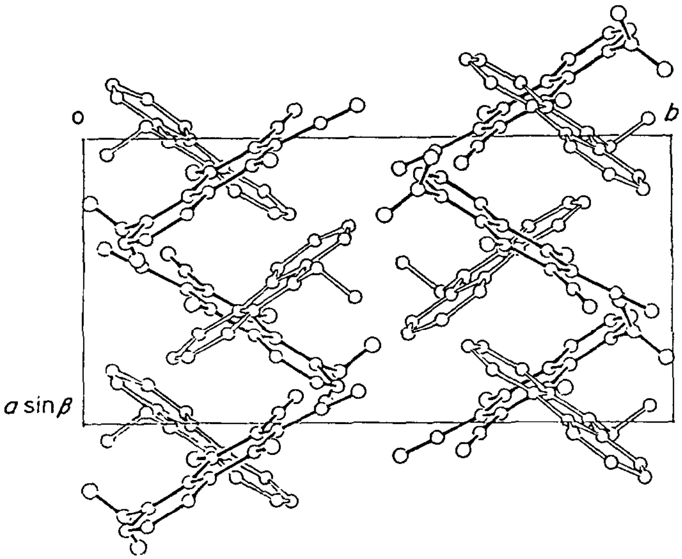


Fig. 5. Crystal structure of the CT complex **I** viewed along the *c*-axis.

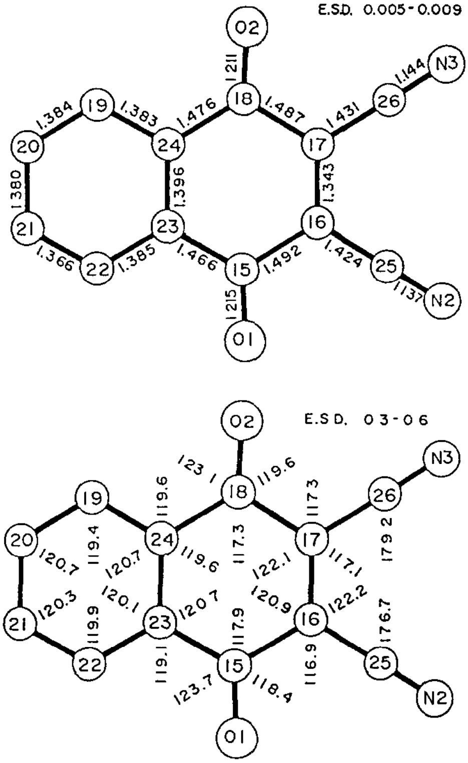


Fig. 6. Interatomic distances (in Å) and bond angles (in degrees) of 2,3-dicyano-1,4-naphthoquinone, **3**,

The crystals of complex **II** belong to the triclinic space group PI with four pairs of **1** and **3** residues in the unit cell. The crystal data of the complex **II** are shown in Table 1. The molecular arrangements in complex **II** are shown in Figs 7, 8 and 9. Complex **II** is arranged in the 1:1 stoichiometry of **1** and **3**. The donors and acceptors are stacked on top of each other to form a column along the *a*-axis. One column is surrounded by six columns at the normal van der Waals distance. In the column the molecular planes are almost parallel to each other (within 2·7°). Four kinds of overlap patterns of donor and acceptor molecules were observed, as shown in Fig. 8, with interplanar separations of 3·38 Å (mode 1), 3·37 Å (mode 2), 3·30 Å (mode 2), and 3·26 Å (mode 3) as shown in Fig. 9. These interplanar separations are a little larger than those in complex **I**, suggesting that **3** is a weaker acceptor than **2**. From these results it was concluded that the strength of the interaction in crystals can be correlated with the strength of the charge-transfer character from the donor to the acceptor.

The overlap patterns of modes 1 and 2 are very similar, as shown in Fig. 9, and correspond to the more overlapped patterns in the case of complex **I**.

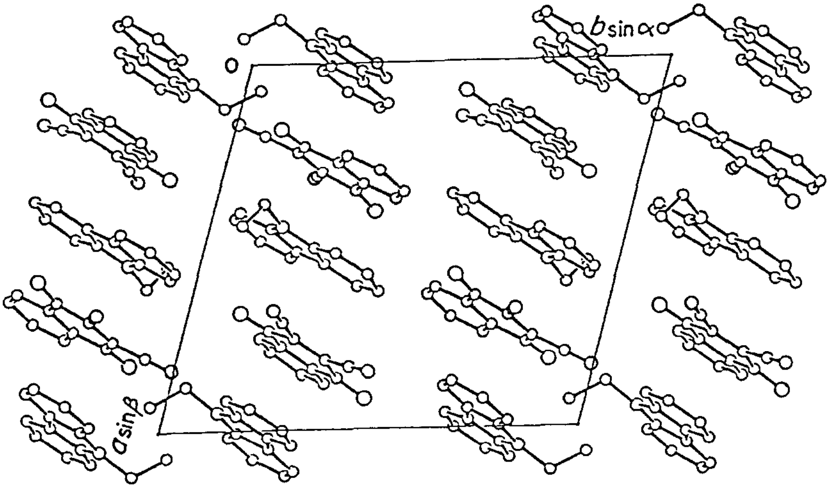
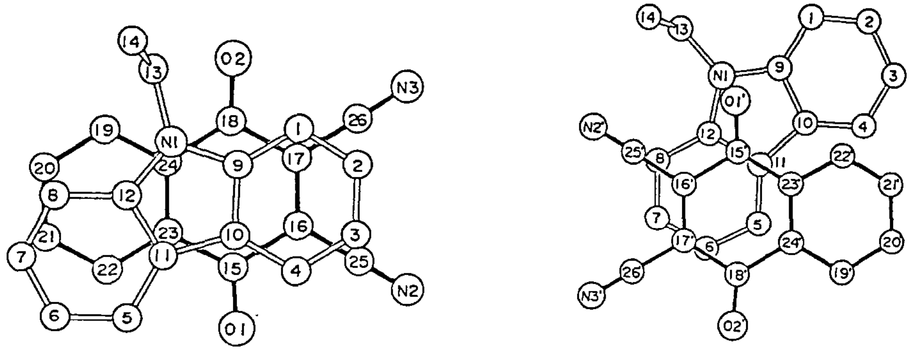
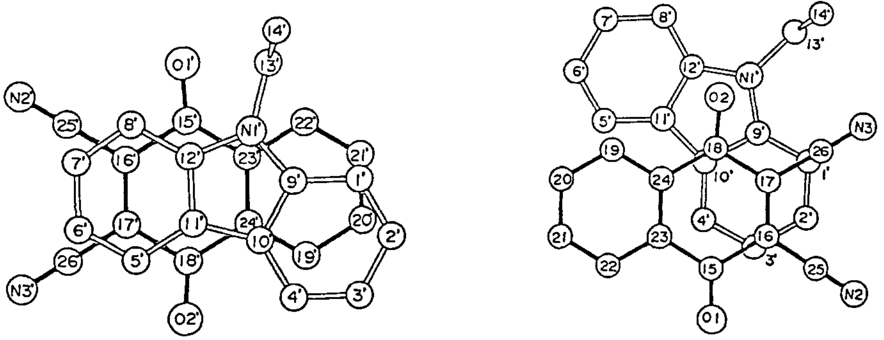


Fig. 7. Crystal structure of the CT complex **II** viewed along the *c*-axis.



(mode 1)

(mode 3)



(mode 2)

(mode 4)

Fig. 8. Overlapping mode of **1** and **3** viewed perpendicular to the molecular plane.

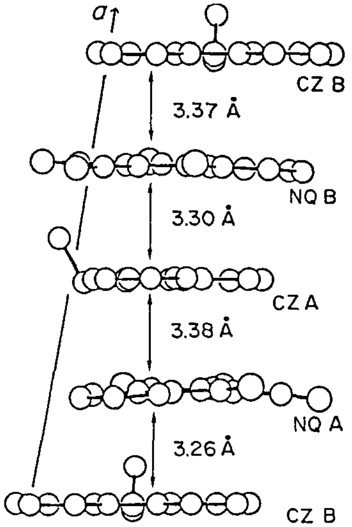


Fig. 9. Alternate stacking mode of **1** and **3** along the *a*-axis, the interplanar separations being given.

Also, the overlap patterns of modes 3 and 4 are similar: the patterns of those modes are less overlapped. It was found that the less overlapped pattern is arranged so as to deviate from the axis perpendicular to the molecular plane in complex **I**, while modes 1 and 2 are arranged along this axis in the complex **II**, since the steric hindrance caused by the nitro group in the complex **I** did not exist in the complex **II**.

There are common molecular units between complexes **I** and **II**. In the **2** and **3** moieties, the bond (bond distance 1·342 Å) between the two carbon atoms to which the cyano group is bonded is almost a double bond and resembles the C=C bond of tetracyanoethylene (TCNE). For all overlap patterns, this bond is located on top of the central part of the aromatic ring, as in the CT complex dyes containing the aromatic molecule and TCNE (see Figs 4 and 8).[6] Hence it can be considered that the charge transfer takes place mainly in this region.

3 EXPERIMENTAL

The crystal samples for X-ray analysis were obtained as dark blue crystals by slow evaporation of a methylene chloride solution of **1** and **2** or **1** and **3**.[2]

X-ray intensities were measured by a four-circle automatic diffractometer with Mo-Kα radiation up to 55°. Altogether 4897 reflections were measured, of which 2301 reflections with $|F_0| > 3(F_0)$ were used for the structure determination. The structure was solved by the direct method using the program MULTAN 78,[7] and was refined by the least-squares method. All the hydrogen atoms were found and they were included in the least-squares calculations. The final residual index *R* was 0·078 for complex **I** and 0·412 for complex **II**.

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