# Stacking Structure with Trimolecular Units of Donor-Acceptor-Donor in a Charge-transfer Complex of Dinaphtho[1,2-*b*:1',2'-*e*]-1,4-dithiin with Tetracyanoquinodimethane

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Dinaphtho[1,2-b:1',2'-e]-1,4-dithiin (DND) was prepared as an electron-donor species and upon reaction with the electron-acceptor species 7,7,8,8-tetracyanoquinodimethane (TCNQ) was found to form a charge-transfer complex with a donor: acceptor ratio of 2:1. The crystal and molecular structure of this complex has been determined. The molecules are arranged in a mixed stack composed of the trimolecular donor-acceptor-donor units, which are further linked by the donor-donor overlap. The donor molecules are folded along the S–S axis with a dihedral angle of 140.6°.

Intensive interest has focused upon organic charge-transfer complexes with metal-like conductivity, and in the chemistry of their component donor and acceptor species.<sup>1</sup> Planarity is considered an important requirement for  $\pi$ -donors and/or  $\pi$ acceptors in order to form charge-transfer complexes, since this allows a large face-to-face overlap. The need for planar molecules arises not only in segregated stacks with high conductivities, but also in mixed stacks in which the donors and acceptors alternate. In this context, thianthrene provides a characteristic family of electron donors, since it adopts a folded structure.<sup>2</sup> Treatment of thianthrene with 7,7,8,8-tetracyanoquinodimethane (TCNQ) fails to give crystalline chargetransfer complexes. However, a thianthrene derivative bearing electron-donating substituents, i.e. 2,3,7,8-tetramethoxythianthrene, forms a crystalline 1:1 complex with TCNQ,<sup>3</sup> even though it shows no conductor properties. Klar and his coworkers have elucidated its X-ray crystal structure.<sup>4</sup> As expected for insulators, the components alternate. In the stacks each of the folded donor molecules is arranged in such a way that one of the phenyl rings of the donor molecule is coplanar with the TCNQ molecules.

### **Results and Discussion**

Preparation of DND and the Charge-transfer Complex.—The DND framework was built up according to a procedure used for the preparation of 1,4-dithiins,<sup>5</sup> starting from the  $\alpha$ -bromoketone (1) and via the Bunte salt (2). Treatment of (2) with acid leads to a condensation reaction in a head-to-tail manner; therefore the regiochemistry is uniquely established, precluding the possibilities of the formation of other dinaptho-1,4-dithiin isomers.

Oxidation of compound (3) by *m*-chloroperbenzoic acid gave the corresponding monosulphone (4). The n.m.r. spectrum of (4) exhibited two sets of signals ascribable to  $-CH_2CH_2$ - groups, which confirms the structure of (4) having no symmetry plane. Compound (3) was readily dehydrogenated with dichlorodicyanobenzoquinone (DDQ) in boiling benzene to give DND (72%).

The charge-transfer complex of DND was precipitated as dark brownish needles from a hot acetonitrile solution containing an equivalent amount of DND and TCNQ. The donor: acceptor ratio of 2:1 was determined by elemental analysis. Charge-transfer complexes with segregated stacks of



donor and acceptor species and with compositions other than the 1:1 ratio of simple salts usually exhibit high electric conductivities owing to mixed valency. Here the 2:1 complex exhibited only poor conductivity below  $10^{-6}$  (S cm<sup>-1</sup>) as measured on a single crystal at room temperature. This is probably due to the closed-shell nature of the components, reminiscent of the mixed stack of the donor and acceptor molecules in the crystal, which is revealed in an X-ray crystallographic analysis described below.

Crystal Packing.—Figure 1 shows the three-dimensional packing arrangement in the crystal. The large molecular size of the DND molecules as compared with the substituted thianthrene donors and also with the TCNQ acceptor affects the crystal packing significantly (Figure 1). There are two crystallographically non-equivalent TCNQ molecules (TCNQ, and TCNQ<sub>b</sub>). Both form crystallographically independent trimolecular units of DND'a-TCNQb-DNDa and DNDb-TCNQ<sub>2</sub>-DND'<sub>b</sub> where the primes (') indicate molecules centrosymmetrically related to the corresponding non-primed molecules. Each (DND-TCNQ-DND') trimolecular unit has an axis joining the overlapping sections of the molecules which is roughly parallel to a  $[10\overline{1}]$  direction. One of the naphthalene rings of DND<sub>a</sub> is roughly parallel to TCNQ<sub>b</sub> with the interplanar angle of 2.3° and the interplanar spacing of 3.47 Å. Similarly, one of the naphthalene rings of DND<sub>b</sub> is parallel to TCNQ<sub>a</sub>, the interplanar angle being 4.2° and the interplanar spacing 3.47 Å.

The two crystallographically independent trimolecular units are linked alternatively by presumably strong van der Waals interactions between the parallel overlapping ring system of folded DND<sub>a</sub> and DND<sub>b</sub> molecules (and between DND'<sub>a</sub> and DND'<sub>b</sub> as well). Thus, DND<sub>a</sub> overlaps with DND<sub>b</sub> with the interplanar angle of 1.4° and the interplanar spacing of 3.62 Å to form a mixed stack of D·A·D–D·A·D–D·A·D– (where D = the donor species DND, and A = the acceptor species TCNQ). The total stack of trimolecular units linked infinitely through the crystal can be described as parallel to [101]. The overlap of the adjacent molecules in a stack is shown in Figure 2. There are no abnormally short intermolecular constants.

It is noteworthy that the acceptor groups, lying side-by-side, form the sheets parallel to the *ab* plane. Thus, the TCNQ molecules are arranged between the layers made by the dimeric units of the donor group. The building pattern observed is rarely encountered and represents a rather unusual type of structure for charge-transfer complexes.

Molecular Structure.—The bond lengths and bond angles of the  $DND_a$  molecule are shown in Figure 3 and those of the  $DND_b$  molecule are in Figure 4. Positional co-ordinates are given in the Table.

The C-S bond distances in DND are *ca.* 1.77 Å. These values are found in many compounds, indicating that the  $\pi$ delocalization is not spread over the whole molecule of DND including the central sulphur atoms. Thus, the degrees of bond alternation observed in the naphthalene rings in DND resembles that found in naphthalene itself.<sup>6</sup> The DND molecules are folded along the S-S axis with a fold angle of 140.6°; thus the DND molecules adopt a more planar conformation than thianthrene<sup>1</sup> and tetramethoxythianthrene<sup>2</sup> but are not as planar as phenothiazine.<sup>7</sup> The naphthalene rings and the sulphur atoms lie on the same plane.

The bond distances and the bond angles for the TCNQ molecules are given in Figure 5. The structural data are consistent with the usual quinonoid structure for this molecule.<sup>8</sup> This finding, together with the absence of short interatomic distances, substantiates our view that we are dealing with an almost neutral charge-transfer complex.

## Experimental

Melting points are uncorrected. <sup>1</sup>H N.m.r. spectra were obtained on a Varian EM-390 spectrometer in CDCl<sub>3</sub> using Me<sub>4</sub>Si as an internal standard.

3,3,4',4'-*Tetrahydrodinaphtho*[1,2-b;1',2'-e]-1,4-*dithiin* (3). A mixture of 2-bromo-1,2,3,4-tetrahydronaphthalen-1-one (1)<sup>9</sup> (18.5 g, 82.2 mmol), sodium thiosulphate pentahydrate (20.6 g, 83.1 mmol), and water (30 ml) was stirred vigorously and heated



Figure 1. Crystal packing of the  $DND_2$ -TCNQ complex viewed along the *b* axis



Figure 2. Overlap of the adjacent molecules: (a)  $DND_a$ -TCNQ<sub>b</sub>; (b)  $DND_a$ -DND<sub>b</sub>; (c) TCNQ<sub>a</sub>-DND<sub>b</sub>

428



Figure 3. Bond lengths (Å) and bond angles (°) for DND<sub>4</sub>; e.s.d.s in the S-C bonds are 0.007-0.008 Å and those in the C-C bonds are 0.010-0.012 Å. E.s.d.s in the C-S-C angles are  $0.3^{\circ}$ , in the C-C-S angles are  $0.5^{\circ}$ , and in the C-C-C angles are  $0.6-0.8^{\circ}$ 



Figure 4. Bond lengths (Å) and bond angles (°) for  $DND_b$ ; e.s.d.s are the same as shown in  $DND_a$ 

Atom	x	у	Z
<b>S</b> (1)	1 574(1)	1 416(3)	1 154(1)
S(2)	1 681(1)	-2 446(3)	1 439(1)
$\dot{\mathbf{C}(1)}$	666(4)	285(9)	1 194(2)
C(2)	-113(4)	1 126(9)	1 081(2)
C(3)	- 190(4)	2 820(9)	926(2)
C(4)	-968(5)	3 565(10)	822(2)
C(5)	-1686(5)	2 565(11)	832(2)
C(6)	-1638(4)	929(11)	964(2)
C(7)	-845(4)	124(10)	1 095(2)
C(8)	-770(4)	-1558(10)	1 233(2)
C(9)	3(4)	-2323(9)	1 353(2)
C(10)	722(4)	-1352(9)	1 324(2)
C(11)	2 369(4)	-951(8)	1 742(2)
C(12)	2 994(4)	-1 510(9)	2 093(2)
C(13)	3 086(4)	- 3 205(9)	2 230(2)
C(14)	3 736(5)	-3 667(11)	2 574(3)
C(15)	4 315(5)	-2 462(10)	2 785(2)
C(16)	4 243(4)	-806(10)	2 663(2)
C(17)	3 582(4)	-311(9)	2 313(2)
C(18)	3 477(4)	1 422(9)	2 189(2)
C(19)	2 850(4)	1 954(9)	1 848(2)
C(20)	2 308(4)	701(9)	1 619(2)
S(3)	3 386(1)	9 373(3)	3 764(1)
S(4)	3 165(1)	13 234(3)	3 479(1)
C(21)	2 617(4)	10 032(9)	3 305(2)
C(22)	2 103(4)	8 742(10)	3 076(2)
C(23)	1 453(4)	9 201(10)	2 744(2)
C(24)	1 322(4)	10 892(9)	2 615(2)
C(25)	653(4)	11 358(11)	2 263(2)
C(26)	546(5)	12 980(11)	2 134(2)
C(27)	1 094(5)	14 264(11)	2 337(3)
C(28)	1 751(4)	13 867(10)	2 683(2)
C(29)	1 872(4)	12 174(9)	2 828(2)
C(30)	2 512(4)	11 699(8)	3 182(2)
C(31)	4 152(4)	12 268(8)	3 584(2)
C(32)	4 841(4)	13 285(9)	3 559(2)
C(33)	5 632(4)	12 661(9)	3 682(2)
C(34)	5 761(4)	10 982(9)	3 825(2)
C(35)	6 573(4)	10 318(11)	3 971(2)
C(36)	6 679(5)	8 696(11)	4 115(2)
C(37)	5 993(5)	/ 619(10)	4 119(2)
C(38)	5 189(4)	8 210(9)	39/2(2)
C(39)	5 050(4)	9 908(9)	3 831(2)
C(40)	4 255(4)	10 028(8)	$\frac{5}{15(2)}$
C(41)	4 398(4)	11 220(8)	4 850(2)
C(42)	4 151(4)	9 382(8)	4 985(2)
C(43)	2 208(4) 2 800(4)	11 393(8)	4 000(2)
C(44) C(45)	3 890(4) 3 035(4)	12 403(8)	4 /0/(2)
C(43)	2 933(4) 4 011(4)	12 104(9)	4 077(2)
C(40)	4011(4)	14 030(9)	4571(2)
N(1)	2 241(4) 4 178(4)	15 346(8)	4034(2)
C(47)	712(4)	8 995(8)	123(2)
C(48)	-105(4)	8 277(8)	00(2)
C(40)	- 105(4) 700(4)	10 751(8)	21(2)
C(50)	1 410(4)	8 018(8)	21(2)
C(51)	1 338(4)	6 268(9)	339(2)
C(52)	2 235(4)	8 641(9)	272(2)
N(3)	1 256(4)	4 893(8)	409(2)
N(4)	2 897(4)	9 099(8)	293(2)
= ( )	=(-)	(-)	

Table. Final atomic parameters ( $\times 10^4$ )

under reflux for 1 h. The solution was cooled in an ice-bath to give the Bunte salt (2) as a white solid, which was filtered off, washed (ethanol), and dried. The salt (2) was then added to a solution of ethanol (15 ml) and concentrated hydrochloric acid (30 ml). The mixture was stirred and heated at the reflux temperature for 4 h, then cooled, and extracted with dichloromethane. The organic layer was washed with aqueous

429





Figure 5. (a) Bond lengths (Å) and bond angles (°) of TCNQ<sub>a</sub>. (b) Bond lengths (Å) and bond angles (°) of TCNQ<sub>b</sub>. E.s.d.s in the C-C(CN) bonds are 0.009—0.010 Å and those in the C-C-CN angles are 0.6—0.7°. The e.s.d.s values of other bonds and angles are about the same as for the C-C and C-C-C in DND<sub>a</sub>

sodium carbonate, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure. The residual solid was recrystallized from ethanol to give (3) (7.4 g, 56%) as white needles, m.p. 158—160 °C (Found: C, 74.9; H, 5.0; S, 20.05. Calc. for  $C_{20}H_{16}S_2$ : C, 74.99; H, 5.03; S, 19.98%).

Oxidation of (3). To a solution of (3) (2.0 g, 6.3 mmol) in dichloromethane (30 ml) *m*-chloroperbenzoic acid (2.2 g, 12.7 mmol) in dichloromethane was added during 15 min and the solution was refluxed for 1 h. The mixture was diluted further with dichloromethane (50 ml), washed with aqueous sodium hydroxide, and dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation gave the sulphone (4) (1.9 g, 68%), which was purified by recrystallization from ethanol, m.p. 192–194 °C (Found: C, 68.3; H, 4.55; S, 18.05. Calc. for C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub>: C, 68.15; H, 4.58; S, 18.19%).

Dinaphtho[1,2-b: 1',2'-e]-1,4-dithiin (DND).—A mixture of (3) (3.2 g, 10.0 mmol) and DDQ (4.6 g, 20.2 mmol) in benzene (100 ml) was refluxed for 1 h. The solid was filtered off, the solution was concentrated and chromatographed on silica gel to afford DND (5) (2.3 g, 72%) as white needles, m.p. 177—179 °C (Found: C, 75.8; H, 3.9; S, 20.15. Calc. for  $C_{20}H_{12}S_2$ : C, 75.94; H, 3.82; S, 20.23%).

Complexation of DND with TCNQ.—A hot solution of acetonitrile containing approximately equivalent amounts of

DND and TCNQ was allowed to cool at room temperature overnight. Dark brownish needles precipitated, m.p. 207 °C [Found: C, 74.65; H, 3.3; N, 5.8; S, 15.35. Calc. for (DND)<sub>2</sub>(TCNQ),  $C_{52}H_{28}N_4S_4$ : C, 74.64; H, 3.35; N, 6.70; S, 15.31%].

X-Ray Crystallography.—The crystal employed for the data collection had dimensions  $0.3 \times 0.3 \times 0.4$  mm. The space group and the unit-cell parameters were determined from precession and Weissenberg photographs. Intensity data were collected with a Ragaku four-circle diffractometer using graphite-monochromated Mo- $K_{\alpha}$  radiation in the range  $1^{\circ} < \theta < 25.0^{\circ}$  of the  $\omega/\theta$  scan mode. The intensities were corrected for Lorentz and polarization factors but not for absorption. 4 400 Reflections had  $F \ge 3\sigma(F)$  and were used in the structure refinement. Hydrogen atoms were not located.

Crystal Data.— $(C_{20}H_{12}S_{2})_2(C_{12}H_4N_4)$ , M = 837.1. Monoclinic, space group  $P2_1/c$ , a = 16.397(5), b = 7.981(2), c = 30.971(6) Å,  $\beta = 101.47(3)^\circ$ , U = 3.972.0 Å<sup>3</sup>, Z = 4,  $D_c = 1.40$  Mg m<sup>-3</sup>, F(000) = 1.728,  $\lambda = 0.710.59$  Å,  $\mu$ (Mo- $K_a$ ) = 0.28 mm<sup>-1</sup>.

Structure Analysis and Refinement.—The structure was solved by the direct method using MULTAN 82 and refined on F by full-matrix least-squares procedures. A series of difference Fourier syntheses and least-squares refinements gradually revealed all the non-hydrogen atoms. The refinement with anisotropic temperature factors on all non-hydrogen atoms gave the final R factor of 0.085. The weakness of the intensity would be responsible for the rather high R value. All the computations were carried out at the Computer Center of the University of Tokyo with the Unics III program system. The final atomic co-ordinates are listed in the Table.

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#### References

- 1 (a) M. R. Bryce and L. M. Murphy, *Nature*, 1984, **309**, 119; (b) R. L. Greene and G. B. Street, *Science*, 1984, **226**, 651; (c) D. O. Cowan and F. W. Wiygul, *Chem. Eng. News*, 1986, July 21, 28.
- 2 (a) H. Lynton and E. G. Cox, J. Chem. Soc., 1956, 4886; (b) I. Rowe and B. Post, Acta Crystallogr., 1958, 11, 372.
- 3 (a) R. C. Wheland and J. L. Gillson, J. Am. Chem. Soc., 1976, 98, 3916; (b) R. C. Wheland, J. Am. Chem. Soc., 1976, 98, 3926.
- 4 W. Hinrichs and G. Klar, J. Chem. Res. (M), 1982, 3540.
- 5 K. Kobayashi and C. L. Gajurel, Sulfur Rep., 1986, 7, 123.
- 6 V. I. Ponomarev, O. S. Filipenko, and L. O. Atovmyan, Kristallografiya, 1976, 21, 392 (Chem. Abstr., 1976, 84, 187972).
- 7 J. D. Bell, J. F. Blount, O. V. Briscoe, and H. C. Freeman, Chem. Commun., 1968, 1656.
- 8 S. Flandrois and D. Chasseau, Acta Crystallogr., Sect. B, 1977, 33, 2744.
- 9 K. G. Rutherford and C. L. Stevens, J. Am. Chem. Soc., 1955, 77, 3278.

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