Crystal Structure of 1 : 2 Charge Transfer Complex of 2,7-Bis(methylthio)-1,6-dithiapyrene (MTDTPY) and Tetrahydrobarreleno-tetracyanoquinodimethane (THBTCNQ)

Kazuhiro Nakasuji,* Mitsuru Sasaki, Ichiro Murata,* Atsushi Kawamoto,† and Jiro Tanaka†
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560
†Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

(Received May 24, 1988)

Synopsis. The crystal structure of a 1 : 2 complex of bis(methylthio)dithiapyrene and tetrahydrobarreleno-TCNQ contained face-to-face packings of acceptor-donor-acceptor units which are isolated from each other. The IR spectrum, geometry, and absorption spectrum showed the neutral nature of this complex.

Recently, we reported the synthesis and properties of three-dimensionally modified tetracyanoquinodimethanes (TCNQ's). An interesting result was the formation of relatively highly conducting charge transfer (CT) complexes.[1] More recently, we have explored new donor molecules, such as 2,7-bis(methylthio)-1,6-dithiapyrene (MTDTPY) and 2,3 : 7,8-bis(ethylenedithio)-1,6-dithiapyrene (ETDTPY), which are classified into peri-condensed Weitz-type donors[2] having alkylthio substituents. MTDTPY produced metallic CT complexes with TCNQ, chloranil, and bromanil.[3] In this report, we present the crystal structure and some physical properties of the title 1 : 2 CT complex, which is composed of MTDTPY and one of the three-dimensionally modified TCNQ derivatives, tetrahydrobarreleno-TCNQ (THBTCNQ).

Experimental

Preparation of Single Crystals of MTDTPY-(THBTCNQ)$_2$ Complex. A solution of the donor and the acceptor in dichloromethane (ca. 0.02 M) was allowed to evaporate at room temperature. After several days, black prisms of MTDTPY-(THBTCNQ)$_2$ were grown: mp 202—204 °C. The stoichiometry was deduced from an X-ray analysis.

Crystal Structure Analysis. Crystal data: $C_{52}H_{36}S_4N_8$, FW =901.15, triclinic, space group $P\bar{1}$, a=14.589 (3), b= 15.4421 (3), c=7.367 (1) Å, α=93.32 (2), β=92.50 (2), γ=139.22 (1), V=1072.3 Å^3, d_{obs}=1.400 g cm^{-3}, d_{calc}=1.396 g cm^{-3}, Z=1. A prism-like crystal with dimensions of 0.5×0.5×0.3 mm was used for data collection on a Rigaku automated four-circle diffractometer (AFC-5) using graphite-monochromated Cu $K\alpha$ radiation (λ=1.5418 Å). 2θ-ω scan mode was employed ($2\theta_{max}$=126°). The structures were solved by the Monte-Carlo direct method[4] with a MULTAN-78[5] program system using 3061 non-zero unique reflections and refined on F^2 by a full-matrix least-squares program with absorption corrections made by an analytical method.[6] The donor molecule turned out to contain an orientational disorder. The occupancy ratio for disordered sulfur and carbon atoms of SC1 and SC2 was assumed to be 1 : 1. Anisotropic temperature factors were used for the refinement of non-H atoms. The final R value ($R=\sum||F_o|-|F_c||/\sum|F_o|$) is 0.057. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[7] All calculations were made on FACOM M-382 computer at the computer center of Nagoya University. The complete F_o-F_c data and the temperature parameters are deposited as Document No. 8845 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The atomic coordinates as well as the bond lengths and angles are listed in Tables 1—3, respectively. An ORTEP drawing of the molecular structures and numbering schemes are shown in Fig. 1. As shown in the crystal structures (Figs. 2 and 3), the donor (D) and the acceptor (A) form an ADA-type arrangement in which each donor molecule lies on an inversion center. The interplanar spacing between D and A is 3.5 Å. One of the $C\equiv N$ bonds is tilted away from the quinodimethane moiety (Fig. 3): the deviation from the plane of the six-membered ring is 0.446 Å for C19 and 0.701 Å for N3. Methylthio groups also deviate from

Table 1. Atomic Coordinates and Equivalent Isotropic Temperature Parameters[a] with Estimated Standard Deviations in Parentheses for MTDTPY-(THBTCNQ)$_2$

Atom	x	y	z	B_{eq}/Å^2
SC1	0.2186(2)	0.9986(2)	0.8704(2)	9.2(1)
SC2	−0.0597(1)	0.7390(1)	0.9799(2)	6.5(1)
S2	0.1549(1)	0.7770(1)	0.8517(1)	8.0(1)
N1	0.5028(4)	1.0582(3)	0.7452(5)	9.3(2)
N2	0.9226(3)	1.3211(3)	0.6568(5)	7.7(2)
N3	0.5271(3)	0.4804(2)	0.7486(4)	6.2(2)
N4	0.9008(3)	0.7852(3)	0.5201(4)	6.9(2)
C2	0.0976(3)	0.8415(3)	0.9021(4)	5.3(2)
C3	−0.0765(3)	0.8340(3)	1.0159(4)	5.1(2)
C4	0.0185(3)	0.9693(3)	0.9818(3)	4.3(2)
C5	0.1485(3)	1.0429(3)	0.9125(3)	5.1(2)
C6	0.2353(3)	1.1718(3)	0.8770(4)	5.1(2)
C7	−0.2002(3)	0.7674(3)	1.0871(4)	5.3(2)
C8	−0.0027(5)	0.6002(4)	0.8442(8)	9.0(3)
C9	0.6748(3)	0.9759(3)	0.6717(4)	4.8(2)
C10	0.5497(3)	0.8368(3)	0.6940(4)	5.0(2)
C11	0.5499(3)	0.7480(3)	0.6788(4)	4.6(2)
C12	0.6756(3)	0.7908(3)	0.6426(3)	4.2(2)
C13	0.7953(3)	0.9269(3)	0.6062(4)	5.0(2)
C14	0.7956(3)	1.0140(3)	0.6227(4)	4.8(2)
C15	0.6888(3)	1.0753(3)	0.6890(4)	5.1(2)
C16	0.5818(3)	1.0602(3)	0.7240(4)	6.1(2)
C17	0.8199(3)	1.2110(3)	0.6706(4)	6.0(2)
C18	0.6893(3)	0.7109(3)	0.6407(3)	4.3(2)
C19	0.5947(3)	0.5827(3)	0.7007(4)	4.9(2)
C20	0.8093(3)	0.7553(3)	0.5756(4)	5.0(2)
C21	0.4068(3)	0.6060(3)	0.6883(5)	5.7(2)
C22	0.4070(3)	0.7704(3)	0.7267(6)	7.3(2)
C23	0.3007(4)	0.5662(4)	0.5348(6)	7.4(2)
C24	0.2990(4)	0.6633(4)	0.5613(7)	7.3(2)
C25	0.3596(4)	0.5987(4)	0.8732(6)	9.2(3)
C26	0.3672(5)	0.7042(4)	0.9017(7)	9.0(3)

a) $B_{eq}=8/3\pi^2\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$.

Table 2. Bond Distances with Estimated Standard Deviations in Parentheses for MTDTPY-(THBTCNQ)$_2$

Bond	*l*/Å	Bond	*l*/Å
SC1-C2	1.635(3)	C11-C21	1.506(3)
SC1-C5	1.635(7)	C12-C13	1.444(3)
SC2-C2	1.678(3)	C12-C18	1.391(7)
SC2-C3	1.671(6)	C13-C14	1.340(7)
C2-S2	1.753(6)	C15-C16	1.432(8)
C3-C4	1.433(4)	C15-C17	1.433(3)
C3-C7	1.387(5)	N1-C16	1.146(9)
C4-C5	1.427(5)	N2-C17	1.149(4)
C4-C4′	1.423(10)	C18-C19	1.426(4)
C5-C6	1.380(5)	C18-C20	1.436(6)
C6-C7′	1.387(8)	N3-C19	1.152(5)
S2-C8	1.791(4)	N4-C20	1.140(6)
C9-C10	1.449(4)	C21-C23	1.542(7)
C9-C14	1.447(6)	C21-C25	1.525(7)
C9-C15	1.384(7)	C22-C24	1.535(5)
C10-C11	1.371(7)	C22-C26	1.538(7)
C10-C22	1.512(6)	C23-C24	1.520(10)
C11-C12	1.448(6)	C25-C26	1.547(11)

Table 3. Selected Bond Angles with Estimated Standard Deviations for MTDTPY-(THBTCNQ)$_2$

Angle	*ϕ*/°	Angle	*ϕ*/°
C2-SC1-C5	104.7(3)	C10-C11-C12	121.0(3)
C2-SC2-C3	103.6(2)	C11-C12-C13	117.2(4)
C2-S2-C8	103.1(3)	C11-C12-C18	124.9(3)
SC1-C2-SC2	132.7(4)	C13-C12-C18	117.9(4)
SC2-C3-C4	128.0(3)	C12-C13-C14	121.6(4)
C4-C3-C7	119.5(5)	C9-C14-C13	122.0(3)
C3-C4-C5	121.6(5)	C9-C15-C16	127.0(3)
C3-C4-C4′	118.8(4)	C9-C15-C17	121.3(4)
C5-C4-C4′	119.6(3)	C16-C15-C17	111.7(5)
SC1-C5-C4	129.0(3)	N1-C16-C15	174.0(4)
C4-C5-C6	119.7(5)	N2-C17-C15	177.4(7)
C5-C6-C7′	121.0(4)	C12-C18-C19	127.1(4)
C3-C7-C6′	121.3(3)	C12-C18-C20	120.6(3)
C10-C9-C14	117.0(4)	C19-C18-C20	112.4(4)
C10-C9-C15	126.3(4)	N3-C19-C18	174.3(5)
C14-C9-C15	116.7(3)	N4-C20-C18	177.1(3)
C9-C10-C11	121.0(4)		

the almost planar DTPY skeleton: 0.508 Å for C8. The molecular overlap mode is shown in Fig. 4. There are no shorter intermolecular distances between ADA units than the van der Waals contacts. In this sense, ADA units are isolated from each other.

This complex can be classified into a neutral complex, as inferred from the following evidence. The stretching frequency of the C≡N bonds for the complex appeared at 2219 cm^{-1}, which is almost the same as that of the neutral THBTCNQ, itself (2213 cm^{-1}).[1] From the bond-length-ratio procedure of Kistenmacher et al.,[8] the degree of CT was calculated to be 0.25 by using the average bond lengths of the assumed *mmm* molecular symmetry. Although such a calculation is too primitive to draw a precise ionicity, both the stretching frequency and the molecular geometry show the neutral nature of the complex.

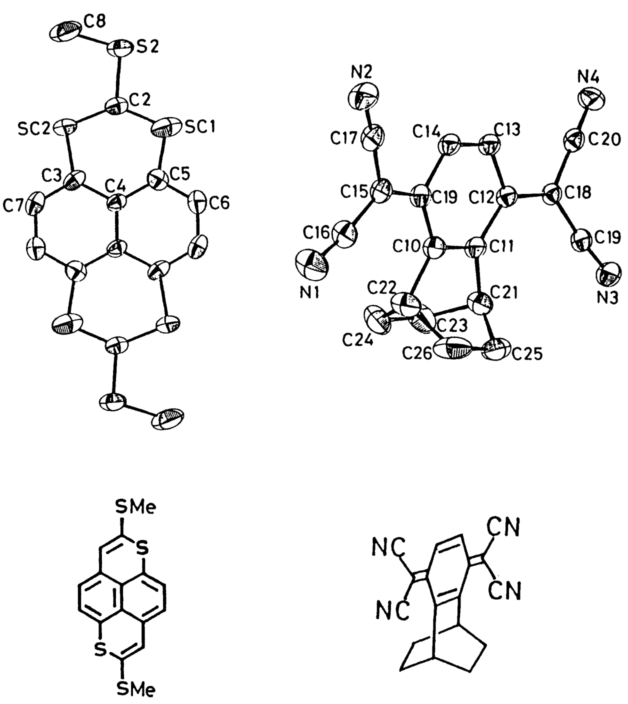

Fig. 1. ORTEP drawings and atomic numbering schemes of MTDTPY and THBTCNQ.

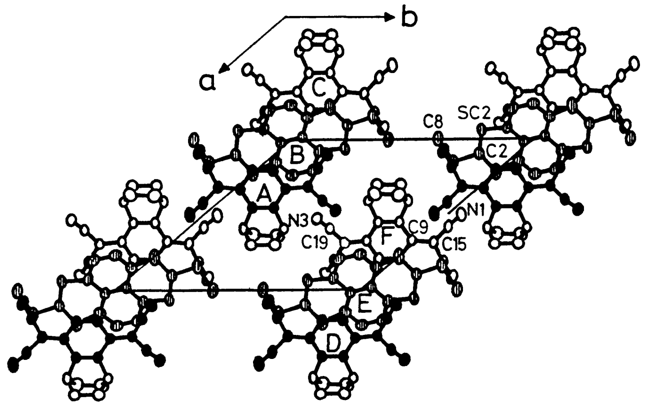

Fig. 2. Crystal structure of MTDTPY-(THBTCNQ)$_2$ viewed along the c axis.

The ionicity of CT complexes can be conveniently predicted from $\Delta E^{\mathrm{o,r}}$ which denotes the difference between the oxidation potential of the donor and the reduction potential of the acceptor. The value of $\Delta E^{\mathrm{o,r}}$ for MTDTPY and THBTCNQ is 0.23 eV, which falls within the range of neutral to partial-ionic complexes. Therefore, the neutral nature of the complex is consistent with such a prediction. $\Delta E^{\mathrm{o,r}}$ exhibits a further utility when the CT transition energy is taken into account for discussion. Torrance et al. reported a simple V-shape correlation between the energy of the CT absorption band ($h\nu_{\mathrm{CT}}$) and $\Delta E^{\mathrm{o,r}}$ for mixed stacking complexes. In the electronic spectrum of this complex dispersed in KBr, a strong absorption band at 23900 cm^{-1} and a weak band at 5800 cm^{-1} are assignable to the molecular absorption band of both neutral THBTCNQ[1] and MTDTPY,[3] and a CT band

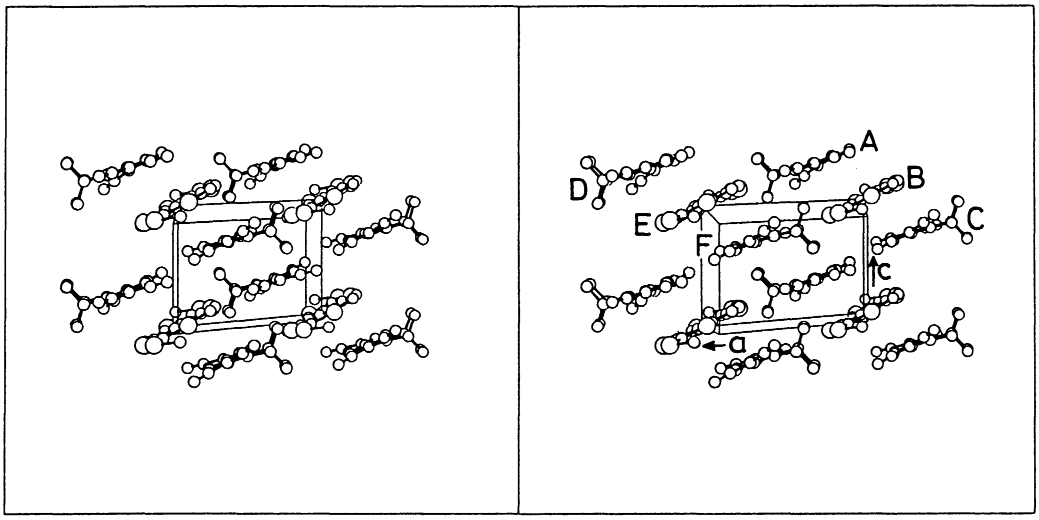

Fig. 3. Stereoview of the crystal packing viewed along the b axis.

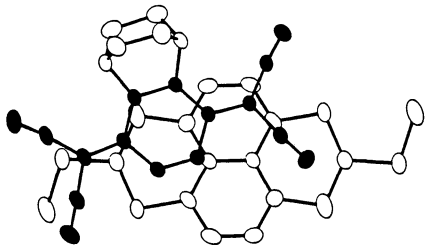

Fig. 4. The mode of molecular overlap between the donor and the acceptor.

between two component molecules, respectively. Although this complex cannot be classified into the usual mixed stacking complexes, it essentially contains a DA-type overlap mode. Therefore, we could estimate the CT transition energy for the complex by the empirical formula,[1,10] $h\nu_{\mathrm{CT,N}}=\Delta E^{\mathrm{o,r}}+0.5$ (eV), deduced from the V-shape correlation. The estimated value, 0.73 eV, is very close to the observed one, 0.72 eV (5800 cm^{-1}). Such a result suggests the potential applicability of the V-shape correlation to a wider range of CT complexes with DA-type overlap modes, although more data are needed to make this argument conclusive. However, such rough information regarding the electronic structure, which can be obtained readily from 1 mg of powdered sample, is especially valuable for chemists exploring new component molecules of organic conductors.

References

1) K. Nakasuji, M. Nakatsuka, H. Yamochi, I. Murata, S. Harada, N. Kasai, K. Yamamura, J. Tanaka, G. Saito, T. Enoki, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **59**, 207 (1986).

2) K. Nakasuji, H. Kubota, T. Kotani, I. Murata, G. Saito, T. Enoki, K. Imaeda, H. Inokuchi, M. Honda, C. Katayama, and J. Tanaka, *J. Am. Chem. Soc.*, **108**, 3460 (1986).

3) K. Nakasuji, M. Sasaki, T. Kotani, I. Murata, T. Enoki, K. Imaeda, H. Inokuchi, A. Kawamoto, and J. Tanaka, *J. Am. Chem. Soc.*, **109**, 6970 (1987).

4) A. Furusaki and A. Furusaki, *Acta Crystallogr., Sect. A*, **35**, 220 (1979).

5) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, MULTAN-78, University of York, York, England and Louvain, Belgium, (1978).

6) C. Katayama, N. Sakabe, and K. Sakabe, *Acta Crystallogr., Sect. A*, **28**, S207 (1972).

7) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, 1974, Vol. IV.

8) T. J. Kistenmacher, T. J. Emge, A. N. Bloch, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **38**, 1193 (1982).

9) a) R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, **98**, 3916 (1976); b) J. B. Torrance, *Acc. Chem. Res.*, **12**, 79 (1979); c) G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, **53**, 2141 (1980).

10) J. B. Torrance, J. E. Vazquez, J. J. Mayerle, and V. Y. Lee, *Phys. Rev. Lett.*, **46**, 253 (1981).