July, 1993] © 1993 The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn.*, **66**, 2115—2117(1993) 2115

Crystal Structure of an Alternated Stacking Charge-Transfer Complex of 2,7-Bis(methylthio)-1,6-dithiapyrene (MTDTPY) with Tetracyano-2,6-naphthoquinodimethane (TNAP)

Jiro TOYODA, Akio ODA,† Ichiro MURATA,† Atsushi KAWAMOTO,†† Jiro TANAKA,†† and Kazuhiro NAKASUJI*
Institute for Molecular Science, Myodaiji, Okazaki 444
†Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560
††Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

(Received January 13, 1993)

Synopsis. The charge-transfer complex of 2,7-bis(methylthio)-1,6-dithiapyrene (MTDTPY) with tetracyano-2,6-naphthoquinodimethane (TNAP) showed an alternated stacking mode of crystal structure. There are no short intermolecular contacts. The ionicity was estimated to be neutral based on an analysis of the IR stretching frequency of the CN groups and the transition energy of the charge-transfer band.

We recently reported that 2,7-bis(methylthio)-1,6-dithiapyrene (MTDTPY) produced metallic conducting charge-transfer (CT) complexes with tetracyanoquinodimethane (TCNQ), chloranil, and bromanil.[1)] Among them, the TCNQ complexes formed two distinct crystalline phases, which contain a segregated stacking and an alternated stacking mode of the donor and the acceptor components. The segregated complex showed a metallic conducting behavior. An extended conjugated-type acceptor of TCNQ, tetracyanonaphtho-2,6-quinodimethane (2,6-bis(dicyanomethylene)-2,6-dihydronaphthalene), (TNAP), is known to have a stronger acceptor ability than dose TCNQ (Chart 1).[2)] Although our efforts to prepare metallic CT complexes with TNAP by a diffusion method have not been established so far, an alternated stacking mode of the complex (MTDTPY–TNAP) is obtained as black plates. Our present report concerns a rare example of the crystal structure and some solid state properties for the CT complex of TNAP having an alternated stacking mode.[3)]

Experimental.

Single Crystals. Black needles and plates were obtained by a diffusion method using 2,7-bis(methylthio)-1,6-dithiapyrene (MTDTPY, 1.0 mg) and tetracyanonaphthoquinodimethane (TNAP, 0.8 mg) in dichloromethane (5 ml).

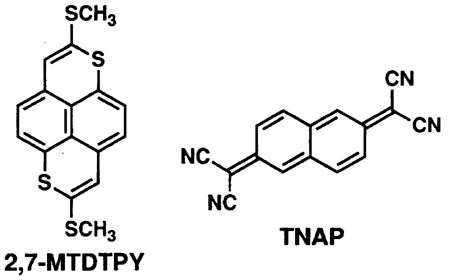

Chart 1.

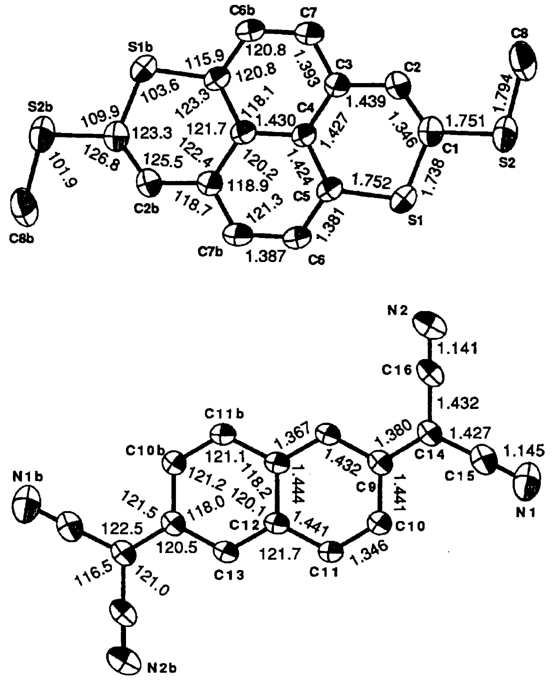

Fig. 1. Molecular dimensions in the MTDTPY and TNAP molecules. The thermal ellipsoids are drawn at the 50% probability level. The esd's are: C–C 0.003—0.005 Å, S–C 0.003—0.004 Å and N–C 0.004 Å. The esd's of the angles are 0.1—0.3°.

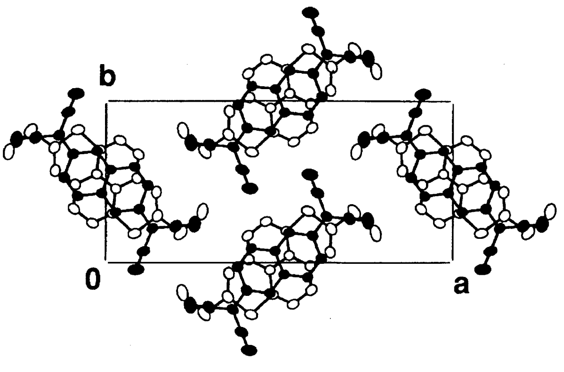

Fig. 2. Crystal packing in MTDTPY–TNAP as viewed along the *c*-axis.

The experiments in higher concentrations (1.5 and 2 times, for example) gave smaller crystals. We used a plate-like single crystal for the crystal structure analysis.

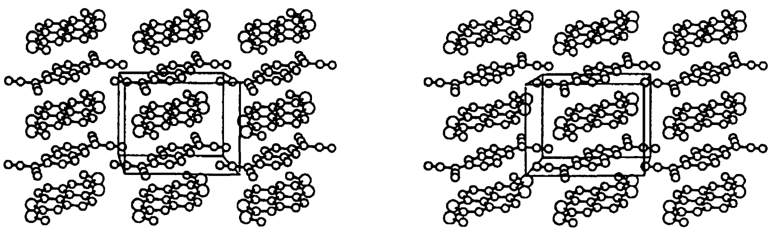

Fig. 3. Stereoview of the crystal packing in MTDTPY–TNAP along the *a*-axis.

Crystal Structure Analysis. The structure was solved by the Monte-Carlo direct method[4] using *MULTAN78*[5] program system. Full-matrix least-squares on $\Sigma w(|F_o|^2-|F_c|^2)$ with an analytical absorption correction were used.[6] Anisotropic temperature factors were used for the refinement of non-H atoms. All of the H atoms were located from a difference Fourier map, and were refined with isotropic temperature factors equivalent to that for the bonded carbon atoms. Final values of R and R_w were 0.039 and 0.050, respectively. Atomic scattering factors were used from International Tables for X-ray Crystallography.[7] Calculations were carried out on the FACOM M780 computer at the Computer Center of Nagoya University. The crystal data: $C_{32}H_{18}N_4S_4$; M_r=586.76; monoclinic; $P2_1/a$; a=20.177(2), b=9.308(1), c=7.245(1) Å, β=93.21(1)°; V=1358.5(3) Å^3; Z=2; D_m=1.450, D_x=1.435 g cm^{-3}; λ(Cu $K\alpha$)=1.54184 Å; crystal dimensions; 0.25×0.10×0.05 mm^3. The data collection: Rigaku AFC-5R diffractometer and graphite monochromatized Cu$K\alpha$: ω-2θ scan; 1964 independent reflections. Tables of the structure factors, anisotropic temperature parameters for non-H atoms, positional parameter for H atoms, the intramolecular bond distances and angles have been deposited as Document No. 66026 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Result and Discussion

The final atomic parameters for non-H atoms are listed in Table 1. The bond lengths and angles of the centrosymmetric MTDTPY and TNAP molecules are given in Fig. 1. Although the methyl group (C(8)) deviates by 0.192 Å from the least-squares plane of the MTDTPY molecule, the dithiapyrene skeleton is nearly planar with a maximum deviation of 0.05 Å for S(1). The TNAP skeleton is also nearly planar with a maximum deviation of 0.04 Å for N(2). The crystal-packing mode is an alternated stack with a uniform distance between the donor and acceptor, as shown in Figs. 2 and 3. The mean separation between the slightly non parallel components is 3.40 Å. The angle between the plane's normals for the two components is 4.46°. The intermolecular S···S and S···N distances in and between the alternated stacks are longer than the sum of the van der Waals radii. Therefore, no special shorter intermolecular heteroatom contacts were found.

Table 1. Final Atomic Coordinates (×10^4, for S Atoms ×10^5) and Equivalent Isotropic Thermal Parameters (Å^2)

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

	x	y	z	B_{eq}
S1	8092(3)	18120(6)	43222(11)	5.19(9)
S2	21548(3)	18359(9)	32912(10)	5.45(9)
N1	7444(1)	7606(3)	11870(4)	6.5(1)
N2	9138(2)	10423(3)	10894(5)	8.1(1)
C1	1476(1)	2900(3)	3823(4)	4.1(1)
C2	1448(1)	4345(3)	3829(4)	4.1(1)
C3	878(1)	5189(3)	4247(3)	3.6(1)
C4	273(1)	4555(2)	4779(3)	3.4(1)
C5	193(1)	3038(3)	4884(3)	3.7(1)
C6	−392(1)	2449(3)	5436(4)	4.3(1)
C7	919(1)	6680(3)	4128(4)	4.2(1)
C8	2782(2)	3162(4)	2956(5)	6.2(1)
C9	9055(1)	6687(3)	10721(3)	3.7(1)
C10	8801(1)	5244(3)	10814(4)	3.9(1)
C11	9188(1)	4101(3)	10499(4)	3.8(1)
C12	9871(1)	4279(2)	10058(3)	3.4(1)
C13	10269(1)	3127(3)	9737(4)	3.7(1)
C14	8663(1)	7864(3)	11057(4)	4.1(1)
C15	7986(1)	7732(3)	11509(4)	4.6(1)
C16	8922(2)	9293(3)	10963(4)	5.2(1)

TNAP is an extended conjugated acceptor of TCNQ and possesses a higher first reduction potential, +0.23 V (vs. SCE),[8] than that of TCNQ. Generally, the metallic conducting organic charge-transfer complexes are characterized by the crystal structures of segregated stacks of the donor and the acceptor molecules, and by the ionicity of a partial charge transfer from the donor to the acceptor. The partial charge transfer might be realized by matching of the strengths and the sizes of the donor and acceptor molecules. Matching of the strength was estimated from the difference ($\Delta E^{\text{o,r}}$) between the first oxidation potential (E_1^{ox}) and the first reduction potential (E_1^{red}), i.e., $\Delta E^{\text{o,r}}=E_1^{\text{ox}}-E_1^{\text{red}}$. For metallic conduction, it is required to combine the donor–acceptor so as to keep the $\Delta E^{\text{o,r}}$ values small, near to zero.[9] The $\Delta E^{\text{o,r}}$ value (+0.34−0.23=+0.11 V) for MTDTPY and TNAP meets such a requirement. Furthermore, these two molecules have similar sizes. However, we have so far obtained only an alternated stacking mode of the CT complex. Most of the metallic conducting CT complexes with segregated stacking modes contain shorter intermolecular heteroatom contacts. As mentioned above, the crystal structure analysis for MTDTPY–TNAP showed no such heteroatom contacts.

Usually, the ionicity for CT complexes can be approximately and conveniently estimated by analyzing the IR stretching frequencies or the geometries of the TCNQ type component molecules. The latter procedure cannot be applied, since no reliable bond-length data of the crystal structure containing the TNAP molecule have been reported. We therefore estimated the ionicity by the former procedure.[10] The stretching frequencies of the cyano group of TNAP, itself, MTDTPY–TNAP and Na·TNAP,[2] were observed at 2210, 2212, and 2175 cm^{-1}, respectively, indicating the neutral nature of the CT complex. Furthermore, the electronic absorption spectra also suggest a neutral ionicity. Thus, a V-shape correlation between the CT transition energy ($h\nu_{\mathrm{CT}}$) and $\Delta E^{\mathrm{o,r}}$ is proposed for the alternated stacking modes of CT complexes.[11] From the equation $h\nu_{\mathrm{CT}} = \Delta E^{\mathrm{o,r}} + 0.5$ for neutral complexes (in eV unit)[11,12] we obtained 0.61 eV as an estimated $h\nu_{\mathrm{CT}}$ for MTDTPY–TNAP. The observed $h\nu_{\mathrm{CT}}$ of the complex is 0.75 eV, measured as a compressed pellet of powders dispersed in KBr. The difference of 0.14 eV is an allowable error, since the equation is an approximate correlation. In addition, we observed a strong absorption band for the complex at 2.56 eV, which can be assigned to the local excitation band for TNAP. The corresponding values reported for TNAP, itself, and Na·TNAP are 2.62 and 1.80 eV, respectively.[13] All of the data described above suggest the neutral nature of MTDTPY–TNAP, although more data are needed to make any final conclusion.

This research was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture.

References

1) 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).

2) J. Diekmann, W. R. Hertler, and R. E. Benson, *J. Org. Chem.*, **28**, 2719 (1963).

3) For the segregated CT complexes of TNAP, see: a) K. Bechgaard, C. S. Jacobsen, and N. H. Anderson, *Solid. State Commun.*, **25**, 875 (1978); b) P. A. Berger, D. J. Dahm, G. R. Johnson, M. G. Miles, and J. D. Wilson, *Phys. Rev.*, **B12**. 4085 (1975).

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

5) S. Main, P. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, "MULTAN78," University of 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) M. L. Kaplan, R. C. Haddon, F. B. Bramwell, F. Wudl, J. H. Marshall, D. O. Cowan, and S. Gronowitz, *J. Phys. Chem.*, **84**, 427 (1980).

9) a) R. C. Wheland, *J. Am. Chem. Soc.*, **98**, 3926 (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. S. Chappel, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, *J. Am. Chem. Soc.*, **103**, 2442 (1981).

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

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

13) K. Yakushi, Y. Sato, I. Ikemoto, and H. Kuroda, *Bull. Chem. Soc. Jpn.*, **54**, 1964 (1981).