

Charge-transfer Complex of a Twin Donor based on its Inclusion Ability

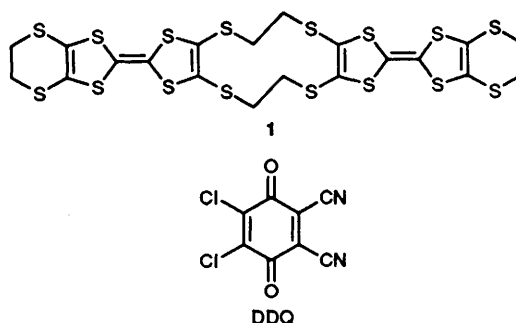
Tatsuya Tachikawa, Akira Izuoka and Tadashi Sugawara*

Department of Pure and Applied Sciences, College of Arts and Sciences, University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

A novel twin donor in which two tetrathiafulvalene moieties are connected by a thiocrown ring has inclusion properties associated with its U-shaped donor conformation and affords an inclusion complex with the organic acceptor, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, through charge-transfer interactions.

Specific formation of inclusion complexes between host and guest molecules is based on molecular recognition *via* hydrophobic, or van der Waals interaction, and/or formation of hydrogen bonds at several centres.¹ Recently, the twin donor **1**, in which two tetrathiafulvalene (TTF) units are connected by a thiocrown ring has been designed and prepared in an attempt to increase the dimensionality in organic conductors.² The crystal structure[†] of the neutral twin donor **1** was determined for a single crystal obtained from carbon tetrachloride-carbon disulfide. The neutral molecule has a U-shaped conformation and includes a cavity made by the two

donor units (Fig. 1). The cavity is occupied with the donor unit of another donor in the crystal. The thiocrown moiety has stable torsional angles corresponding to *gauche* and *anti* conformations. As the size of cavity can vary flexibly as a result of conformational changes of the thiocrown ring, **1**



[†] Crystal data: C₂₀H₁₆S₁₆, *M* = 769.31, triclinic, space group *P* $\bar{1}$, *a* = 15.393(3), *b* = 18.189(7), *c* = 12.215(4) Å, α = 118.92(2), β = 95.54(4), γ = 90.72(4)°, *V* = 2973(2) Å³, *Z* = 4, *D*_c = 1.719 g cm⁻³; Mo-K α radiation (graphite monochromator, λ = 0.71069 Å), final conventional *R* factor 5.5% for 6237 observed reflections [*F* ≥ 3 σ (*F*)] and 714 parameters.

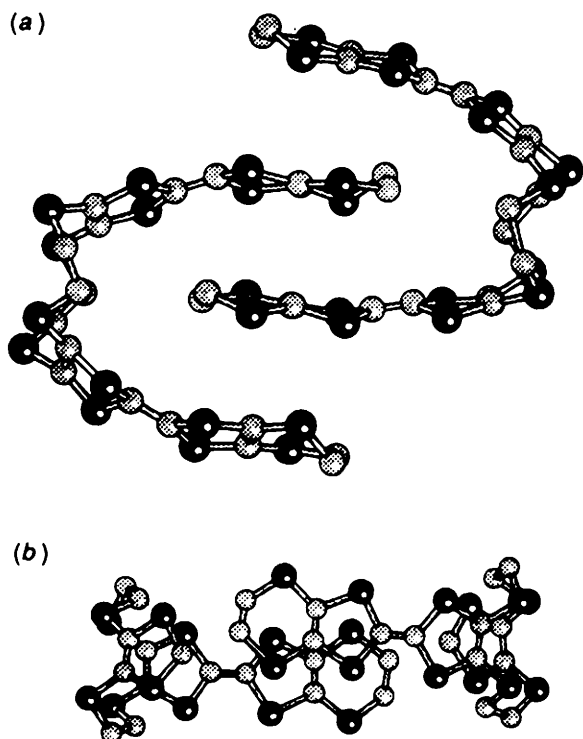


Fig. 1 Dimeric structure of neutral 1: (a) viewed along the molecular short axis; (b) the overlap within the dimer: a part of the donor units is omitted for clarity.

should afford the inclusion complexes with planar molecules which are about 3.5 Å in thickness or with spherical molecules which are about 10 Å in diameter. The cavity size in the latter case is as large as that of γ -cyclodextrin (9–10 Å).³ Charge transfer interactions may enhance not only the inclusion ability but also the specificity of host molecules.⁴

As expected, the twin donor 1 was found to afford an inclusion complex with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), which was formed as black plates by a diffusion method in tetrahydrofuran (THF)–carbon disulfide (1:1). X-Ray crystallographic analysis[†] showed that the DDQ molecule is clipped by two donor units of the twin donor as shown in Fig. 2. The DDQ molecule penetrates deep inside the donor cavity. The structure of the donor units is characterized by the interplanar angles between the three C_2S_4 planes for each donor unit. One donor unit (D_α) is almost planar and the angles between the C_2S_4 plane containing the central C=C double bond and the C_2S_4 planes containing the edge C=C double bond are 5.0 and 12.0°, respectively. On the other hand, the other donor unit (D_β) has a concave shape with corresponding angles of 15.1 and 20.7°, respectively. The difference in the shape of the donor units suggests that the positive charge is mainly located in D_α .

The IR spectrum of the complex shows the C≡N stretching mode at 2206 cm^{-1} ; the C=O stretching frequency was not detected. The C≡N stretching is shifted to low frequency by 27

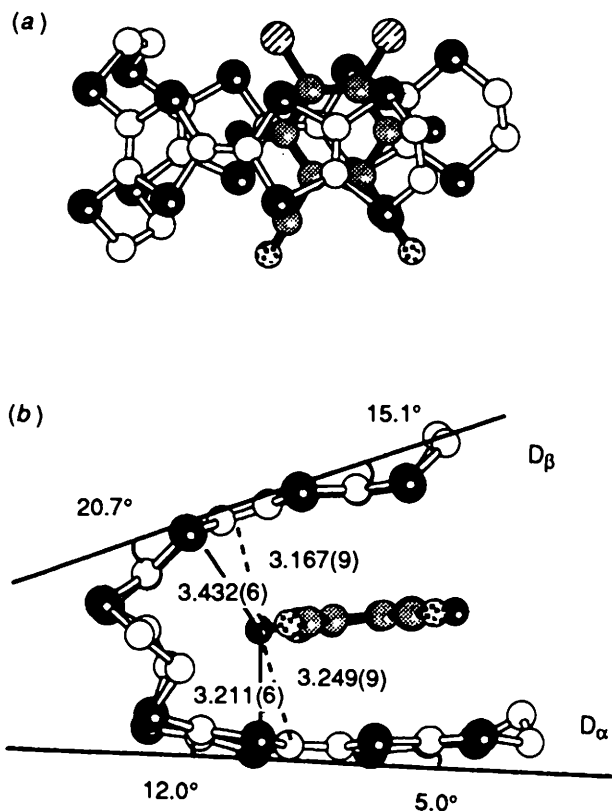


Fig. 2 Molecular structure of the inclusion complex 1·DDQ: (a) top view; (b) side view (distances in Å)

Table 1 Bond lengths for DDQ and $[DDQ]^{·-}$ ($r/\text{Å}$)

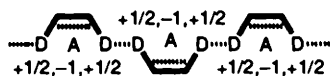
| Distance | DDQ | $[Et_4N]^+[DDQ]^{·-}$ | 1·DDQ |
|-------------|-------|-----------------------|-------|
| $r(C1-C1')$ | 1.343 | 1.386 | 1.406 |
| $r(C1-C2)$ | 1.497 | 1.444 | 1.438 |
| $r(C2-C3)$ | 1.482 | 1.463 | 1.453 |
| $r(C3-C3')$ | 1.339 | 1.363 | 1.366 |
| $r(C1-C4)$ | 1.436 | 1.430 | 1.422 |
| $r(C4-N)$ | 1.134 | 1.140 | 1.148 |
| $r(C2-O)$ | 1.203 | 1.246 | 1.258 |
| $r(C3-Cl)$ | 1.697 | 1.716 | 1.705 |

cm^{-1} compared with neutral DDQ. § The bond lengths of the DDQ molecule in 1·DDQ are compared with those of neutral DDQ⁶ and its anion radical⁷ in $[NEt_4]^+[DDQ]^{·-}$ in Table 1. They coincide well with those of $[NEt_4]^+[DDQ]^{·-}$. The UV–near IR spectrum of 1·DDQ shows absorptions for the DDQ anion radical⁵ and TTF cation radical at 450 and 900 nm, respectively. These results suggest that the host donor and the guest acceptor afford the radical ion salt with complete electron transfer. The crystal structure of the inclusion complex may be described as follows. The twin donors (D) which include the acceptor (A) form a DAD·DAD·DAD mixed stack, bridging units being stacked alternately. The

† Crystal data: $C_{28}H_{16}F_2N_2O_2S_{16}$, $M = 1489.97$, triclinic, space group $P\bar{1}$, $a = 12.521(2)$, $b = 16.018(5)$, $c = 9.743(3)$ Å, $\alpha = 99.27(2)$, $\beta = 102.04(2)$, $\gamma = 94.38(2)^\circ$, $V = 1873.8(8)$ Å³, $Z = 2$, $D_c = 1.095$ g cm^{-3} ; Mo-K α radiation (graphite monochromator, $\lambda = 0.71069$ Å), final conventional R 7.6%, R_w 7.2% for 4693 observed reflections [$F > 3\sigma(F)$] and 450 parameters.

For both structures atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The frequencies of the corresponding modes of neutral DDQ are observed at 2233 and 1701 cm^{-1} , respectively, while the frequency of the C≡N stretching shifts to 2217 cm^{-1} and the C=O stretching absorption disappears when DDQ forms the anion radical salt with tetraethylammonium cation. $[NEt_4]^+[DDQ]^{·-}$.⁵



..... intra- and inter-molecular interaction

Fig. 3 Mixed-valent state in the mixed stack column consisting of twin donors including an acceptor (DAD)

charged donor units (D_{α}) have close contacts not only with the included $[DDQ]^{-}$ anion radicals but also with the $[DDQ]^{-}$ in the adjacent stacks, the distances between the sulfur atoms of D_{α} and the nitrogen atoms of the cyano groups of the acceptor being 3.146(9) and 3.230(9) Å. The electrical conductivity of the salts was $5 \times 10^{-4} \text{ S cm}^{-1}$, as measured by the four-probe method along the crystal c axis.

In summary, the twin donor **1** provides the first example of an inclusion complex with DDQ based on complete electron transfer which shows semiconducting properties. If the included acceptor has a uniform charge transfer interaction between the two donor units, the twin donor exists in a mixed-valent state (Fig. 3). In such cases, the charge transfer salts may not only exhibit high conductivity but also have three-dimensional interactions between the donor molecules. Therefore the twin donor **1** may provide new possibilities in host-guest chemistry for developing interesting physical properties.

The present work was supported (in part) by a Grant-in-Aid for the new Program 'Intelligent Molecular Systems with

Controlled Functionality' (03NP0301) from the Ministry of Education, Science, and Culture of Japan.

Received, 22nd March 1993; Com. 3/01650A

References

- 1 J. Rebek, Jr., B. Askew, P. Ballester, C. Buhr, S. Jones, D. Nemeth and K. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 5033; A. D. Hamilton and D. V. Engen, *J. Am. Chem. Soc.*, 1987, **109**, 5035; R. E. Sheridan and H. W. Whitlock, Jr., *J. Am. Chem. Soc.*, 1988, **110**, 4071; H. M. Colquhoun, E. P. Goodings, J. M. Maud, J. F. Stoddart, J. B. Wolstenholme and D. J. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1985, 607.
- 2 A. Izuoka, R. Kumai, T. Tachikawa and T. Sugawara, *Mol. Cryst. Liq. Cryst.*, 1992, **218**, 213; T. Tachikawa, A. Izuoka, R. Kumai, T. Sugawara and Y. Sugawara, *Solid State Commun.*, 1992, **82**, 19.
- 3 M. L. Bender and M. Komiyama, *Cyclodextrin Chemistry*, Springer 1978; W. Saenger, *Inclusion Compounds*, vol. 2, ed. J. L. Atwood, J. E. D. Daves and D. D. MacNicol, Academic Press, 1984, p. 207.
- 4 S. C. Zimmerman and W. Wu, *J. Am. Chem. Soc.*, 1989, **111**, 8054; S. C. Zimmerman and C. M. Van Zyl, *J. Am. Chem. Soc.*, 1987, **109**, 7894; S. C. Zimmerman, M. Mrksich and M. N. Baloga, *J. Am. Chem. Soc.*, 1989, **111**, 8528; C.-W. Chen and H. W. Whitlock, Jr., *J. Am. Chem. Soc.*, 1978, **100**, 4921.
- 5 J. S. Miller, P. J. Krusic, D. A. Dixon, W. M. Reiff, J. H. Zhang, E. C. Anderson and A. J. Epstein, *J. Am. Chem. Soc.*, 1986, **108**, 4459.
- 6 G. Zanotti, R. Bardi and A. Der Pre, *Acta Crystallogr., Sect. B*, 1980, **36**, 168.
- 7 G. Zanotti, A. Der Pre and R. Bardi, *Acta Crystallogr., Sect. B*, 1982, **38**, 1225.