Crystal Structure of Benzene–Bis[1,2,5]thiadiazolotetracyanoquinodimethane (BTDA) Complex: A Weak Charge-transfer Complex Stabilized by Inclusion Behaviour

Takanori Suzuki,[a] Chizuko Kabuto,[b] Yoshiro Yamashita,[a] Toshio Mukai,[a] and Tsutomu Miyashi*[a]

[a] *Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980, Japan*
[b] *Instrumental Analysis Center for Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980, Japan*

An *X*-ray structural analysis of the title charge-transfer complex revealed an unusual cage-like network formed by S- -N≡C interactions of bis[1,2,5]thiadiazolotetracyanoquinodimethane (BTDA) (1) in which benzene was tightly included; the stabilization observed may be attributed to this inclusion behaviour.

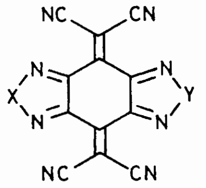
Some large organic molecules such as cyclodextrins[1] possess cavities in which smaller molecules may be included, thus forming host–guest complexes in the crystalline state. These complexes are stabilized by van der Waals interaction and their formation is facilitated by hydrogen bonding in some cases.[2] The title molecule BTDA (**1**)† forms a charge-transfer (CT) complex with tetrathiafulvalene (TTF) in which BTDA molecules are connected to each other by S- -N≡C interactions to form cavities incorporating TTF molecules. This complex can be regarded as of the host–guest type.[3] It is intriguing that the molecule (**1**) exhibits inclusion behaviour, since it is essentially planar,[4] with neither a cavity nor hydroxy groups for hydrogen bonding. Although S- -N≡C interactions are also observed in anion radical salts of (**1**),[5] inclusion behaviour has not been observed; thus such behaviour does not occur in complexes where strong CT interaction is present. We report here the crystal structure of a CT complex of (**1**) with benzene as weak electron donor, where inclusion behaviour is predominant and a unique cage-like network is formed.

The benzene–BTDA (1:2) complex (**2**) [m.p. 130—140 °C (decomp.); i.r.(KBr) $\nu_{max.}$ 2223 cm^{-1}] was obtained by recrystallization of (**1**) from benzene, and was stable without loss of benzene for several months at ambient temperature. Reflectance data were collected at −60 °C for accurate structural analysis.‡ In the crystal of (**2**), two different kinds of molecule (**1**) exist; one lies on the centre of symmetry (BTDA-1) and the other on the two-fold axis (BTDA-2). BTDA-2 forms an alternating mixed stack with benzene, in which the benzene is just overlapped with the central six-membered rings of BTDA-2 (molecules **A** and **B** in Figure 1) in parallel and rotated around the two-fold axis by an angle

---

† Benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole-4,8-diylidenebis(malononitrile).

‡ *Crystal data* for (**2**): $C_{30}H_6N_{16}S_4$, *M* 718.75, monoclinic, space group *C*2/*c*, $a = 29.703(2)$, $b = 6.666(1)$, $c = 15.637(1)$ Å, $\beta = 108.01(1)°$, $U = 2944.6(3)$ Å^3, $Z = 4$, $D_c = 1.62$ g cm^{-3}. A total of 3410 reflections within $2\theta = 55°$ was collected using graphite-monochromated Mo-K_α radiation while the crystal was kept at −60 °C by a liquid nitrogen flow method. The final *R* value was 4.25% for 2766 reflections with $|F_o| > 3\sigma|F_o|$. Estimated standard deviations for the bond lengths and angles are 0.002—0.004 Å and 0.1—0.3° for (**1**) and 0.007 Å and 0.4° for benzene. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1988.



BTDA (**1**) X = S , Y = S
(**2**) $C_6H_6\cdot(BTDA)_2$
TSDA (**3**) X = S , Y = Se
BSDA (**4**) X = Se , Y = Se

of *ca.* 30° from superimposition, suggesting CT interaction between benzene and BTDA-2. The interplanar distances are 3.28 Å for molecule **A** and 3.39 Å for molecule **B**, indicating that a stronger CT interaction exists in the former overlap than in the latter. However, the bond lengths and angles for BTDA-2 are similar to those for neutral (**1**),[4] showing that the degree of charge transfer is small. On the other hand, BTDA-1 molecules (**E**—**H**) are intercalated between the mixed stacks without significant interaction with benzene. The BTDA-1 molecules are connected with BTDA-2 (molecules **A**—**D**) by several S--N≡C interactions (3.28 and 3.40 Å), thus locking the benzene by forming an unusual cage-like network (Figure 1). Thus, one benzene molecule is held by four BTDA-2 molecules from the top, the bottom, and two sides, and further encircled by four BTDA-1 molecules in the cage network. It is also intriguing that the BTDA-2 overlapped with benzene is deformed into a butterfly shape, with a dihedral angle of 167.0° between the two heterocycles. Such a deformation has never been found previously in CT complexes or anion radical salts of (**1**),[3—5] indicating that it is not a favoured conformation for the BTDA molecule. However, as a result of the deformation of BTDA-2, the cage network can hold the benzene more tightly, giving a denser crystal structure with large stabilization; this could cancel the disadvantage caused by the molecular deformation. The driving force for the formation of complex (**2**) may be the CT interaction, which also exists in solution [K_{CT} 0.08 mol^{-1} dm^3 in CH_2Cl_2 at 30 °C (ε 1 580 at 450 nm)]. This is suggested by the fact that TSDA (**3**) and BSDA (**4**), weaker electron acceptors than (**1**), did not afford corresponding benzene complexes although (**3**) and (**4**) crystallize isomorphously with (**1**).[6]

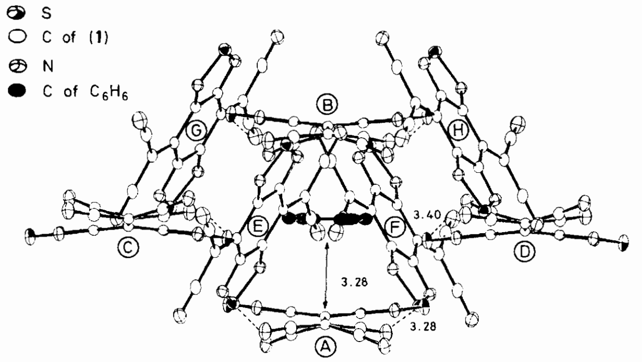


Figure 1. Cage-like network in structure (**2**). The S--N≡C interactions (3.28 and 3.40 Å) are indicated by broken lines. Molecules **A**—**D** are BTDA-2, and molecules **E**—**H** BTDA-1.

However, the stabilization of the crystal of (**2**) may also be due to the novel inclusion behaviour with S--N≡C interactions; this is suggested by the deformation of BTDA-2 as well as the existence of BTDA-1 which locks the benzene in without CT interaction.

Received, 9th February 1988; Com. 8/00444G

References

1 M. L. Bender and M. Komiyama, 'Cyclodextrin Chemistry,' Springer-Verlag, Berlin, 1978.
2 D. E. Palin and H. M. Powell, *Nature (London)*, 1945, **156**, 334; T. C. W. Mak, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1435.
3 T. Suzuki, C. Kabuto, Y. Yamashita, and T. Mukai, *Bull. Chem. Soc., Jpn.*, 1987, **60**, 2111.
4 C. Kabuto, T. Suzuki, Y. Yamashita, and T. Mukai, *Chem. Lett.*, 1986, 1433.
5 T. Suzuki, C. Kabuto, Y. Yamashita, T. Mukai, T. Miyashi, and G. Saito, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 483.
6 T. Suzuki, C. Kabuto, Y. Yamashita, G. Saito, T. Mukai, and T. Miyashi, *Chem. Lett.*, 1987, 2285.