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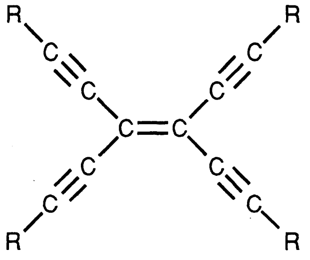
A New Type of Inclusion Compounds Composed of a Charge-Transfer Complex between Tetrakis(phenylethynyl)ethene and 2,4,7-Trinitrofluorenone

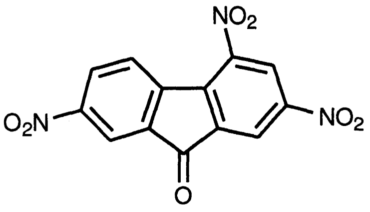
Hiroshi TANIGUCHI,* Koji HAYASHI,† Keiko NISHIOKA,† Yuji HORI,††
Motoo SHIRO,††† and Tsugio KITAMURA*†
Kurume College of Technology, Komorino-cho Kurume 830
† Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University 36,
Hakozaki, Higashi-ku, Fukuoka 812
†† Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Honjo, Saga 840
††† Rigaku Corporation, Matsubara-cho 39-12, Akishima, Tokyo 196

Tetrakis(phenylethynyl)ethene and 2,4,7-trinitrofluorenone form a deep red charge-transfer complex which gives the inclusion compound with benzene. The crystal structure of the inclusion compound with benzene was determined. The inclusion compound is composed of new frameworks possessing cavities for recognition of benzene molecules. Other examples of the inclusion compound are described.

Tetraethynylethenes (**1** and **2**) are attractive molecules because of their important chemical and physical properties, i.e., tetraethynylethenes possess cross-conjugated π systems, provide charge-transfer complexes, and are potent of anticancer agents and π-electron materials by the Bergman reaction.1-3)



(**1**) R = H; (**2**) R = Ph



TNF

Twenty-four years ago we prepared for the first time tetrakis(phenylethynyl)ethene (**2**),1) and reported that **2** forms a deep red charge-transfer complex with 2,4,7-trinitrofluorenone (TNF) composed of a 1:2 molecular ratio of **2** and TNF. The interesting behavior of the charge-transfer complex is the incorporation of a solvent molecule and the exclusion of the solvent on heating. For example, the charge-transfer complex with TNF [**2**-TNF (1:2)] uptakes a benzene molecule. The new inclusion compound excludes the benzene at 127 °C and melts at 167 °C which temperature is the same as the melting point of the **2**-TNF (1:2) complex.1) Our interest has been focused on the structure of the charge-transfer complex and the inclusion compound, especially, how the benzene molecules are incorporated and released. Thus, we analyzed and determined the crystal structures of the charge-transfer complex of **2**-TNF (1:2)5,6) and the inclusion compound. In this communication, we report a new framework controlled by a charge-transfer complex, which can transform the framework for recognition.

Suitable single crystals of the charge-transfer complex **2**-TNF (1:2)7) and the inclusion compound7) with benzene were obtained by a slow cooling of the solution in ethanol or benzene. The crystal structures of the **2**-TNF (1:2) complex and the inclusion compound are depicted in Figs. 1 and 2. Fig. 1 clearly shows that the charge-transfer complex **2**-TNF (1:2) is composed of one tetraethynylethene **2** and two TNF molecules. Bond lengths and angles in **2** are within the range obtained from the X-ray data for only **2**.4) Two TNF molecules lie on the two phenyl rings, respectively The crystal packing diagram of the charge-transfer complex of **2**-TNF (1:2) shows infinite stacks of alternate **2** and TNF molecules and is accord with a generally observed structure of a parallel arrangement of donor and acceptor molecules. The unit cell contains two kinds of the charge-transfer complex of **2**-TNF (1:2), which stack along c-axis, respectively Tetraethynylethene **2** is essentially planer No cavities or channels are exist in the complex of **2**-TNF (1:2). The structure of the charge-transfer complex **2**-TNF (1:2) is almost identical to that very recently reported by Diederich et al.6)

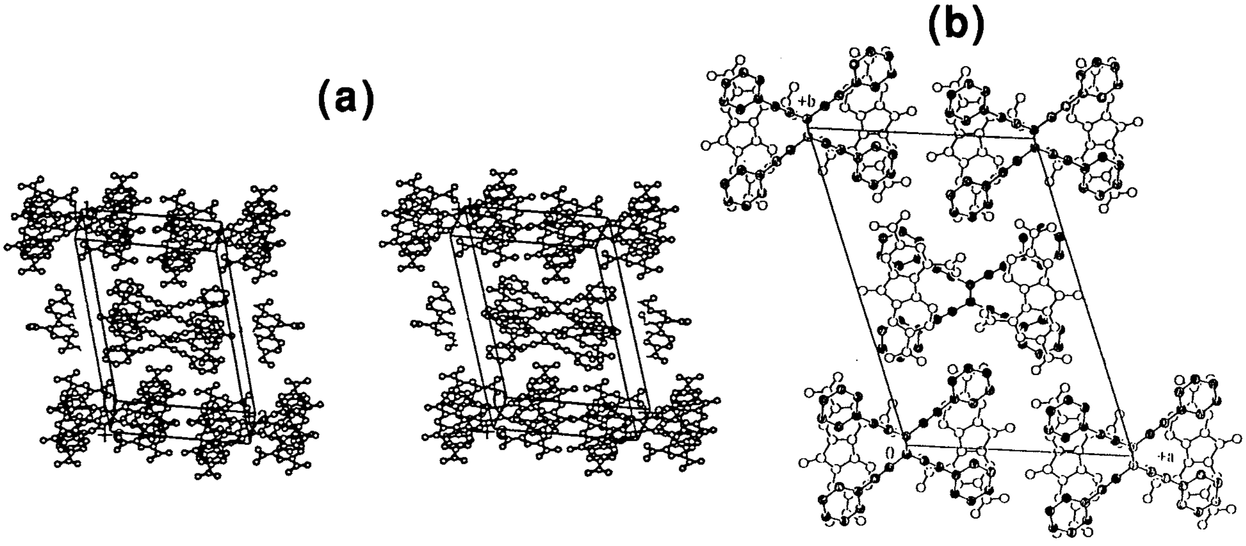


Fig. 1. Crystal structure of the charge-transfer complex **2**-TNF (1:2). (a) Stereoscopic packing diagram. (b) Overlapping of **2** and TNF viewed along the c axis. Molecules **2** are shaded.

However, Fig. 2 exhibits that the inclusion compound forms a different framework from the complex of **2**-TNF (1:2). Interestingly even in the inclusion compound molecules **2** and TNF keep donor-acceptor pairs which are consist of a 1:2 molecular ratio of **2** and TNF. Compared with the charge-transfer complex **2**-TNF (1:2), one layer containing the complex **2**-TNF (1:2) moves by 1/2 unit and makes new frameworks where the complex **2**-TNF (1:2) stacks along the c axis to form cavity channels. The X-ray crystal structure clearly shows that the benzene molecules lie in the cavity channels rather than forming the new stacks of benzene molecules. As the result, the inclusion compound consists of **2**, TNF, and benzene with a molecular ratio of 1:2:1. The bond lengths and angles of molecule **2** in the inclusion compounds are essentially same as those of the charge-transfer complex **2**-TNF (1:2) or tetrakis(phenylethynyl)ethene **2** itself.

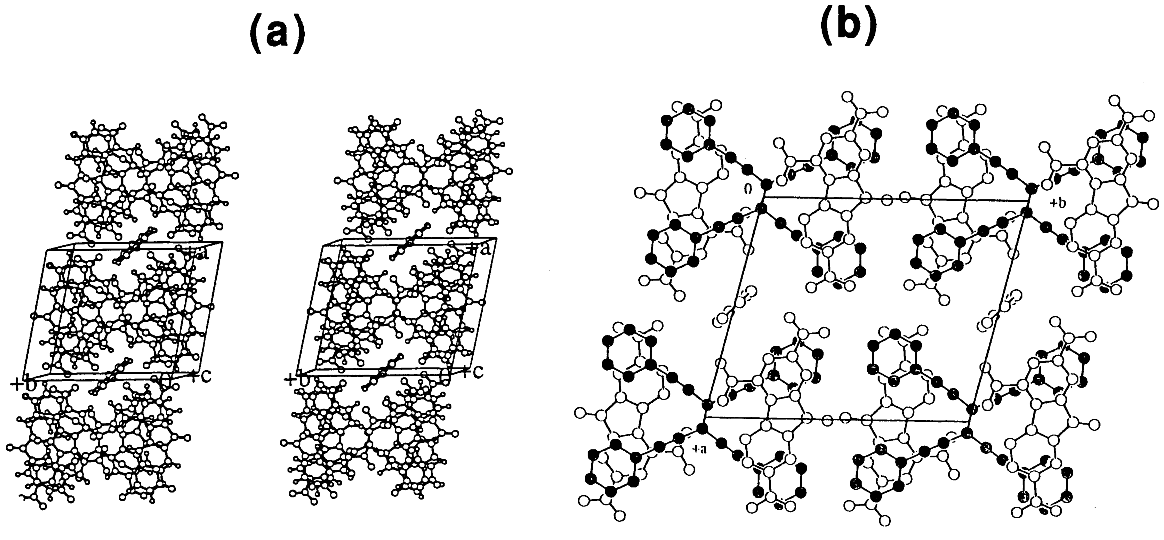


Fig. 2. Crystal Structure of the inclusion compound with benzene. (a) Stereoscopic packing diagram. (b) Overlapping of **2** and TNF viewed along the c axis. Molecules **2** are shaded.

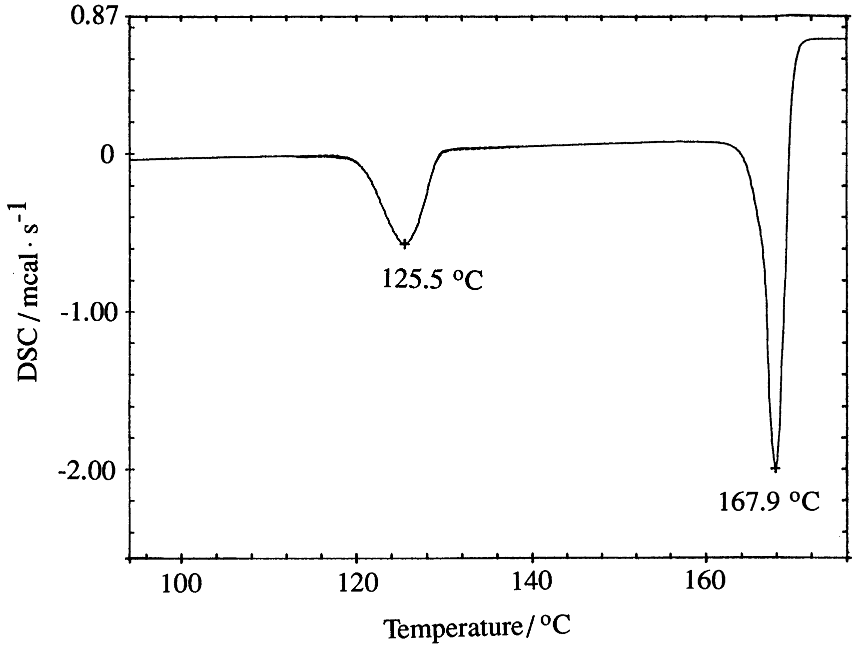


Fig. 3. DSC curve of the inclusion compound with benzene (1 cal = 4.184 J).

Fig. 3 indicates the DSC curve of the inclusion compound with benzene. The first endotherm is ascribed to the desorption of benzene but the second endotherm corresponds to the melting point of the charge-transfer complex **2**-TNF (1:2). When the inclusion compound is heated and the guest molecule, benzene, is allowed to escape, the inclusion host compound changes to the original charge-transfer complex of **2**-TNF (1:2). The X-ray crystal structure of the charge-transfer complex **2**-TNF (1:2) do not show the existence of such a cavity to hold a guest molecule. Accordingly, the desorption of the guest molecule on heating means the change of the framework of host molecules to the original stacking of **2** and TNF where no cavity channels exist.

Other several molecules are included in the charge-transfer complex **2**-TNF (1:2). All of the inclusion compounds indicates the second endotherm corresponding to the melting point of **2**-TNF (1:2). Molecules included in the charge-transfer complex **2**-TNF (1:2) are benzonitrile(97.6 °C), *p*-diethynylbenzene(125.2 °C), fluorobenzene (112.1 °C), chlorobenzene (112.4 °C), iodobenzene (92.9 °C), *p*-xylene (98.2 °C), toluene (103.8 °C), pyridine (91.7 °C), and phenylacetylene(87.0 °C). The values in parentheses are the desorption temperature of the guest molecule determined by DSC. Mesitylene, *m*-xylene, ethylbenzene, and nitrobenzene did not become incorporated into the charge-transfer complex **2**-TNF (1:2).

In summary, we have disclosed the structures of the charge-transfer complex of **2** and TNF and the inclusion compound with benzene molecules. The cavity channels holding guest molecules exist only in the inclusion compound and do not in the charge-transfer complex of **2** and TNF. The frameworks composed of the charge-transfer complex **2**-TNF (1:2) transform new frameworks possessing cavities for recognition of benzene molecules.

References

1) Y. Hori, K. Noda, S. Kobayashi, and H. Taniguchi, *Tetrahedron Lett.*, **1969**, 3563.
2) H. Hauptmann, *Angew. Chem., Int. Ed. Engl.*, **14**, 498 (1975); *Tetrahedron*, **32**, 1293 (1976).
3) Y. Rubin, C. B. Knobler, and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, **30**, 698 (1991).
4) H. Hopf, M. Kreutzer, and P. G. Jones, *Chem. Ber.*, **124**, 1471 (1991).
5) In preparation of this manuscript, we found a paper which reported a crystal structure of the complex **2**-TNF (1:2) by Diederich, Philp, and Seiler.⁶⁾
6) F. Diederich, D. Philp, and P. Seiler, *J. Chem. Soc., Chem. Commun.*, **1994**, 205.
7) Crystal data of **2**-TNF (1:2): $C_{60}H_{30}N_6O_{14}$, FW = 1058.93, crystal dimensions 0.300 x 0.300 x 0.050 mm, triclinic, space group P1 (#2), a = 15.189(4), b = 21.779(5), c = 8.297(2) Å, α = 93.42(2), β = 102.98(2), γ = 108.31(2)°, V = 2513(1) Å^3, Z = 2, D_c = 1.399 g/cm^3. All measurements were made on a Rigaku AFC 5R diffractometer with graphite monochromate CuKα radiation. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3720 observed reflections [$I > 3.00\sigma(I)$] and 722 variable parameters and converged with unweighted and weighted agreement factors of R = 0.049 and R_w = 0.059.
Crystal data of the inclusion compound: $C_{36}H_{21}N_3O_7$, FW = 607.58, crystal dimensions 0.300 x 0.100 x 0.050 mm, triclinic, space group P1 (#2), a = 12.804(4), b = 14.782(4), c = 7.322(1) Å, α = 89.99(2), β = 94.05(2), γ = 104.54(2)°, V = 1337.9(6) Å^3, Z = 2, D_c = 1.508 g/cm^3. All measurements were made on a Rigaku AFC 7R diffractometer with graphite monochromate CuKα radiation. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1393 observed reflections [$I > 1.50\sigma(I)$] and 389 variable parameters and converged with unweighted and weighted agreement factors of R = 0.066 and R_w = 0.059.

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