Structure of the 1:1 Charge-Transfer Complex between Trithia[5]heterohelicene and 3,5-Dinitrobenzoic Acid. Deformation of Helicene Molecules in Crystals

Koh-ichi Yamada,*,a Eiji Oguma[a], Hiroko Nakagawa[a], Hiroshi Kawazura[a] and Hiroshi Miyamae[b]

[a]Faculty of Pharmaceutical Sciences, Josai University, Sakado, Saitama 350-02, Japan and [b]Faculty of Science, Josai University, Sakado, Saitama 350-02, Japan

Yamada, K., Oguma, E., Nakagawa, H., Kawazura, H. and Miyamae, H., 1996. Structure of the 1:1 Charge-Transfer Complex between Trithia[5]heterohelicene and 3,5-Dinitrobenzoic Acid. Deformation of Helicene Molecules in Crystals. – Acta Chem. Scand. 50: 438–442. © Acta Chemica Scandinavica 1996.

The crystal and molecular structure of the title charge-transfer (CT) complex was determined by X-ray crystallographic analysis. Thieno[3,2-e:4,5-e']di[1]-benzothiophene ([5]TH) and 3,5-dinitrobenzoic acid are alternately aligned with a separation of ca. 3.8 Å to produce one-dimensional columns along the b-axis. Within a column, the chirality of [5]TH, having a labile helical structure, is confined to either type of enantiomer. A comparison of three CT complexes of [5]TH with different acceptors showed the propensity for planarity of the [5]TH molecule in the complex to increase with reduction of the electron affinity of the acceptors.

Helicenes with an inherently twisted skeleton seem reluctant to act as π-donors to form crystalline charge-transfer (CT) complexes with ordinary π-acceptors, presumably because of a difficulty in forming an effective planar overlap in the donor–acceptor pair. In fact in CT complexes of helicenes, the structures which have so far been disclosed by X-ray crystallographic analyses have been restricted to complexes with acceptors having a strong electron affinity, such as 4-bromo-2,5,7-trinitrofluorenone,[1] tetracyanoquinodimethane (TCNQ),[2] and 2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid (TAPA).[3] Thus, it seems of interest to learn to what extent helicene molecules can be brought sufficiently close to planar molecules in CT interactions.

In the course of our study on the structures of a series of thiaheterohelicenes and their CT interactions, we have inadvertently obtained single crystals of the CT complex between thieno[3,2-e:4,5-e']di[1]benzothiophene (trithia-[5]heterohelicene, [5]TH) and 3,5-dinitrobenzoic acid (DNB) by leaving an equimolar mixture of both components in CHCl₃ for several months. This is in marked contrast to the complexation of [5]TH with TCNQ or TAPA, for which crystals of their CT complexes could be obtained after <24 h in CHCl₃. Such a tardy crystallization habit of [5]TH with DNB may be explicable partly in terms of a weak bonding energy between the

reactants because of the weaker electron-accepting ability of DNB compared with that of TCNQ or TAPA. We describe herein the crystal and molecular structure of the 1:1 CT complex obtained between [5]TH and DNB and discuss the deformation of the [5]TH molecule in the crystals, in comparison with the [5]TH molecules in the crystals of [5]TH itself,[4] the [5]TH-TCNQ complex and the [5]TH-TAPA complex.

[5]TH DNB
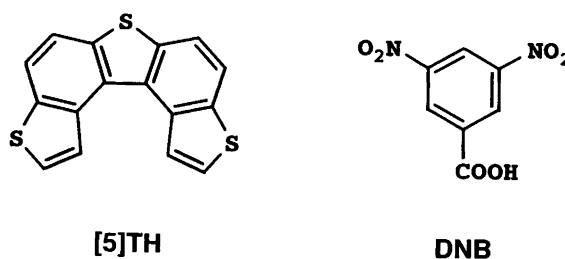
Experimental

[5]TH was prepared by oxidative photocyclization of the precursor olefin according to the previously described method.[5] DNB was obtained from Wako Chemicals and crystallized from ethanol. The title 1:1 charge-transfer complex formed orange needle-like crystals from an equimolar mixture of [5]TH and DNB in CHCl₃ (concentration ca. 2×10^{-3} M) after several months in darkness at room temperature. Found: C 54.15; H 2.42; N 5.66.

---

* To whom correspondence should be addressed.

Calc. for $C_{23}H_{12}N_2O_6S_3$: C 54.32; H 2.38; N 5.51. Electronic absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer.

The X-ray diffraction data for the complex obtained were collected on a Rigaku AFC-5 automatic four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.710\,69$ Å). The unit-cell parameters were refined from the least-squares fits of 24 centered reflections in the range $27 < 2\theta < 32°$.

Crystal data: $C_{23}H_{12}N_2O_6S_3$, FW $= 508.56$, crystal size $0.4 \times 0.3 \times 0.15$ mm, monoclinic, space group $P2_1/a$, $a = 29.873(5)$, $b = 7.662(2)$, $c = 9.192(2)$ Å, $\beta = 91.75(2)°$, $V = 2102.9(8)$ Å^3, $Z = 4$, $D_c = 1.607$ g cm^{-3}, $D_m = 1.59(1)$ g cm^{-3} (floatation in ZnBr$_2$ aqueous solution), $F(000) = 1040$, $\mu(Mo\ K\alpha) = 3.82$ cm^{-1}. The measurements were performed at room temperature.

The intensity data were collected by the θ–2θ scan technique up to $2\theta = 55.0°$ (h: -38–38, k: 0–9, l: 0–11) with a scan width of $(1 + 0.5\ \tan\theta)°$ and a scan rate of $4°$ min^{-1} on θ. During the data collection three standard reflections were monitored every 150 reflections, and the maximum variation in their intensities was 0.041. The total number of measured reflections was 5480, of which 3214 independent reflections with $|F_o| > 4.0\sigma(|F_o|)$ were used for the structure determination. The data set was corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by the direct method MULTAN 78.[6] Refinements of all positional parameters and anisotropic thermal parameters for the non-hydrogen atoms were carried out by a block-diagonal least-squares method with the minimized function of $Sw(|F_o| - |F_c|)^2$ where $w = 1/(\sigma^2 + 0.02F_c^2)$. The isotropic thermal parameters for the hydrogen atoms were refined by difference syntheses. All the parameter shifts in the final cycle of the refinement were less than 0.114, and $|\Delta\rho|_{max}$ in the final difference Fourier map was 1.19 e Å^{-3}. The final R value converged to 0.074 and the R_w value to 0.079.

The neutral atomic-scattering factors were taken from Ref. 7. All the computations were performed on a FACOM M770/8 computer at Josai University using the UNICS III[8] and ORTEP[9] programs. The final positional and thermal parameters with standard deviations are given in Table 1. Data regarding structure factors, anisotropic thermal parameters, coordinates of the hydrogen atoms, bond lengths and bond angles, together with the least-squares planes, can be obtained from one of the authors (H. N.).

Results and discussion

Structure of the CT complex. The 1:1 complex between [5]TH and DNB is stable in air and has a bright orange color in the crystalline style. The complex displays a CT absorption maximum at ca. 420 nm (a weak and broad band) in CHCl$_3$ solution in comparison with the pale yellow crystals of [5]TH itself, which exhibits a longest-wavelength absorption maximum at 350 nm in CHCl$_3$.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters.

Atom	x	y	z	$B_{eq}/Å^{2a}$
S(1)	2559.6(5)	$-987(2)$	346(2)	4.48(5)
S(2)	581.5(4)	1230(2)	$-286(1)$	4.49(4)
S(3)	872(1)	3884(2)	5999(1)	5.11(5)
O(1)	112(1)	$-1114(5)$	3429(4)	4.76(11)
O(2)	545(1)	$-713(5)$	5418(3)	4.10(11)
O(3)	2107(1)	$-2556(6)$	5286(4)	6.29(14)
O(4)	2339(1)	$-4132(6)$	3536(4)	6.52(14)
O(5)	1373(1)	$-5124(5)$	$-686(4)$	4.52(11)
O(6)	706(1)	$-4045(6)$	$-753(4)$	5.61(13)
N(1)	2051(1)	$-3302(6)$	4121(4)	4.05(13)
N(2)	1064(1)	$-4336(5)$	$-147(4)$	3.57(12)
C(1)	2573(2)	173(7)	1928(5)	4.31(16)
C(2)	2174(2)	891(7)	2236(5)	3.53(14)
C(3)	1822(1)	503(6)	1191(5)	2.81(12)
C(4)	2003(2)	$-470(6)$	40(5)	3.26(13)
C(5)	1748(2)	$-915(7)$	$-1228(5)$	4.00(15)
C(6)	1321(2)	$-381(7)$	$-1357(5)$	3.77(15)
C(7)	1130(2)	535(6)	$-204(5)$	3.24(13)
C(8)	1364(1)	974(6)	1098(4)	2.69(12)
C(9)	1064(1)	1853(6)	2105(5)	2.89(13)
C(10)	639(2)	2115(7)	1438(5)	3.59(14)
C(11)	288(2)	2990(8)	2092(6)	4.73(17)
C(12)	355(2)	3631(7)	3461(6)	5.11(18)
C(13)	755(2)	3307(6)	4209(5)	3.70(15)
C(14)	1119(1)	2414(6)	3588(5)	2.88(13)
C(15)	1465(2)	2154(7)	4663(5)	3.90(15)
C(16)	1378(2)	2873(8)	5968(5)	4.65(17)
C(17)	855(1)	$-2156(6)$	3405(4)	2.73(12)
C(18)	1266(1)	$-2327(6)$	4101(4)	2.86(12)
C(19)	1606(1)	$-3154(6)$	3393(5)	2.87(13)
C(20)	1550(1)	$-3829(6)$	2014(5)	3.08(13)
C(21)	1138(1)	$-3643(6)$	1349(4)	2.75(12)
C(22)	785(1)	$-2821(6)$	1999(5)	2.94(13)
C(23)	476(2)	$-1264(6)$	4139(5)	3.28(13)

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

The perspective drawing of the molecular structure of the CT complex is shown in Fig. 1, together with the atom-numbering scheme and an indication of the rings. As seen from the figure both molecules in the complex are aligned with each other to produce a parallel stack having a large overlap with a separation of ca. 3.8 Å between the F ring of DNB and the C ring of [5]TH. The [5]TH molecule in the complex manifests a geometry that is characteristic for the helicene family with a cylindrical helix. However, it loses an intramolecular C_2 symmetry axis through the S(2) atom and the center of the C(8)–C(9) bond observed for the molecules in [5]TH crystals. Each aromatic ring in the [5]TH molecule in the complex holds a fairly flat configuration: the maximum deviation of the constituent atoms from each of the mean planes is found to be only 0.035(4) Å in the D ring. Therefore, tilts between the aromatic rings in the molecule are thought mainly to be responsible for the formation of the helical framework, in common with other thiaheterohelicenes. Dihedral angles between the adjacent rings are observed as follows: A–B 4.9(2)°, B–C 2.3(2)°, C–D 3.9(1)° and D–E 5.4(2)°, giving an average value of 4.1°. These values are considerably smaller than
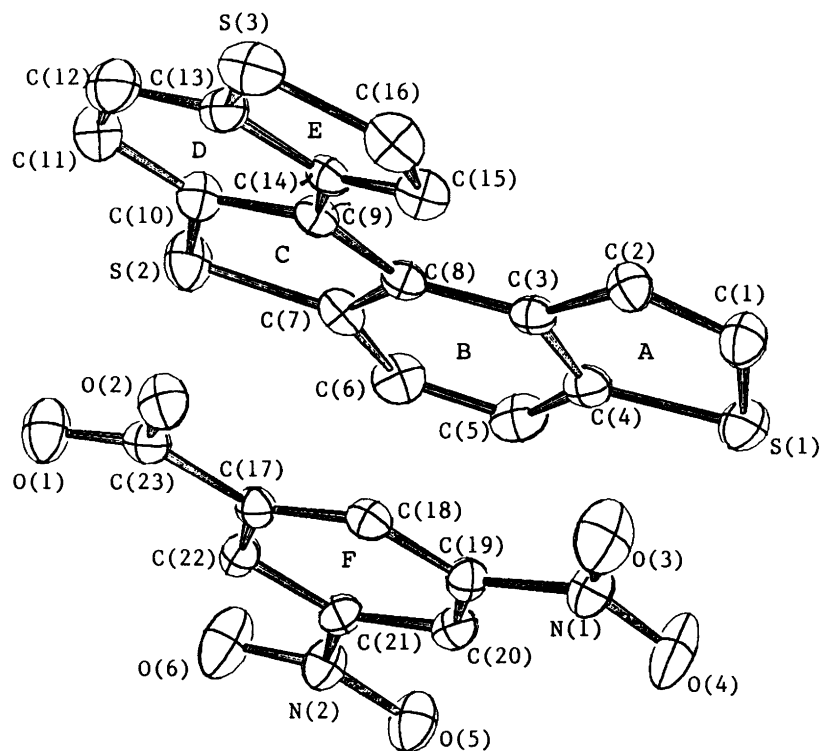
Fig. 1. A perspective drawing of the CT complex between thieno[3,2-e:4,5-e']di[1]benzothiophene and 3,5-dinitrobenzoic acid. The hydrogen atoms are omitted for clarity.

observed in the crystal study of [5]TH [A–B and D–E 10.6(1)°, B–C and C–D 7.9(2)° with an average value of 9.3°], implying an increase in the intramolecular planarity and thus a less torsional structure for the [5]TH molecule in the complex. This may be due to a reduction in the inclination angle between the terminal five-membered rings (A and E) from 36.6(1)° in [5]TH to 15.2(2)° in the present complex. The value of this inclination angle can therefore be used as a measure of the planarity of the [5]TH molecule; the smaller the value, the more planar the molecule.

The bonds constituting the skeletal structure of the [5]TH molecule exhibit the characteristics of helicenes: for example, the longest C–C bond lengths appear in the inner core (average value 1.425 Å), the shortest ones in the outer core (1.352 Å), and medium lengths for the radial bonds (1.413 Å). Each bond length and bond angle in the complex is similar to the corresponding one in the molecules in [5]TH crystals.

As for the structure of DNB in the complex, this moiety is also found to be essentially planar. The maximum deviation of the component carbons from the mean plane of the F ring is 0.002(3)Å. The planes of the carboxy and the two nitro groups rotate slightly out of the F ring by 1.7(2)° and by 6.1(3) and 4.6(3)°, respectively. These rotation angles seem somewhat smaller than the values of 2.2, 1.6 and 11.5° reported for ethyl 3,5-dinitrobenzoate.[10] The F ring is located on an almost complete parallel with the C ring of [5]TH, the dihedral angle between the F and C rings being 0.1(2)°.

Therefore, the planes of the carboxy and the two nitro groups make dihedral angles with the C ring of 1.8(2), 6.1(3) and 4.6(3)°, respectively. All bond lengths and bond angles in the DNB molecule in the complex resemble the corresponding ones in ethyl 3,5-dinitro-benzoate.[10]

Figure 2 shows a stereoview of the packing diagram of the CT complex in the crystals. It is seen that two DNB molecules are linked together through hydrogen bonds between two carboxyl groups with a center of symmetry. The distance between O(1) (symmetry operation x, y, z) and O(2) $(-x, -y, 1-z)$ is 2.657(5) Å, which is as expected for associated carboxylic acids.[11] For each of the DNB molecules linked with hydrogen bonds, alternating stacks of [5]TH and DNB are observed to form a pair of one-dimensional columns along the b-axis. A sole non-bonded atomic contact within 3.5 Å between the columns is found except for the contacts in the hydrogen-bond moieties; this contact is 3.281(6) Å between O(6) (x, y, z) and C(11) $(-x, -y, -z)$. It is noteworthy that the configuration of [5]TH within a column is recognized to be confined to one type, the P or the M enantiomer. Thus, a certain column displays a molecular array of ···(P)[5]TH–DNB–(P)[5]TH–DNB–(P)[5]TH···, while the adjacent column possesses an array of ···(M)[5]TH–DNB–(M)[5]TH–DNB–(M)[5]TH···.

This type of molecular alignment is in contrast to the alignments observed in [5]TH crystals and in the TCNQ–[5]TH CT crystals. In crystals of [5]TH a colum-
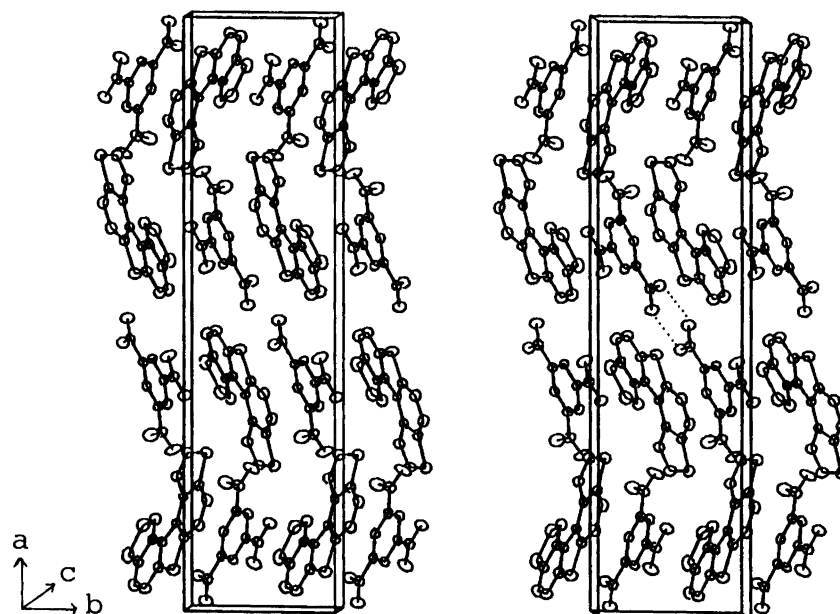
Fig. 2. A stereoview of the molecular packing of the CT complex between thieno[3,2-e:4,5-e']di[1]benzothiophene and 3,5-dinitrobenzoic acid. The hydrogen bonds are shown as dotted lines. The hydrogen atoms are omitted for clarity.

nar stacking of the [5]TH molecules is observed with alternating configurations of $\cdots(P)$[5]TH–(M)[5]TH–(P)[5]TH–(M)[5]TH$\cdots$. In the crystals of the TCNQ–[5]TH CT complex each TCNQ molecule is interposed between molecules of [5]TH, resulting in an one-dimensional column of donor–acceptor pairs like $\cdots(P)$[5]TH–TCNQ–(M)[5]TH–TCNQ–(P)[5]TH–TCNQ–(M)[5]TH$\cdots$. These differences in the molecular array must presumably be based upon the different sterical environments in the crystals. These molecular arrays can be easily understood by consideration of the crystallographic symmetry for each of the crystals. These phenomena seem intriguing from the viewpoint of the chirality recognition encountered in CT interactions between a chiral donor and an achiral acceptor.

Deformation of the [5]TH molecule in the CT interaction. The change in the conformation of the [5]TH molecules in the CT interaction was investigated in comparison with that of the [5]TH molecules in crystals. Table 2 summarizes the CT absorption maximum in $CHCl_3$ solution, the color of the crystals, the A–E dihedral angle and the $C(2)\cdots C(15)$ distance between the non-bonded terminal carbons for each of the DNB–, TAPA– and TCNQ–[5]TH complexes, together with the correspond-

ing data for the [5]TH molecule. Taking into consideration the wavelengths of the CT absorption maxima in solution, the bonding energy between a donor and an acceptor is presumed to decrease in the order TCNQ > TAPA > DNB complex, an order which coincides with the order of electron affinity of the acceptors. This relation concerning the binding energy may be expected to hold approximately for the complexes in solid state by taking account of the color of the crystals.

The dihedral angle between the terminal A and E rings was found to be smaller for each of the CT complexes than of [5]TH itself, implying an increase in planarity of the molecule during the complexations. The extent of planarity of the [5]TH molecule as estimated from these angles increases in the order TCNQ < TAPA < DNB complex, which seems to be the inverse order of electron affinity of the acceptors, i.e. the binding energy of the complexes. Moreover, an increase in planarity of the [5]TH molecule results in a spreading out of the distance between $C(2)$ and $C(15)$ to reduce the mutual steric repulsion. Consequently, it may be noted that as the electron affinity of an acceptor decreases to cause weak binding with the [5]TH molecule, the [5]TH molecule itself may alter its conformation to a structure that is as flat as possible to achieve an improved overlap with the

Table 2. Comparison of [5]TH and its CT complexes.

Compound	CT Band ($CHCl_3$)/nm	Color of crystals	A–E/°	$C(2)\cdots C(15)$/Å
[5]TH–DNB	ca. 420	Orange	15.2 (2)	3.269 (7)
[5]TH–TAPA[3]	505	Dark red	23.5 (5)	3.26 (2)
[5]TH–TCNQ[2]	ca. 675	Dark green	29.6	3.246 (6)
[5]TH[4]	—	Pale yellow	36.6 (1)	3.239 (4)

acceptor. This type of phenomenon exerted by the helical molecule may be considered as a sort of molecular recognition developed in an intermolecular interaction.

References

1. Mackay, I. R., Monteath Robertson, J. and Sime, J. G. *J. Chem. Soc., Chem. Commun.* (1969) 1470.
2. Konno, M., Saito,Y., Yamada, K. and Kawazura, H. *Acta Crystallogr., Sect. B 36*, (1980) 1680.
3. Nakagawa, H., Yamada, K. and Kawazura, H. *J. Chem. Soc., Chem. Commun.* (1989) 1378.
4. Nakagawa, H., Yamada, K. Kawazura, H. and Miyamae, H. *Acta Crystallogr, Sect. C40* (1984) 1039.
5. Yamada, K., Ogashiwa, S., Tanaka, H., Nakagawa, H. and Kawazura, H. *Chem. Lett.* (1981) 343.
6. Main, P., Lessinger, L., Woolfson, M. M., Germain, G. and Declercq, J. P. MULTAN78. *A System of Computer Programs for the Automatic Solution of Crystal Structure from X-Ray Diffraction Data.* Universities of York, UK and Louvain, Belgium 1978.
7. *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch Press, Birmingham 1974.
8. Sakurai, T. and Kobayashi, K. *Rep. Inst. Phys. Chem. Res.* 55 (1979) 69.
9. Johnson, C. K. ORTEP II, Report ORNL-3794, revised, Oak Ridge National Laboratory, Oak Ridge, TN 1974.
10. Hughes, D. L. and Trotter, J. *J. Chem. Soc. A* (1971) 2358.
11. Pimentel G. C. and McClellan A. L. *The Hydrogen Bond*, W. H. Freeman, San Francisco 1960, p. 284.