Total Conversion of Racemic [5]Thiaheterohelicene into a Single Enantiomer by a Diastereoisomeric Charge-transfer Complex Formation

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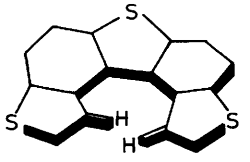
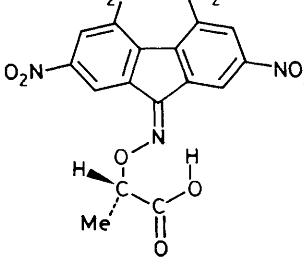
Racemic thieno[3,2-*e*: 4,5-*e*′]di[1]benzothiophene was totally converted into a single enantiomer on crystallizing the charge-transfer complex with (*S*)-2-(2,4,5,7-tetranitro-9-fluorenylidene-amino-oxy)propionic acid; the structure of the complex was determined by *X*-ray crystallographic analysis.

The crystallization-induced asymmetric transformation which permits the total resolution of one enantiomer from a racemate[1] has recently aroused interest from the standpoint of chiral discrimination between chiral molecules and a synthetic application to important chiral intermediates.[2] So far, the propulsion of the asymmetric transformation, by an interaction between different kinds of chiral molecules, has been used substantially for salt formation between chiral acids and chiral bases;[1] there have been few reports on the use of transformation for charge-transfer complex formation. The present paper describes how racemic heterohelicene was totally converted into one enantiomer by forming a diastereoisomeric charge-transfer complex with the chiral acceptor 2-(2,4,5,7-tetranitro-9-fluorenylidene-amino-oxy)propionic acid (TAPA).[3] The molecular shape of thieno-[3,2-*e*: 4,5-*e*′]di[1]benzothiophene ([5]thiaheterohelicene = [5]TH) as a donor is helical owing to the steric repulsion between the terminal hydrogens which gives an alternating pile of *P* and *M* enantiomers in the crystals as revealed by *X*-ray analysis.[4] The intramolecular inversion of the helix, however, occurs easily in solution, causing so rapid a racemization that the enantiomers cannot be resolved at room temperature.[5]



(*P*) [5]TH



(*S*)TAPA

Equimolar amounts of racemic [5]TH and (*S*)TAPA were dissolved into a mixed solvent of MeCN and $CHCl_3$ (1 : 1), and allowed to stand for several days to yield deep-red needle-like crystals of 1 : 1 adduct. First, in order to investigate the chirality of the [5]TH molecules in these crystals we measured the circular dichroism (CD) spectra in solution and in the solid state. The $CHCl_3$ solution of the crystals only exhibited the CD absorption of (*S*)TAPA [Figure 1, (a)]. However, the measurement of the solid using a KBr disk† gave a quite different spectrum. The similarities between the CD spectra in solution and in the solid state were examined using (*P*)-bisthieno[3′,2′:4,5]benzo[1,2-*b*:4,3-*b*′]di[1]benzothiophene {(*P*)[7]TH}, a homologue of [5]TH, which underwent no racemization under the present conditions, because of the overlap between the terminal skeletons of the molecule.[5,6] Both spectra obtained demonstrated marked similarity [Figure 1, (b) and (c)] except for small red shifts and a little broadening of the absorptions in the solid. These indicate that the absorptions of the solid in question are virtually due to the enantiomeric [5]TH, presumably due to the (*P*)enantiomer as predicted by comparison with [7]TH, and that in the solution of the complex the enantiomeric [5]TH racemizes rapidly to give no CD spectral absorptions. Furthermore, only the characteristic CD absorption of (*S*)TAPA was detected from the filtrate after the crystals were removed. The enantiomeric excess of the [5]TH residue in the filtrate may also be converted into the racemic form. Moreover, the equimolar mixture of [5]TH and (*S*)TAPA after grinding in an agate mortar, turned red in colour, but only (*S*)TAPA exhibited a CD absorption spectrum in a KBr disk.

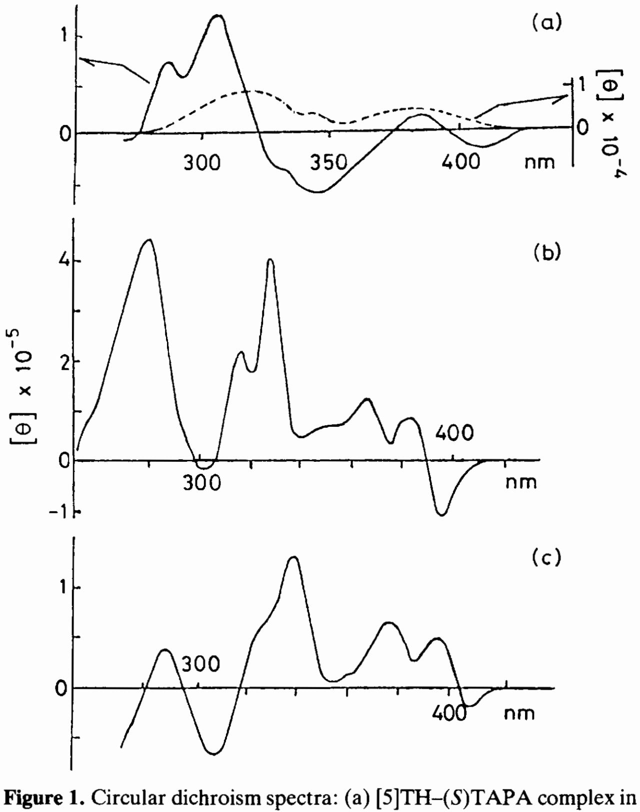


Figure 1. Circular dichroism spectra: (a) [5]TH–(*S*)TAPA complex in $CHCl_3$ solution (dashed line) and in a KBr disk (solid line); (b) (*P*)[7]TH in $CHCl_3$ solution; and (c) (*P*)[7]TH in a KBr disk. Molecular ellipticities ([θ]) are expressed as deg kg cm^{-1} mol^{-1} for the solid samples and deg l cm^{-1} mol^{-1} for the solution samples.

All these facts lead us to the following inferences; (*S*)TAPA molecules may undertake chiral discrimination towards racemic [5]TH and select only the one-sided enantiomer when crystallizing the charge-transfer complex, followed by a rapid racemization of the [5]TH left in the enantiomeric excess solution, and subsequently, only the crystals of (*S*)TAPA-(*P*)[5]TH were produced from the racemic [5]TH solution.

The crystal and molecular structures of the complex were determined by *X*-ray crystallographic analysis,‡ as shown in

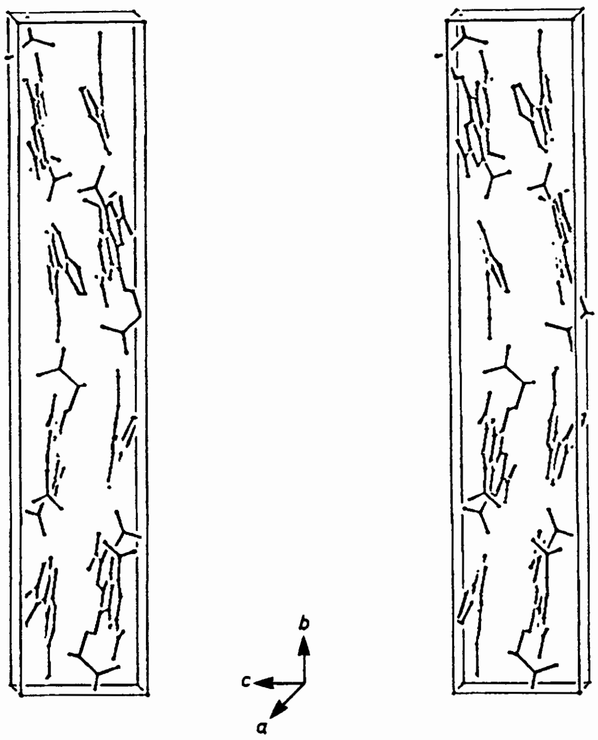


Figure 2. Projection of the [5]TH–(*S*)TAPA complex along the *a* axis.

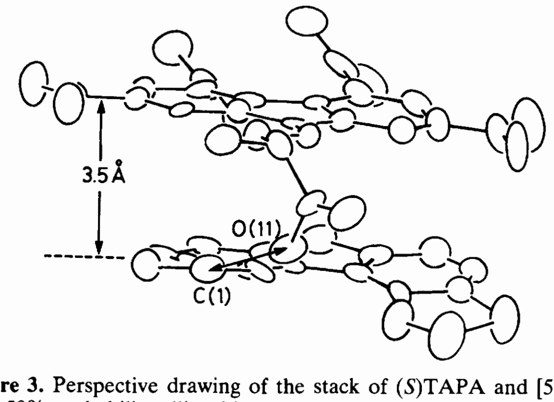


Figure 3. Perspective drawing of the stack of (*S*)TAPA and [5]TH with 50% probability ellipsoids.

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† Usually 250 mg of KBr and *ca.* 1 mg of solid sample were mixed to make a disk 0.07—0.15 mm thick. All the KBr disks of the complex (made of large crystals, small crystallites, or powders) gave the same spectra.

‡ *Crystal data*: $C_{32}H_{17}N_5O_{11}S_3$, orthorhombic, space group $P2_12_12_1$, $a = 11.149(1)$, $b = 38.571(4)$, $c = 7.308(1)$ Å, $U = 3142.6(5)$ Å^3, $Z = 4$, $D_c = 1.57$ g cm^{-3}, $F(000) = 1520$, $\mu = 27.42$ cm^{-1}, (Cu-K_α) radiation ($\lambda = 1.5418$ Å), $\omega/2\theta$ scan technique, 2287 independent reflections, 2147 [$I > 2.5\ \sigma(I)$] used in refinement, $R = 0.092$, $R_w = 0.076$ [$w = 1/\{\sigma^2(F) + 0.02 \times F^2\}$]. 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.

Figures 2 and 3, respectively. In a TAPA molecule the tetranitrofluorenylidene moiety plays the role of charge-transfer interaction and the oxypropionic acid moiety that of chiral recognition.[7] The chirality of the [5]TH molecule in the crystals was disclosed to be the right-handed helicity (P) in agreement with the results of the CD spectral studies. The planarity of the molecule increases as a whole, the dihedral angle between the terminal thiophene rings is 23.5° in comparison with 36.6° in the [5]TH crystals (racemic)[3] or 29.6° in the [5]TH (racemic)–TCNQ charge-transfer complex crystals.[8] This is presumably due to the parallel stacks of the fluorenylidene ring of TAPA with the π system of [5]TH, with separation of *ca.* 3.5 Å, suggesting a strong interaction between them. Close contacts are observed between the propionic acid chain of TAPA and the terminal ring of [5]TH. The closest contact is 3.00(1) Å between O(11) in the carboxyl group and C(1) in the [5]TH end ring; several contacts within the sum of the van der Waals radii of atoms are observed in that vicinity, implying the chiral discrimination effectuated around these moieties.

When the same experiments concerning the alternative combination, [5]TH and (R)TAPA, were carried out, the same results were obtained except for the difference in the handedness of the [5]TH molecules. Thus, it is concluded for thiaheterohelicene, the charge-transfer interaction is strong enough to exert the total conversion of a racemate into a single enantiomer on crystallizing a diastereoisomeric complex.

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