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Chiral switching and fast reversible molecular movement phenomena in crystals

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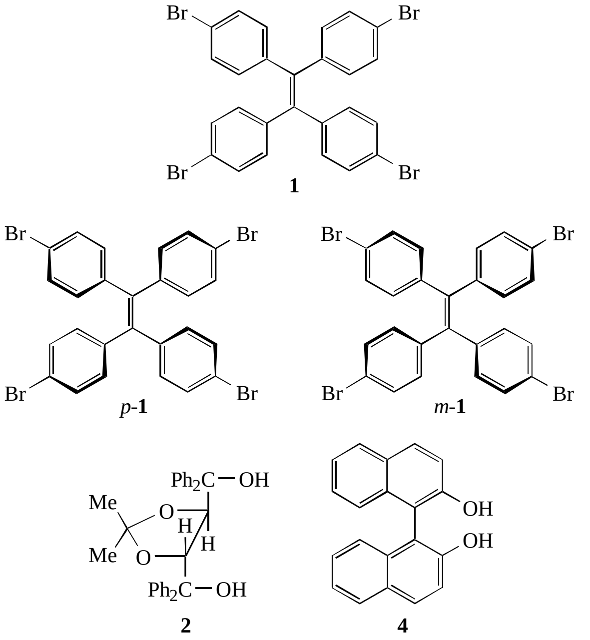
As found using FTIR, powder diffraction and CD spectrometry, in reversible inclusion complexation between crystalline hosts and gaseous guests, host molecules showed novel chiral switching phenomena: fast and reversible molecular displacement, rotation around the C–C bond, and switching between different hydrogen-bonding patterns.

Inclusion complexation between crystalline hosts and gaseous guests in the solid state occurs reversibly.[1] Namely, contact of powdered host with gaseous guest gives their inclusion compound, which converts to the original components upon heating. This process can be done repeatedly. The stereochemistry of host and guest molecules also changes the reversible inclusion process. For example, 1,2-dichloroethane is accommodated as an eclipsed form in an inclusion crystal with a host compound, although it exists as a gauche form.[2] In some cases, achiral molecules are accommodated in a chiral form with a chiral host compound, and the chirality can be fixed by a chemical reaction to give an optically active product.[3]



a *rac*-form
b (+)-form
c (–)-form

Scheme 1

When the reversible inclusion complexation between crystalline hosts and gaseous guests proceeds by changing stereochemistry or chirality of the host and/or guest molecule, these phenomena are interesting in relation to stereochemical or chiral switching in a crystal. Although various examples of stereochemical switching in a crystal have been reported,[1] chiral switching in a crystal has not been reported. As we are aware, chiral switching in the inclusion crystal of tetra(*p*-bromophenyl)ethene **1** with gaseous guests such as THF, dioxane, benzene, *p*-xylene and β-picoline has been known as a sole example.[4] Contact of powdered **1** with THF vapour, for example, at room temperature, gave a 1:2 inclusion crystal of **1** and THF, in which achiral molecules of **1** were arranged in a chiral form. The chirality of **1** is generated by the twisting of *p*-bromophenyl groups to one direction from the plane of the ethene moiety, as depicted in *p*-**1** and *m*-**1**. Evaporation of THF from

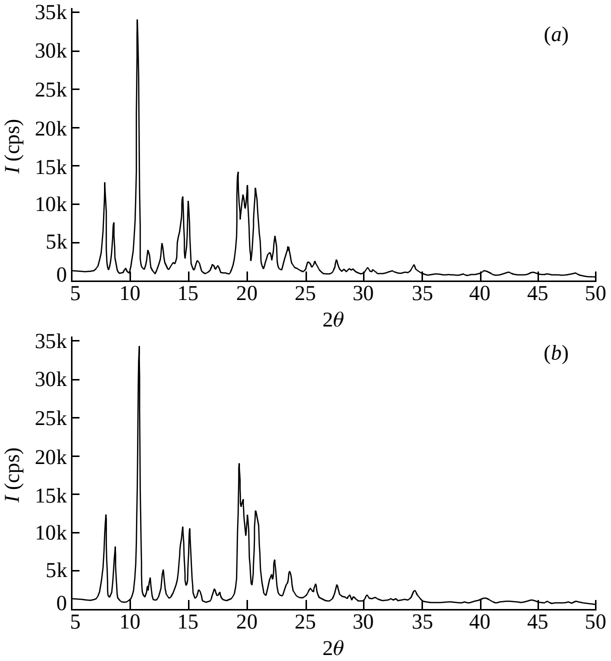


Figure 1 X-ray powder diffraction patterns of (*a*) parent **2a** and (*b*) **2a** recovered by evaporation of acetone from **3a**.

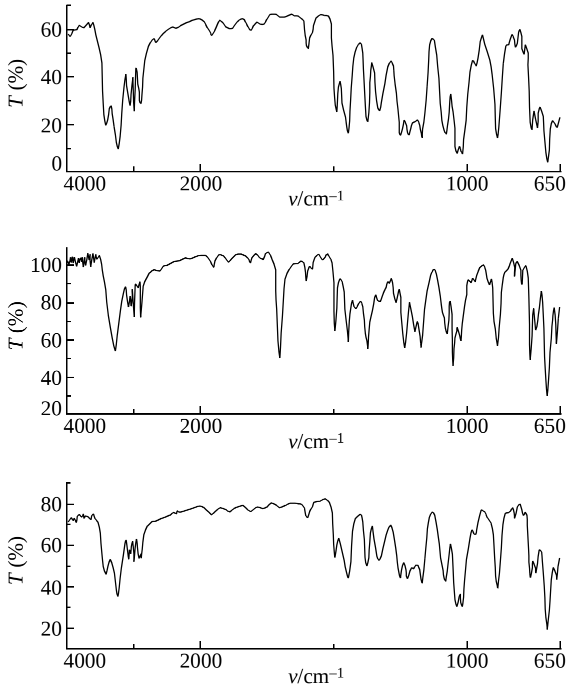


Figure 2 FTIR spectra of (*a*) parent **2a**; (*b*) 1:1 complex of **3a** with acetone; and (*c*) **2a** recovered by acetone evaporation from **3a**.

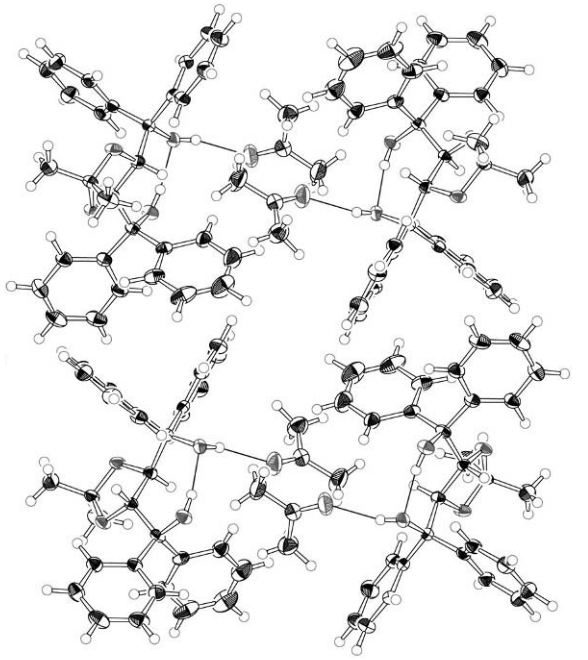


Figure 3 X-ray structure of (1:1) complex **3a** of **2a** and acetone.

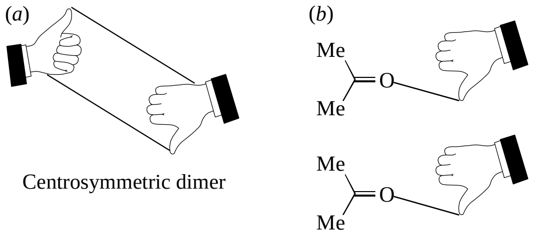


Figure 4 Schematic representation of the molecular symmetry: (*a*) H-bonded centrosymmetric dimers found in *rac*-BNO (**4a**, from ref. 5) and (*b*) homochiral aggregates with H-bonded acetone molecules found in complex **3a**.

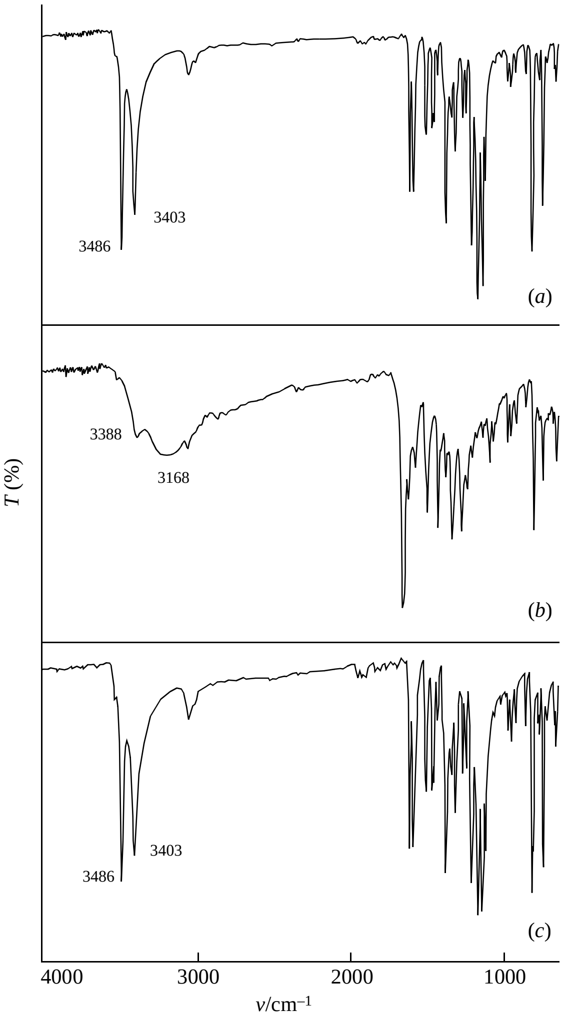


Figure 5 FTIR spectra of (*a*) parent **4a**, (*b*) 1:2 complex of **5a** with DMF and (*c*) **4a** recovered after DMF evaporation from **5a**.

the complex gave the original achiral crystal of **1**. In this case, chiral switching is attributed to the rotation of *p*-bromophenyl groups around the single bond connecting the aromatic groups to the ethene moiety. Supramolecular interactions between an achiral host and an achiral guest create a chiral object that forms an inclusion complex, which crystallises in a non-centrosymmetric space group. Such a phase transition lowers the conjugation of the system and requires fast and reversible misplacements of the host molecules in order to form the inclusion complex and come back to the parent structure.

The exact mechanism of such solid phase phenomena involving drastic movement of molecules in a crystal is unknown. Therefore, we have been looking for another model system where reversible inclusion complexation with vapour guests could be studied. The first host compound considered was *rac-trans*-4,5-bis(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane **2a**[5] derived from *rac*-tartaric acid. By contact of powdered **2a** with acetone vapour, 1:1 inclusion compound **3a** was formed as colourless crystals. This process was studied by IR spectroscopy and X-ray powder diffraction.[†] Inclusion compound **3a** was identical to that prepared by recrystallization of **2a** from acetone as evidenced from powder FTIR spectra. The FTIR spectra and X-ray powder diffraction patterns of parent compound **2a** and the solid phase obtained by the evaporation of acetone are identical (Figures 1 and 2).

The X-ray analysis of a monocrystal of **3a** showed that two (+)-molecules of **2b** accommodate two acetone guest molecules, and two (–)-molecules of **2c** accommodate two acetone guest molecules *via* hydrogen bond formation. These two enantiomerically different units are arranged alternatively (Figure 3). Contrarily, molecules of **2b** and **2c** in racemic **2a** are arranged so that a classic centrosymmetric dimer is formed through hydrogen bonds [Figure 4(*a*)].[6] Each dimer has a hydrophilic domain inside and a lypohilic surface outside. During exposure to gaseous acetone, hydrogen bonds in two nearby dimers are broken, and molecules flip in order to make hydrogen bonds with acetone molecules. The aggregate thus formed contains two molecules of the same chirality [Figure 4(*b*)]. It is surprising that this fast molecular movement occurs in the crystal lattice so effectively.

Second, molecular rearrangement was studied using racemic compound **4a** and optically active 2,2′-dihydroxy-1,1′-binaphthyl host compounds **4b**, **4c**.[7] When powdered **4a** contacted

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[†] IR spectra were measured in KBr pellets. CD spectra were measured in Nujol mulls. Powder X-ray diffraction spectra were measured at room temperature. X-ray diffraction data for **3a** and **5a** were collected on monocrystalline diffractometers at 150 and 283 K, respectively.

Crystal data for **3a**: $C_{34}H_{36}O_5$, $M = 524.66$, monoclinic, space group $P2_1/c$, $a = 18.917(3)$ Å, $b = 7.939(2)$ Å, $c = 21.094(5)$ Å, $\beta = 115.63(2)°$, $V = 2856(1)$ Å^3, $Z = 4$, $d_{\text{calc}} = 1.220$ g cm^{-3}; residuals: R = 0.046, Rw = = 0.046; GOF = 0.93, reflections/parameter, 5.08.

Crystal data for **5a**: monoclinic, space group Cc, $a = 14.2537(6)$ Å, $b = 10.8106(7)$ Å, $c = 28.1048(14)$ Å, $\beta = 96.313(6)°$, $V = 4304.4(4)$ Å^3, $Z = 8$, $d_{\text{calc}} = 1.251$; residuals: $R_1 = 0.1198$, $wR_2 = = 0.3671$ for 3610 experimental data and 541 parameters.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 214872 and 214873. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2003.

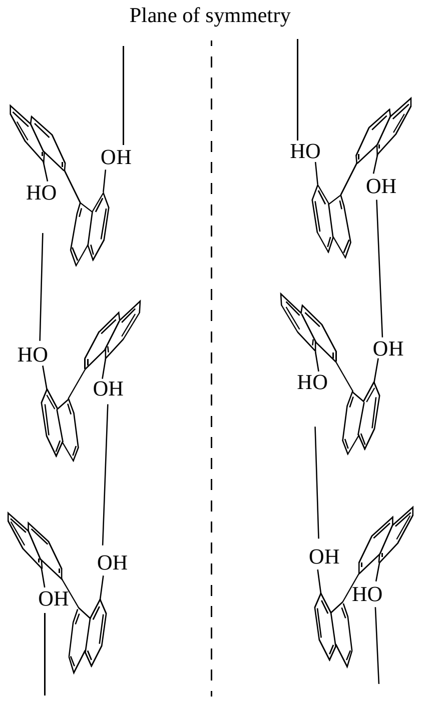

Figure 6 Schematic representation of the molecular symmetry found in **4a**: two homochiral 3_1 helices related by a plane of symmetry (from ref. 5).

with DMF vapour overnight, 1:2 inclusion complex **5a** was formed as colourless crystals. Heating of **5a** at 80 °C at 30 Torr for 3 h recovered unchanged **4a**. This switching occurs repeatedly. The IR spectrum of **4a** left after evaporation of DMF from **5a** was identical to that of compound **4a** initially used for the inclusion complexation (Figure 5).

In order to know the type of molecular movement between **4a** and **5a**, the X-ray crystal structure of **5a**† was analysed and compared with that of **4a**.[5]

In the crystal of racemic **4a**, the enantiomeric molecules **4b** and **4c** are arranged so as to form a hydrogen-bonded helical structure down a two-fold axis (Figure 6).[9] Namely, clockwise helices of **4b** molecules and anticlockwise helices of **4c** molecules are arranged alternatively in a crystal of **4a**. Although the space group of the racemic form is non-centrosymmetric (*Iba*2), two chiral helices are related by a glide plane. However, in complex **5a**, helical structure has been broken. Instead, hydrogen-bonded aggregates of non-crystallographic two-fold symmetry have been formed, each consisting of two homochiral hosts bound and three DMF molecules. (Figures 7 and 8). In this case, switching between the helical structure of **4a** and the aggregate structure of **5a**, *i.e.*, between two different hydrogen-bonding patterns requires misplacements of the two homochiral helices in order to accomodate DMF molecules and mutual rotation of the two naphthyl units in order to form new hydrogen bonds. As a remining of this complicated molecular displacement disorder of one DMF molecule and large thermal motions of both guests and at the periphery of the host molecules are observed. However, attempts to refinement in centrosymmetric space group *C*2/*c* failed, giving unreasonable geometry (*e.g.*, the non-planarity of aromatic rings), unstable refinement and high *R*-factor (*ca.* 0.21). Finally, structure was solved in *Cc* space group with an asymmetric unit consisting of two binaphthyl and three DMF molecules. It is surprising that such drastic and reversible molecular movements occur effectively in a crystal.

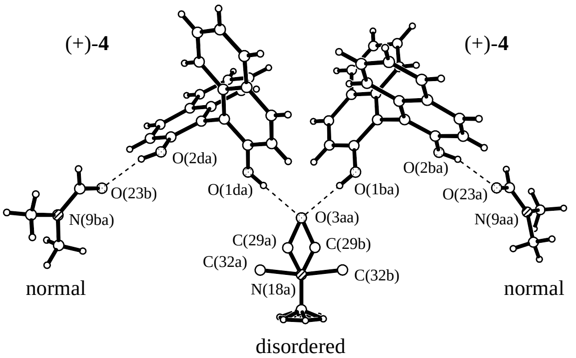

Figure 7 Hydrogen bond pattern of a (2:3) *rac*-BNO complex with DMF (some H-atoms omitted for clarity). Two DMF molecules are located in general position, the other is disordered over two positions related by non-crystallographic two-fold symmetry.

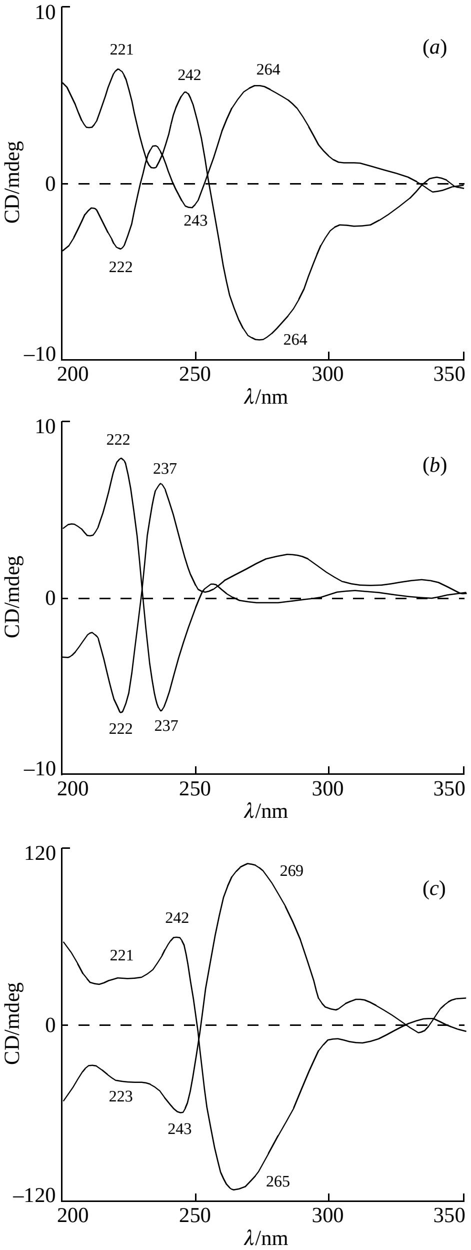

Figure 8 CD spectra in Nujol mull: (*a*) enantiomeric **4b** and **4c**, (*b*) their complexes with DMF **5b** and **5c**, (*c*) **4b** and **4c** recovered by DMF evaporation from **5b** and **5c**, respectively.

Furthermore, it was also disclosed that a similar process occurs for an optically acive host compound **4b** or **4c**. For example, **4b** formed a 1:1 inclusion complex with DMF (**5b**), which gave **4b** upon heating *in vacuo*. The switching was monitored by CD spectral measurements (Figure 8). As expected, **4b** and **4c** showed mirror imaged spectra [Figure 8(*a*)]. By inclusion complexation of **4b** and **4c** with DMF, these spectra changed drastically [Figure 8(*b*)]. Evaporation of DMF from **5b** and **5c** reproduced the respective CD spectra of **4b** and **4c** [Figure 8(*c*)].

Fast and reversible molecular displacements observed between powdered achiral or chiral host compounds and achiral guest vapours (acetone, DMF) resulted in various phase transitions, including formation of chiral crystals (‘chiral switching’). Our studies showed that molecular movements in crystals involved rotation around a single C–C bond and switching between different hydrogen bonding patterns.

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