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Comparison of the X-ray structures of concomitant pseudodimorphs formed between a diquinoline host and *d*-chloroform guest

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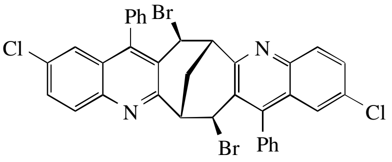
The X-ray structures of two lattice inclusion compounds formed simultaneously from a solution of substituted diquinoline derivative 1 in *d*-chloroform are described and contrasted in crystal engineering terms.

We are currently exploring the chemistry of molecules designed around the general principles illustrated diagrammatically in Figure 1.[1–4] If the sensor group is a bromine atom, these compounds function as lattice inclusion hosts,[5,6] whereas no such properties result if this group is simply hydrogen. Strong hydrogen bonding is not involved in the self-assembly of host and guest molecules into the resulting lattice inclusion (clathrate) compounds. These materials, therefore, provide an excellent means of exploring the roles of less familiar weak intermolecular forces in crystal engineering.[7,8]

In this work, we investigated racemic diquinoline derivative **1**, which has both chloro and phenyl substitution present on the aromatic wings. The eighteen-line proton-decoupled ^{13}C NMR spectrum[†] indicated that the molecule of **1** adopts C_2 symmetry in solution with hindered phenyl group rotation resulting in the magnetic non-equivalence of *o*,*o*'- and *m*,*m*'-CH groups.



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A solution of **1** in *d*-chloroform was allowed to stand at room temperature for two days. By this time two crystals of different appearance had formed: a small orthorhombic crystal and a much larger triclinic one. The structures of the complete small crystal and a cut-off portion of the larger crystal were determined by X-ray crystallography. These proved to have the compositions **1**·$CDCl_3$ and **1**·2$CDCl_3$, respectively.[‡]

When polymorphs crystallise simultaneously in the same container under identical conditions, they are described as concomitant polymorphs,[13,14] and the term pseudopolymorphism describes solvated forms of a compound with different crystal structures.[15] Hence, the outcome of this experiment is a case of concomitant pseudodimorphism. It offers a rare opportunity to investigate this unusual phenomenon by comparing these substances from a crystal engineering perspective.

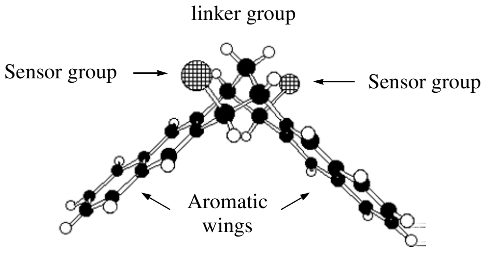

Figure 1 A general schematic design for obtaining new families of lattice inclusion hosts. The molecules involve three modular units: aromatic wings, an alicyclic central linker group, and *exo*-cyclic sensor groups.

Both crystals contain only one host molecule in their asymmetric unit, and both involve layer structures. Otherwise, however, their packing arrangements are entirely different.

In the orthorhombic structure of **1**·$CDCl_3$, space group $Pna2_1$, each *d*-chloroform guest molecule is hydrogen bonded to one of the host nitrogen atoms with $C–D\cdots N$ and $C–D\cdots N$ distances of 2.75 and 3.63 Å, respectively, and an angle of 146°. The torsion angles between the quinoline wings and phenyl substituents (Figure 2) are $t_1 = 102.0°$ and $t_2 = 103.0°$ (for the wing associated with $CDCl_3$).

The lattice comprises layers of host molecules of the same chirality but with adjacent stacked layers having opposite handedness. Within each layer, the **1**·$CDCl_3$ units are arranged around two different twofold screw axes. One (*A*, Figure 2) has the host methano-bridge vertices pointing outwards, and the other (*B*) has them pointing inwards. In the case of *A*, the host molecules are associated by *endo*,*endo*-facial aromatic offset face–face (OFF)[16,17] interactions of 3.6 Å. The host chlorine atoms

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[†] Compound **1**: ^{13}C NMR ($CDCl_3$) δ: 21.58 (CH_2), 45.38 (CH), 52.20 (CH), 125.40 (CH), 127.88 (C), 128.15 (C), 128.57 (CH), 128.73 (CH), 129.00 (2CH), 130.45 (CH), 130.74 (CH), 131.47 (CH), 133.07 (C), 133.72 (C), 146.57 (C), 149.18 (C), 156.35 (C).

[‡] *Crystallographic data for* **1**·$CDCl_3$ at 294 K: $C_{35}H_{22}Br_2Cl_2N_2\cdot CDCl_3$, orthorhombic, space group $Pna2_1$, $a = 19.815(4)$ Å, $b = 13.931(5)$ Å, $c = 12.173(2)$ Å, $V = 3360(1)$ Å^3, $Z = 4$, $M = 821.7$, $d_{\rm calc} = 1.62$ g cm^{-3}, μ(MoKα) = 2.818 mm^{-1}, final $R = 0.045$ for 1905 independent observed reflections and 186 variables [$I/\sigma(I) > 2$].

Crystallographic data for **1**·2$CDCl_3$ at 294 K: $C_{35}H_{22}Br_2Cl_2N_2\cdot 2CDCl_3$, triclinic, space group $P\bar{1}$, $a = 12.110(4)$ Å, $b = 13.425(4)$ Å, $c = 13.600(5)$ Å, $\alpha = 64.03(3)°$, $\beta = 80.87(3)°$, $\gamma = 74.43(3)°$, $V = 1913(1)$ Å^3, $Z = 2$, $M = 942.1$, $d_{\rm calc} = 1.64$ g cm^{-3}, μ(MoKα) = 2.692 mm^{-1}, final $R = 0.049$ for 3998 independent observed reflections and 210 variables [$I/\sigma(I) > 2$].

Reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in a $\theta/2\theta$ scan mode using graphite-monochromated molybdenum radiation ($\lambda = 0.7107$ Å). Data for the orthorhombic crystal (but not the triclinic one, as the crystal shape was poorly defined) were corrected for absorption.[9] Reflections with $I > 2\sigma(I)$ were considered observed. The positions of all atoms in the asymmetric unit were determined by direct phasing (SIR92).[10] Hydrogen atoms were included in calculated positions. For each structure, the pendant phenyl rings of the host were refined as rigid groups of *mm*2 symmetry, while the remaining atoms of the host were refined by full matrix least squares. The $CDCl_3$ molecules were treated as threefold symmetric rigid groups with a single C–Cl variable. The Br and host Cl atoms were refined with anisotropic thermal motion.[11] Thermal parameters for the remaining atoms of the host molecules were described by three 15 parameter *TLX* groups (where *T* is the translation tensor, *L* is the libration tensor, and *X* is the origin of libration), one for each of the phenyl rings and one for the remaining atoms of the host. The guest molecules were also refined with a 15 parameter *TLX* rigid body thermal parameter for each. Reflection weights used were $1/\sigma^2(F_0)$, with $\sigma(F_0)$ being derived from $\sigma(I_0) = [\sigma^2(I_0) + (0.04I_0)^2]^{1/2}$. The weighted residual is defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_0^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were taken from International Tables for X-ray Crystallography.[12]

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 212041 and 212042. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

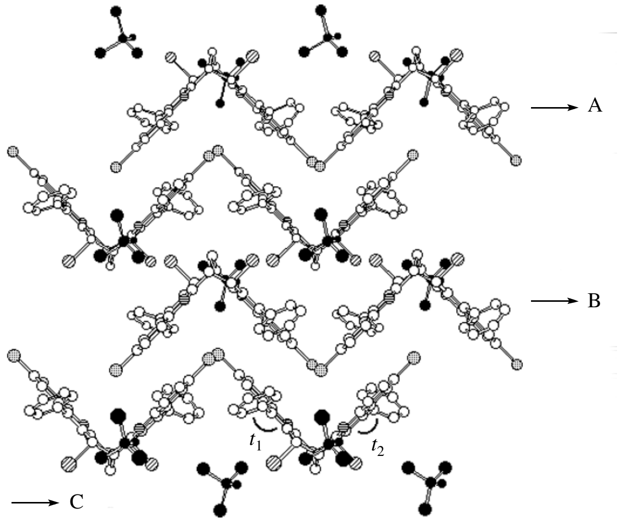

Figure 2 Part of one layer of the structure of **1**·CDCl$_3$ viewed tilted from the *bc* plane. Host hydrogen atoms are omitted for clarity. Host atom code: N (horizontal hatching), Br (diagonal hatching), and Cl (stippling). The atoms of the chloroform guests are indicated by black spheres. Twofold screw axes are present between each horizontal chain of molecules. Only one enantiomer of **1** is present in each layer.

both participate in π-halogen (differently at each end of **1**),[18,19] and Cl···Cl interactions (3.91 Å).

The second twofold screw axis *B* is a region of multiple host–guest interactions. Guest molecules participate in Cl···Br (3.45, 4.00 and 4.06 Å), Cl···N (3.86 Å) and Cl···Cl–Ar (3.66 Å) motifs, but there are no host–host Br···Br or guest–guest Cl···Cl contacts[20,21] under 4.20 Å.

In the triclinic structure of **1**·2CDCl$_3$, space group $P\overline{1}$, one of the *d*-chloroform guest molecules is hydrogen bonded to one of the host nitrogen atoms (C–H···N angle of 156°), with C–*D*···*N* and *C*–D···*N* distances of 2.22 and 3.17 Å, respectively. These values are considerably shorter than for the first compound. In marked contrast, however, the second guest molecule is not hydrogen bonded to nitrogen. The torsion angles between the quinoline wings and phenyl substituents (defined as before) are now $t_1 = 105.3°$ and $t_2 = 99.4°$.

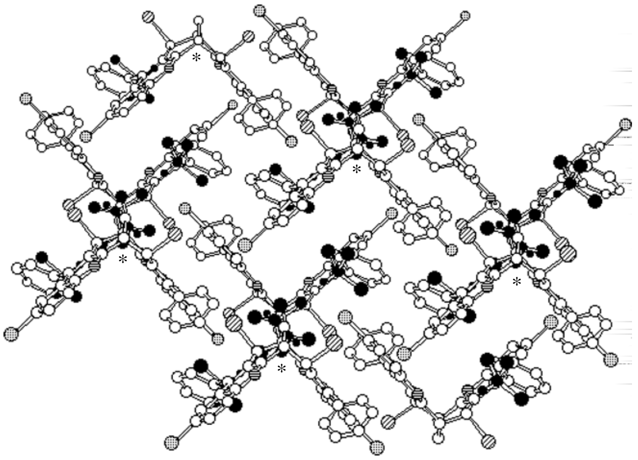

Figure 3 Part of one layer of the structure of **1**·2CDCl$_3$ viewed tilted from the *ac* plane. Host hydrogen atoms are omitted for clarity. Host atom code: N (horizontal hatching), Br (diagonal hatching), and Cl (stippling). The atoms of the chloroform guests are indicated by black spheres. Both enantiomers of **1** are present in each layer, molecules of the second enantiomer being indicated by * symbols.

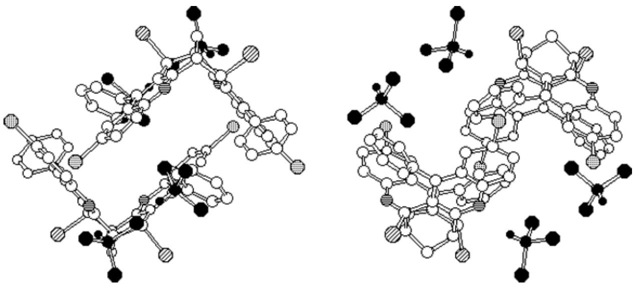

Figure 4 Two orthogonal views of the repeat unit in the structure of **1**·2CDCl$_3$. This is a centrosymmetric *endo*,*endo*-facial combination of two **1**·2CDCl$_3$ units.

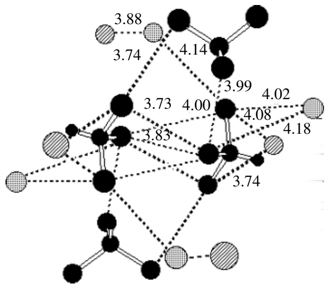

Figure 5 The centrosymmetric network of halogen–halogen interactions (dashed lines) present in and around the tetrameric (CDCl$_3$)$_4$ unit in the structure of **1**·2CDCl$_3$. Numerical values are interatomic distances in Å, and only the participating halogen atoms of the guest molecule structures are drawn. Atom codes: guest atoms, black; host chlorines, stippled; and host bromines, diagonally hatched.

The lattice again comprises stacked layers, but now these contain both enantiomers of the host. Within each layer (Figure 3), the repeat unit is the centrosymmetric *endo*,*endo*-facial arrangement of two **1**·2CDCl$_3$ units shown in Figure 4. There are no OFF or aromatic edge-face (EF) motifs within this, but there are OFF (3.7 Å, along *c*) and pairs of EF interactions[16,17] (–*C*–H···*C* 4.1 Å, along the *ab* diagonal) between repeat units.

The guest molecules are arranged as a centrosymmetric tetramer located near the *ab* plane at $c = 0$ (Figure 5). A pair of CDCl$_3$ molecules (hydrogen bonded to N) form Cl···Cl interactions[20,21] of 3.73, 3.83 and 4.00 Å, and further Cl···Cl interactions of 3.74 and 3.99 Å to a pair of non-nitrogen hydrogen bonded guests, which complete the tetrameric unit. The pair of CDCl$_3$ guests (not hydrogen bonded to N) hydrogen bond C–D···Cl to the guests (hydrogen bonded to N) with C–*D*···*Cl* of 2.82 Å, *C*–D···*Cl* of 3.86 Å and an angle of 168°. The tetrameric unit also interacts with a total of six surrounding host molecules (of which only the interacting halogens are shown in Figure 5) *via* Cl(guest)···Cl(host) and Cl(guest)···Br(host) distances of about 4 Å. There is one Cl(host)···Br(host) interaction of 3.88 Å but no Br(host)···Br(host) contacts under 4.2 Å.

It is fascinating to compare how these dimorphs solve the same problem of combining **1** with *d*-chloroform. Our results show that the compound **1**·CDCl$_3$ has a rather simple crystal structure that meets the needs of both components by means of OFF, halogen–halogen, and hydrogen bonding attractions. Its weakness is that considerable enantiomer separation is required to produce the layers containing chirally pure host molecules.

The compound **1**·2CDCl$_3$ has a more complicated structure, but the opposite host enantiomers are not required to separate and can form favourable centrosymmetric motifs. The host molecules hydrogen bond much more efficiently to one of the guests but not at all to the other. However, inclusion of this second guest molecule permits the formation of complex networks of halogen–halogen interactions.

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