Supramolecular networks *via* pyridine *N*-oxide CH···O hydrogen bonding in the crystal structures of 2,2′-dithiobis(pyridine *N*-oxide) and its complexes with 1,2,4,5-tetracyanobenzene and pyromellitic dianhydride

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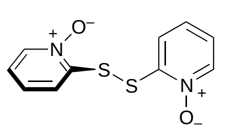
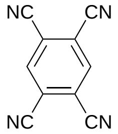
CH··O hydrogen bonding in crystals of 2,2′-dithiobis(pyridine *N*-oxide) (DTPO) supports network formation.

Crystal packing depends critically upon molecular geometry and directional intermolecular forces. Conventional hydrogen bonding (X–H··Y; X, Y = N or O) has been extensively employed to command supramolecular network formation in organic solids.[1,2] By comparison, the construction of networks *via* weak CH···O hydrogen bonding[3] is much less advanced, despite the widespread importance of these interactions.[4] Here, we present a set of new supramolecular networks constructed from pyridine *N*-oxide (PO) CH···O hydrogen bonds in the crystal structures of 2,2′-dithiobis(pyridine *N*-oxide) (DTPO) and its complexes with tetracyanobenzene (TCNB) and pyromellitic dianhydride (PMDA).


DTPO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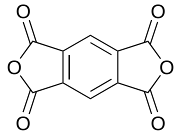
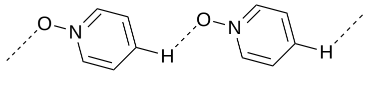
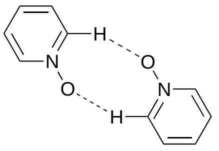

PMDA

Precedence for PO self association *via* hydrogen bonding can be found in the Cambridge Structure Database (CSD).[5]† Both chain propagating (**X**) and chain termination (**Y**) modes of CH···O bonding occur, the former being much more common than the latter. For DTPO, self-association in at least two dimensions *via* CH···O interactions should be possible if the conformational preference of aryl disulfides (twisted orientation of aryl rings) survives in the solid. Thus, we have investigated the CH···O network formation ability of DTPO in the solid state.


o,m CH•••O also possible

X


Y

Crystals of DTPO **1** [mp 205 °C (decomp.)] were grown from nitromethane and analysed by X-ray diffraction.‡ The crystal structure is a three-dimensional CH···O bonded racemic supernetwork in which each DTPO molecule participates in eight (four unique) CH···O hydrogen bonds (see Fig. 1). By virtue of the disulfide conformational preference for a 90° C–S–S–C twist angle,[6] the DTPO molecule is axially dissymmetric. Both DTPO enantiomers are present in crystal **1**. We refer to the lattice as a supernetwork because it is composed of two interpenetrated three-dimensional homochiral DTPO networks which associate *via* two (of eight) CH···O hydrogen bonds per DTPO molecule.

The open network character of the homochiral fragments of **1** suggested that guest inclusion in a DTPO lattice might be possible. To test this possibility, DTPO was crystallized in the presence of electron-deficient additives TCNB and PMDA.[7]

Light yellow crystals of $(DTPO)_2TCNB(H_2O)_4$ **2** [mp 250 °C (decomp.)] were obtained from nitromethane,‡ Homochiral networks are not observed in **2**, but guest inclusion is observed. In this cocrystal, DTPO molecules self-assemble *via* **X** and **Y** mode CH···O bonding to yield a ladder host array clathrated by TCNB guests, as shown in Fig. 2. The ladder cavity dimensions are 8.4 × 6.5 Å, and the cavity contains π-stacked DTPO dimer donor and TCNB acceptor moieties with an inter-plane distance of *ca.* 3.25 Å, indicative of an attractive donor–acceptor (DA) interaction.[8] Two unique water molecules (not shown) also appear in the lattice between ladders and hydrogen bond to each other and to the DTPO oxygens of the ladder host. These water molecules fill space between the DTPO superstructures and, by OH···O hydrogen-bonding, effectively cross-link adjacent DTPO ladders which orient parallel to each other in the lattice.

In the presence of PMDA in MeCN, DTPO forms dark yellow plates of $(DTPO)_2PMDA$ **3** [mp 220 °C (decomp.)].‡ The crystal structure is shown in Fig. 3. The DTPO host network of **3** closely resembles that of **2**, yielding guest-occupied DTPO

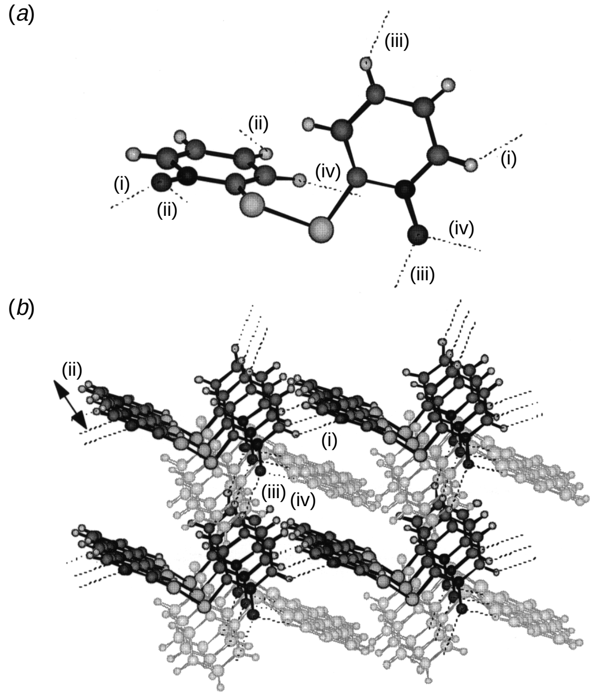


Fig. 1 CH···O hydrogen bonding at DTPO in crystal **1**: (*a*) single DTPO molecule and (*b*) enantiomer-shaded racemic network; [H···O (Å), C(H)···O (Å), CH···O (°)]: (i) 2.36(2), 3.113(2), 137(2); (ii) 2.35(3), 3.170(3), 143(2); (iii) 2.41(2), 3.179(2), 146(2); (iv) 2.44(2), 3.346(2), 157(2)

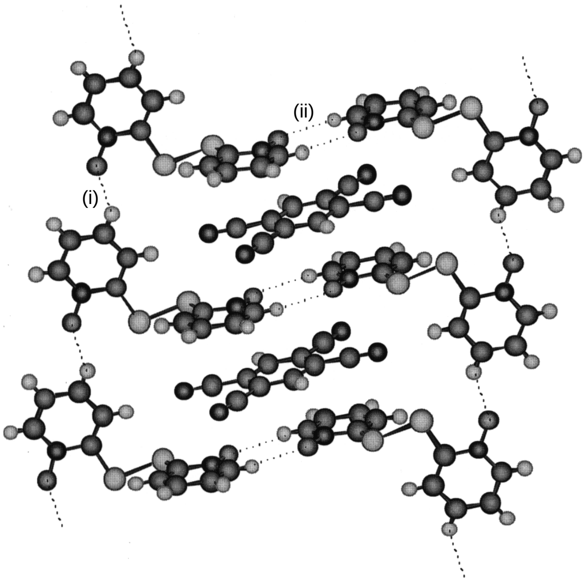


Fig. 2 TCNB-occupied DTPO ladder host network of crystal **2**; [H···O (Å), C(H)···O (Å), CH···O (°)]: (i) 2.48(3), 3.252(3), 142(2); (ii) 2.38(3), 3.281(3), 169(3)

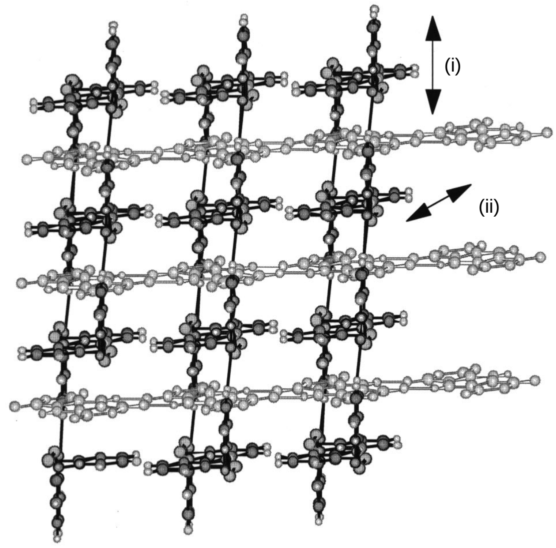
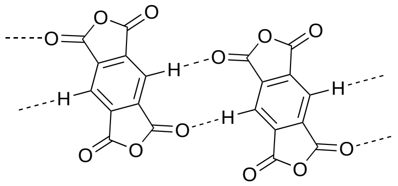


Fig. 3 DTPO ladder host networks (dark) threaded by PMDA stands (light) in crystal **3**: [H···O (Å), C(H)···O (Å), CH···O (°)]: DTPO (i) 2.32(3), 3.130(3), 145(2); DTPO (ii) 2.35(3), 3.220(3), 172(3); PMDA 2.36(3), 3.257(3), 164(2)

ladders. An added feature of **3** is guest self-association. PMDA forms 10-membered rings as CH···O hydrogen bonded dimers,[9] giving PMDA tapes which thread the ladder host cavities to form a two-dimensional host–guest array with a novel supramolecular polypseudorotaxane architecture.[10] The plane-to-plane distance between DTPO and PMDA rings is *ca.* 3.3 Å. Adjacent DTPO ladders on different threads associate *via* a third (interladder) CH···O hydrogen bond‖ between DTPOs to complete three-dimensional ordering of the lattice. From a crystal engineering perspective, **3** is a novel solid in which three distinct supramolecular bonding schemes cooperate to effect three-dimensional molecular organization in the two-component solid.



In summary, the above structures illustrate the propensity of the pyridine *N*-oxide units of DTPO to form networks *via* CH···O bonding in the solid state. Knowledge of such interactions is important to crystal engineering with the POs whose strong molecular dipole makes them attractive substrates for optical or electronic materials preparation. Structures **2** and **3** display an interplay of CH···O and π DA interactions, culminating in three-dimensional host–guest arrays.

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Footnotes and References

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† Although CH···O hydrogen bonding of POs has not previously been exploited for crystal engineering, many previous examples can be found in the CSD. A PO substructure search (CSD, Dec. 1996) found 59 hits, all of which display CH···O close contacts.

‡ *Crystal data* was collected on a Siemons diffractometer ($\lambda = 0.71073$ Å) with a SMART/CCD area detector. Hydrogens were positioned from difference Fourier maps and refined isotropically (SHELXL-93). Final full matrix least-squares refinement was done on F^2 with all data. CH··O geometries refer to normalized (1.08 Å) C–H distances. For **1**: $C_{10}H_8N_2O_2S_2$, triclinic, $P\bar{1}$, $a = 7.0793(2)$, $b = 7.0898(1)$, $c = 10.7979(3)$ Å, $\alpha = 86.800(1)$, $\beta = 73.725(2)$, $\gamma = 89.129(2)°$, $V = 519.43(2)$ Å^3, $Z = 2$, $D_c = 1.613$ g cm^{-3}, $T = 173(2)$ K. Data collection ($1.97 < \theta < 27.92°$) gave 2297 reflections with $I > 2\sigma(I)$ out of 3319 total unique reflections and refinement gave $R_1 = 0.036$, $wR_2 = 0.080$ and GOF = 1.019. For **2**: $C_{15}H_{13}N_4O_4S_2$, triclinic, $P\bar{1}$, $a = 7.1382(2)$, $b = 10.7477(3)$, $c = 11.3481(4)$ Å, $\alpha = 100.566(1)$, $\beta = 99.021(1)$, $\gamma = 91.340(1)°$, $V = 844.05(4)$ Å^3, $Z = 2$, $D_c = 1.485$ g cm^{-3}, $T = 293(2)$ K. Data collection ($1.85 < \theta < 27.89°$) gave 3752 reflections with $I > 2\sigma(I)$ and 5314 total unique reflections and refinement gave $R_1 = 0.55$, $wR_2 = 0.107$ and GOF = 1.163. For **3**: $C_{15}H_9N_2O_5S_2$, triclinic, $P\bar{1}$, $a = 6.9849(2)$, $b = 7.3531(2)$, $c = 15.3700(2)$ Å, $\alpha = 77.007(2)$, $\beta = 77.504(2)$, $\gamma = 81.529(2)°$, $V = 746.93(3)$ Å^3, $Z = 2$, $D_c = 1.607$ g cm^{-3}, $T = 173(2)$ K. Data collection ($1.38 < \theta < 27.87°$) gave 3307 reflections with $I > 2\sigma(I)$ and 4782 total unique reflections and refinement gave $R_1 = 0.063$, $wR_2 = 0.109$ and GOF = 1.038.

‖ The interaction occurs between a ladder rung DTPO CH *ortho* to the disulfide and the NO oxygen of an adjacent ladder rail with H···O 2.38(3), C(H)···O = 3.136(3) and CH···O = 139(2) Å.

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