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A Chiral 2-D Donor–Acceptor Array of a Bipyrazine *N*-Oxide and Tetracyanoethylene

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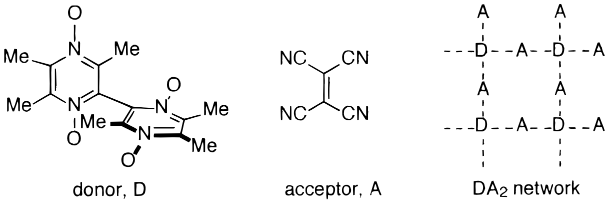
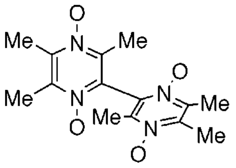
ABSTRACT



Hexamethylbipyrazine-*N*,*N*′,*N*′′,*N*′′′-tetraoxide (1) is synthesized in racemic form and cocrystallized with tetracyanoethylene to give a donor–acceptor (DA) networked lattice. The resulting DA$_2$ cocrystal contains homochiral 2-D DA arrays (layers) cohered by 2.7 Å NO$\cdots$C=C DA bonds with periplanar O p-orbital/C=C orientations. Layer formation is stereoselective, while interlayer relations yield a racemic lattice.

The synthesis of orientationally constrained molecular networks requires the use of anisotropic molecular association modes for cohesion. Within a crystal lattice, control of supramolecular order is known as crystal engineering.[1] In an effort to develop new tools for crystal engineering, we have been evaluating new, localized organic electron donor−acceptor[2] (DA) associations and their effect on crystal growth.[3] We report here the cocrystallization of bipyrazine *N*-oxide (**1**) and tetracyanoethylene (TCNE).



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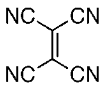
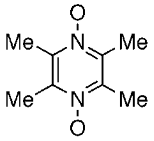


TCNE



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Previous work showed that heterocyclic *N*-oxides such as **2** bind to TCNE in a manner that supports cocrystallization with $(DA)_n$ or $(D_2A)_n$ chain formation in the lattice.[4] A hallmark of the DA bonding in such cocrystals is a short NO$\cdots$C=C intermolecular contact of 2.77−2.91 Å, which is significantly shorter than the nonbonded O,C van der Waals distance[5] of 3.22 Å. The previous cocrystal structures suggested that a bipyrazine tetra-*N*-oxide (BPTO) such as **1** might serve as a chain crossing linker to afford two-dimensional DA arrays in a hypothetical BPTO/TCNE cocrystal.

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(1) Some reviews are (a) Desiraju, G. R. *Crystal Engineering, The Design of Organic Solids*; Elsevier: Amsterdam, 1989. (b) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309. (c) *The Crystal as a Supramolecular Entity. Perspectives in Supramolecular Chemistry*; Desiraju, G. R., Ed.; Wiley: New York, 1996. (d) Weber, E. *Top. Curr. Chem.* **1998**, *198*, 1.

(2) For reviews of organic donor−acceptor complexation, see: (a) Bent, H. A. *Chem. Rev.* **1968**, *68*, 587. (b) Mulliken, R. S.; Person, W. B. *Molecular Complexes: A Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969. (c) Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: New York, 1969. (d) Herbstein, F. H. *Persp. Struct. Chem.* **1971**, *4*, 166.

(3) (a) Blackstock, S. C.; Poehling, K.; Greer, M. L. *J. Am. Chem. Soc.* **1995**, *117*, 6617. (b) Greer, M. L.; Blackstock, S. C. *J. Am. Chem. Soc.* **1997**, *119*, 11343. (c) Greer, M. L.; Blackstock, S. C. *Mol. Cryst. Liq. Cryst.* **1998**, *313*, 55.

(4) (a) Greer, M. L.; McGee, B. J.; Rogers, R. D.; Blackstock, S. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1864. (b) Greer, M. L.; Duncan, J. R.; Duff, J. L.; Blackstock, S. C. *Tetrahedron Lett.* **1997**, *38*, 7665. (c) Bodige, S. G.; Selby, T. D.; McKay, S. E.; Blackstock, S. C. *Trans. Am. Cryst. Assoc.* **1998**, *33*, 135.

(5) For van der Waals radii in crystals, see: (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Rowland, R. S.; Taylor, R. *J. Phys. Chem.* **1996**, *100*, 7384.

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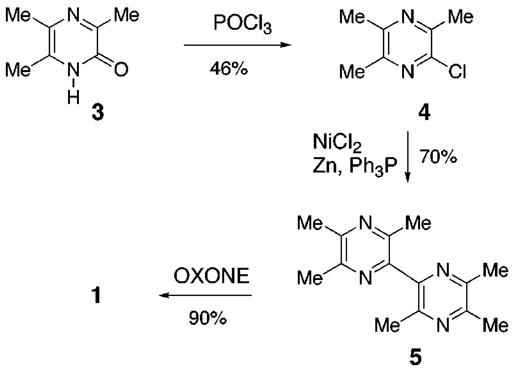
To avoid CH•••O hydrogen bonded self-aggregation of the *N*-oxide moiety that might compete with DA-mediated aggregation modes,[4c,6] the permethylated BPTO **1** was desired as a target donor structure. Scheme 1 shows the synthesis of **1**. Treatment of trimethylpyrazinone **3**[7,8] with $POCl_3$ gave **4**,[8] whose Nickel-mediated coupling using a procedure derived from Constable et al.[9] yielded bipyrazine **5**. Oxygenation of **5** with OXONE gave tetra-*N*-oxide **1**.

Scheme 1



The mixture of colorless **1** and TCNE in CH_2Cl_2 yields a red solution that features a new visible absorption band with λ_m = 496 nm (Figure 1). This absorption is assigned to the charge-transfer excitation of the **1**/TCNE DA complex. Benesi–Hildebrand analysis[10] of **1**/TCNE mixtures in CH_2Cl_2 provides an estimate of K_f (3.6 ± 0.1 M^{-1}) for complexation and of ϵ (4686 cm^{-1} M^{-1} at 490 nm) for the complex. A plot (Figure 2) of absorbance at 496 nm as a function of continuous variation of the D:A molar ratio (according to the method of Job) shows a maximum at D:A = 1:1, suggesting that an assumed 1:1 stoichiometry of complexation is valid under the solution conditions.

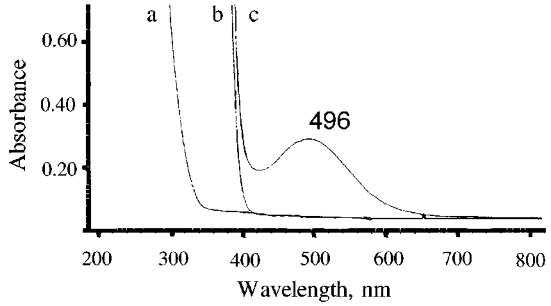


Figure 1. UV–vis spectra in CH_2Cl_2 of (a) 49 mM TCNE, (b) 1.2 mM **1**, and (c) 49 mM TCNE + 1.2 mM **1**.

Cooling of concentrated 2:1 TCNE/**1** solutions in CH_2Cl_2 at −20 °C under an ether atmosphere afforded bright red DA_2 cocrystals for which X-ray diffraction analysis at −100 °C has been performed.[11] DA aggregation is observed in the lattice as two-dimensional (2-D) supramolecular layers (grids) of $(DA_2)_n$ composition (Figure 3). Each donor binds to four acceptors, and each acceptor binds to two donors to cohere the array. In a supramolecular sense, crossed DA chains form a thatched layer with the BPTO donors serving as the chain intersection points. The component connectivity pattern is denoted below.

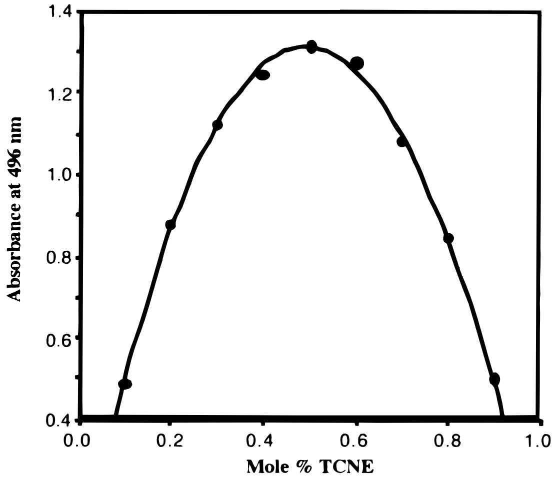


Figure 2. Job plot for **1**/TCNE absorption at 496 nm with [**1**] + [TCNE] = 0.020 M in CH_2Cl_2 at 25 °C.

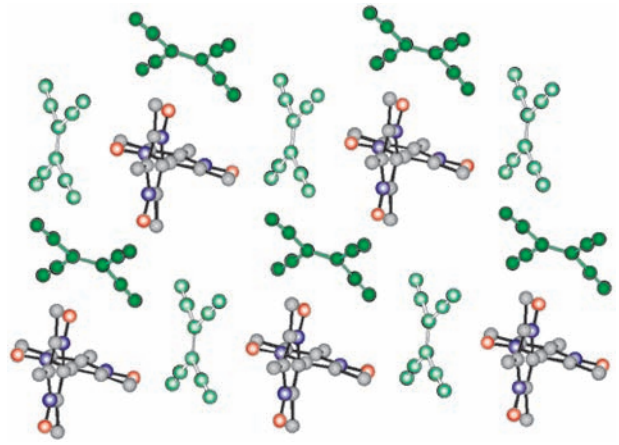


Figure 3. $(DA_2)_n$ layer in (**1**)$(TCNE)_2$ cocrystal.

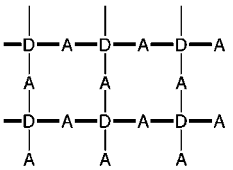


Figure 4 shows the DA connections. Intermolecular D–A contacts of 2.6–2.7 Å are observed. These contacts are 0.5

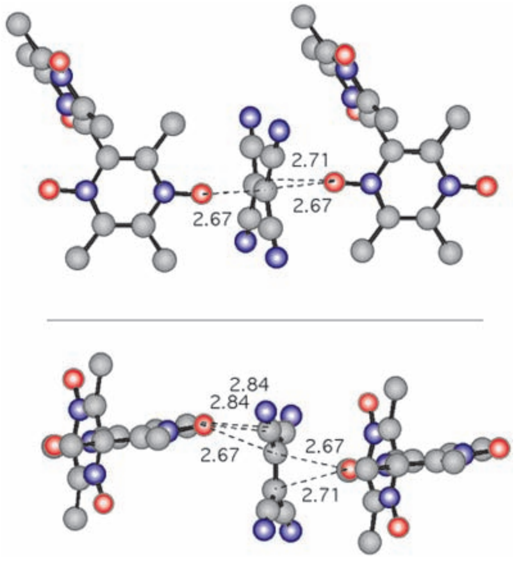
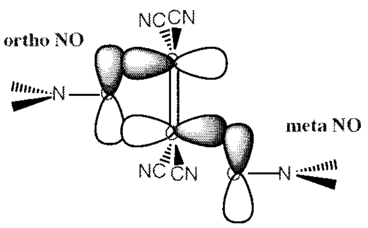
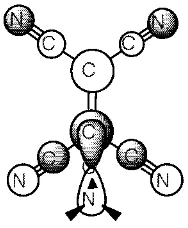


Figure 4. DA bonding in the (**1**)(TCNE)$_2$ cocrystal lattice. Dashed distances are in Å. Top and bottom views are orthogonal perspectives about the horizontal axis.

Å shorter than the van der Waals radii sum and clearly represent DA attractions in the lattice between *N*-oxide and TCNE functional groups that we shall refer to as DA bonds. The DA bond orientations are similar to those previously found in azodioxide/TCNE[13] and pyrazine dioxide/TCNE[4a,b] arrays in which the p-orbital axis of the *N*-oxide orients parallel to the C═C bond of TCNE. This geometry is favorable for HOMO/LUMO orbital overlap, which appears to play a significant structural role, along with dipolar coulombic attractions, in the N−O···TCNE DA bonding. Figure 5 shows the HOMO of **1** and LUMO of TCNE as calculated by AM1.

The ortho and meta NO groups of **1** bind to TCNE with slightly different geometries. The "bisected" ortho NO···TCNE and "slipped" meta NO···TCNE linkages are depicted below with FMO overlap. Both DA bonds have short 2.7 Å noncovalent NO···C═C lengths and parallel oxygen p-orbital, TCNE C═C bond orientations. For the ortho NO···TCNE bond, a cyclic DA interaction between the oxide oxygen and the two carbons of the C═C linkage occurs with a "bisected" topology that could be described, in Dewar−Zimmerman terms,[12] as an $\omega 2a + \pi 2s$ Möbius aromatic pericyclic array. For the meta NO···TCNE bond a "slipped" version of the DA interaction is observed, with the oxide oxygen located to one end of the C═C linkage. In both DA bond geometries, constructive FMO overlap is apparent. The presence of two different DA interaction geometries in the (**1**)(TCNE)$_2$ cocrystal may be caused by the different molecular environments of the ortho and meta NO groups or by other intermolecular close-packing constraints in the lattice. The "loose" DA bonds will have soft potentials that allow them to undergo distortion in response to other energetically demanding features of molecular packing. We speculate that the "slipped" DA bonds of the (**1**)(TCNE)$_2$ lattice may result from a collapse or relaxation of the $(DA_2)_n$ grid network that would, were it composed of only rigid bisected DA links, otherwise be strained as a result of porous structure. Of course, optimum interlayer packing may also influence the DA$_2$ grid structure and, in turn, the observed DA bond geometries. Although it seems reasonable to assume that the bisected NO···TCNE bond would be electronically preferred to the slipped one, there is no compelling evidence at this time to support this conjecture. In fact, there is more literature precedence for the slipped NO···TCNE bond geometry.[4a,b,13]





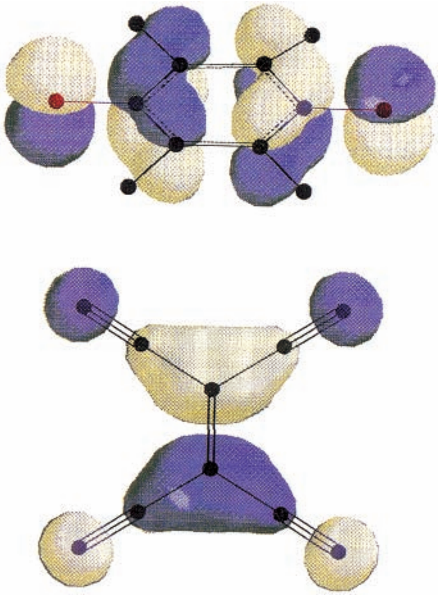


Figure 5. (above) HOMO of **1** and (below) LUMO of TCNE as calculated by AM1.

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(6) For preliminary reports of heterocyclic *N*-oxide CH···O hydrogen bonding in crystal lattices, see: (a) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063. (b) Bodige, S. G.; Zottola, M. A.; McKay, S. E.; Blackstock, S. C. *Cryst. Eng.* **1998**, *1*, 243.

(7) MacDonald, J. C.; Bishop, G. G.; Mazurek, M. *Tetrahedron* **1976**, *32*, 655.

(8) Karmas, G.; Spoerri, P. E. *J. Am. Chem. Soc.* **1952**, *74*, 1580.

(9) Constable, E. C.; Morris, D.; Carr, S. *New J. Chem.* **1998**, 287.

(10) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

(11) Monoclinic $C2/c$ lattice: $a = 18.1957(6)$, $b = 10.0687(1)$, $c = 18.1772(6)$ Å and $\alpha = \gamma = 90°$, $\beta = 118.699(2)°$. Data/parameter = 2522/227, structure refinement on F^2 gave R_1 ($I > 2\sigma(I)$) = 0.0514, wR$_2$ = 0.1074. See Supporting Information for complete details.

(12) (a) Zimmerman, H. E. *Acc. Chem. Res.* **1971**, *4*, 272. (b) Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761.

Since donor **1** is a chiral structure by virtue of its slow bond rotation about the bipyrazine linkage,[14] there exists an issue of the stereochemical integrity of DA layer assembly. It is observed that the $(DA_2)_n$ arrays of the (**1**)$(TCNE)_2$ cocrystal are homochiral, i.e., they contain only one enantiomer of **1**. However, the crystal lattice as a whole is racemic because alternate layers are of alternate chirality. Presumably, chiral layer formation is favored because such layers propagate most readily and/or pack together (in racemic form) in optimal fashion. Figure 6 displays a packing diagram of the (**1**)$(TCNE)_2$ lattice with color-coded layers.

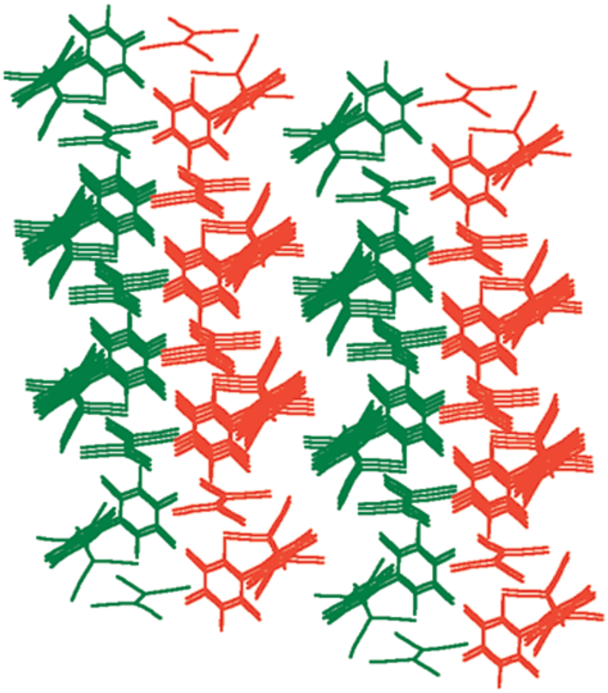

Figure 6. Packing diagram for (**1**)$(TCNE)_2$ cocrystal showing alternating chiral layers.

To test for the presence of polymorphic cocrystals of **1**/TCNE, a powder diffractogram of the bulk sample was obtained and compared to the calculated powder spectrum. As seen from Figure 7, bulk material has the same powder peaks as expected for the observed (**1**)$(TCNE)_2$ crystal and no additional peaks. This result suggests that little or no polymorphic cocrystal formation occurred under our crystal growth conditions.

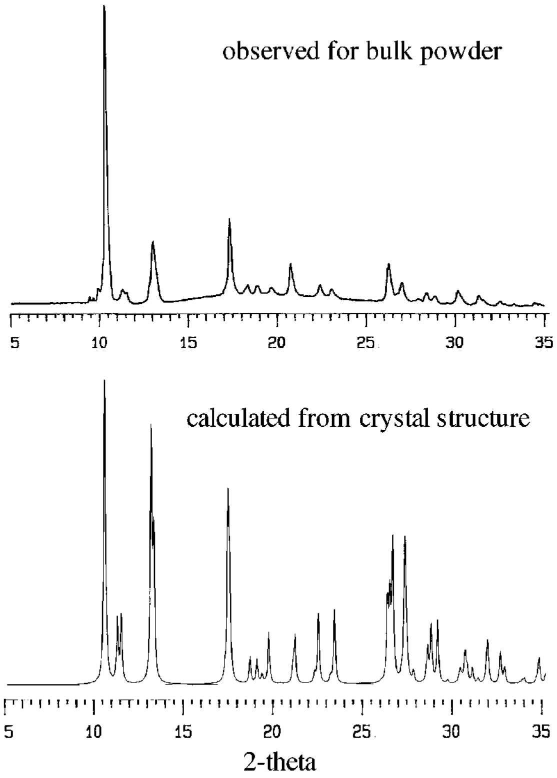

Figure 7. Powder X-ray diffractograms for bulk (**1**)$(TCNE)_2$ and for its single-crystal structure.

In conclusion, we have shown that a bipyrazine tetra-*N*-oxide donor molecule functions as a chain intersection linker to form 2-D $(DA_2)_n$ grids with TCNE in the solid state. Extremely short NO···C=C DA bonds are observed, having lengths 0.55 Å shorter than van der Waals contact (or 31% of the way from a nonbonded O···C distance toward that of a single C−O bond). The orientational preference of these *N*-oxide/TCNE DA bonds is consistent with HOMO/LUMO overlap optimization. Finally, the stereoselectivity of the $(DA_2)_n$ layer formation in (**1**)$(TCNE)_2$ is noted.

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Supporting Information Available: Synthetic procedures, material purifications and spectral data, Benesi−Hildebrand analysis, Job plot, X-ray tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Greer, M. L.; Blackstock, S. C. *J. Org. Chem.* **1996**, *61*, 7895.

(14) Resolution of **1** is being attempted. The report of isolated (*S*)-3,3′-dimethyl-2,2′-biquinoline-*N*,*N*′-dioxide strongly suggests that **1** also exists as isolable enantiomeric rotamers. See: Nakajima, M.; Saito, M.; Shiro, M.; Hashimoto, S. *J. Am. Chem. Soc.* **1998**, *120*, 6419.