Pergamon

*Tetrahedron Letters*, Vol. 38, No. 44, pp. 7665-7668, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10089-2

# Solid-State Complexes of Quinoxaline- and Phenazine-N,N′-dioxide Donors with Tetracyanoethylene. Crystal Engineering via Donor-Acceptor Interactions

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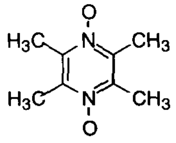
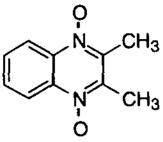
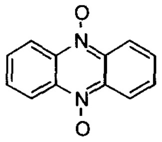
***Abstract:*** 2,3-Dimethylquinoxaline-N,N'-dioxide (DMQDO) and phenazine-N,N'-dioxide (PDO) bind to tetracyanoethylene (TCNE) in solution, with complexation constants of 4.8(7) and 1.2(7) $M^{-1}$, respectively in $CH_2Cl_2$. Crystallization of the mixtures affords two-component solids which contain weakly bound one-dimensional donor-acceptor arrays. The DA interactions create DA ladder domains in the $(DMQDO)_2TCNE$ solid and single-stranded DA chains in the (PDO)TCNE crystal.

The discovery of attractive functional group interactions in solids aids the development of crystal engineering[1] and organic material science and also expands our basic knowledge of chemical bonding. In this context, we have been exploring donor-acceptor[2] (DA) interactions between organic NO-containing donors and electron poor olefins.[3] Recently, we reported the formation of crystalline DA networks of a pyrazine-N,N'-dioxide (TMPDO) and tetracyanoethylene (TCNE).[4] Now, we present the TCNE complexation of two larger heterocyclic-N-oxide ring systems, 2,3-dimethylquinoxaline-N,N'-dioxide (DMQDO) and phenazine-N,N'-dioxide (PDO).


TMPDO


DMQDO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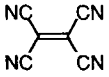
TCNE

In $CH_2Cl_2$, mixtures of DMQDO[5] and TCNE are red and possess a broad absorption band ($\lambda_{max}$ 536 nm) which we assign to DMQDO/TCNE complex charge-transfer (CT) excitation. A Benesi-Hildebrand analysis[6] of this mixture yields a complex formation constant, $K_f$, of 4.8(7) $M^{-1}$.[7]

Cooling DMQDO/TCNE mixtures in $CH_3CN$ affords red $(DMQDO)_2TCNE$ crystals whose structure has been determined by X-ray diffraction.[8] This two-component solid contains ladder-like 1D $(D_2A)_n$ arrays (Figure 1b) whose structure is mediated by close contacts between DMQDO oxygens and TCNE olefinic carbons at distances of 2.806(3) and 2.853(3) Å. These contacts are much shorter than the sum of atomic van der Waals radii[9] (3.22 Å for O--C). Keeping in mind the solution association of DMQDO and TCNE, we ascribe these close contacts to weak DA bonding in the mixed solid. Four donors surround each TCNE molecule with oxygen atoms positioned at the $\pi^*$ orbital lobes of the acceptor olefin in a rectangular geometry

(Figure 1a). Adjacent DMQDO donors in the ladder array have parallel ring planes at roughly 3.3 Å separation and are slipped by 1.3 Å along the ladder axis, presumably to allow favorable inter-donor NO dipole alignment. The $(D_2A)_n$ ladder strands pack in parallel fashion to form the bulk lattice.

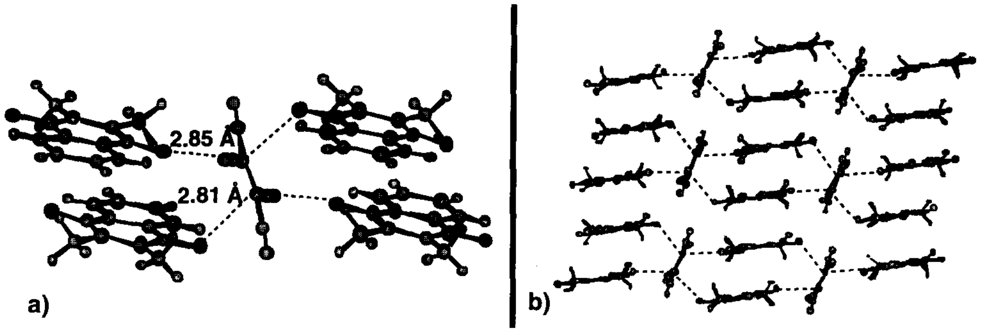

**Figure 1.** The $(DMQDO)_2TCNE$ crystal structure a) DA connectivity and b) adjacent ladder chains.

Solution mixtures of PDO[10] and TCNE are deep violet in color and show a CT band with $\lambda_{max}$ 586 nm in $CH_2Cl_2$. $K_f$ for this DA complex is 1.2(7) $M^{-1}$.[11] Dark purple needles of (PDO)TCNE are grown from cooled 1:1 mixtures in $CH_2Cl_2$. The (PDO)TCNE crystal structure[12] shows prominent intermolecular interactions between donor and acceptor which conform to 1D -D-A-D-A- chains in the lattice. The closest DA contacts are between PDO oxygens and TCNE olefinic carbons at 2.819(1) Å (Figure 2). In contrast to other azaaromatic-N-oxide/TCNE DA arrays (Fig. 1 and ref 4), only two donors bind at each TCNE.

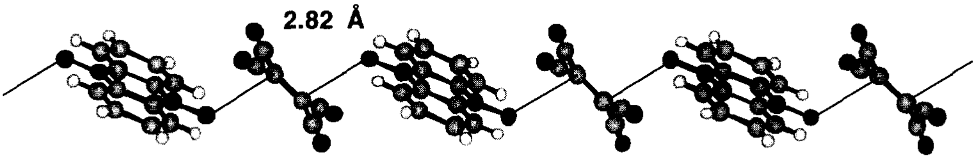

**Figure 2.** The (PDO)TCNE crystal structure $(DA)_n$ chain.

Close inspection of the (PDO)TCNE crystal structure reveals the presence of additional intermolecular close contacts in the lattice. These are PDO-PDO CH--O and PDO-TCNE CH--N contacts of 2.40 - 2.50 Å with CH--O and CH--N angles of 121 - 165 degrees. These contacts are inside of O--H and N--H van der Waals distances which are 2.72 and 2.75 Å, respectively and have geometries consistent with CH--X hydrogen bonding interactions,[13] although the true nature of these contacts awaits more detailed spectroscopic analysis of the material.[14] If we tentatively assume that the short CH--X contacts are weak hydrogen bonds, then the (PDO)TCNE lattice may be considered to be three-dimensionally ordered, with putative CH-O hydrogen bonding aligning the $(DA)_n$ chains in one direction and putative CH--N hydrogen bonding ordering the $(DA)_n$ chains in the orthogonal direction as illustrated in Figure 3. We further speculate that the conjectured H-bonding in the (PDO)TCNE crystal may be either a cause or consequence of the change from ladder to chain

DA array stoichiometry in this crystal structure. Close CH--O or CH--N contacts are not found in the related crystalline DA arrays of (TMPDO)$_2$TCNE or (DMQDO)$_2$TCNE.

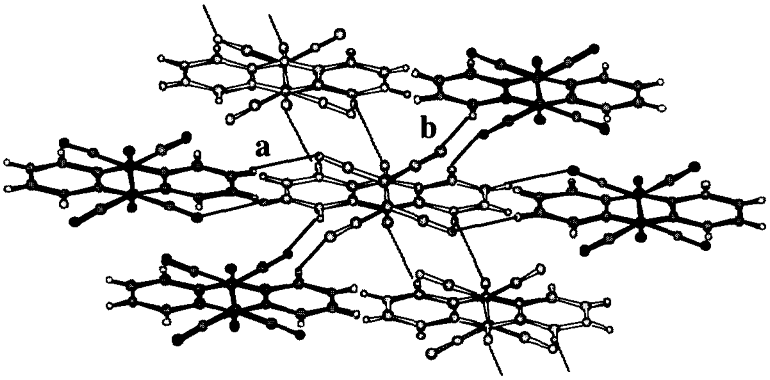

**Figure 3.** The (PDO)TCNE crystal lattice viewed along the (DA)n strand axis showing CH--O contacts between (lightened) strands with CH--O = 2.444(1) Å, C(H)--O = 3.139(1) Å, and CH--O = 120.9(1)° and CH--N contacts (darkened) between PDO and TCNE molecules with (a) CH--N = 2.402(1) Å, C(H)--N = 3.456(2) Å, and CH--N = 164.9(1)° and (b) CH--N = 2.500(1) Å, C(H)--N = 3.4829(2) Å, and CH--N = 150.8(1)°.[15]

The above DA arrays assemble in the crystals as a consequence of rather localized DA bonding between azaaromatic-N-oxides and TCNE, which affords one-dimensional control of the crystal structure. The nature of these weak DA "bonds" is postulated to be both electrostatic and covalent as judged by the strongly dipolar nature of the components, the 2.8 Å distance, the observed interaction topology, and the calculated O--C overlap population (0.016) determined by a single point 6-31G* RHF calculation.[16] These results help establish the azaaromatic-N-oxide/TCNE array as a new and viable crystal engineering synthon.

**Acknowledgments:** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support of this work. We also thank Prof. R. D. Rogers and L. Rogers for assistance with X-ray crystallography.

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2. Some reviews include: 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; Ch 8; d) Herbstein, F. H. *Persp. Struct. Chem.* **1971**, *4*, 166.
3. For earlier work see a) Blackstock, S. C.; Poehling, K.; Greer, M. L. *J. Am. Chem. Soc.* **1995**, *117*, 6617; b) Greer, M. L.; Blackstock, S. C. *J. Org. Chem.* **1996**, *61*, 7895.
4. Greer, M. L.; McGee, B. J.; Rogers, R. D.; Blackstock, S. C. *Angew. Chem., Int. Ed. Engl.*, in press.
5. DMQDO (0.55 g, 90 %) was prepared by treatment of 0.50 g 2,3-dimethylquinoxaline (Aldrich) in 50 ml of $CH_2Cl_2$ with 1.53

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g of mCPBA (75%) (2.1 molar equiv) and purified by recrystallization from methanol.

6. Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
7. Benesi-Hildebrand conditions of [DMQDO] = 2.42 mM and [TCNE] = 24.6, 40.2, 53.9, 68.7, and 96.9 mM in $CH_2Cl_2$ were used and absorbances at 500, 540, and 580 nm (with derived $\varepsilon$ values of 1655, 2140, and 1665 $M^{-1}cm^{-1}$, respectively) were monitored to calculate $K_f$, assuming 1:1 complexation.
8. Crystal data: $C_{13}H_{10}N_4O_2$, monoclinic, $a$ = 7.3041(5), $b$ = 10.0917(7), $c$ = 16.2913(10) Å, $\alpha$ = 90, $\beta$ = 96.626(2), $\gamma$ = 90 °, $V$ = 1192.82(14) $Å^3$, space group $P2_1/c$, $Z$ = 4, $D_{calc}$ = 1.329 g/cm$^3$, F(000) = 492, $\mu$(Mo-K$\alpha$) = 0.094 mm$^{-1}$. A total of 7211 data ($\theta_{max}$ = 27.88 °) were collected at 173 K on a Siemens diffractometer equipped with a CCD area detector and graphite-monochromated (Mo-K$\alpha$) radiation ($\lambda$ = 0.71073 Å). Merging gave 2760 unique reflections ($R_{int}$ = 0.0535), of which 2760 had I > 2$\sigma$(I). The structure was solved by direct methods and refined on $F^2$ with the non-H atoms allowed anisotropic thermal motion. Hydrogen atoms were found and refined isotropically. At final convergence $R_1$ = 0.0618 and $wR_2$ = 0.1258 for 213 refined parameters, g.o.f. on $F^2$ = 1.028.
9. 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.
10. PDO (1.71 g, 70 %) was prepared by treatment of 2.01 g phenazine (Aldrich) in 35 ml of $CH_2Cl_2$ with 6.40 g mCPBA (75%) (2.5 molar equiv) and was purified by recrystallization from $CH_2Cl_2$.
11. Benesi-Hildebrand conditions of [PDO] = 2.07 mM and [TCNE] = 31.2, 57.0, 69.5, 86.3, and 91.9 mM in $CH_2Cl_2$ were used and absorbances at 560, 586, and 610 nm (with derived $\varepsilon$ values of 3858, 5716, and 5814 $M^{-1}cm^{-1}$, respectively) were monitored to calculate $K_f$, assuming 1:1 complexation.
12. Crystal data: $C_9H_4N_3O$, triclinic, $a$ = 6.64650(10), $b$ = 7.5710(2), $c$ = 7.8963(3) Å, $\alpha$ = 88.454(2), $\beta$ = 81.7500(10), $\gamma$ = 87.0510(10) °, $V$ = 392.64 (2) $Å^3$, space group P-1, $Z$ = 2, $D_{calc}$ = 1.439 g/cm$^3$, F(000) = 174, $\mu$(Mo-K$\alpha$) = 0.100 mm$^{-1}$. A total of 2475 data ($\theta_{max}$ = 27.84°) were collected at 173 K on a Siemens diffractometer equipped with a CCD area detector and graphite-monochromated (Mo-K$\alpha$) radiation ($\lambda$ = 0.71073 Å). Merging gave 1730 unique reflections ($R_{int}$ = 0.0159), of which 1728 had I > 2$\sigma$(I). The structure was solved by direct methods and refined on $F^2$ with the non-H atoms allowed anisotropic thermal motion. Hydrogen atoms were initially placed in geometrically calculated positions and thereafter allowed to ride on their parent C atoms with $U_{iso}$(H) = 1.2 $U_{eq}$(C). At final convergence $R_1$ = 0.0397 and $wR_2$ = 0.1137 for 119 refined parameters, g.o.f. on $F^2$ = 1.038.

13 For recent reviews of CH--O hydrogen bonding see a) Steiner, T. *Chem. Commun.* **1997**, 727; b) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441.

14. We have observed similar CH--O close contacts for pyridine-N-oxides in the solid state which appear to greatly influence the crystal packing for this azaaromatic-N-oxide function (Bodige, S. G.; Rogers, R. D.; Blackstock, S. C. *J. Chem. Soc., Chem. Commun.*, in press). In addition, similar close associations are found for pyrazine-N,N′-dioxides (manuscript in preparation).
15. CH--O and CH--N geometric data uses normalized CH bond lengths of 1.08 Å.
16. The crystal structure $(DMQDO)_2TCNE$ complex geometry was calculated using the Gaussian 94 Program from Gaussian, Inc., Pittsburgh, PA, 1995 was used. This Mulliken overlap density is comparable in magnitude to that calculated for weak hydrogen bonds.

(*Received in USA* 20 *May* 1997; *revised* 30 *July* 1997; *accepted* 28 *August* 1997)