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Pericyclic Arrays in the Solid State. Azooxide and Azodioxide Donor−Acceptor Complexes with Tetracyanoethylene

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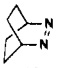
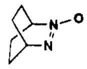
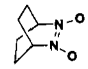
Noncovalent interactions between molecules control how molecules recognize each other[1] and are fundamentally important in many areas of chemistry, including enzyme−substrate binding, biochemical signaling, and switching mechanisms for synthetic molecular devices. Intermolecular "forces" also affect molecular ordering in condensed phases. One class of noncovalent molecular interaction which is largely electrostatic-based is the electron donor−acceptor (DA) interaction.[2] How donors and acceptors interact is relevant not only to the structure and energetics of a large class of molecular complexes but also to understanding mechanistically bimolecular reactions between electrophiles and nucleophiles.[3] We report here on the nature of some DA complexes between tetracyanoethylene (TCNE) and two donors, an azoalkane *N*-oxide and an azoalkane *N,N'*-dioxide. These substrates form cyclic DA complexes in the solid state which we suggest may be viewed as "aromatic" pericyclic arrays.

It is known that azoalkanes complex strong acceptors, and in the case of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), a 2:1 DA complex has previously been isolated with TCNE as the acceptor.[4] This complex is a DBO sandwich of TCNE in which the azo nitrogen lone pair orbitals point at the π C−C bond of TCNE, with one donor positioned on each face of the acceptor π-system.[5] We were intrigued by the apparent "local" electronic interactions in this complex. The DBO··TCNE orientation suggests that the DA association could be described in terms of $\sigma 4_s$ (donor) + $\pi 2_s$ (acceptor) orbital overlap,[6,7] and we wondered how important such "pericyclic" interactions are to the geometry of the complex. To probe this question, we have investigated how oxygenated azo donors interact with TCNE. Here, we present our findings of the DBO-oxide and DBO-dioxide interactions with TCNE.[8]


DBO


DBO-oxide


DBO-dioxide

Electrochemical analysis of DBO-oxide shows no anodic peak <2.0 V vs SCE by cyclic voltammetry in CH$_3$CN. Despite the thermodynamic difficulty with which DBO-oxide is oxidized, it forms a DA complex (orange, λ_m = 330 nm, K_f = 1.3 M^{-1} in CH$_3$CN)[9] when mixed in solution with TCNE (Figure 1a). Furthermore, slow cooling of 1:1 solutions of DBO-oxide and TCNE in ethyl acetate affords selective crystallization of an orange solid which proves to be a 2:1 complex of DBO-oxide with TCNE. The X-ray crystal structure of the complex is shown in Figure 2.

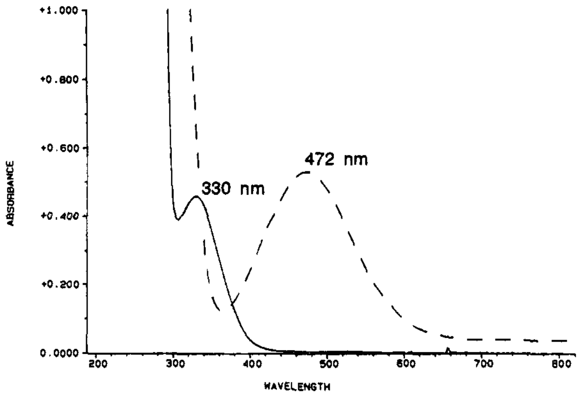


Figure 1. UV−vis spectrum in CH$_3$CN of (a, solid line) DBO-oxide (8.7 mM) and TCNE (0.27 M) and (b, dashed line) DBO-dioxide (14 mM) and TCNE (32 mM).

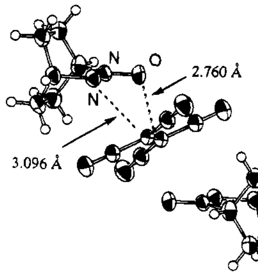


Figure 2. X-ray structure of (DBO-oxide)$_2$·TCNE complex. R = 0.036, R_w = 0.049.

The orange crystal consists of canted, π-stacked D$_2$A sandwiches in which intermolecular FMO interactions are apparent in the D··A··D assembly, just as observed earlier in the (DBO)$_2$·TCNE structure.[4] The observed intermolecular topology of the complex is that which is most "bonding" according to a Woodward−Hoffmann,[10] Dewar−Zimmerman,[11] or Fukui[12] analysis of the substrate π-interactions and contains what could be described as an "aromatic" $\pi 4_s + \pi 2_s$ DA array. Of course, the D··A··D assembly of Figure 2 is actually a termolecular rather than a bimolecular complex and is thus perhaps more accurately characterized as a net Hückel pericyclic array of $\pi 4_s + \pi 2_s + \pi 4_s$ components.[13] However, as in fused aromatic molecules such as naphthalene, we expect that the local 6-electron Hückel cycles will be more energetically important to the complex than the perimeter 10-electron array (vide infra).[14] Azomonooxides such as DBO-oxide are, in fact, 1,3-

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(1) For a recent review, see: *Molecular Recognition: Chemical and Biochemical Problems II*; Roberts, S. M., Ed.; Royal Society of Chemistry: Cambridge, 1992; and references therein.

(2) For some reviews, see: (a) Foster, R. *Organic Charge-Transfer Complexes*; Academic: New York, 1969. (b) Foster, R., Ed. *Organic Molecular Association*; Academic: New York, 1975 and 1979; Vols. 1 and 2, and references therein.

(3) For examples, see: (a) Kochi, J. K. *Acc. Chem. Res.* **1992**, *25*, 39. (b) Kochi, J. K. *Chimia* **1991**, *45*, 277.

(4) Blackstock, S. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2484.

(5) For discussions of other organic DA crystalline solids, see ref 2a, p 216, and Herbstein, F. H. *Persp. Struct. Chem.* **1971**, *4*, 166.

(6) Here, adjacent filled lone pair orbitals of the azoalkane are referred to as σ-components because these orbitals are hybrid orbitals with substantial *s* character, even though the lone pair−lone pair interaction is π-like in nature.

(7) We note that this sort of orbital analysis is consistent with Mulliken's original "whole-complex MO" treatment of donor−acceptor complexes. For a summary and references to earlier work, see: Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.

(8) Both DBO-oxide (ref a) and DBO-dioxide (ref b,c) are known. We synthesized these substrates by DBO oxygenation using oxone (ref d). (a) Bandurco, V. T.; Snyder, J. P. *Tetrahedron Lett.* **1969**, 4643. (b) Snyder, J. P.; Heyman, M. L.; Suciu, E. N. *J. Org. Chem.* **1975**, *40*, 1395. (c) Singh, P. *J. Org. Chem.* **1975**, *40*, 1405. (d) Greer, M. L.; Sarker, H.; Mendicino, M. E.; Craft, W. D.; Blackstock, S. C. *J. Am. Chem. Soc.*, submitted for publication.

(9) Formation constants were determined by UV−vis spectroscopy according to the Benesi−Hildebrand method: Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. See also: Tamres, M.; Strong, R. L. *Mol. Assoc.* **1979**, *2*, 340.

(10) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, and Academic Press: New York, 1970.

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

(12) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57.

(13) The central $\pi 2$ component is interacting from both faces of its π-system but is labeled $\pi 2_s$ because it interacts only suprafacially with each of the other π-systems in the complex.

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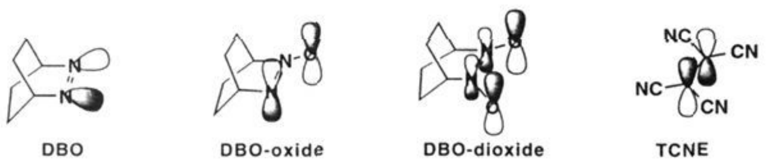

Figure 3. HOMOs for azo, azooxide, and azodioxide molecular series and LUMO for TCNE.

dipoles but do not undergo dipolar cycloaddition reactions, presumably because the thermodynamics for such are unfavorable.[15] The chemical inertness of DBO-oxide as a 1,3-dipole is, of course, what allows isolation of the reactant complex. In essence, then, we gain a glimpse of a 1,3-dipole/TCNE interaction along the reaction coordinate of a "would-be" dipolar cycloaddition reaction.[16,17]

Next, we turn our attention to the anticipated DBO-dioxide interaction with TCNE. Because pericyclic FMO interactions appear to be prominent in the D···A···D geometries of DBO and DBO-oxide complexes with TCNE, it might be expected that they will be a factor in the DBO-dioxide/TCNE complexation as well. Figure 3 shows the HOMOs of DBO, DBO-oxide, and DBO-dioxide along with the LUMO of TCNE. Both DBO and DBO-oxide HOMOs possess appropriate symmetry for constructive suprafacial overlap with the LUMO of TCNE—all orbitals have out-of-phase p-lobes at their termini. However, the DBO-dioxide HOMO has in-phase p-orbitals at its terminal O atoms and thus is of the wrong symmetry for suprafacial interaction (π-stacking) with TCNE. This change in HOMO symmetry for DBO-dioxide heightened our interest in this donor as a good test case to establish the extent to which orbital symmetry really influences the noncovalent interactions between these donors and TCNE.

Greene and Gilbert[18] first showed that *cis*-azodioxides form DA complexes with TCNE in solution. We find that DBO-dioxide ($E^{\circ\prime} = 1.65$ V vs SCE)[6d] and TCNE give a colored solution upon mixing in CH_3CN and that a weak DA complex (red, $\lambda_m = 472$ nm, $K_f = 0.4\ M^{-1}$)[9] forms (Figure 1b). Cooling concentrated 1:1 mixtures of DBO-dioxide/TCNE in CH_2Cl_2 affords deep red crystals of the DA complex.[19] The X-ray diffraction structure of a single crystal is shown in Figure 4.[20]

There is a change in the topology of the DA interaction for (DBO-dioxide)$_2$·TCNE from that found in the monooxide series. While a D_2A assembly is again obtained in the solid state, π-stacking is not observed in the dioxide·TCNE complex. Instead, the dioxide component appears to interact antarafacially with the TCNE C=C bond (which interacts suprafacially), consistent with the pericyclic array prediction of the structure. Thus, if viewed as a precycloaddition complex, the (DBO-dioxide)$_2$·TCNE structure gives a "snapshot" along the reaction path of a would-be $\pi 6_a + \pi 2_s$ cycloaddition. More precisely, the complete D···A···D structure consists of two fused $\pi 6_a + \pi 2_s$ Möbius arrays, yielding a net Hückel cycle of $\pi 6_a + \pi 2_s + \pi 6_a$ components. It is noteworthy that the perimeter Hückel cycle of 14 electrons could be achieved by either a $\pi 6_a + \pi 2_s + \pi 6_a$ array or a $\pi 6_s + \pi 2_s + \pi 6_s$ array, but only the former is observed, presumably because the latter would possess disfavored antiaromatic 8-electron Hückel arrays in the important smaller internal closed loops.

We have tried to revive these "dead" cycloaddition reactions of DBO-oxide and DBO-dioxide with TCNE by photo charge-transfer (CT) excitation of the DA complexes in solution and in the solid state. The radical ion pair formed upon photolysis might possess enough internal energy for exothermic adduct formation at low temperature, conditions under which the adducts might survive. However, no detectable photo CT chemistry of these complexes has yet been observed, possibly because back electron transfer within the contact ion pair excited state (or ion pair dissociation) may be much faster than ion pair reaction.

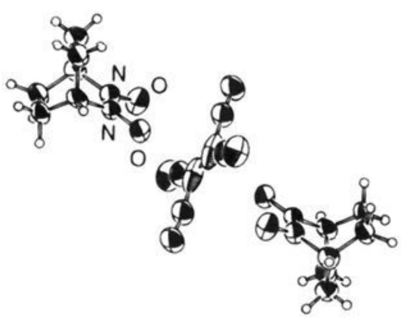

Figure 4. X-ray structure of (DBO-dioxide)$_2$·TCNE complex. $R = 0.067$, $R_w = 0.082$.

In summary, we find that the *N*-oxide and *N,N'*-dioxide of DBO associate with TCNE in solution and in the solid state. Crystalline complexes are isolable and amenable to X-ray diffraction analysis. These solid state complexes show 2:1 D···A···D sandwich structures in which the topology of the D···A···D interaction is effectively described as a pericyclic array, with local D···A cycles apparently influencing the geometry of the noncovalent interactions in the solid state. The *degree* to which the pericyclic arrays found here actually *control* the preferred DA geometry in the solid state is not known. At least for this series of structures, we can conclude that the pericyclic analysis is sufficient to predict the observed topology of cyclic DA interaction, and the concept of "aromatic complexation" appears useful.[21] Future experiments to investigate the interaction of bifunctional azooxide and azodioxide donors with TCNE are planned to determine if the local noncovalent forces found in this series of DA solids can be used to propagate oriented ···A·D—D·A·D—D··· chains in the crystalline state and to probe the utility of the pericyclic array as a tool in crystal engineering.

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Supplementary Material Available: X-ray diffraction crystal data summary, tables of fractional coordinates and thermal parameters (5 pages). This material is contained in many libraries on microfiche, immediately follows the article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(14) (a) Hess, B. A., Jr.; Schaad, L. J.; Agranat, I. *J. Am. Chem. Soc.* **1978**, *100*, 5268. (b) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444.

(15) For a review of azooxide 1,3-dipolar addition chemistry, see: Storr, R. C. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley, 1984; Vol. *2*, Chapter 10, p 162.

(16) The D and A components are located just within van der Waals contact distances, which according to Bondi are 3.22 and 3.25 Å for C···O and C···N, respectively. Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(17) For examples of the application of solid state structures to the modeling of reaction dynamics, see: Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153 and references therein.

(18) Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409.

(19) In fact, two types of colored crystalline complexes are isolated: a lighter 2:1 DA solid and a darker 1:1 DA solid. Only the 2:1 structure is presented here, as it is most analogous to the D_2A solid structures of the DBO and DBO-oxide complexes. The 1:1 solid exhibits D···A interactions similar to those reported here but contains an additional bridging TCNE group which interacts laterally with one oxygen on each of two adjacent DBO-dioxide units. This structure will be reported elsewhere.

(20) The thermal ellipsoids for the TCNE central C atoms suggest the presence of some in-plane disorder in this part of the structure (or in-plane thermal motion of the TCNE) which we believe to be due to backward and forward rotation of the TCNE unit in order to achieve closer intermolecular C···O contacts and whose *average* is the vertical C—C bond shown in Figure 5 (with average C···O contacts of 3.16 Å). While this disorder lowers the resolution of the structural data for this complex, it does not affect conclusions based on the topology of the donor and acceptor interaction.

(21) How applicable this paradigm will be for describing the cyclic DA interactions of other functional groups and how this effect compares in magnitude to dipolar, steric, and closest packing factors are important questions which remain to be answered.