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Structure and Stability of an Azoalkane−Iodine Complex

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Halogen complexes of aromatic hydrocarbons,[1−3] olefins,[4−6] amines,[7,8] and other donors[9,10] have been known for many decades, but charge-transfer (CT) complexes of azoalkanes were discovered more recently.[11] In the course of investigating the oxidation of 1,2-dialkylhydrazines by halogens, we found that azoalkanes also form CT complexes with halogens, which are $x\sigma$-type acceptors.[12] While earlier workers[11] had mentioned the color change that occurred on mixing of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) with iodine, we were able to isolate a single crystal of this complex and determine its X-ray structure. Hydrazine also forms complexes with halogens;[13] hence, the halogen oxidation of hydrazines to azoalkanes may be complicated by both hydrazine and azo CT complexes.

Mixing a heptane solution of I_2 (4.88×10^{-5} M) with one of DBO (0.00775−0.0493 M) gave immediate rise to a light yellow color caused by a weak band at 424 nm and to a stronger band at 266 nm, both attributed to the CT complex (cf. Figure 1).[14,15] The longer wavelength of the of DBO−I_2 CT band (266 nm) than of the analogous pyridine−I_2 band (236 nm)[16] is in the direction expected from the lower IP of DBO (8.19 eV)[17] than pyridine (9.26 eV).[18] We determined the absorbance of the 266 nm band at 25 °C as a function of DBO concentration with DBO in 100-fold excess and used the Scott equation (7 points, $r = 0.9998$)[19] to calculate the extinction coefficient and the equilibrium constant. The value of ϵ (18 500) is similar to that of aliphatic amine−I_2 complexes ($\epsilon \sim 25\,000$)[20] but is smaller than that of pyridine−I_2 ($\epsilon = 51\,700$).[16] Our ϵ cannot be compared with that of previously known DBO CT complexes because no short-wavelength band was reported.[11] The extinction coefficient of our 424 nm band is ~2000, comparable to that of DBO−TCNE[11] and to the 422 nm band of pyridine−I_2.[16] The observed value of K (153 M^{-1}) is far larger than that of other known DBO complexes: TCNE (1 M^{-1}), CBr_4 (5 M^{-1}), or $AgNO_3$ (1 M^{-1})[11] is smaller than the highly structure-dependent values for amines ($K = 530$−$12\,100$)[20] but is very similar to that of R_2S−I_2 [21] and pyridine−I_2 complexes.[16] This last result is in accord with the sp^2 hydridization of nitrogen in both cases but does not reflect the lower IP of DBO.[9]

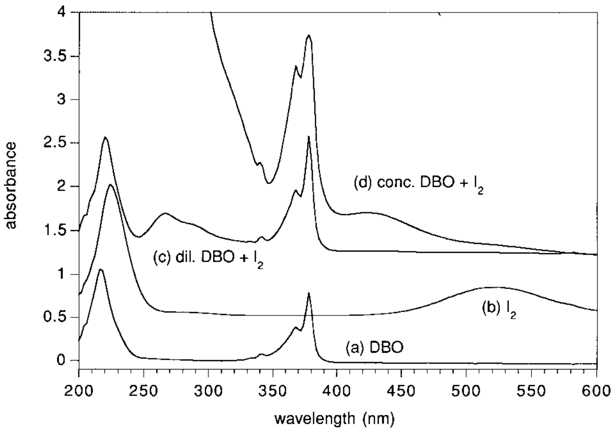

Figure 1. UV−vis absorption spectrum in *n*-heptane of (a) 0.00406 M DBO, (b) 4.11×10^{-4} M I_2, offset = +0.5, (c) 0.00775 M DBO + 4.88×10^{-5} M I_2, offset = +1.2, and (d) 0.0205 M DBO + 4.57×10^{-4} M I_2, offset = +1.2.

The enthalpy of complexation was calculated from the 266 nm absorbance of a sealed, degassed, and N_2 backfilled heptane solution of 0.0207 M DBO and 4.61×10^{-5} M I_2 in a quartz cuvette at four temperatures from 8.8 to 30.6 °C. A plot of ln K vs $1/T$ yielded $\Delta H = -6.2$ kcal/mol ($r = 0.9987$), which was combined with our K(25 °C) to yield $\Delta S = -11$ eu. These values are similar to those for I_2−ether complexes.[15]

A single crystal of the DBO−I_2 complex was grown by slow diffusion of ether into a MeCN solution of the components at −5 °C. Because the crystal was unstable to X-rays at room temperature, the data were acquired at −100 °C. The refined structure ($R = 0.0382$, cf. Figure 2) reveals that the geometry of the DBO moiety resembles that of DBO itself.[22] DBO is close to C_{2v} symmetry, as shown by the C_3−N_2−N_1−C_6 dihedral angle of 1.5° and the nearly eclipsed conformation (5.3° deviation) about the C_4−C_3 and C_7−C_8 bonds. Whereas the two C−N=

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(1) Hubig, S. M.; Jung, W.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 6233.

(2) Turner, D. E.; O'Malley, R. F.; Sardella, D. J.; Barinelli, L. S.; Kaul, P. *J. Org. Chem.* **1994**, *59*, 7335.

(3) Joens, J. A. *J. Org. Chem.* **1989**, *54*, 1126.

(4) Maier, G.; Senger, S. *Justus Liebigs Ann./Recueil* **1997**, 317.

(5) Brown, R. S.; Nagorski, R. W.; Bennet, A. J.; McClung, R. E. D.; Aarts, G. H. M.; Klobukowski, M.; McDonald, R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1994**, *116*, 2448.

(6) Bellucci, G.; Chiappe, C.; Bianchini, R.; Lenoir, D.; Herges, R. *J. Am. Chem. Soc.* **1995**, *117*, 12001.

(7) Hassel, O.; Romming, C. *Rev. Chem. Soc.* **1962**, *16*, 1.

(8) Blair, L. K.; Parris, K. D.; Hii, P. S.; Brook, C. P. *J. Am. Chem. Soc.* **1983**, *105*, 3649.

(9) Andrews, L. J.; Keefer, R. M. *Molecular Complexes in Organic Chemistry*; Holden Day: San Francisco, 1964.

(10) Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: London, 1969.

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

(12) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 801.

(13) Margerum, D. W.; Jia, Z.; Salaita, M.; Liu, R. M. In *Abstracts of the 213th ACS National Meeting,* San Francisco, CA, Apr 13, 1997; American Chemical Society: Washington, DC, 1997. paper no. 805. Liu, R. M.; Margerum, D. W. *Inorg. Chem.* **1998**, *37*, 2531.

(14) Tamres, M.; Brandon, M. *J. Am. Chem. Soc.* **1960**, *82*, 2134.

(15) Brandon, M.; Tamres, M.; Searles, S. *J. Am. Chem. Soc.* **1960**, *82*, 2129.

(16) Bist, H. D.; Person, W. B. *J. Phys. Chem.* **1967**, *71*, 2750.

(17) Engel, P. S.; Gerth, D. B.; Keys, D. E.; Scholz, J. N.; Houk, K. N.; Rozeboom, M. D.; Eaton, T. A.; Glass, R. S.; Broeker, J. L. *Tetrahedron* **1988**, *44*, 6811.

(18) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. *Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions*; Nat. Stand. Ref. Data Ser. Nat. Bur. Stand.: Washington, D.C., 1969; Vol. NSRDS-NBS 26.

(19) Scott, R. L. *Rec. Trav. Chim.* **1956**, *75*, 787.

(20) Yada, H.; Tanaka, J.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1660.

(21) Strom, E. T.; Orr, W. L.; Snowden, B. S.; Woessner, D. E. *J. Phys. Chem.* **1967**, *71*, 4017.

(22) Ottersen, T.; Romming, C.; Snyder, J. P. *Acta Chem. Scand. B* **1976**, *30*, 407.

S0022-3263(98)00265-5 CCC: $15.00

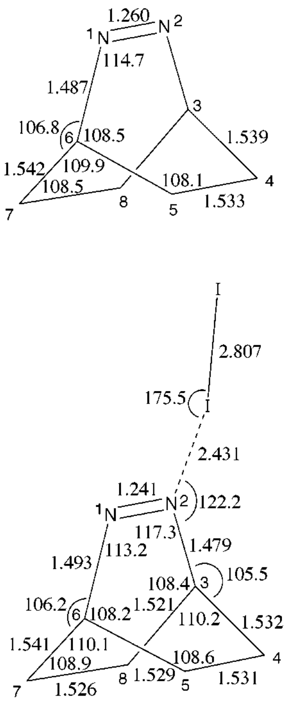

Figure 2. Structural comparison of DBO with its iodine complex. Bond lengths are in angstroms and bond angles are in degrees.

N angles in DBO are equal, those of the complex differ by 4°. Likewise, the C−N bonds of DBO are equal, but those of the complex are 1.479 and 1.493 Å. Thus, complexation with I_2 opens the C−N=N angle of the I_2-bound nitrogen, shortens its C−N bond, and also shortens the N=N bond from 1.260 Å in DBO to 1.241 Å in the complex. The skeletal distortion of DBO in the complex is probably due to its relatively high strength and to its asymmetry. In the earlier DBO complexes,[11] both nitrogens were associated with an acceptor moiety and the skeleton was not distorted.

The N−I and I−I distances of 2.431 and 2.807 Å may be compared with those of 4-picoline−I_2 (2.31 and 2.83 Å, respectively),[23] Me_3N-I_2 (2.27 and 2.83 Å, respectively),[24] and I_2 itself (2.715 Å).[25] The longer N−I and shorter I−I length in DBO−I_2 than the amine complexes is interesting but is probably unrelated to the value of *K*.[10] The other noteworthy aspects of the structure are the deviation from linearity of the N−I−I moiety and the alignment of the I−I bond with one nitrogen lone pair, indicating a σ complex or hypervalent iodine compound[8] rather than a π complex.

In view of the known electron-transfer photochemistry of azoalkanes,[26−29] it is not surprising that the DBO−I_2 complex is photolabile. This aspect of DBO−I_2, the role of complexes in the halogen oxidation of hydrazines, and the chemistry of other azoalkane−halogen complexes are currently under investigation in this laboratory.[30]

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Supporting Information Available: X-ray data for $C_6H_{10}N_2{\cdot}I_2$ (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(23) Hassel, O.; Romming, C.; Tufte, T. *Acta Chem. Scand.* **1961**, *15*, 967.

(24) Stromme, K. O. *Acta Chem. Scand.* **1959**, *13*, 268.

(25) Bolhuis, F. v.; Koster, P. B.; Migchelsen, T. *Acta Crystallogr.* **1967**, *23*, 90.

(26) Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964.

(27) Zona, T. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5879.

(28) Adam, W.; Sendelbach, J. *J. Org. Chem.* **1993**, *58*, 5316.

(29) Adam, W.; Moorthy, J. N.; Nau, W. M.; Scaiano, J. C. *J. Am. Chem. Soc.* **1997**, *119*, 6749.

(30) We find, for example, that DBO forms an isolable, light yellow bromine complex whose structure is very similar to that of the iodine complex.