trans, and "phantom", for which the "perpendicular" twisted geometry (Figure 1) is reasonable.[6]

In the simple HMO treatment of twisting about the central carbon–carbon bond, the energetics of this deformation of stilbene dianion and triplet are identical. While the shortcomings of HMO theory are well known, this does not alter the fact that similar twisting potentials for the two species are indicated. Indeed, the electronic structures of the two species are similar in such a way that virtually any MO theory is expected to yield qualitatively similar predictions for geometries of the two species.

On this basis, the two lines of evidence for twisting in the dianion and triplet are mutually reinforcing.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

[6] J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2515, 2516 (1963); see also G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964).

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Photoisomerization of the $B_{20}H_{18}^{-2}$ Ion

Sir:

Photoisomerization reactions are well known in the realm of organic chemistry, but no reactions of this type have yet been reported which involve the boron hydrides or their derivatives. We have recently observed the smooth photoisomerization of the $B_{20}H_{18}^{-2}$ (I) ion[1–3] and the reconversion of the photo-$B_{20}H_{18}^{-2}$ (II) to I.

Irradiation of acetonitrile solutions of bis(triethylammonium) I in Pyrex vessels with a mercury lamp resulted in the rapid loss of the characteristic yellow color of I. Removal of solvent followed by recrystallization from ethanol afforded bis(triethylammonium) II, mp 155–156, in 88% yield. *Anal.* Calcd for $[(C_2H_5)_3NH]_2B_{20}H_{18}$: B, 49.30; C, 32.84; H, 11.48; N, 6.39; equiv wt, 219.4; apparent mol wt, 146.3. Found: B, 49.35; C, 32.74; H, 11.71; N, 6.10; equiv wt, 224; apparent mol wt, 149 (osmotic, acetonitrile solution). The infrared spectrum of II salts contained an absorption band at 1750–1780 cm^{-1} which is characteristic of B–H–B bridge linkages. The 19.3-Mc/sec ^{11}B nmr spectrum of II contained a low-field doublet[4] (+3.3 ppm, J = 152 cps) and a broadened, less well-defined doublet at higher field (+27.0 ppm, J = 109 cps). Under identical conditions, completely deuterated II exhibited two singlets at +3.3 and +27.0 ppm.[4]

Solutions of II salts in acetonitrile were readily converted to the corresponding salts of I by thermal soaking at 100° for 36 hr. Yields of isolated I salts obtained by this procedure were of the order of 70–80%. Attempts to follow the rate of II to I conversion were thwarted by the formation of unidentified metastable intermediates which obscured the spectrophotometric analytical method.

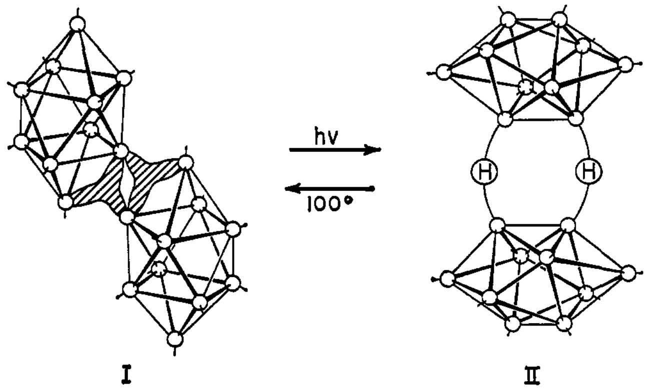

Figure 1. Structures of $B_{20}H_{18}^{-2}$ (I) and photo-$B_{20}H_{18}^{-2}$ (II).

Reduction of II with sodium in liquid ammonia resulted in a 98% yield of $B_{20}H_{18}^{-4}$ (e^2 isomer[5]). The reaction of II with aqueous hydroxide ion resulted in the consumption of 2 equiv of base per II ion and the formation of a previously undescribed[6] isomer (III) of $B_{20}H_{17}OH^{-4}$. *Anal.* Calcd for $K_4B_{20}H_{17}OH \cdot 3H_2O$: B, 46.94; H, 5.25; K, 33.93; H_2O, 11.72; equiv wt, 461. Found: B, 46.23; H, 5.70; K, 34.28; H_2O, 10.01; equiv wt, 453. Acid-catalyzed rearrangement[5,6] of III in aqueous solution resulted in the formation of a second previously unreported $B_{20}H_{17}OH^{-4}$ isomer.[7]

The ^{11}B nmr spectrum of II closely resembles that of a $B_{10}H_{10}^{-2}$ ion with nonequivalent equatorial positions and equivalent apical positions. The presence of B–H–B bridge linkages detected in the infrared spectrum of II and the requirement that the two B_{10} polyhedra be joined by a pair of three-center interactions suggests that II is composed of two B_{10} polyhedra joined by a pair of B–H–B bridge linkages at equatorial positions. This model for bonding in II could generate two isomers depending upon the equatorial positions selected for bridge bonding.[8] The preliminary results of a single-crystal X-ray diffraction study[9] of bisrubidium II has located the boron atom positions and confirmed the structure of II as that isomer which contains a mirror plane. Figure 1 indicates the remarkable rearrangement of I to II. The earlier suggestion[2] that a $B_{20}H_{18}^{-2}$ ion could be composed of two B_{10} polyhedra linked by a pair of hydrogen bridge bonds has thus been confirmed.

The mechanism of the photochemical transformation of I to II is not clearly indicated by evidence at hand although the inclusion of polyhedral rearrangement steps in the transformation of I to II and the corresponding retro-rearrangement reaction appears as a possibility.

The isolation of a second $B_{20}H_{18}^{-2}$ isomer lends additional support to the suggestion[6] that I is in equilibrium

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[1] A. Kaczmarczyk, R. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

[2] W. N. Lipscomb, *ibid*, **47**, 1791 (1961).

[3] R. L. Pilling, M. F., Hawthorne, and E. A. Pier, *J. Am. Chem. Soc.*, **86**, 3568 (1964).

[4] Chemical shifts measured in acetonitrile solution relative to boron trifluoride etherate (external standard).

[5] M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, *J. Am. Chem. Soc.*, **87**, 1893 (1965).

[6] M. F. Hawthorne, R. L. Pilling, and P. M. Garrett, *ibid.*, **87**, 4740 (1965).

[7] Satisfactory elemental analyses and characterization data were obtained.

[8] One isomer would have no mirror planes and no center of symmetry while the second isomer would contain a mirror plane between B_{10} polyhedra.

[9] The authors are greatly indebted to B. G. De Boer, A. Zalkin, and D. H. Templeton for communicating these results prior to publication.

with an isomeric ion which reacts much more rapidly with hydroxide ion than I itself.

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Acylation through a Sulfonium Ion Intermediate. Coupled Conversion of a Carboxylic Acid to an Acid Anhydride during Oxidation of a Thioether to a Sulfoxide[1]

Sir:

Earlier studies in our laboratory had suggested that oxidation of thioethers in the presence of aqueous phosphate buffer may be mediated by formation of an energetic phosphate bond.[2] The catalytic role has also been observed for a series of carboxylate species especially among those capable of forming a ring structure.[3] We wish to present direct evidence which strongly suggests that the energy derived from oxidation of alkyl sulfides to sulfoxide can drive such dicarboxylic acids to their more energetic anhydride form.

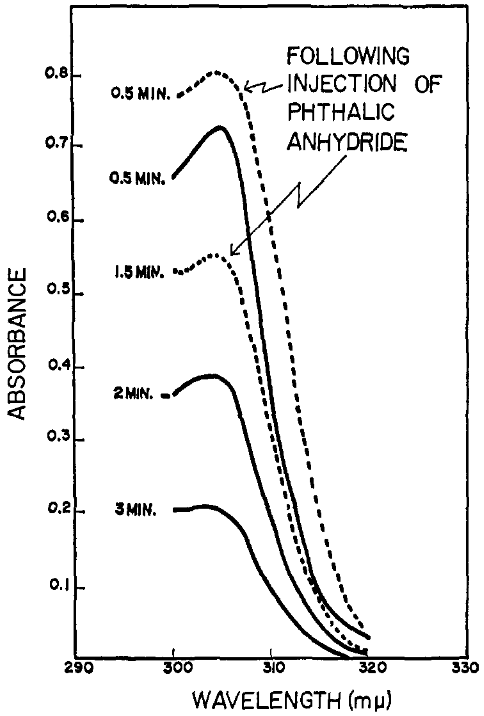
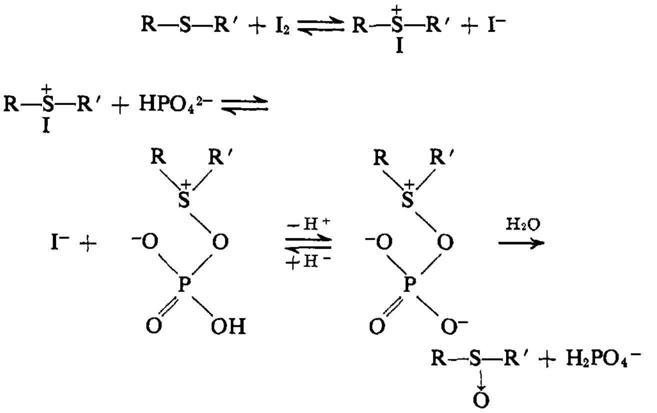


Figure 1. Comparison of spectra shown as solid lines obtained following injection of iodine into an aqueous solution of tetramethylene sulfide in phthalate buffer with spectra shown as dotted lines obtained by direct injection of a stoichiometrically equivalent amount of phthalic anhydride in dioxane into a comparable system. The change in spectra with time is assumed to be due to the hydrolysis of phthalic anhydride. In both instances the phthalate buffer concentration was 0.06 M at pH 5.1. Approximately 7 x 10^{-4} M iodine and phthalic anhydride were injected in the respective cases.

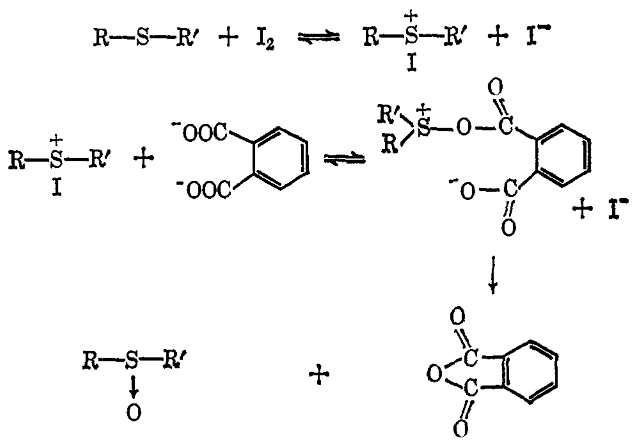


$$R{-}S{-}R' + I_2 \rightleftharpoons R{-}\overset{+}{\underset{I}{S}}{-}R' + I^-$$

$$R{-}\overset{+}{\underset{I}{S}}{-}R' + HPO_4^{2-} \rightleftharpoons$$

$$R{-}\underset{\underset{O}{\downarrow}}{S}{-}R' + H_2PO_4^-$$

Thioethers in the absence of catalytic species react exceedingly slowly with iodine. On addition of certain nucleophiles the reaction proceeds very rapidly, apparently involving intermediate formation of acylsulfonium species. Thus in the case where phthalate ion acts as the nucleophile we presume that it is driven to its anhydride through the following sequence.



$$R{-}S{-}R' + I_2 \rightleftharpoons R{-}\overset{+}{\underset{I}{S}}{-}R' + I^-$$

The evidence for formation of the anhydride is based on observation of appearance of a peak at 304 mμ characteristic of phthalic anhydride when tetramethylene sulfide was oxidized with iodine in the presence of 0.06 M phthalate buffer (pH 5.1). Although free iodine in the system may be expected to interfere with spectral measurements, the halogen reacts extremely rapidly under these conditions, being essentially all consumed in less than a second. In Figure 1 is shown the spectrum of the solution in the range 300–320 mμ 30 sec after disappearance of added iodine (7×10^{-4} M), after approximately 2 min, and after 3 min. In the same figure, spectra of only the phthalate buffer containing added sulfide are shown following injection of approximately stoichiometric equivalence of phthalic anhydride (in 40 μl of dioxane) at two time intervals. The general spectral agreement strongly supports the presumed formation of the anhydride.

The identity of the reactive species formed in phthalate buffer during the oxidation of the sulfide to sulfoxide is further supported by the observed hydrolytic rate of the absorbing substance. Spectrophotometric kinetic measurements on these systems following oxida-

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[1] This work was supported in part by grants from the National Institutes of Health (GM-05830 and AM-03437).

[2] T. Higuchi and K.-H. Gensch, unpublished work.

[3] T. Higuchi and K.-H. Gensch, in preparation.