tions are effected with insufficient base, are larger than experienced when the decompositions are effected in aprotic environments. It thus appears that minor cationic processes (eq 1) give bicyclo[1.1.0]butanes without incorporation of external label.

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On Twisted Arylethylene Dianions and Triplets

Sir:

Twisted structures (Figure 1) have been proposed for arylethylene dianions.[1] Aside from theoretical considerations, the best evidence for this has been that anion radicals of sterically strained arylethylenes (tetraphenylethylene, triphenylethylene) tend to disproportionate *via* electron transfer to a much greater extent than stilbene.[2] Disproportionation (eq 1)

$$2R_2\dot{C}{-}\bar{C}R_2 \rightleftharpoons R_2\bar{C}{-}\bar{C}R_2 + R_2C{=}CR_2 \qquad (1)$$

would be accompanied by relief of steric strain for each of the former pair of anion radicals, but not for the latter, if the dianions could readily assume twisted geometries but the anion radicals were constrained to seek planarity.

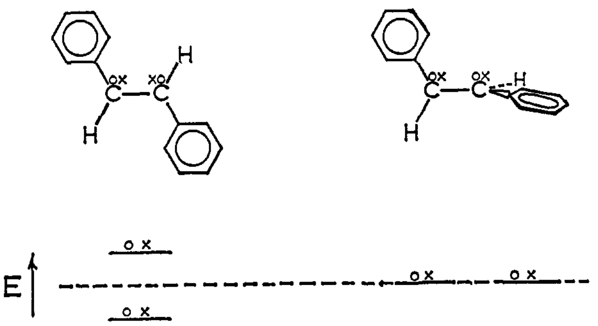

Figure 1. Partial HMO diagrams of stilbene triplets and dianions showing planar (left) and "perpendicular" (right) geometries. The circles represent electrons of the lowest energy π–π^* triplet state. The circles and x's together represent electrons of the corresponding dianion. Only the two highest energy occupied orbitals are shown. The remainder of the electrons are identically described for both the triplet and the dianion in this theory. Since the orbital diagram is symmetric about $E = \alpha$ (dashed line), the net contribution of the depicted electrons is zero for both the triplet and the dianion at all angles of twist about the central carbon–carbon bond. Thus, identical twisting potentials are predicted by HMO theory for the two species.

Since there is another reasonable and obvious explanation for the same trend, the evidence cited above is ambiguous. The alternative explanation is that electron–electron repulsions are relatively greater in the stilbene dianion than in those of tri- and tetraphenylethylene even if these are all planar.[1a,3]

This ambiguity is not present in considerations of the data presented here.

A comparison of the disproportionation tendencies of stilbene and α-methylstilbene anion radicals shows that the latter are much more prone to disproportionate than the former. Representative data, together with some for tri- and tetraphenylethylene anion radicals, are presented in Table I.[4]

Table I. Disproportionation of Sodium Arylethylenes in 2-Methyltetrahydrofuran at 25°

Hydrocarbon	K^a
α-Methylstilbene	$\geqslant 1000$
Stilbene	0.09
Triphenylethylene	36
Tetraphenylethylene	$\geqslant 1000$

[a] K is the equilibrium constant for disproportionation of ion pairs to give a netural triple ion. The concentrations of ionic species ranged from *ca.* 10^{-5} to *ca.* 10^{-3} M. K is concentration independent through this range.

The effect of methyl substitution of stilbene is large. It is in the opposite direction from that which might be expected if a steric effect on the magnitude of the Coulombic interactions in the ionic aggregates were the important factor, since the dianion should be more sensitive to this kind of strain than the anion radical. It is difficult to view the large effect of methyl substitution as other than a steric effect reflecting a change in geometry accompanying disproportionation.[5]

Occasionally data from two different and independent areas of study are interrelated in such a way that each problem bears on the other. Such is the case for the problems of the geometries of arylethylene triplet states and the corresponding dianions.

Hammond and Saltiel were forced to postulate nonvertical energy transfer to *cis*-stilbene. They proposed the possibility that three varieties of the lowest lying π–π^* triplet state of stilbene are metastable: *cis*,

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(1) (a) N. S. Hush and J. Blackledge, *J. Chem. Phys.* **23**, 514 (1955); (b) M. J. S. Dewar and P. Gray, Special Publication No. 12, The Chemical Society, London, 1958, pp 164–166; (c) J. F. Garst, E. R. Zabolotny, and R. S. Cole, *J. Am. Chem. Soc.*, **86**, 2257 (1964); (d) R. C. Roberts and M. Szwarc, *ibid.*, **87**, 5542 (1965).

(2) E. R. Zabolotny and J. F. Garst, *ibid.*, **86**, 1645 (1964).

(3) Steric interactions would prevent complete planarity in the strained systems, but the calculations of ref 1a presume planarity.

(4) Data are presented for sodium counterion and 2-methyltetrahydrofuran solvent because under these conditions the formal equilibrium constant, K_F, for disproportionation is very nearly concentration independent in the range about 10^{-4} M for the systems for which it is measureable. K_F is computed from the concentrations of species measured without regard to state of ionic aggregation. The lack of concentration dependence of K_F indicates negligible dissociation of ion pairs, a factor which cannot be ignored in the more polar ethers (tetrahydrofuran and 1,2-dimethoxyethane).[1c,d] Under the experimental conditions of this report, the directly measured K_F can be taken as the equilibrium constant for the disproportionation of ion-pair anion radicals to give neutral triple ion dianion species. The same trend with hydrocarbon structure that is reported here is also observed for other counterion–solvent combinations.

The experimental methods employed here were the same as previously reported. The visible spectra of α-methylstilbene ions are nearly identical with those of the stilbene ions.[1c]

(5) The "twisting" discussed here is, of course, only one of several possible modes of change in geometry.

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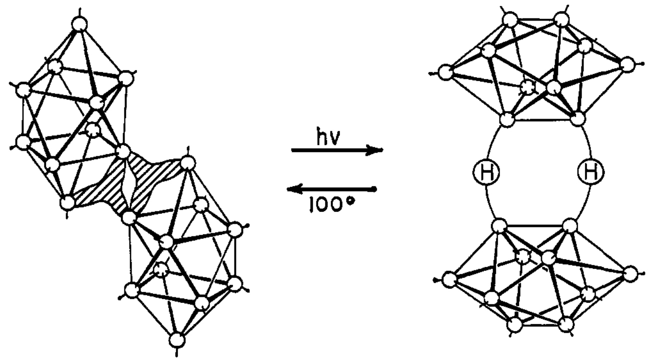
Photoisomerization of the $B_{20}H_{18}^{-2}$ Ion

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.



I

II

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.