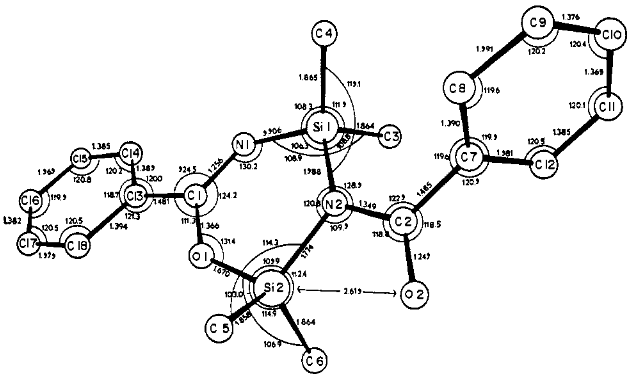

Figure 2. The molecular structure of cyclobis(benzamidodimethylsilane) with bond distances and angles indicated. Typical standard errors, as computed from the variance–covariance matrix, are ±0.003 Å for Si–N, Si–C, and Si–O distances; ±0.006 Å for C–C, C–N, and C–O distances; and ±0.3° for the angles.

distances ranging between 2.116 and 2.344 Å found in caged pentacoordinate silicon compounds.[3] The C(5)–Si(2)–C(6), C(5)–Si(2)–N(2), and C(6)–Si(2)–N(2) angles are seen to have opened considerably from the tetrahedral values, presumably to provide room for the Si···O interaction. The bond angles at N(2) have also distorted in a manner that permits O(2) to approach C(2): the Si(2)–N(2)–C(2) angle has closed down to 109.7°, while Si(1)–N(2)–C(2) has opened up to 128.3°. On the other hand no evidence can be found for a transannular Si(2)···N(1) interaction; this distance is 3.187 Å. The disilaoxadiazine heterocycle is nearly planar with a maximum deviation of 0.13 Å from the least-squares plane.

Some other features of the structure are worth noting. The C(1)–N(1) distance of 1.256 Å shows that these two atoms are in fact doubly bonded.[1] The exocyclic C(2)–N(2) bond length of 1.349 Å and the C(2)-O(2) distance of 1.247 Å are close to the corresponding values in benzamide[4] (1.31 and 1.24 Å). The geometry at Si(1) is more nearly tetrahedral, and the other bond distances and angles in the system are in excellent agreement with literature values.

The incipiently pentacoordinate structure found for I suggests that the lower energy tautomerization governed by r_1 may proceed through the eight-membered cyclic intermediates E and G (Figure 1) *via* carbonyl attack at Si(2)[5] and cleavage of the Si(2)–N(2) bond. The higher temperature r_2 process could then result from an alternative attack by oxygen at Si(1) yielding a different pair of eight-membered cyclic intermediates, F and H. We note that this mechanism differs formally from that postulated by Klebe[1] in that the r_2 process exchanges tautomers A ↔ D and B ↔ C instead of A ↔ C and B ↔ D. The r_1 process may occur at lower energy because the greater inductive ability of oxygen (*vs.* nitrogen) predisposes Si(2) to accept an electron pair However, the rotation barrier[6] about the amidic C(2)–N(2) bond may play a role in limiting the rate of the r_2 process since the carbonyl group must be rotated from a position near Si(2) (structures A–D) to one near Si(1) (structures A′–D′). The mechanism proposed here has the advantage of not requiring hexacoordinate transition states and is consistent with the known ability of eight-membered rings, such as cyclooctatetraenes[7] and diazocines,[8] to undergo transannular rearrangements.

Acknowledgment. We thank James Gaidis and John Flynn for their kind assistance with the experimental work and are grateful to Francis Johnson for helpful discussions.

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(3) J. W. Turley and F. P. Boer, *J. Am. Chem. Soc.*, 90, 4026 (1968); F. P. Boer, J. W. Turley, and J. J. Flynn, *ibid.*, 90, 5102 (1968). Distances of 2.116 and 2.344 Å were found in *m*-nitrophenyl(2,2′,2″-nitrilotriethoxy)silane and in methyl(2,2′,3-nitrilodiethoxypropyl)silane, respectively (F. P. Boer and J. W. Turley, *ibid.*, in press).

(4) B. R. Penfold and J. C. B. White, *Acta Cryst.*, 12, 130 (1959).

(5) In this discussion Si(2) is defined as the silicon bonded directly to a nitrogen and an oxygen, and Si(1) is the atom bonded to two nitrogens.

(6) Rotation barriers in amides typically have free energies of 15–25 kcal: M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

(7) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 11 (1948).

(8) W. Metlesics and L. H. Sternbach, *J. Am. Chem. Soc.*, **88**, 1077 (1966).

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The Norbiphenylene Anion

Sir:

We wish to report evidence for the synthesis of the norbiphenylene anion (I) and the conversion of the latter to an unusual dimeric hydrocarbon on protonation. Anion I is particularly interesting in that it is isoelectronic with biphenylene, from which it differs structurally only by replacement of a benzene ring by a cyclopentadienide ring. Molecular orbital calculations predict a total π energy of 15.025β for this anion.[1]

The previously reported dicarboxylic acid II[2] was converted *via* the liquid diethyl ester III[3] to the crystalline dihydrazide IV, mp 251–252°. Reaction of IV with nitrous acid gave the diazide V, pyrolysis of which in benzyl alcohol yielded the benzylurethan VI, mp 145–146°. Hydrogenolysis of urethan VI gave the diamine VII, which was converted by formaldehyde and formic acid to the tertiary amine VIII, which in turn afforded the dimethiodide IX, mp 311–312°, on

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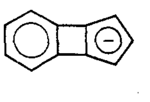
(1) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, N. Y., 1965.

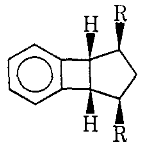
(2) H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

(3) All new compounds gave elemental analyses and spectral data in accord with the assigned structures.

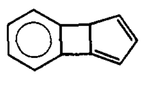
treatment with methyl iodide. Reaction of IX with potassium *t*-butoxide in *t*-butyl alcohol gave, after aqueous work-up, neither of the expected monomeric hydrocarbons X or XI, but rather a mixture of two crystalline dimers $C_{22}H_{16}$: dimer A, mp 132°, and dimer B, mp 201°. Whereas no color formation was observed during the *t*-butoxide elimination reaction of IX, a similar elimination reaction of IX using dimethyl sulfoxide anion in DMSO gave a stable deep brown solution (λ_{max} 590 mμ, shoulder at 500 mμ), the color of which we attribute to anion I. Addition of water to the brown solution caused immediate decolorization with the formation of dimers A and B; addition of D_2O led to the formation of dimers A and B, each containing two deuteriums.[4] In a control experiment, undeuterated dimer B was found not to give the brown anion with DMSO anion in DMSO and was recovered undeuterated after treatment with D_2O.



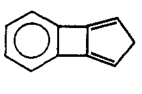
I



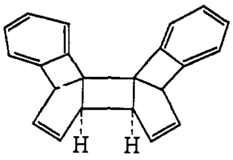
II, R = CO_2H
III, R = $CO_2C_2H_5$
IV, R = $CONHNH_2$
V, R = CON_3
VI, R = $NHCOOCH_2C_6H_5$
VII, R = NH_2
VIII, R = $N(CH_3)_2$
IX, R = $N(CH_3)_3I$



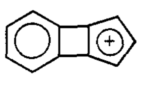
X



XI



XII



XIII

The above observations are consistent with the formation of the norbiphenylene anion (I) from IX by DMSO anion and its protonation by water at the predicted position of highest electron density[1] to give the highly strained, unstable monomer X. Cyclodimerization of X involving the strained central double bond could result in any of four possible dimers, all of which would have nmr spectra in general accord with those observed for dimers A and B. Such a dimeric structure was indeed determined by X-ray analysis for dimer B as explained below.

Dimer B crystallizes in the monoclinic system with unit cell parameters $a = 27.67 \pm 0.04$, $b = 6.015 \pm 0.009$, $c = 38.89 \pm 0.06$ Å, $\beta = 27.74 \pm 0.01°$. The observed and calculated densities ($Z = 8$) are 1.24 and 1.23 g/cc, respectively. Systematic absences are consistent with space groups I2/c and Ic. The intensities of 2187 independent data ($\theta_{Mo} \leqslant 22.5°$) were measured *via* the moving crystal–moving counter method with Mo Kα radiation on a Picker automatic four-circle diffractometer. The centrosymmetric space group was assumed to be the correct one, and iterative application of the Sayre equation[5] to the corrected intensities yielded the locations of all 22 carbon atoms. Preliminary isotropic least-squares refinement has yielded a crystallographic discrepancy factor, R_1, of 0.11.

The crystallographic results show dimer B to have the structure XII and to possess idealized C_s-m symmetry.

Work is in progress aimed toward the X-ray structure determination of dimer A and toward the generation of the ten-π-electron norbiphenylene cation XIII.[6]

Acknowledgment. Support of this work by the National Science Foundation (Grant GP-4931) and by the Petroleum Research Fund (PRF Grant 841-G), administered by the American Chemical Society, is gratefully acknowledged.

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[4] The two protons appearing at δ 4.48 in the undeuterated dimer B are completely absent in the nmr spectrum of the deuterated sample.

[5] D. Sayre, *Acta Cryst.*, **5**, 60 (1952); R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis (Part III), University of California at Los Angeles, 1965.

[6] R. Breslow, W. Washburn, and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 196 (1969), have very recently reported the detection of the cyclobutadienocyclopentadienyl anion, a species closely related to anion I. Protonation of the cyclobutadienocyclopentadienyl anion gave, *via* an unstable monomer, a material which was tentatively assigned the structure of a Diels–Alder dimer. However, subsequent work (private communication from Professor Breslow) shows that this was instead a difficultly separable mixture of two isomeric dimers formed by 2 + 2 cycloaddition of the strained double bond, as in our dimer XII.

[7] National Defense Education Act Fellow.

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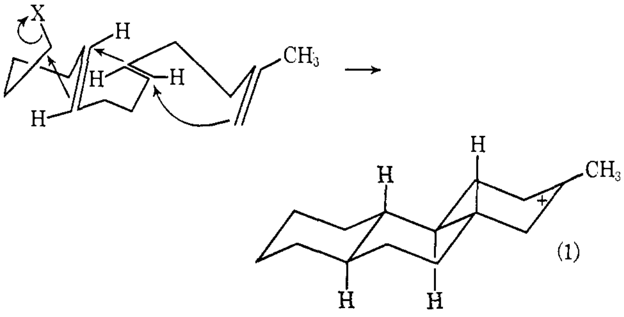
Nucleophilic Participation by a Carbon–Carbon Double Bond in an Intramolecular Analog to the SN2′ Displacement Reaction

Sir:

One rationale for the remarkable stereospecificity which attends the solvolytic cyclization of certain di- and trienyl sulfonate esters (*e.g.*, eq 1)[1] postulates that the cyclization is a concerted process in which *trans* addition occurs simultaneously at each double bond involved in the cyclization process.[1] If this mechanism were operative, it would necessitate nucleophilic attack by one carbon–carbon double bond upon another. The ability of carbon–carbon double bonds to function as nucleophiles in simple displacement reactions is now well established.[2] There is at present, however, little



(1)

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[1] A review: W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

[2] For a summary of leading references, see: (a) G. D. Sargent, N. Lowry, and S. D. Reich, *J. Am. Chem. Soc.*, **89**, 5985 (1967); (b) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *ibid.*, **89**, 880 (1967); (c) P. D. Bartlett, E. M. Nicholson, and R. Owyang, *Tetrahedron Suppl.*, **8**, Part II, 399 (1966), and previous papers in this series therein cited; (d) F. C. Uhle, *J. Org. Chem.*, 31, 4193 (1966), footnote 26; (e) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms 1966," Interscience Publishers, New York, N. Y., 1967, pp 24–31; (f) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms 1965," Interscience Publishers, New York, N. Y., 1966, pp 37–42; (g) B. Capon, *Quart. Rev.* (London), **18**, 45 (1964); (h) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; *Chem. Rev.*, **56**, 571 (1956).