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Molecular Rods: Synthesis and Properties[1]

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Our earlier synthetic methodology affording bicyclo[2.2.2]octyl [1]-rod and [2]-rod systems proved inadequate for [4]-rods. New synthetic approaches were developed, and [3]- and [4]-rod molecules were obtained. Sodium–potassium coupling was employed to afford the longer rod units. A radical anion approach gave lower yields. Hybrid rods with aromatic rings interposed were also synthesized. Rods of 9.2-, 9.7-, 13.4-, 13.9-, and 18.2-Å length were included in this study. Consideration of rod chirality suggests each bicyclooctane rod unit to be stereogenic, either *P* (clockwise) or *M* (anticlockwise). Thus, in a [1]-rod there are enantiomers and in a [2]-rod there are diastereomers. Molecular mechanics treatment of rod stereoisomerization was carried out. Interconversion of enantiomers of the [1]-rod and diastereomers of the [*n*]-rods should be very rapid at room temperature. X-ray analysis of the 4,4′-dimethoxy-[2]-rod reveals an achiral conformation. AM1 quantum mechanics computations were carried out on [*n*]-rod radical cations and bridgehead cations.

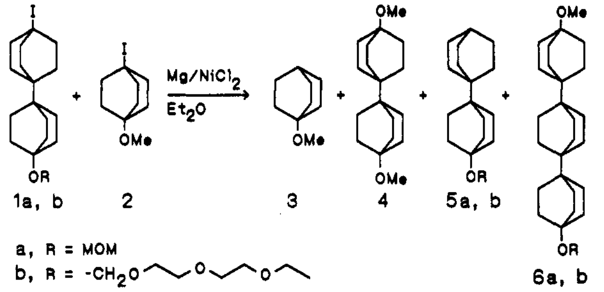
Introduction

Previously[2,3] we described the concept and synthesis of rodlike molecules composed of rigid, linear units. This was in connection with studies of excitation and electron transmission through such rodlike units as bicyclo[2.2.2]octane. In these studies we observed both singlet and triplet "through bond" energy transfer. The utility of this phenomenon was further demonstrated by Dervan and co-workers[4] who described singlet energy transfer through these molecular units.

The synthesis of longer rods was of specific interest in determining whether the observed excitation transfer was really "through bond" or "through space". Furthermore, the longer rods constitute a unique type of supermolecule. It was with these goals that the present research began.

Results

[3]-Rod Syntheses: Traditional and New Methodology. Our previous efforts resulting in the [2]-rod syntheses[3,5] utilized dimerization of iodo bridgehead substituted [1]-rod (i.e. bicyclo[2.2.2]octyl) units with magnesium and a nickel catalyst. We began with the reaction of 4-iodo-4′-(methoxymethoxy)-[2]-rod **1a** and 4-iodo-4-methoxy-[1]-rod **2** with magnesium and nickel chloride. The ether end group was designed to enhance solubility, a factor discussed in detail below. The reaction afforded a 6% yield of [3]-rod[3b] product **6a** after separation from the anticipated byproducts such as 4,4′-dimethoxy-[2]-rod **4**, 4-(methoxymethoxy)-[2]-rod **5a**, and 1-methoxy-[1]-rod **3**. The reaction is shown in eq 1.



(1)

An alternative approach was devised using sodium–potassium alloy (1:3) in dimethoxyethane (DME), and a protecting end group derived from diethylene glycol monoethyl ether was employed affording 4-methoxy-4″-(1,3,6,9-tetraoxaundecyl)-[3]-rod (**6b**) in 10% yield. This conversion is included in eq 1.

[4]-Rod Syntheses: New Methodology. In the synthesis of [4]-rods it was found that the traditional magnesium–nickel chloride approach, which had been successfully employed in the dimerization of 1-iodo-4-methoxy-[1]-rod, when applied to the dimerization of 4-iodo-4′-methoxy-[2]-rod, was unsuccessful. Instead of [4]-rod dimer, 4-methoxy-[2]-rod **7** resulted, presumably by hydrogen abstraction from solvent by the [2]-rod free radical (vide infra). Hence, new approaches were needed.

It was surmised that successful dimerization required high concentrations of combining bridgehead free radicals, and low solubilities were characteristic of the longer rod compounds. Additionally, it appeared that reaction on a metal surface favored dimerization over hydrogen abstraction. Finally, available evidence[6] suggested that lower temperatures enhanced dimerization relative to hydrogen abstraction in free radicals. The more reactive sodium–potassium alloy promised to permit the use of lower temperatures and also to provide a metal surface. The EOEOEOM ethers (i.e. 1,3,6,9-tetraoxaundecyl) seemed likely to have higher solubilities. The [2]-rod EOEOEOM ether was prepared as described in Scheme I. The product iodo EOEOEOM ether **1b** had a solubility in DME of 1.0 M versus 0.02 M for the corresponding methyl ether.

The dimerization of the 4-iodo-4′-EOEOEOMO-[2]-rod is outlined in Scheme II. The product mixture was directly hydrolyzed with acid to afford 78% of 4-hydroxy-[2]-rod **12** and 21% of 4,4‴-dihydroxy-[4]-rod **11a**. The [4]-rod product melted above 525 °C and was virtually insoluble in the common solvents. Nevertheless, mass spectral analysis revealed the most intense peak to be at 466 mass units, corresponding to the intact dihydroxy-[4]-rod ion. In addition, mass peaks were observed corresponding to the dehydroxylated parent [4]-rod ion, a

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[1] (a) This is paper 226 of our general series. (b) For Publication 225, see: Zimmerman, H. E. The Di-π-Methane Rearrangement. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York, 1991; Vol. 11.

[2] Zimmerman, H. E., McKelvey, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 3638–3645.

[3] (a) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933–3951. For more recent synthetic work, note ref 3b. (b) King, R. K. Ph.D. Thesis, University of Wisconsin–Madison, 1985.

[4] (a) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090. (b) Note also: Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571–5573 and related references.[4c] (c) Reference 4b utilizes our [1]- and [2]-rod spacers, syntheses, and the basic concept with citation only of ref 4a.

[5] The rod compounds are composed of bicyclo[2.2.2]octyl moieties bonded bridgehead to bridgehead; convenient nomenclature designates rods composed of *n* units as an [*n*]-rod. The conventional numbering leads to the terminal bridgehead positions being labeled 1 and 4 for the [1]-rods; 4 and 4′ for the [2]-rods; 4 and 4″ for the [3]-rods; and 4 and 4‴ for the [4]-rods.

[6] Berger, K. C. *Makromol. Chem.* **1975**, *176*, 3575.

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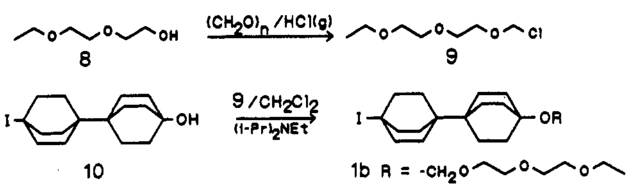
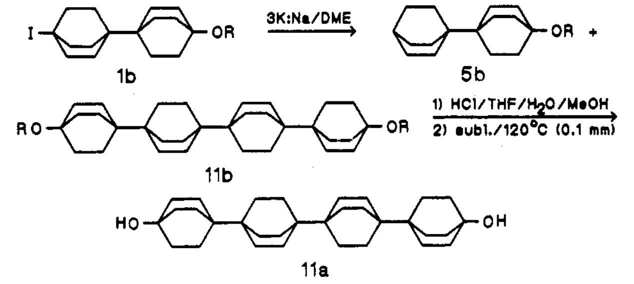
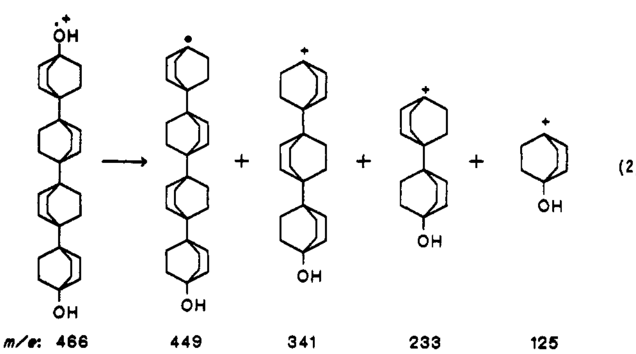
Scheme I. Preparation of the 4-Iodo-4′-EOEOEOMO-[2]-rod



Scheme II. Dimerization of the 4-Iodo-4′-EOEOEOMO-[2]-rod



hydroxy-[3]-rod cation resulting from loss of a hydroxybicyclo[2.2.2]octyl unit, and loss of such hydroxybicyclo[2.2.2]octyl fragments as depicted in eq 2. Proper analysis



(2)

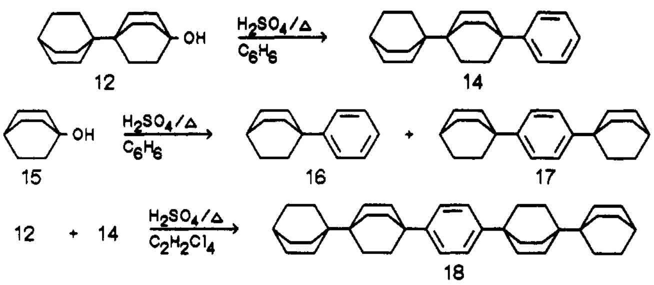
of the [4]-rod was obtained by derivatization of the 4,4‴-dihydroxy-[4]-rod with neat *n*-octanoyl chloride at 185 °C to afford the corresponding dioctanoate **13**. The effect of this terminal substitution was to lower the melting point to 360 °C dec and to enhance solubility—thus permitting recrystallization from chloroform–hexane, NMR spectral characterization, and elemental analysis.

Syntheses of the Hybrid Aromatic Bicyclo[2.2.2]octyl Rods. It was of interest to investigate rod-like molecules in which various rod units were replaced by an aromatic moiety such as *p*-phenylene. We term the [3]-rod having a given unit replaced by the phenylene group, an [x-Ph,3]-rod, where "x" is "a", "b", "c", etc., depending on its placement. These syntheses are outlined in Scheme III. Our first hybrid rod was the [a-Ph,3]-rod **14** which was prepared by Friedel–Crafts alkylation of benzene by 4-hydroxy-[2]-rod **12**. The melting point of this compound was 228 °C, and the compound was reasonably soluble in solvents such as benzene and could be recrystallized without difficulty.

In the course of preparing the known 1-phenylbicyclo[2.2.2]octane **16**[7] from the Friedel–Crafts reaction of 1-hydroxybicyclo[2.2.2]octane **15** with benzene, [b-Ph,3]-rod **17** was also obtained. This melted at 287 °C and could be recrystallized from methylene chloride in hexane. This chemistry is included in Scheme III.

The [c-Ph,5]-rod **18** was obtained from the Friedel–Crafts alkylation of [a-Ph,3]-rod **14** with 4-hydroxy-[2]-rod **12** in *s*-tetrachloroethane giving a 28% conversion to material insoluble in virtually all solvents (e.g. tetrachloroethane, chloroform) even at elevated temperatures. This insolubility precluded recrystallization as in the case of 4,4‴-dihydroxy-[4]-rod, and purification was effected by extraction with successive solvents. The identity of this product was suggested by its high-resolution mass spectral analysis which revealed a parent peak at *m*/*e* 510.4239.

Scheme III. Syntheses of the Hybrid Rods



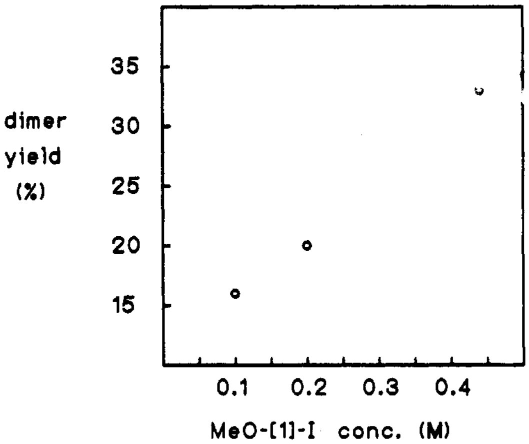


Figure 1. Dimerization yields with naphthalene radical anion as a function of concentration.

Radical Anion Dimerization. Although the potassium–sodium alloy approach had proved useful for rod dimerization, we attempted a dimerization using, instead, naphthalene radical anion as an electron source. The reaction of 1-iodo-4-methoxybicyclo[2.2.2]octane **2** in THF or DME did afford 4,4′-dimethoxy-[2]-rod product **4** in 15–30% yield. The major product observed was 70–80% of 1-methoxybicyclo[2.2.2]octane **3**. The method suffers from the inherent dilution resulting from the addition of the naphthalene radical anion solution, thus diminishing the ratio of dimerization to hydrogen abstraction by bridgehead radicals. This is illustrated graphically in Figure 1 with a minimal three-point plot of 4,4′-dimethoxy-[2]-rod dimer **4** yield versus reactant 1-iodo-4-methoxy-[1]-rod **2** concentration. The use of alternative radical anions, such as biphenylyl and 4,4′-di-*tert*-butylbiphenylyl, led to quite similar results.

Molecular Mechanics Considerations and X-ray Structure of 4,4′-Dimethoxy-[2]-rod. Since an understanding of the conformations of the bicyclo[2.2.2]octane-based rods seemed critical to our efforts, we pursued both Allinger molecular mechanics and an X-ray determination of the system. Thus MM2[8a] computations on the aliphatic rods and MMP[8b] on the hybrid rod compounds were carried out. In each case, a variety of starting conformations was employed in an approach to global opti-

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(7) Chapman, N. B.; Sotheeswaran, S.; Toyne, K. J. *J. Org. Chem.* **1970**, *35*, 917–923.

(8) (a) Allinger, N. L.; Flanagan, H. L. *J. Comput. Chem.* **1983**, *4*, 399–403. (b) Gilbert, K. E.; Gajewski, J. J. Indiana University, Bloomington, IN, 1984.

Table I. Rod Lengths Determined by Molecular Mechanics

rod	compd	length[a]	length[b]	dihedral[c]
H-[1]-H	**19a**	4.82	2.58	10.4
H-[2]-H	**19b**	9.10	6.86	17.6
H-[3]-H	**19c**	13.39	11.15	17.2, 22.4
H-[4]-H	**19d**	17.66	15.42 (4.28)	17.6, 21.6
HO-[1]-OH	**20a**	5.38	2.55	9.4
HO-[2]-OH	**20b**	9.65	6.83	17.1
HO-[3]-OH	**20c**	13.95	11.12	14.7, 22.8
HO-[4]-OH	**11a**	18.22	15.40 (4.28)	17.0, 21.7
MeO-[1]-OMe	**21**	5.44	2.60	10.1
MeO-[2]-OMe	**4**	9.71	6.87 (4.27)	18.0
I-[1]-I	**22a**	6.94	2.60	0.3
I-[2]-I	**22b**	11.24	6.90 (4.30)	18.0
[a-Ph,3]	**14**	13.48	11.26	17.7, 18.7
[b-Ph,3]	**17**	13.40	11.17	10.0
[c-Ph,5]	**18**	21.93	19.70	17.9, 19.1

[a] Length defined as the distance (Å) between terminal substituent atoms. [b] Defined as the distance between terminal carbon atoms; value in parentheses denotes average increase for series. [c] Twist angle (°) defined as dihedral angle between bridgehead carbon atoms through the ethano bridge; second value (when applicable) corresponds to the twist of the internal bicyclo[2.2.2]octyl unit.

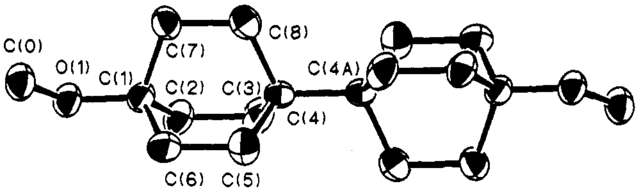

Figure 2. ORTEP diagram of 4,4′-dimethoxy-1,1′-bibicyclo[2.2.2]octane.

mization. The length of various rods given by molecular mechanics coordinates is summarized in Table I. The unit length of each bicyclo[2.2.2]octane unit was determined to be 4.28 (±0.02) Å with this being defined as the increment in rod length with each added unit.

An X-ray determination of the structure of the 4,4′-dimethoxy-[2]-rod **4** was carried out, both for comparison with the molecular mechanics predictions and for conformational purposes (vide infra). An ORTEP drawing of the structure is given in Figure 2. The rod length, from oxygen to oxygen, was determined as 9.88 Å. The bridgehead carbon to carbon distance was 6.84 Å. A comparison of the X-ray with the molecular mechanics results is delayed for consideration in the Discussion.

Interestingly, the molecular mechanics determinations of 1,4-dimethoxy-, 1,4-dihydroxy-, and 1,4-dihydro-[1]-rods (**21**, **20a**, and **19a**, respectively) revealed these to be twisted along the molecular axis by approximately 10° and therefore chiral. In contrast, the 1,4-diiodo-[1]-rod **22a** was untwisted (±0.3°) and hence achiral. The [2]-rods were all twisted with diastereomeric conformations which are designated *P*–*P* (or *M*–*M*) and *P*–*M* with single rod contributions of *P* (clockwise) or *M* (anticlockwise).[9] The intraunit twist in the [2]-rods was 17–18°. The twists in the central rod unit of the [3]-rods were still greater, averaging 22–23°, while the end units were twisted to the extent of 16–17°, close to that of the [2]-rods. The various twist angles are included in Table I.

For 4,4′-dihydro-[2]-rod **19b** the difference in energy of the *P*–*P* (or *M*–*M*) and the *P*–*M* diastereomers was 1.5 kcal/mol with the *P*–*P* (or *M*–*M*) diastereomer being lower in energy than the *P*–*M* isomer. An estimate of the activation energy for interconversion of the *P*–*M* to the *P*–*P* diastereomer was obtained by using molecular mechanics and constraining one rod unit of the 4,4′-dihydro-[2]-rod **19b** in an eclipsed and achiral conformation which then simulated the transition state. This transition state conformer was obtained by replacing the twisted [1]-rod unit at one end by the untwisted moiety obtained from 1,4-diiodo-[1]-rod and then varying the central [1]-rod to [1]-rod distance to minimize the energy. The activation energy obtained was 5.1 kcal/mol; in the reverse direction this corresponds to an activation energy of 6.6 kcal/mol.

Interpretative Discussion

Factors Controlling Rod Syntheses. All of the saturated rod syntheses employed in the present study involve bimolecular bridgehead free-radical dimerization. The main factor limiting the dimerization yields is competing hydrogen abstraction by the bridgehead radical from solvent. However, since dimerization is second order in free-radical concentration, while the undesired hydrogen abstraction is pseudo-first order, the yields of rod dimers should be linear with the instantaneous free-radical concentration. Hence, it was not surprising that the yields increased with increased concentrations of the free-radical precursors. Additionally, the most successful methods utilized two-phase media having a metal surface. It seems likely that the success of these conditions results from the greater probability of two radicals colliding on a two-dimensional surface as opposed to solution chemistry with its three-dimensional volume.

The requirement for high concentrations was made difficult to accomplish by the limited solubility of the rod compounds, especially as the rod length was increased. In addition, synthetic operations on the rod compounds proved difficult with the less soluble members of the series. However, the use of solubilizing end groups provided a means of minimizing these difficulties up to a point (vide infra). Methoxymethyl ether, 1,3,6,9-tetraoxaundecyl, and octanoyl groups did markedly enhance solubility (vide supra). However, while the octanoates may be of value in effecting some transformations, they were clearly unsuitable for dimerizations. An additional factor is the sheer molecular weight of the longer solubilizing groups plus the basic rod unit. For example, the octadecoxy group was considered as a possibility for solubilizing iodo-[4]-rod. However, the molecular weight of this substituted [4]-rod is 827 and the neat compound, assuming a density of unity, thus has a molarity of 1.2 which is diminished by the solvent required for reaction. With increasing rod length or solubilizing group size, the dilution and hence the problem worsens.

The Mass Spectra of the Rod Compounds. One especially important aspect of our mass spectral analyses of

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(9) *IUPAC Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F,* and *H*; Pergamon Press: Elmsford, NY, 1979.

Table II. Salient Features of the Mass Spectra

rod compd	mass peak (assignment)[a]
HO-[2]-OH	232 (P), 125 (C–C)
HO-[4]-OH	466 (P), 449 (P–OH), 341 (C–C), 233 (C–C), 125 (C–C)
MeO-[1]-OMe	170 (P), 138 (P–MeOH), 84 ($C_5H_{10}O$)
MeO-[2]-OMe	278 (P), 246 (P–MeOH), 139 (C–C), 84 ($C_5H_{10}O$)
MeO-[4]-OMe	494 (P), 462 (P–MeOH), 246 (C–C), 138 (C–C), 84 ($C_5H_{10}O$)
I-[1]-I	362 (P), 235 (P–I)
I-[2]-I	470 (P), 343 (P–I), 107 (P–I and C–C)
I-[1]-OAc	294 (P), 167 (P–I), 107 (P–I–AcOH)
I-[2]-OAc	275 (P–I), 215 (P–I–AcOH), 125 (P–I and C–C), 107 (C–C)
H-[2]-H	218 (P), 109 (C–C)
H-[2]-I	343 (P), 217 (P–I), 109 (C–C)
H-[2]-OAc	276 (P), 216 (P–I–AcOH), 109 (C–C)
H-[2]-OMe	248 (P), 139 (C–C), 109 (C–C)

[a] The peak assignments in parentheses correspond to the following fragments: (P) parent ion; (P–I), (P–AcOH), or (P–MeOH) loss of bridgehead substituent; (C–C) denotes bridgehead to bridgehead carbon–carbon bond cleavage.

the rod compounds is its relevance to the structure proof of [4]-rod diol **11a**. Not only did the base peak correspond to the parent ion, but additionally the most salient features of the spectrum resulted from loss of one, two, and three [1]-rod units. This evidence for the structure of [4]-rod was confirmed by the elemental analysis obtained for the dioctanoate derivative **13**.

The mass spectra of the [1]-, [2]-, and [3]-rods were analogous. Each showed the parent ion, however not necessarily as the base peak. The most common mode of fragmentation for these compounds was loss of a bridgehead group—hydroxy, methoxy, iodo, or acetoxy. In addition, bridgehead to bridgehead fragmentation was also common for the [2]- and [3]-rods. Note Table II.

In the case of the 1,4-dimethoxy-[1]-rod **21** a curious fragmentation was encountered giving *m/e* 84, corresponding to a composition of C_5H_8O. The same peak was seen in the 4,4′-dimethoxy-[2]-rod and 4,4‴-dimethoxy-[4]-rod. This seems most likely to be due to 2-methoxybutadienyl radical cation in the ion stream.

Rod Length. The rod lengths in Table I for the 4,4′-dimethoxy-[2]-rod (6.87 Å, terminal bridgehead C to C), determined by molecular mechanics, are remarkably close (within 2%) to the X-ray measurement (6.84 Å). We also note that the present investigation has provided the longest known rod compounds. Thus, the [4]-rod measures 15.4 Å from bridgehead to bridgehead. In the following discussion we confine our definition of organic "rods" to our original proposal.[3] Thus, although Verhoeven[10] has adopted our terminology in describing molecules lacking a symmetry axis, these are really not "rod compounds" in the same sense. Still, the longest molecule described by Verhoeven and Paddon-Row is 14.9 Å.[11] Prior to our own work, steroids had been utilized as chromophore separators. While these are not rod compounds either, it is of interest that the C3 to C17 separation is 15 Å.[12] Some nonlinear polybicyclo[1.1.0]butane derivatives were described by Szeimies in 1984.[13]

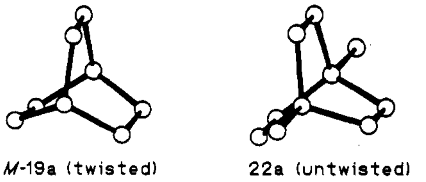

Figure 3. Chiral 1,4-dihydro- and achiral 1,4-diiodo-[1]-rod.

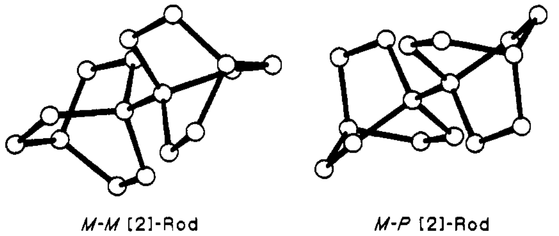

Figure 4. 4,4′-Dihydro-[2]-rod conformations.

In contrast to these nonrodlike molecules, [2]- and [3]-rods composed of bicyclo[1.1.1]pentane units were first described by Wiberg.[14] Schlüter described the polymerization of [1.1.1]propellane derivatives to obtain mixtures of oligomers.[15] [2]-, [3]-, [4]-, and [5]-rods have been described by Michl.[16] In the case of the bicyclopentane rods, the [5]-rod measures 15.1 Å, bridgehead to bridgehead. Finally, rods with cubanyl units have been reported by Eaton.[17]

Conformational Considerations: Chirality. The molecular mechanics computations on 1,4-dihydro-[1]-rod **19a**, 1,4-dihydroxy-[1]-rod **20a**, and 1,4-dimethoxy-[1]-rod **21** all revealed a preference for a twisted conformation having a *P* (i.e. plus, or clockwise) or *M* (i.e. minus, or anticlockwise) twist. Hence, these molecules are chiral. This is illustrated in Figure 3. The dihedral angles measured for C1–C2–C3–C4 are collected in Table I and average 11°. Strikingly, the 1,4-diiodo-[1]-rod **22a** is untwisted and achiral. This seems to result from minimization of iodine–methylene hydrogen van der Waals repulsions.

With [1]-rod chirality, we thus can understand the possibility of the existence of [2]-rod diastereomers, the *P–P* and *M–M* diastereomer and the *P–M* diastereoisomer. The preferred interunit conformation had the methylenes of one rod unit oriented between the methylenes of the

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(11) (a) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258–3269. (b) Warman, J. M.; Haas, M. P. de; Overing, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Oliver, A. M.; Hush, N. S. *Chem. Phys. Lett.* **1986**, *128*, 95–99. (c) The "rod" terminology and concept of transfer through the bonds of such systems may be coincidental with these authors in refs 10 and 11 being unware of our prior efforts, since we find no citations to the earlier work in ref 3.

(12) (a) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670–671. (b) Somewhat larger distances were obtained using a bis-steroidal system (ca. 21.5 Å). However, the conformational freedom of the chromophores neccessitates variations in the overall length.[11c] (c) Latt, S. A.; Cheung, H. T.; Blout, E. R. *J. Am. Chem. Soc.* **1965**, *87*, 995.

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Table III. Linear Rods and Their Attributes

structural unit[a]	synthetic method	[*n*][b]	yield (%)	mp (°C)
bicyclo[2.2.2]octyl[c]	Mg/NiCl$_2$	[2]	65	165
(4.28 Å)	Na:K	[2]	55	-
	Na:K	[4]	21	>525
bicyclo[1.1.1]pentyl[d]	radical polymerization	[1]	*e*	32–33
(3.30 Å)		[2]	13	142–144
		[3]	9	240–242
		[4]	6	290, dec
		[5]	2	290, dec
2,4-dimethylenebicyclo[1.1.1]pentyl[f]	anionic polymerization			
	tert-butyllithium		50	303, dec
	phenyllithium		35	*e*
cubanyl[g]	metal–halogen exchange			
(4.24 Å)	*n*-butyllithium	[2]	30	*e*

[a] Value in parentheses denotes the incremental length increase for "rods" larger than the parent. [b] The number of structural units is denoted by "[*n*]". [c] Reference 3 and this work. [d] Reference 16b. [e] Not reported. [f] Reference 15c. [g] Reference 17. Length increment estimated from X-ray crystal structures of bicubyl and cubane.

other. (Note Figure 4 for a three-dimensional drawing of the [2]-rod diastereomers.) In contrast to the [1]-rod situation, the 4,4′-diiodo-[2]-rod **22b** was twisted.

Despite the molecular mechanics prediction of diastereomers, we note that no direct experimental evidence could be adduced for the actual existence of these diastereomers. Thus, in the case of the [2]-rods the syntheses utilized invariably afforded only one crystal with a sharp melting point. However, the single X-ray obtained from the 4,4′-dimethoxy-[2]-rod 4 revealed an achiral structure, and we must conclude that intermolecular crystal forces have overcome the intramolecular tendency to twist which was seen from molecular mechanics (vide supra) to be small. With a 5.1 kcal/mol barrier (vide supra), an interconversion rate constant of 1.2×10^9 s^{-1} is predicted, making NMR detection not readily accessible. In the case of the [3]- and [4]-rod compounds a larger number of diastereoisomers might be possible, but no evidence of lack of homogeneity of any compounds was adduced. It seems likely that the barrier suggested by molecular mechanics is sufficiently small so that the presence of diastereomers goes undetected.

Comparison of Various Rod Types: Synthetic Considerations, Physical Properties, and Molecular Properties. Table III lists the known linear rod types and a comparison of some of their properties and synthetic yields. Clearly polymerization giving longer rods provides a facile generation of these; however, the disadvantage of this approach is the need for separation and the exceptionally low yields obtained for any one homogeneous [*n*]-rod. The bicyclo[1.1.1]pentyl rods also are less thermally stable due to the strained ring system. For electronic energy and electron transmission studies, the [1.1.1]-rods differ from the [2.2.2]-rods in having strained σ bonds and thus lower insulating properties; depending on intention, this can be an advantage or a disadvantage. The difference in the preparation is in the [2.2.2]-rods resulting from directed syntheses while the [1.1.1]-rods are formed more readily but require separation of oligomers.

Theoretical Analysis of the Bridgehead Cations of the Rods. Consideration of electron delocalization in our rod molecules was of general interest. Also, in our mass spectral analysis of the dihydroxy-[*n*]-rods two types of peaks were among the most common. The first corresponded to the bridgehead cations, and it was of interest to treat these species quantum mechanically. Considering the size of the largest of the rods, AM1[18] along with the Weinhold NBO analysis[19] was selected. This analysis has the advantage of giving electron densities in the various bonds rather than in randomly oriented atomic orbitals. The geometry employed was MM2 optimized as described above.

Table IV. NBO Analysis of Bond Electron Densities in the Bridgehead Cations

type	HO[4]+ occupancy[a]	HO[3]+ occupancy	HO[2]+ occupancy	HO[1]+ occupancy
a1	1.9744	1.9746	1.9744	1.9741
b1	1.9090	1.9076	1.9090	1.9139
c1	1.9730	1.9727	1.9730	1.9722
a2	1.9724	1.9723	1.9723	
b2	1.9798	1.9797	1.9794	
c2	1.9738	1.9740	1.9715	
a3	1.9733	1.9733		
b3	1.9803	1.9898		
c3	1.9741	1.9730		
a4	1.9735			
b4	1.9800			
c4	1.9731			
d1	1.95234	1.95107	1.95261	
d2	1.96259	1.96307		
d3	1.96322			
e	1.98636	1.98622	1.98584	1.98133

[a] Occupancies are given in electron densities per bond of each type.

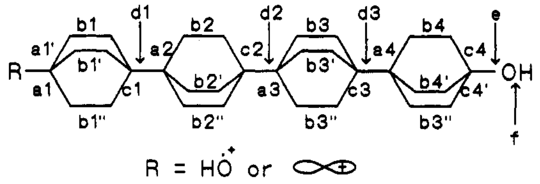

Figure 5. Bond designations as applied to the [4]-rod species.

The results of the computations are summarized in Table IV. In this we have labeled six types of bonds—a, b, c, d, e, and f. This labeling is defined in Figure 5 for the [4]-rod system. The bonds in different bridges of the same type are designated with primed letters (e.g. a, a′, and a″) while bonds in the sequential rod units are labeled 1, 2, 3, and 4, thus giving bond labels as a1, a2′, etc. For the cations, bond numbering begins at the positive center.

The most interesting point is the diminished electron density in certain bonds which are parallel to the molecular axis (i.e. bonds of type b1 and d). Bonds of type a and c do not lose appreciable electron density to the cationic bridgehead, a reasonable result considering their lesser

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Table V. Bond Electron Densities in the Radical Cations of the Rod Diols

type	HO[4]OH occupancy[a]	HO[3]OH occupancy	HO[2]OH occupancy	HO[1]OH occupancy
a1	1.9701	1.8952	1.8956	1.7372
b1	1.9796	1.9693	1.9748	1.9767
c1	1.9611	1.9687	1.9694	1.7394
a2	1.9048	1.8730	1.9730	
b2	1.9795	1.9979	1.9788	
c2	1.8783	1.9742	1.9734	
a3	1.9554	1.9737		
b3	1.9798	1.9789		
c3	1.9707	1.9735		
a4	1.9730			
b4	1.9798			
c4	1.9730			
d1	1.9629	1.9676	1.9683	
d2	1.9650	1.9692		
d3	1.9637			

[a] Occupancies are given in electron densities per bond of each type.

ability to overlap and conjugate with the axially symmetric orbital system. Another point of interest is that the electron deficiency falls off with distance from the cationic center.

Theoretical Considerations Applied to the Diol Radical Cations. The same theoretical treatment applied to the radical cation species encountered in the mass spectra of the compounds led to the bond electron densities listed in Table V, and the same bond nomenclature is employed. Note Figure 5, again. In this case a major factor in considering the electron deficiency is the lack of perfect symmetry in the species utilized. This results in an artificial localization of charge in particular bridges and also at one end of the rod. However, a trend is seen in the electron deficiency being found in bonds of type a and c, in contrast to the situation for the bridgehead cation.

Conclusion. The linear rod system composed of bicyclo[2.2.2]octane units provides a particularly fascinating set of supermolecules with well-defined geometry and unusual physical properties. The powerful crystal packing forces and high melting points suggest the utility of these molecules as thermally stable organic molecules.

Experimental Section[20]

1,4-Dimethoxycyclohexa-1,4-diene.[21] The method of Birch was used with modification to give 1,4-dimethoxycyclohexa-1,4-diene as a white solid after recrystallization from pentane, mp 51–53 °C (lit.[21] mp 54 °C).

1,4-Dimethoxybicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic Acid Anhydride.[22] The method of Brown was modified in scale to give 1,4-dimethoxybicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic acid anhydride as colorless prisms after recrystallization from ethyl acetate, mp 127–129 °C (lit.[22] mp 123–125 °C).

1,4-Dimethoxybicyclo[2.2.2]octane-2,3-dicarboxylic Acid Anhydride.[22] Minor modification of the method of Brown gave 1,4-dimethoxybicyclo[2.2.2]octane-2,3-dicarboxylic acid anhydride as an off-white solid, mp 108–109 °C (lit.[22] mp 100–103 °C), used without further purification.

1,4-Dimethoxybicyclo[2.2.2]octane-2,3-dicarboxylic Acid.[22] This material was prepared by the method of Brown to give the diacid as a white solid, mp 163–164 °C (lit.[22] mp 160–165.5 °C).

1,4-Dimethoxybicyclo[2.2.2]oct-2-ene.[22] The method of Brown gave 1,4-dimethoxybicyclo[2.2.2]oct-5-ene as a colorless oil, bp 63–65 °C (1.5 mmHg) (lit.[22] bp 91 °C (10 mmHg)).

1,4-Dimethoxybicyclo[2.2.2]octane (21).[22] This material was prepared after the method of Brown to give 1,4-dimethoxybicyclo[2.2.2]octane as a colorless oil, bp 65 °C (2.0 mmHg) (lit.[22] bp 77 °C (4.0 mmHg)).

1,4-Diiodobicyclo[2.2.2]octane (22a). A stirring solution of 17.9 g (0.105 mol) of 1,4-dimethoxybicyclo[2.2.2]octane and 100 mL of constant hydriodic acid[23] was heated moderately, collecting iodomethane and water until a constant distillate temperature had been attained (110 °C). The distillation apparatus was replaced with a condenser and the solution refluxed for 18 h. The white sublimate was collected by filtration, washed with water, and dried to give 36.0 g (94%) of 1,4-diiodobicyclo[2.2.2]octane, mp 239–241 °C subl (lit.[24] mp 240 °C).

4-Iodo-1-bicyclo[2.2.2]octyl Acetate.[3] The method of Zimmerman et al. was employed with modifications to give the iodo acetate as a white solid after recrystallization from ether in hexane, mp 126–127 °C (lit.[3] mp 128.2–129.2 °C).

4-Iodobicyclo[2.2.2]octan-1-ol.[3] The method of Zimmerman et al. was employed to give the iodo alcohol as fine white needles, mp 162–164 °C (lit.[3] mp 162–162.2 °C).

1-Iodo-4-methoxybicyclo[2.2.2]octane (2).[3] Utilization of the method of Zimmerman et al. gave 1-iodo-4-methoxybicyclo[2.2.2]octane as colorless prisms after recrystallization from hexane, mp 76–78 °C (lit.[3] mp 79.6–79.8 °C).

4,4′-Dimethoxy-1,1′-bibicyclo[2.2.2]octane (4).[3] Modification of the method of Zimmerman gave 4,4′-dimethoxy-1,1′-bibicyclo[2.2.2]octane after recrystallization from ether in hexane as colorless needles, mp 169–170 °C (lit.[3] mp 168.1–168.5 °C).

Single-Crystal X-ray Structure of 4,4′-Dimethoxy-1,1′-bibicyclo[2.2.2]octane (4). Crystals of 4,4′-dimethoxy-1,1′-bibicyclo[2.2.2]octane were prepared by slow crystallization from methanol. X-ray data were collected with Cu Kα radiation on a Nicolet (Syntex) P-1 diffractometer from a monoclinic shaped crystal of dimensions 0.5 × 0.2 × 0.05 mm. Unit cell parameters were obtained by least-squares refinement of 25 reflections (48° $< 2\theta <$ 88°). Data were collected in the (hkl) range (−6,0,−13) to (3,10,13) with three reflections monitored every 45. A total of 922 unique data was collected, with 818 of $F > 4\sigma(F)$. Lorentz and polarization corrections were applied, and the structure was solved under $P2_1/c$ symmetry by direct methods using SHELXTL PLUS (VMS).[25] Hydrogen atoms were located from difference Fourier synthesis, and full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Refinement of 95 parameters converged to $R_1(F) = 0.0536$ and $R_w(F) = 0.0733$. Results and structural parameters are available as supplementary material.

Dimerization of 1-Iodo-4-methoxybicyclo[2.2.2]octane Using Sodium Naphthalenide. In a typical reaction, a solution of 250 mg (0.939 mmol) of 1-iodo-4-methoxybicyclo[2.2.2]octane in 1.0 mL of DME at 25 °C was treated with 1.3 mL of a 1.0 M solution of sodium naphthalenide[26] in DME. After stirring for 1 h at 25 °C, 1.0 mL of methanol was added. Neutral workup[20] gave a mixture of 1-methoxybicyclo[2.2.2]octane and 4,4′-dimethoxy-1,1′-bibicyclo[2.2.2]octane (4). The product ratio was determined by monitoring the ^{1}H NMR signals at δ 3.14 (OCH_3,

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(20) Melting points were determined on a Mel-Temp heating block and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 37921-1750. All reactions were performed under an atmosphere of dry nitrogen. Neutral workup refers to quenching the reaction with water, extraction with the indicated solvent, washing with water and brine, drying, filtering, and concentration in vacuo. Anhydrous magnesium sulfate was the drying agent. Column chromatography was performed on silica gel (Matheson, Coleman, and Bell, grade 62, 60–200 mesh) or neutral alumina (Fischer Scientific, Inc., 80–200 mesh, and slurry packed in hexane or the indicated solvents. Preparative thick-layer chromatography was carried out with MN-Kieselgel G/UV 254 silica gel. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled successively, under a nitrogen atmosphere, from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. Diethyl ether was distilled from sodium benzophenone ketyl. Benzene was distilled from calcium hydride. Methylene chloride was distilled from phosphorus pentoxide. Sonification was with a 300-W Branson immersion apparatus.

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dimer 4) and δ 3.16 (OCH_3, 1-methoxybicyclo[2.2.2]octane).

4′-Iodo-1,1′-bibicyclo[2.2.2]octan-4-ol (10).[3] The method of Zimmerman et al. was employed to give 4′-iodo-1,1′-bi(bicyclo[2.2.2]octan)-4-ol as white needles, mp 200–201 °C (lit.[3] mp 196.6–197.7 °C).

4-(1,3-Dioxabutyl)-4″-methoxy-1,1′:4′,1″-terbicyclo[2.2.2]octane (6a).[5] In a typical run, 7.4 g (0.304 mol) of magnesium was added to a solution of 1.74 g (4.31 mmol) of 4-(1,3-dioxabutyl)-4″-iodo-1,1′-bibicyclo[2.2.2]octane,[5] 8.70 g (32.7 mmol) of 1-iodo-4-methoxybicyclo[2.2.2]octane and 4.80 g (37.0 mmol) of anhydrous nickel chloride in 20.0 mL of ether. The reaction was sonicated for 2 h. Neutral workup[20] with chloroform gave 8.67 g of a crude product mixture. The combined crude products from two such runs were dissolved in 200 mL of a 1:1 mixture of chloroform and ether. This solution was treated with 100 mL of a 1:1 solution of water and concd hydrochloric acid and stirred at ambient temperature for 4 h. Column chromatography on silica gave 506 mg of material suspected to be 4″-methoxy-1,1′:4′,1″-terbicyclo[2.2.2]octan-1-ol. Methoxymethylation in 50 mL of chloroform with 40.0 mL of dimethoxymethane and 5.5 g (38.7 mmol) of phosphorus pentoxide for 2.25 h at ambient temperature gave, after neutral workup[20] and chromatography on alumina, 132.2 mg (6.2%) of 4-(1,3-dioxabutyl)-4″-methoxy-1,1′:4′,1″-terbicyclo[2.2.2]octane, mp (sealed tube) 413–420 °C dec.

The spectral data were the following: IR ($CHCl_3$) 3000, 2950, 2915, 2865, 1460, 1350, 1145, 1095, 1040, 995, 985, 940, 915, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.68 (s, 2 H, acetal), 3.33 (s, 3 H, OCH_3), 3.14 (s, 3 H, OCH_3), 1.65–1.46 (m, 24 H, $CH_2CH_2C(O)$), 1.25 (s, 12 H, CH_2CH_2 internal); MS *m/e* 416.3291 (calcd for $C_{24}H_{44}O_3$ *m/e* 416.3292).

Anal. Calcd for $C_{24}H_{44}O_3$: C, 77.84; H, 10.64. Found: C, 77.66; H, 10.54.

1-Chloro-2,5,8-trioxadecane (9). Adaptation of the method of Corey[27] was employed. A stirring suspension of 18.5 g (0.616 mol) of anhydrous paraformaldehyde in 75.0 mL (74.9 g, 0.558 mol) of 2-(2-ethoxyethoxy)ethanol was treated with anhydrous hydrogen chloride gas at 0 °C for 1.5 h until the solution had become homogeneous. The solution was poured into 600 mL of pentane at 0 °C containing 70 g of anhydrous magnesium sulfate and stored at 0 °C for 12 h. Removal of solids by suction filtration followed by concentration in vacuo gave 68.5 g of a colorless oil. Distillation at reduced pressure gave 47.1 g (46%) of 1-chloro-2,5,8-trioxadecane as a colorless oil, bp 67 °C (1.1 mmHg). Repetitive distillation afforded an analytical sample, bp 53.5–54.0 °C (0.20 mmHg).

The spectral data were the following: IR (neat) 2975, 2930, 2875, 1470, 1455, 1375, 1360, 1350, 1320, 1245, 1110, 1045, 1005, 945, 845 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.55 (s, 2 H, OCH_2Cl), 3.86 (m, 2 H, $C\mathit{H}_2OCH_2Cl$), 3.72 (m, 2 H, $C\mathit{H}_2CH_2OCH_2Cl$), 3.69–3.48 (m, 6 H, OCH_2), 1.21 (t, $J = 6.8$ Hz, 3 H, CH_3); MS *m/e* ($M - C_2H_5O$) 137.0382 (calcd for $C_5H_{10}O_2Cl$ *m/e* 137.0369).

Anal. Calcd for $C_7H_{15}ClO_3$: C, 46.03; H, 8.28. Found: C, 45.72; H, 8.01.

4-Iodo-4′-(1,3,6,9-tetraoxaundecyl)-1,1′-bibicyclo[2.2.2]octane (1b). To a stirring solution of 1.52 g (4.21 mmol) of 4′-iodo-1,1′-bi(bicyclo[2.2.2]octan)-4-ol in 15.0 mL of methylene chloride was added 4.00 mL of *N,N*-diisopropylethylamine and 1.30 mL (1.36, 7.43 mmol) of 1-chloro-2,5,8-trioxadecane. The solution was heated at reflux for 8 h. Neutral workup[20] gave 2.95 g of a yellow oil that was chromatographed on a 3- × 32-cm neutral alumina column packed in 5% ether in hexane; elution with 15% ether in hexane provided the following fractions: fraction 1, 75 mL, nil; fraction 2, 75 mL, 1.50 g of a yellow oil which crystallized upon standing. Fraction 2 was recrystallized from the melt in 5.0 mL of anhydrous methanol to give 1.26 g (59%) of 4-iodo-4′-(1,3,6,9-tetraoxaundecyl)-1,1′-bibicyclo[2.2.2]octane as white spheroids, mp 52.0–53.5 °C.

The spectral data were the following: IR ($CHCl_3$) 2955, 2920, 2870, 1460, 1350, 1300, 1235, 1190, 1170, 1110, 1040, 1000, 945, 915, 910, 900, 860, 815 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.73 (s, 2 H, OCH_2O), 3.72–3.45 (m, 10 H, OCH_2), 2.35 (m, 6 H, $C(I)CH_2$), 1.73–1.30 (m, 18 H, CH_2), 1.21 (t, 3 H, CH_3); MS *m/e* (M − I) 379.2852 (calcd for $C_{23}H_{39}O_4$ *m/e* 379.2848).

Anal. Calcd for $C_{23}H_{39}IO_4$: C, 54.55; H, 7.76. Found: C, 54.73; H, 7.61.

4-Methoxy-4″-(1,3,6,9-tetraoxaundecyl)-1,1′:4′,1″-terbicyclo[2.2.2]octane (6b) and 4″-Methoxy-1,1′:4′,4″-terbicyclo[2.2.2]octan-1-ol (6c). A solution of 491 mg (0.970 mmol) of 4-iodo-4′-(1,3,6,9-tetraoxaundecyl)-1,1′-bibicyclo[2.2.2]octane and 1.15 g (4.33 mmol) of 1-iodo-4-methoxybicyclo[2.2.2]octane in 5.30 mL of DME at 0 °C was treated with 350 μL of a 5:1 (w/w) alloy of potassium and sodium and sonicated for 1 h. Neutral workup[20] with methylene chloride gave 825 mg of a yellow oil. Recrystallization from ether in hexane gave 12.1 mg (2.4%) of 4-methoxy-4″-(1,3,6,9-tetraoxaundecyl)-1,1′:4′,1″-terbicyclo[2.2.2]octane as a lustrous white solid, mp 318–329 °C.

Acid hydrolysis of the crystallization filtrates in 100 mL of a 40:40:10:10 tetrahydrofuran–methanol–water–hydrochloric acid mixture gave 25.1 mg (6.7%) of 4″-methoxy-1,1′:4′,4″-terbicyclo[2.2.2]octan-1-ol, mp 430 °C dec. Recrystallization from chloroform in ethyl acetate gave 11.3 mg (3.0%), mp (sealed tube) 400 °C subl.

The spectral data for 4-methoxy-4″-(1,3,6,9-tetraoxaundecyl)-1,1′:4′,1″-terbicyclo[2.2.2]octane were the following: IR ($CHCl_3$) 2950, 2915, 2865, 1460, 1350, 1235, 1095, 1075, 1040, 1025, 925, 920, 905, 895, 890, 650 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.76 (s, 2 H, OCH_2O), 3.68–3.51 (m, 10 H, OCH_2), 3.14 (s, 3 H, OCH_3), 1.72–1.40 (m, 24 H, CH_2CH_2CO), 1.25 (s, 12 H, CH_2CH_2), 1.21 (t, $J = 8$ Hz, 3 H, $OCH_2C\mathit{H}_3$); MS *m/e* 518.3983 (calcd for $C_{32}H_{54}O_5$ *m/e* 518.3973).

Anal. Calcd for $C_{32}H_{54}O_5$: C, 74.09; H, 10.49. Found: C, 73.70; H, 10.39.

The spectral data for 4″-methoxy-1,1′:4′,4″-terbicyclo[2.2.2]octan-1-ol were the following: IR (KBr) 3425 (OH), 2945, 2865, 1450, 1385, 1350, 1235, 1170, 1125, 1100, 1060, 1035, 1005, 940, 855, 825 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.14 (s, 3 H, OCH_3), 1.52 (m, 12 H, $C\mathit{H}_2C(O)$), 1.47 (m, 12 H, $C\mathit{H}_2CH_2C(O)$), 1.25 (s, 12 H, CH_2CH_2); MS *m/e* 372.3028 (calcd for $C_{25}H_{40}O_2$ *m/e* 372.3028).

Anal. Calcd for $C_{25}H_{40}O_2$: C, 80.59; H, 10.82. Found: C, 80.01; H, 10.59.

1,1′:4′,1″:4″,1‴-Quaterbicyclo[2.2.2]octane-4,4‴-diol (11a). In a sonication bath at 0 °C a solution of 1.009 g (1.99 mmol) of 4-iodo-4′-(1,3,6,9-tetraoxaundecyl)-1,1′-bibicyclo[2.2.2]octane in 2.50 mL of DME was treated with 130 μL of a 3:1 alloy of potassium and sodium. After 1.5 h the solution was carefully quenched by the addition of water. Neutral workup[20] with chloroform gave a tan solid. Acid hydrolysis of the crude product in 100 mL of 10:1:1:1 tetrahydrofuran–methanol–water–hydrochloric acid gave 400.3 mg of a mixture of alcohols. Fractional sublimation (135 °C (0.25 mmHg)) afforded 1,1′-bibicyclo[2.2.2]octan-4-ol, 364.9 mg (78%) as a white solid, mp 243–245 °C subl. (lit.[3] mp 254.5–255.5 °C). The residual off-white solid, 94.9 mg (21%), was identified as 1,1′:4′,1″:4″,1‴-quaterbicyclo[2.2.2]octane-4,4‴-diol, mp >525 °C.

The spectral data for 1,1′-bibicyclo[2.2.2]octan-4-ol were the following: IR (KBr) 3440, 2945, 2915, 2860, 1460, 1350, 1255, 1155, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.55–1.41 (m, 18 H, CH_2), 1.33–1.28 (m, 7 H, CH_2, CH); MS *m/e* 234.1973 (calcd for $C_{16}H_{27}O$ *m/e* 234.1984).

The spectral data for 1,1′:4′,1″:4″,1‴-quaterbicyclo[2.2.2]octane-4,4‴-diol were the following: IR (KBr) 3495 (OH), 2950, 2920, 2865, 1460, 1405, 1385, 1350, 1310, 1235, 1170, 1150, 1125, 1095, 1030, 985, 940, 875 cm^{-1}; IR (Nujol mull) 3495 (OH), 3380 (OH), 2860, 1350, 1235, 1150, 1095, 1030, 985, 940, 875 cm^{-1}; MS *m/e* 466.3789 (calcd for $C_{32}H_{50}O_2$ *m/e* 466.3811).

1,1′:4′,1″:4″,1‴-Quaterbicyclo[2.2.2]octane-4,4‴-diyl Dioctanoate (13). A mixture of 26.7 mg (0.0572 mmol) of finely divided 1,1′:4′,1″:4″,1‴-quaterbicyclo[2.2.2]octane-4,4‴-diol and 1.00 mL (0.953 g, 5.86 mmol) of octanoyl chloride was heated at 185 °C for 13 h. Excess octanoyl chloride was removed in vacuo (40 °C (0.17 mmHg)). The residual solids were suspended in ether–hexane and collected by suction filtration to give 36.9 mg of a tan solid mp 350–360 °C dec. Recrystallization from chloroform in hexane gave 34.0 mg (85%) of 1,1′:4′,1″:4″,1‴-quaterbicyclo[2.2.2]octane-4,4‴-diyl dioctanoate as a lustrous, waxy solid, mp 350–360 °C dec.

The spectral data were the following: IR (film) 2945, 2930, 2865, 1730 (C=O), 1460, 1380, 1350, 1265, 1235, 1185, 1150, 1115, 1045,

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[27] Corey, E. J.; Gras, J.-L.; Ulrich, P. *Tetrahedron Lett.* 1976, 809–812.

1030, 950 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.17 (t, J = 6.0 Hz, 4 H, CH$_2$C(O)), 1.88 (m, 12 H, C*H*$_2$CO), 1.45 (m, 12 H, C*H*$_2$CH$_2$CO), 1.26 (s, 16 H, CH$_2$), 1.22 (br s, 24 H, CH$_2$), 0.87 (t, J = 6 Hz, 6 H, CH$_3$); partial ^{13}C NMR (CDCl$_3$, 500 MHz) δ 35.59, 34.98, 33.73, 31.69, 30.01, 28.98, 25.95, 25.26, 25.13, 22.62, 14.10; MS *m/e* (M − C$_8$H$_{14}$O$_2$) 576.4924 (calcd for C$_{40}$H$_{64}$O$_2$ *m/e* 576.4906).

Anal. Calcd for C$_{48}$H$_{78}$O$_4$: C, 80.17; H, 10.93. Found: C, 80.33; H, 10.92.

1-Bicyclo[2.2.2]oct-1-ylbenzene (16) and 1,4-Dibicyclo[2.2.2]oct-1-ylbenzene (17). To a stirred solution of 219 mg (1.74 mmol) of bicyclo[2.2.2]octan-1-ol[28] in 25 mL of benzene was added 0.25 mL of concd sulfuric acid. The mixture was refluxed for 6.5 h and poured over 25 g of crushed ice. Neutral workup[20] gave 312 mg of a white solid. Chromatography on a 20 × 20 cm thick-layer silica gel plate eluting twice with hexane gave the following: band 1, R_f = 0.45, 188 mg of 1-bicyclo[2.2.2]oct-1-ylbenzene; band 2, R_f = 0.05, 17.8 mg of 1,4-dibicyclo[2.2.2]oct-1-ylbenzene.

The 1-bicyclo[2.2.2]oct-1-ylbenzene was recrystallized from ether in hexane to give 138 mg (43%) of white plates, mp 82.5–84.0 °C (lit.[7] mp 78–80 °C). The 1,4-dibicyclo[2.2.2]oct-1-ylbenzene was recrystallized from methylene chloride in hexane to give 10.4 mg (4.1%) of white flakes, mp 285–287 °C.

The spectral data for 1-bicyclo[2.2.2]oct-1-ylbenzene were the following: IR (CHCl$_3$) 3065, 3035, 2940, 2920, 2865, 1600, 1495, 1455, 1445, 1350, 1335, 1265, 1035, 920, 910, 900, 895, 655, 650, 535 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.32–7.15 (m, 5 H, arom), 1.77 (m, 6 H, CH$_2$), 1.72 (m, 7 H, CH$_2$CH); MS *m/e* 186.1397 (calcd for C$_{14}$H$_{18}$ *m/e* 186.1409); UV (cyclohexane) $\lambda_{\max}$ 214 nm (ϵ 3500).

Anal. Calcd for C$_{14}$H$_{18}$: C, 90.26; H, 9.74. Found: C, 90.54; H, 9.87.

The spectral data for 1,4-dibicyclo[2.2.2]oct-1-ylbenzene were the following: IR (CHCl$_3$) 2940, 2920, 2865, 1520, 1505, 1455, 1335, 1265, 995, 915, 895, 830, 820, 570 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.22 (s, 4 H, arom), 1.74 (m, 12 H, CH$_2$), 1.69 (m, 14 H, CH$_2$CH); MS *m/e* 294.2355 (calcd for C$_{22}$H$_{30}$ *m/e* 294.2349); UV (cyclohexane) $\lambda_{\max}$ 220 (ϵ 5600).

Anal. Calcd for C$_{22}$H$_{30}$: C, 89.73; H, 10.27. Found: C, 89.95; H, 10.22.

4-Phenyl-1,1′-bibicyclo[2.2.2]octane (14). To a stirred solution of 266 mg (1.13 mmol) of 1,1′-bibicyclo[2.2.2]octan-4-ol in 30 mL of benzene was added 0.25 mL of concd sulfuric acid. The mixture was refluxed for 4 h and poured over 25 g of crushed ice. Neutral workup[20] gave 302 mg of a white solid. Recrystallization from benzene gave 212 mg (63%) of 4-phenyl-1,1′-bibicyclo[2.2.2]octane, mp 226–228 °C.

The spectral data were the following: IR (KBr) 3080, 3060, 3030, 2945, 2935, 2915, 2910, 2860, 1935, 1860, 1795, 1600, 1495, 1455, 1385, 1350, 1255, 1205, 1080, 1035, 1000, 990, 955, 910, 900, 850, 820, 760, 695, 535 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.36–7.14 (m, 5 H, arom), 1.74 (m, 6 H, CH$_2$), 1.53–1.31 (m, 19 H, CH$_2$, CH); MS *m/e* 294.2351 (calcd for C$_{22}$H$_{30}$ *m/e* 294.2349); UV (cyclohexane) $\lambda_{\max}$ 212 nm (ϵ 6300).

Anal. Calcd for C$_{22}$H$_{30}$: C, 89.73; H, 10.27. Found: C, 89.93; H, 10.39.

1,4-Bis(1,1′-bibicyclo[2.2.2]oct-4-yl)benzene (18). To a stirring solution of 92.3 mg (0.394 mmol) of 1,1′-bibicyclo[2.2.2]octan-4-ol and 104 mg (0.354 mmol) of 4-phenyl-1,1′-bibicyclo[2.2.2]octane in 10 mL of *s*-tetrachloroethane was added 3 drops of concd sulfuric acid, and the mixture was refluxed for 16 h. The precipitate was collected by suction filtration and washed with acetone to give a deeply colored solid, 53.9 mg (28%) of material identified as 1,4-bis(1,1′-bibicyclo[2.2.2]oct-4-yl)benzene, mp 505 °C subl.

The spectral data were the following: IR (KBr) 2940, 2915, 2860, 1515, 1455, 1385, 1350, 1255, 1240, 1200, 1160, 1035, 995, 910, 820, 565 cm^{-1}; MS *m/e* 510.4239 (calcd for C$_{38}$H$_{54}$ *m/e* 510.4228).

1,1′-Bibicyclo[2.2.2]octane-4,4′-diyl Diacetate. Occasionally a poorly soluble organic compound was isolated from the reaction of 4,4′-dimethoxy-1,1′-bibicyclo[2.2.2]octane with constant hydriodic acid. It was suspected that the material might be a partially converted intermediate 1,1′-bibicyclo[2.2.2]octane-4,4′-diol, mp 392–394 °C (lit.[29] mp 230–233 °C).

The spectral data for this material were the following: IR (KBr) 3445, 3405, 2950, 2865, 1455, 1425, 1405, 1350, 1335, 1260, 1235, 1175, 1150, 1125, 1100, 1060, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.54–1.45 (m, 24 H, CH$_2$), 1.22 (br s, 2 H, OH); MS *m/e* 250.1928 (calcd for C$_{16}$H$_{26}$O$_2$ *m/e* 250.1933).

Confirmation of this identification was provided by conversion to the diacetate. A stirring solution of 231 mg (0.921 mmol) of 1,1′-bibicyclo[2.2.2]octane-4,4′-diol in 17 mL of acetic anhydride was refluxed for 3 h. Excess solvent was removed in vacuo, and the residuals were dissolved in methylene chloride. Neutral workup[20] gave 255 mg (83%) of pure product, mp 243–247 °C (lit.[29] mp 224–226 °C).

The spectral data for 1,1′-bibicyclo[2.2.2]octane-4,4′-diyl diacetate were the following: IR (KBr) 2950, 2925, 2875, 1730, 1460, 1440, 1370, 1355, 1250, 1230, 1040, 1000, 870, 730, 610 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.93 (s, 6, H, CH$_3$), 1.85 (m, 12 H, CH$_2$CO), 1.46 (m, 12 H, CH$_2$); MS *m/e* 274.1937 (calcd for C$_{18}$H$_{26}$O$_2$ *m/e* 274.1933).

Anal. Calcd for C$_{20}$H$_{30}$O$_4$: C, 71.83; H, 9.04. Found: C, 71.44; H, 8.95.

4,4′-Diiodo-1,1′-bibicyclo[2.2.2]octane (22b). A solution of 251.3 mg (0.903 mmol) of 4,4′-dimethoxy-1,1′-bibicyclo[2.2.2]octane in 20.0 mL of constant hydriodic acid[23] was refluxed for 12 h. The suspension was diluted with water, and the precipitated solids were collected by suction filtration and dried to give 403.1 mg (95%) of 4,4′-diiodo-1,1′-bibicyclo[2.2.2]octane, mp 351–355 °C dec. Recrystallization from 1,2-dichloroethane gave an analytically pure sample, mp 365–367 °C dec.

The spectral data were the following: IR (KBr) 2950, 2915, 2865, 1470, 1450, 1440, 1345, 1300, 1230, 965, 935, 825, 815, 800, 755, 700, 640 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.37 (m, 12 H, CH$_2$CI), 1.46 (m, 12 H, CH$_2$); MS *m/e* (M − I) 343.0909 (calcd for C$_{16}$H$_{24}$I *m/e* 343.0925).

Anal. Calcd for C$_{16}$H$_{24}$I$_2$: C, 40.87; H, 5.14. Found: C, 40.88; H, 5.16.

1,1′-Bibicyclo[2.2.2]oct-4-yl Acetate. To a flask containing 266.6 mg (1.138 mmol) of 1,1′-bibicyclo[2.2.2]octan-4-ol was added 2.0 mL of acetic anhydride. The mixture was stirred at 135 °C for 3 h. Excess solvent was removed in vacuo to give 298.5 mg of a white solid. Recrystallization from hexane provided 1,1′-bibicyclo[2.2.2]oct-4-yl acetate as fine white flakes, mp 171–173 °C.

The spectral data were the following: IR (CHCl$_3$) 2945, 2920, 2865, 1720 (C=O), 1460, 1370, 1260, 1045 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.94 (s, 3 H, CH$_3$), 1.90 (m, 6 H, CH$_2$CO), 1.47 (m, 12 H, CH$_2$), 1.27 (m, 7 H, CH$_2$, CH); MS *m/e* 276.2083 (calcd for C$_{18}$H$_{28}$O$_2$ *m/e* 276.2089).

Anal. Calcd for C$_{18}$H$_{28}$O$_2$: C, 78.21; H, 10.21. Found: C, 78.00; H, 10.23.

4′-Iodo-1,1′-bibicyclo[2.2.2]oct-4-yl Acetate. A flask containing 204.2 mg (0.5668 mmol) of 4′-iodo-1,1′-bibicyclo[2.2.2]octan-4-ol and 5.0 mL of acetic anhydride was heated at 135 °C for 2.5 h. Excess solvent was removed in vauco to give 220.0 mg of a white solid. Recrystallization from ether gave pure 4′-iodo-1,1′-bibicyclo[2.2.2]oct-4-yl acetate as white needles, mp 282–284 °C.

The spectral data were the following: IR (CHCl$_3$) 2955, 2945, 2870, 1725, 1460, 1370, 1260, 1045 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.39 (m, 6 H, C(I)CH$_2$), 1.93 (s, 3 H, CH$_3$), 1.89 (m, 6 H, CH$_2$CO), 1.46 (m, 12 H, CH$_2$); MS *m/e* (M − I) 275.2027 (calcd for C$_{18}$H$_{27}$O$_2$ *m/e* 275.2011).

Anal. Calcd for C$_{18}$H$_{27}$IO$_2$: C, 53.74; H, 6.76. Found: C, 53.71; H, 6.76.

4-Iodo-4′-(tetrahydropyran-2-yloxy)-1,1′-bibicyclo[2.2.2]octane. The method of Weiss was employed.[30] To a stirring suspension of 282 mg (0.782 mmol) of 4′-iodo-1,1′-bibicyclo[2.2.2]octan-4-ol and 8.1 mg (0.043 mmol) of *p*-toluenesulfonic acid in 10 mL of methylene chloride was added 0.360 mL (329 mg, 3.91 mmol) of dihydropyran. The mixture was stirred at 25

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(28) (a) Doering, W. v. E.; Levitz, M.; Satigh, A.; Sprecher, M.; Whelan, W. P., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 1008. (b) Grob, C. A.; Ohta, M.; Renk, E.; Weiss, A. *Helv. Chim. Acta* **1958**, *41*, 1191–1197.

(29) Adcock, W.; Iyer, V. S. *J. Org. Chem.* **1988**, *53*, 5259–5266.

(30) Bernady, K. F.; Floyd, M. B.; Poletto, J. F.; Weiss, M. J. *J. Org. Chem.* **1979**, *44*, 1438–1446.

°C for 1.5 h and then diluted with 65 mL of ether. The combined organics were washed with 75 mL of a 2:1:1 mixture of water, saturated sodium bicarbonate, and brine. The aqueous phase was back-extracted with an additional 75 mL of ether. The combined organics were dried and concentrated in vacuo to give 515 mg of a pale yellow semisolid. Recrystallization from methylene chloride in hexane gave 260 mg (75%) of 4-iodo-4′-(tetrahydropyran-2-yloxy)-1,1′-bibicyclo[2.2.2]octane, mp 195–196 °C.

The spectral data were the following: IR ($CHCl_3$) 3005, 2950, 2920, 2870, 1460, 1350, 1235, 1220, 1210, 1155, 1130, 1115, 1075, 1030, 1010, 980, 950, 940, 910, 905, 860, 815 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.72 (s, 1 H, acetal), 3.92 (m, 1 H, OC*H*H), 3.42 (m, 1 H, OCH*H*), 2.38 (m, 6 H, CH_2CI), 1.90–1.27 (m, 24 H, CH_2); MS *m/e* ($M - C_5H_9O_2$) 343.0879 (calcd for $C_{16}H_{24}I$ *m/e* 343.0925).

Anal. Calcd for $C_{21}H_{33}IO_2$: C, 57.76; H, 7.48. Found: C, 57.64; H, 7.43.

Molecular Mechanics Calculations. Molecular mechanics calculations were performed with the MM2 program of Allinger[8a] for the "[*n*]-rods" and the MMP program of Gejewski[8b] for the "hybrid rods". An approximation of the transition state for interconversion of diasteromers of 4,4′-dihydro-[2]-rod was modeled on the highly symmetric carbon framework obtained from diiodo-[1]-rod and the carbon framework obtained from 1,4-dihydro-[1]-rod. This system was optimized by minimizing the steric energy from varying the central carbon–carbon bond length.

Acknowledgment. Appreciation is expressed to the National Science Foundation for support of and confidence in these efforts and to the NIH (Grant GM07487) for contribution to its inception.

Registry No. **1a**, 143123-40-4; **1b**, 143123-31-3; **2**, 74467-18-8; **3**, 7697-14-5; **4**, 74467-39-3; **5b**, 143123-32-4; **6a**, 143123-33-5; **6b**, 143123-41-5; **6c**, 143123-42-6; **8**, 111-90-0; **9**, 85232-17-3; **10**, 74467-40-6; **11a**, 143123-35-7; **12**, 74467-48-4; **13**, 143123-36-8; **14**, 143123-37-9; **15**, 20534-58-1; **16**, 23062-62-6; **17**, 143123-38-0; **18**, 143123-39-1; **21**, 59880-84-1; **22a**, 10364-05-3; **22b**, 143123-43-7; $HO[1]^+$, 73428-51-0; $HO[2]^+$, 143123-46-0; $HO[3]^+$, 143123-34-6; $HO[4]^+$, 143123-51-7; $HO[1]OH^{\bullet+}$, 143123-50-6; $HO[2]OH^{\bullet+}$, 143123-49-3; $HO[3]OH^{\bullet+}$, 143123-48-2; $HO[4]OH^{\bullet+}$, 143123-47-1; 1,1′-bibicyclo[2.2.2]octane–4,4′-diyl diacetate, 116278-39-8; 1,1′-bibicyclo[2.2.2]octane–4,4′-diol, 116263-79-7; 1,1′-bibicyclo[2.2.2]oct-4-yl acetate, 143123-44-8; 4′-iodo-1,1′-bibicyclo[2.2.2]oct-4-yl acetate, 143142-47-6; 4-iodo-4′-[(tetrahydropyran-2-yl)oxy]-1,1′-bibicyclo[2.2.2]octane, 143123-45-9.

Supplementary Material Available: X-ray crystallographic study of 4 (4 pages). This material is contained in many 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.

Azaborines: An ab Initio Study

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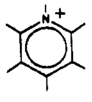
Three different indicators of aromatic electron delocalization have been investigated computationally for 1,2- (**3**), 1,4- (**4**), and 1,3-azaborine (**5**), all of which are experimentally unknown as unsubstituted compounds. MP2/6-31G* optimizations show a varying but considerable degree of electron delocalization. The calculated order of stability (**3** ≫ **4** > **5**) resolves the contradictions of former reports. In contrast to the noncorrelated level, consideration of electron correlation significantly lowers the relative energy of the 1,3-isomer, for which not even substituted derivatives are known. Natural bond orbital (NBO) analyses confirm the expected Lewis structures of the 1,2- and 1,4-isomers but offer an interesting description of the intricate π-system of 1,3-azaborine. Isodesmic equations reveal a resonance energy for **4** similar to stable Hückel aromatics and a somewhat smaller effect for **3**, whereas a hyperhomodesmotic equation assigns half the resonance energy of benzene to **4**. Basic differences in the σ framework of the azaborines are considered to be responsible for the stability of **3**. Computational results are supported by comparison of the scarce NMR data with chemical shifts calculated by the individual gauge localized orbitals (IGLO) method.

Introduction

Replacement of a carbon atom in benzene by one of its neighbors in the periodic table yields the charged, isoelectronic 1-borinate anion **1** or the 1-pyridinium cation **2**. Replacing two carbon atoms by one boron and one nitrogen leads to a series of heterocyclic molecules in which the formal charges in **1** and **2** cancel. Three structural isomers can be constructed: 1,2-dihydrido-1,2-azaborine (**3**), 1,4-dihydrido-1,4-azaborine (**4**), and 1,3-dihydrido-1,3-azaborine (**5**).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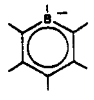
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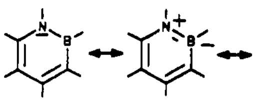
Each isomer has six π-electrons, suggesting some degree of aromatic electron delocalization. The differences in electronegativities of nitrogen and boron should, however, reduce the amount of aromatic character. Accurate calculations on the three isomers would provide valuable information about the balance between charge separation and electron delocalization.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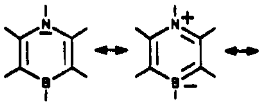
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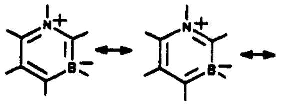
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None of the three parent heterocycles have been isolated. Unsubstituted **3** was detected in the mass spectrometer[1] by Dewar and co-workers, but could not be isolated because it rapidly polymerizes. The least substituted de-

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(1) Davies, K. M.; Dewar, M. J. S.; Rona, P. *J. Am. Chem. Soc.* **1967**, *89*, 6294.