J. Am. Chem. Soc. **1981**, *103*, 3297–3300

Theoretical Studies of Dodecahedrane. 3. Ab Initio Studies of Dodecahedrane and Its Inclusion Compounds

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Abstract: This paper extends our previous studies of dodecahedrane and its inclusion compounds through the use of ab initio molecular orbital calculations. The energetics of dodecahedrane and several of its inclusion compounds, $C_{20}H_{20}X$, with X = H^+, He, Li^+, Be, Be^+, Be^{2+}, Na^+, and Mg^{2+}, were considered at the STO-3G level. The included species were placed at the dodecahedrane midpoint in all cases, while the proton and lithium were placed at various positions along a fivefold axis as well. No barrier was found for passage of the proton through a dodecahedrane pentagonal face. A similar result was obtained by using as the model system planar cyclopentane plus a proton, which was studied at both the STO-3G and 4-31G levels. On the other hand, large barriers were found for the passage of lithium through a dodecahedrane face in $C_{20}H_{20}Li^+$ and for beryllium in the model system $C_5H_{10}Be^{2+}$. The most stable dodecahedrane system found was that with X = Be^{2+}; there, the beryllium was nominally sp^3 hydribidzed. The lowest excited triplet state of $C_{20}H_{20}Be^{2+}$, ^3G_g, was calculated to be 182 kcal/mol above the ground state. This state involves even more charge transfer from the framework to beryllium than the substantial amount which occurs in the ground state.

The dodecahedrane molecule, $C_{20}H_{20}$, continues to be the object of elegant synthetic efforts by the Eaton and Paquette groups[1] as well as the subject of several theoretical studies by semiempirical molecular orbital methods[2a,b] and molecular mechanics[2c–e] methods. In addition, semiempirical molecular orbital theory has been applied to several dodecahedrane inclusion compounds, $C_{20}H_{20}X$, with X contained in the 20-carbon cavity.[2b] Evidence for several stable inclusion compounds was found for X = H^+, Li^+, and especially Be. However, it is well-known that total energies produced by the INDO method can be unreliable. The purpose of the present paper is to reinvestigate these systems using ab initio molecular orbital theory at the STO-3G level[3a] and to study several new ones as well: X = Be^+, Be^{2+} (singlet and triplet), Na^+, and Mg^{2+}.

A further matter of interest regarding $C_{20}H_{20}X$ is whether X would be capable of penetrating a dodecahedron pentagonal face. This has led us to perform an extensive set of calculations for X = H^+ and Li^+ situated on a fivefold axis at the STO-3G level and further calculations for X = H^+ at the 4-31G level[3b] and Be^{2+} at the 6-31G level,[3c] using planar cyclopentane as a model for a dodecahedrane face. The results are described in the following section.

Results

A. Dodecahedrane. An STO-3G calculation on dodecahedrane with the use of R_{CC} = 1.54 Å (the value in diamond) and R_{CH} = 1.09 Å (the value in ethane) can be used to compare the STO-3G orbital energies with those obtained by the MINDO/3 method.[2b] Good agreement is found, particularly for the higher occupied levels. The dodecahedrane total energy at this geometry is −760.1330 au. Optimization of the geometry furnished the slightly improved bond lengths R_{CC} = 1.555 Å and R_{CH} = 1.087 Å and a total energy of −760.1380 au. The R_{CC} = 1.54 Å, R_{CH} = 1.09 Å geometry was used in all $C_{20}H_{20}X$ calculations to enable comparison with prior semiempirical results. Considerations of computer time precluded a reoptimization of each dodecahedrane framework in $C_{20}H_{20}X$. This would have modified our results quantitatively but not qualitatively, and would not affect the conclusions.

Table I. Orbital Energies of Dodecahedrane[a]* (au)

orbital	ab initio	MINDO/3
$2a_g$	−1.1599	−1.71
$2t_{1u}$	−1.0790	−1.43
$2h_g$	−0.9480	−1.11
$2g_u$	−0.8271	−0.87
$2t_{2u}$	−0.7046	−0.72
$3a_g$	−0.6892	−0.71
$2g_g$	−0.6595	−0.65
$3t_{1u}$	−0.6242	−0.61
$3h_g$	−0.5454	−0.52
$3t_{2u}$	−0.4614	−0.45
$4h_g$	−0.4247	−0.41
$3g_u$	−0.4041	−0.40
$1h_u$	−0.3818	−0.37
$3g_g$	−0.3491	−0.36

[a] The CC and CH bond lengths used were 1.54 and 1.09 Å, respectively. The C_{1s} core orbitals transform as a_g, t_{1u}, h_g, g_u, t_{2u}, and g_g and their energies are ca. −11.022 au.

It is amusing to consider whether the STO-3G energy of dodecahedrane is of any value in estimating its heat of formation. Using the "homodesmotic"[4] (or "group separation reaction"[5])

$$\underset{\text{isobutane}}{20(CH_3)_3CH} \rightarrow \underset{\text{dodecahedrane}}{(CH)_{20}} + \underset{\text{ethane}}{30(CH_3)_2} \qquad (1)$$

wherein the types and numbers of CH and CC bonds are matched as closely as possible in reactants and products, we obtain −14.8 kcal/mol for the change in energy of reaction 1. Correcting for zero-point energies[6] and temperatures[3b] this furnishes $\Delta H_{f,298K}$ (dodecahedrane) = −29.4 kcal/mol, in fair agreement with the molecular mechanics values of Engler et al.,[2d] −0.22 kcal/mol, and Allinger,[2a] 22.5 kcal/mol. Unfortunately, the accuracy of the ab initio value is very difficult to assess.

B. Protonated Dodecahedrane ($C_{20}H_{20}H^+$). A proton was placed along the dodecahedrane fivefold axis (z) at various positions from the center (O), z = 0.0 Å, through a pentagonal

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[1] For recent reviews see: (a) P.E. Eaton, *Tetrahedron*, **35**, 2189 (1979); (b) *Top. Curr. Chem.*, **79**, 41 (1979).

[2] (a) J. M. Schulman, T. Venanzi, and R. L. Disch, *J. Am. Chem. Soc.*, **97**, 5335 (1975); (b) J. M. Schulman and R. L. Disch, *Ibid.*, **100**, 5677 (1978); (c) O. Ermer, *Angew. Chem., Int. Ed. Engl.*, **16**, 411 (1977); E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *Ibid*, **95**, 8005 (1973); (e) and N. L. Allinger, *ibid.*, **99**, 8127 (1977).

[3] (a) W. J. Hehre, R. J. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc*, **92**, 4796 (1970); (c) J. S. Binkley and J. A. Pople, *J. Chem. Phys.*, **66**, 879 (1977).

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[5] J. D. Dill, A. Greenberg, and J. F. Liebman, *J. Am. Chem. Soc.*, **101**, 6814 (1979).

[6] For the zero-point energies we have used the calculated value of ref 3 for dodecahedrane and the isobutane value of K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4844 (1956). STO-3G energies of isobutane and ethane were taken from the Supplementary Material Table of ref 9.

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Table II. Energies, Atomic Charges, and Spin Densities for $C_{20}H_{20}X$ with X at Various Locations

X	location[a]	energy,[b] kcal/mol	charges[d]			spin densities		
			P_X	P_C	P_H	X	C	H
		0.0		−0.05	0.05			
H^+	O	−42.4[c]	0.74	−0.08	0.10			
H^+	F	−114	0.33	−0.03[f] to −0.10	0.07[f] to 0.13			
He	O	43.3	0.01	−0.05	0.05			
Li^+	O	−5.24	0.96	−0.09	0.09			
Li^+	F	394	1.07	−0.04 to −0.23	0.07 to 0.12			
Be	O	299	0.12	−0.05	0.04			
Be^+ (^2A_g)	O	107	0.61[e]	−0.07	0.09	0.870	−0.008	0.014
Be^{2+} (^1A_g)	O	−167	1.06	−0.10	0.14			
Be^{2+} (^3G_g)	O	15.0	0.59	−0.07	0.13	0.859	0.02	0.04
Na^+	O	76.0	0.96[g]	−0.09	0.09			
Mg^{2+}	O	−56.7	1.56[h]	−0.12	0.14			

[a] O = geometric center of dodecahedrane; F = center of a pentagonal face of carbon atoms. [b] Energies are relative to X and dodecahedrane at infinite separation, calculated in the STO-3G basis set (without the use of ghost atomic orbitals at the position of X). R_{CC} = 1.54 Å and R_{CH} = 1.09 Å. [c] Inclusion of a hydrogen ghost orbital at O in dodecahedrane changes this energy to −41.8 kcal/mol. [d] Atomic charges in units of electrons. [e] The gross orbital charges on X are 1s, 1.98 e; 2s, 0.29 e; $2p_x = 2p_y = 2p_z$, 0.22 e. [f] The dodecahedrane carbons and hydrogens are no longer all equivalent. The range of charges found is given. [g] The gross orbital charges on Na are 1s, 2.00 e; 2s, 1.93 e; $2p_x = 2p_y = 2p_z$, 1.79 e; 3s, 0.08 e; $3p_x = 3p_y = 3p_z$, 0.22e. [h] The gross orbital charges on Mg are 1s, 1.99 e; 2s, 1.96 e; $2p_x = 2p_y = 2p_z$, 1.88 e; 3s, 0.19 e; $3p_x = 3p_y = 3p_z$, 0.22 e.

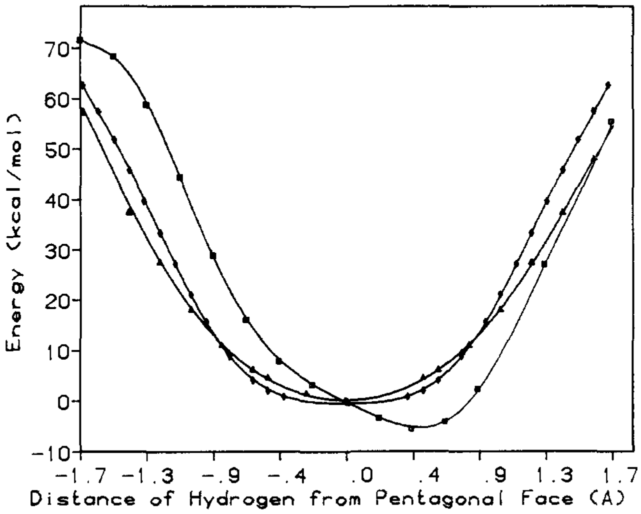

Figure 1. The energies of protonated dodecahedrane (squares) and protonated planar cyclopentane (diamonds, STO-3G; triangles, 4-31G) vs. distance of the hydrogens from the pentagonal face along the fivefold axis. For dodecahedrane, −1.7 Å is the molecular center. The zero of energy corresponds to the face-protonated species.

face (F), z = 1.715 Å, to the exterior of the molecule (see Figure 2 of ref 2b). Figure 1 shows the total energies obtained relative to the energy with the proton at F. A single minimum in the energy is found for the proton exterior to dodecahedrane by ca. 0.4 Å from F. Inside the cavity the energy increases monotonically, reaching a maximum of 71.6 kcal/mol at O relative to F. The atomic charge of the included H is 0.74 e while the hydrogens and carbons of the dodecahedrane framework have atomic charges of 0.10 e and −0.08 e, respectively.

Exterior to the cavity the energy of $C_{20}H_{20}H_+$ increases monotonically as the proton is moved away from its minimum energy position (Figure 1). Calculations were carried out to a proton distance of 3.43 Å, which places the face equidistant from the proton and O. The SCF convergence was still quite good at this geometry and the energy obtained was 55.4 kcal/mol, a lower energy at this position than at O. However, the proton is more stable at O than at infinity by 42.4 kcal/mol (Table II). As a control calculation we placed a hydrogen 1s shell (ghost atom) at O and recalculated the energy of dodecahedrane. The reduction in energy was only 3 kcal/mol relative to the STO-3G result, indicating that most of the −42.4 kcal/mol is not due merely to an expansion of the framework basis.

The most interesting results for protonated dodecahedrane are (i) the external minimum on the fivefold axis ca. 0.4 Å from F with an energy of −120 kcal/mol relative to infinite separation and (ii) the absence of a maximum as the proton passes through a dodecahedrane face, despite the very large attendant increase in nuclear repulsion energy. These results are in qualitative agreement with the previous MINDO/3 calculation[2b] which gave a minimum relative to infinity of −94 kcal/mol at an exterior point 0.6 Å from F. In contrast, the INDO calculations furnished an internal as well as an external minimum and a small barrier at F. We did not attempt to find a global minimum for protonated dodecahedrane, but since the geometry-optimized STO-3G energy of ethane furnishes a proton affinity of 167 kcal/mol,[7] it seems quite likely that the proton would be more stable bridging a dodecahedrane CC bond. Clearly, a rather extensive geometry optimization would be required to establish the exact proton position. Moreover, the STO-3G basis set is not appropriate for calculating accurate proton affinities.

We were intrigued by the rather low energy of $C_{20}H_{21}{}^+$ with the proton on a dodecahedrane face. In order to determine whether this result was unique to dodecahedrane or a consequence of using a minimal basis set, we considered the problem of planar cyclopentane with a proton on its fivefold axis. Calculations were performed with both the STO-3G and 4-31G basis sets. The results, displayed as energies relative to the proton in the plane

Table III. Energies of Protonated Planar Cyclopentane for Various Proton Positions Along the Fivefold Axis (in kcal/mol)

dist of proton from plane of C, A	energy rel to center-protonated cyclopentane	
	STO-3G	4-31G
0.0[a]	0.0[a]	0.0
0.5	2.0	4.6
1.0	21.1	18.2
1.5	51.8	47.9
1.7	62.6	
2.0		65.1
3.0		85.7
4.0		90.4
infinity	96.4[b,c]	92.3[b]

[a] The zero of energy corresponds to the proton in the center of the cyclopentane ring which is taken to be planar with R_{CC} = 1.54 Å, R_{CH} = 1.09 Å, and tetrahedral HCH angles. [b] Total energies of cyclopentane in this geometry were STO-3G, −192.88548 au and 4-31G, −194.87109 au. [c] The cyclopentane STO-3G energy is lowered to −192.88802 au through the use of a ghost atom with hydrogen basis functions at the cyclopentane center. This change is ca. 1.6 kcal/mol.

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(7) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.* **93**, 808 (1971).

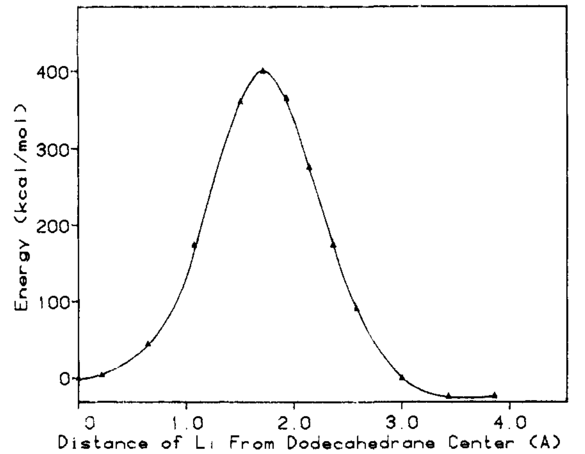

Figure 2. Energy of $C_{20}H_{20}Li^+$ vs. position of the lithium on the fivefold axis. The triangles indicate computed points.

of the ring, are shown in Figure 1, along with the energies of protonated dodecahedrane. It can be seen that (i) the results for cyclopentane are qualitatively similar to those of dodecahedrane, aside from the fact that the cyclopentane curve is necessarily symmetric about the inplane proton configuration whereas the $C_{20}H_{21}^+$ is asymmetric with an exterior minimum, and (ii) the STO-3G and 4-31G results for $C_5H_{11}^+$ are in good agreement. A proton is stable at F in $C_{20}H_{21}^+$ relative to infinite separation by 114.1 kcal/mol; for $C_5H_{11}^+$ the corresponding STO-3G and 4-31G values are 96.4 and 92.3 kcal/mol, respectively.[8] In order to determine how much of the $C_5H_{11}^+$ stabilization was due to the presence of 1s basis functions at the cyclopentane center merely improving the framework, an STO-3G calculation with a ghost atom at the center was performed. The total energy decreased by 1.6 kcal/mol, which is only 2% of the $C_5H_{11}^+$ stabilization energy. From these calculations it is clear that a proton can penetrate a cyclopentane face of dodecahedrane. Whether it will is, of course, another matter.

C. Dodecahedrane + Helium ($C_{20}H_{20}He$). Little needs to be said about this system. The interaction between these two closed shells should be repulsive and indeed it is, by 43.3 kcal/mol (22 kcal/mol in INDO[2b]). The He atomic charge is only 0.01 e and the C and H charges are almost identical with those in dodecahedrane itself.

D. Dodecahedrane + Lithium Ion ($C_{20}H_{20}Li^+$). STO-3G calculations were performed for $C_{20}H_{20}Li^+$ with the lithium located on a fivefold axis. The resulting energies relative to that of lithium at the dodecahedrane center, O, are plotted in Figure 2. The lithium is stable relative to infinite separation by only 5.2 kcal/mol. A barrier to passage through the dodecahedrane face of ca. 400 kcal/mol is found. The minimum energy position along the fivefold axis is exterior to the molecule ca. 1.7 Å from F.

The extent of covalent interaction between the lithium and dodecahedrane moities seems quite small. The gross orbital charges in the lithium 2s and 2p orbitals were only 0.01 e and 0.12 e, respectively. The lithium total charge was nearly unity, 0.96 e.

The present results contrast with the previous INDO study,[2b] which furnished a minimum at O of −162 kcal/mol, an external minimum 1.8 Å from F of −272 kcal/mol, and a barrier at F of 600 kcal/mol. Also, the INDO calculation predicted considerable overlap with the lithium 2s and 2p atomic orbitals, which is not the case in the ab initio calculations. Nonetheless, the INDO calculations were qualitatively correct in predicting an external minimum and a high barrier to passage through a pentagonal face.

E. Inclusion Complexes with Beryllium. The energy of $C_{20}H_{20}Be$ with Be at O (Table II) shows that neutral beryllium is unstable at the dodecahedrane center relative to infinite separation (as dodecahedrane and Be).[9] This result is in marked contrast with the very high stability of $C_{20}H_{20}Be$ given by the INDO method,[2b] which is undoubtedly incorrect. As seen from Table II, $C_{20}H_{20}Be^+$ is also unstable relative to dissociation, by 107 kcal/mol (the unrestricted Hartree–Fock method, UHF, was employed). On the other hand, the system $C_{20}H_{20}Be^{2+}$ is stable by 167 kcal/mol relative to infinite separation as Be^{2+} and $C_{20}H_{20}$. In this dication there is considerable charge transfer (0.94 e) from the framework into the beryllium 2s and 2p orbitals, the beryllium being approximately sp^3 hybridized.

The electron affinity of the $C_{20}H_{20}Be^{2+}$ species is 0.22 au, a value similar to the calculated electron affinity of Be^+, 0.25 au, and much smaller than that of Be^{2+}, 0.65 au. It can be argued that the beryllium of $C_{20}H_{20}Be^{2+}$ is already in the +1 state as it has obtained nearly one electron from the framework.

Because of the high electron affinity of Be^{2+} relative to dodecahedrane, an interesting question is: are the electrons of $C_{20}H_{20}Be^{2+}$ adequately described by the restricted Hartree–Fock (RHF) closed shell approximation or does the high electron affinity of Be^{2+} lead to an open shell triplet or singlet ground state, i.e., a diradical state in which one unpaired electron resides primarily in the beryllium 2s orbital and the other in a framework $3g_g$ orbital? To answer this question UHF calculations were carried out for the lowest triplet and singlet states. The triplet state (^3G_g, only barely spin contaminated) was 182 kcal/mol above the ground state.[10] The atomic charges and spin densities given in Table II show that the beryllium atom in the triplet state is strikingly similar to that in $C_{20}H_{20}Be^+$. Most of the excitation came from the framework as had been expected. The triplet state density matrix was then employed as the starting point for a UHF calculation of the singlet state and the calculation converged to the previous RHF result for the singlet. This result and the high energy of the triplet state imply that the closed shell model is adequate for the ground state of $C_{20}H_{20}Be^{2+}$.

To assess the barrier to entry of Be^{2+} into $C_{20}H_{20}$, we studied cyclopentane plus Be^{2+}, $C_5H_{10}Be^{2+}$, analogous to our model studies of protonated dodecahedrane described in section B. This allowed us to use the extended basis set 6-31G. A minimum energy configuration was found for the beryllium on the fivefold axis at a point 1.2 Å from the cyclopentane midpoint. This system was stable by 135 kcal/mol relative to infinite separation. However, the energy of $C_5H_{10}Be^{2+}$ with the beryllium at the cyclopentane center is 216 kcal/mol greater than at infinite separation. This is a high barrier to passage through a cyclopentane ring by beryllium, unlike the case of a proton.

F. $C_{20}H_{20}Na^+$ and $C_{20}H_{20}Mg^{2+}$. Two systems with X a second-row element at the dodecahedrane center were studied, $C_{20}H_{20}Na^+$ and $C_{20}H_{20}Mg^{2+}$. The former proved to be unstable relative to infinite separation by 76 kcal/mol. As shown in Table II, the atomic charge on sodium was 0.96 e which is identical with that on lithium in $C_{20}H_{20}Li^+$ and nearly the total charge of the system. Approximately 0.2 e was shifted from each 2p orbital to the corresponding 3p orbital and the 3s orbital remained nearly vacant with a population of only 0.08 e.

In contrast to the sodium case, the magnesium dication was stable relative to infinite separation by 57 kcal/mol. The atomic charge on magnesium is 1.56 e, indicating a transfer of 0.44 e from the dodecahedrane framework, more specifically, the hydrogens. This electron density is distributed among the 3s and 3p orbitals of magnesium. The stability of $C_{20}H_{20}Mg^{2+}$ is much less than that of $C_{20}H_{20}Be^{2+}$, which shows a charge transfer of 0.94 e from the dodecahedrane framework. Compared to their first-row counterparts, the X = Na^+, Mg^{2+} systems suggest that no additional stability will be found by descending the periodic table although, admittedly, the role of 3d orbitals has not been assessed for the second row.

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(8) At infinite separation the ground state would undoubtedly be a hydrogen atom and an ionized dodecahedrane. Similarly, the ground state of $C_{20}H_{20}Be^{2+}$ at infinite separation should be Be^+ and ionized dodecahedrane.

(9) Although there is some certainty in the STO-3G beryllium 2s, 2p scaling factor, we have found that a 10% increase or decrease over the value in ref 3a changed our results negligibly.

(10) The RHF triplet state was 91 kcal/mol higher than the UHF triplet.

Conclusions

The present ab initio survey of dodecahedrane inclusion compounds offers no promise of special stability for these systems. The neutral species are unstable, and only limited stability is found for the included ions, which are essentially "unsolvated" by the hydrocarbon framework. Perhaps the most promising candidate is $C_{20}H_{20}Be^{2+}$ which is stable relative to dissociation by −170 kcal/mol. However, just as relevant as the energy is the probable large barrier to inward and outward passage. Thus, the beryllium would have to be synthesized "in situ" and would thereafter remain inside the dodecahedron.

An interesting question regarding $C_{20}H_{21}^+$ (and the other cations) is the role of electrostatic vs. covalent stabilization. The total stabilization energy of $C_{20}H_{21}^+$ with the hydrogen at the center is −42.4 kcal/mol. An SCF calculation was performed with a bare proton (i.e., without basis functions) at the center and it furnished a stabilization energy of only 10.7 kcal/mol. Since this energy includes both electrostatic and charge-induction energies,[11] the bulk of the proton affinity appears to be covalent in origin.

It is interesting to point out that the induction energy does not include charge-induced dipole interactions. As we have previously shown,[1] the lowest nonvanishing permanent moment of dodecahedrane is its 2^6-pole moment. Since the perturbing proton does not lower the I_h symmetry of the system, the induced moment can also be no lower than order 2^6.

Acknowledgment. One of us (J.M.S.) is pleased to acknowledge a grant in aid from the CUNY Research Foundation.

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[11] The STO-3G basis set furnished a polarizability of 13.7 × 10^{-24} cm^3, which is about half that expected from empirical bond polarizability values. We have found similar STO-3G underestimates of polarizabilities in other molecules.

Conformational Interconversions in Pentaalkylhydrazine Cation Tetrafluoroborates

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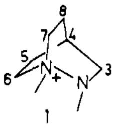
Abstract: Peak coalescence dynamic NMR data gave the results that $\Delta G^\ddagger$ for equilibration of C_6 and C_7 in 1,2-dimethyl-1-diaza-2-azoniabicyclo[2.2.2]octane tetrafluoroborate (**1**) is 9.0 kcal/mol at −70 °C, that for N^+Me_2 interconversion in 1,1,2-trimethylhexahydropyridazinium tetrafluoroborate (**2**) is 11.1 kcal/mol at −20 °C, and that for N^+Me_2 interconversion in 1,1,2-trimethyl-1,2,3,6-tetrahydropyridazinium tetrafluoroborate is 10.4 kcal/mol at −40 °C. From broadenings at C_6 in **2** and **3** it was determined that **2** exists about 0.2 to 0.3% in the axial *N*-methyl form (−80 °C) and **3** about 3.5 to 5.5% (−80 °C). These results are interpreted to indicate that nitrogen inversion barriers are only rather weakly increased by inductive electron withdrawal, that rotational barriers in pentaalkylhydrazines lie between the "passing" and "nonpassing" barriers of the related tetraalkylhydrazines, and that the electronic energy destabilization of the ee relative to the ae form of 1,2-dimethylhexahydropyridazine (**6**) is about 2 kcal/mol.

We have carried out a dynamic carbon NMR study of conformational interconversions in pentaalkylhydrazinium tetrafluoroborates **1**–**3**. These salts were prepared by treatment of



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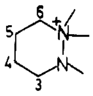

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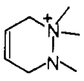

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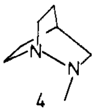
the corresponding iodide salt (e.g., from **4** and MeI) with silver oxide and tetrafluoroboric acid, or by direct methylation of **5** and **6** with Meerwein's salt. Dimethylation was not observed under these conditions, but **4** gave an approximately 70:30 mixture of **1** and **7**, which were separated by crystallization.



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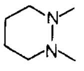

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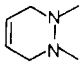

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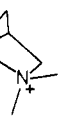

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The carbon NMR shifts observed at ambient temperature, where conformational interconversion is rapid, and at low temperature, where it is slow, are shown in Table I. The rates of exchange between mirror image conformations of **1**, **2**, and **3** were determined by simulation of the NMR spectra at various temperatures, and the activation parameters calculated are summarized in Table II.

Table I. Carbon NMR Shifts for Pentaalkylhydrazine Cations (ppm Downfield from Internal Me_4Si)

compd	ambient *T*, °C	low *T*, °C	assignment
1[a]	49.19	48.74	$N_1{}^+Me$
	37.99	37.55	N_2Me
	58.05	57.58	C_3H_2
	20.91	20.64	C_4H
	22.58	22.30 (br)	C_5, C_8
	56.03	50.03, 60.97	C_6, C_7
2[b]	46.51	36.12, 54.29	$N_1{}^+Me$
	38.22	37.75	N_2Me
	50.79	49.95	C_3H_2
	18.72	18.12	C_4H_2
	22.24	22.01	C_5H_2
	67.07	66.24	C_6H_2
3[c]	46.48	52.12, 36.96	$N_1{}^+Me$
	37.01	36.53	N_2Me
	51.09	50.53	C_3H_2
	116.61	117.42, 117.61	C_4H, C_5H
	63.21	62.70	C_6H_2

[a] Low-temperature spectrum at −102 °C. [b] At −71 °C. [c] At −86 °C.

Discussion

2-Azabicyclooctane Derivatives. The carbon assignments for **1** seem unambiguous. The two sets of two equivalent methylene carbons at ambient temperature, C_6, C_7 and C_5, C_8, differ greatly

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