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Theoretical Investigation of the Hyperconjugation Effect on Nitrogen Inversion Barriers in Aziridines[1]

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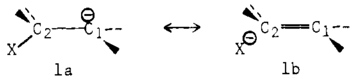
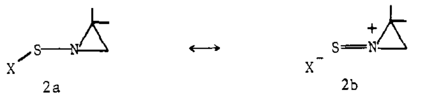
Abstract: Ab initio (STO 3G and 4-31G) SCF-MO calculations were carried out on three systems: CH_3NH_2, FCH_2NH_2, and $H_3N^+CH_2NH_2$. In all three cases the aziridine system was simulated by constraint of the amine HNH angle to 60°. The F and $-NH_3^+$ substituents were chosen as different but typical electron-withdrawing groups which might be involved in anionic hyperconjugation with the nitrogen lone pair. Hyperconjugation was probed by examining effects on geometry (C–N and C–F bond lengths), energetics (barriers to torsion about the C–N bond and nitrogen inversion), and charge transfer (from NH_2 to F or $-NH_3^+$). The valence bond concept of hyperconjugation was related to the PMO concept of two-electron interactions which were probed in the HOMO and LUMO orbitals. It was concluded that all three types of hyperconjugation effects were found in the frontier orbitals but only the first two were substantially reflected in molecular properties. The conclusions of the calculations supported previous assessments of the importance of hyperconjugation in affecting torsional and inversional barriers in sulfenamides made on the basis of experimental studies.

The concept of hyperconjugation arose within the framework of qualitative valence bond (VB) theory as a stabilizing and charge delocalization mechanism for carbocations and intermediates in electrophilic aromatic substitution which could be expressed in terms of bond no-bond canonical structures.[3,4] Later the concept was extended to explain the supposed extra stabilization of carbanions by electron-withdrawing substitutents attached to adjacent carbon atoms (negative or anionic hyperconjugation).[5,6] Thus canonical structures **1a** and **1b** represent the delocalization of charge on C_1 by transfer to the polar substituent X. This picture has been used to explain experimental observations in organo fluorine chemistry,[5,6] although some workers have expressed the view that experimental results could be accommodated without invoking hyperconjugation.[6b] In addition, theoretical evidence has been adduced to support the view that the charge delocalization predicted by canonical structure **1b** is, in fact, negligible.[7]


1a 1b

Recently, hyperconjugation has been used by us[8] and others[9] to rationalize effects on nitrogen inversion barriers. In cases where an electron-withdrawing group (capable of bearing a negative charge) was located α to a nitrogen atom, a substantial decrease in the nitrogen inversion barrier was observed. It was argued that this derived from greater hyperconjugative stabilization of the planar transition state than of the pyramidal ground state. Thus, the barriers to inversion of the ((trihalomethyl)sulfenyl)aziridines (**2**) (X = CCl_3, CF_3) were found to be lower than those in the analogous (alkylsulfenyl)aziridines (X = CH_3, *t*-Bu, Ph).[8a,b] An analysis which took into consideration steric factors indicated that the barriers measured for **2** were ca. 2–2.5 kcal/mol lower than anticipated for aziridines with nonpolar substituents of comparable size. The stabilization of the transition state by polar groups was associated with the greater contribution of canonical structure (**2b**) in the planar transition state where the lone pair on nitrogen occupies a pure p orbital and is better suited for π conjugation.


2a 2b

In this paper we present theoretical evidence which supports our initial qualitative interpretation of polar substituent effects on nitrogen inversion in aziridines. In addition we discuss the structural and energetic consequences of hyperconjugation in this and related systems. Recently, hyperconjugation has been associated mainly with effects in ionic species.[10] In the present study we examine effects in neutral molecules. Finally, we have tried to relate the VB concept of hyperconjugation to the perturbational molecular orbital (PMO) treatment of nitrogen inversion. We shall present evidence that the traditional VB concept of hyperconjugation as a charge delocalization mechanism is not reflected to a significant extent in theoretical results, in accord with the recent findings of Streitwieser and co-workers.[7] The consideration of canonical structures **2a** and **2b** allows a number of structural and energetic consequences. This set of consequences may be regarded as a tentative phenomenological definition of hyperconjugation. Since phenomenological hyperconjugation is subject to experimental verification and quantification, it is useful to enumerate this set of experimental characteristics.

Our goal is to examine experimental and theoretical data to determine which, if any, of these consequences is borne out in practice and to modify, if necessary, the set of criteria to provide a useful working definition of hyperconjugation. Examination of canonical structure **2b** suggests that hyperconjugation should be associated with shortening of the C–N bond, and parallel lengthening of the C–X bond, relative to their standard values

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(1) (a) This paper may be considered as part 38 of the series "Stereochemistry in Trivalent Nitrogen Compounds". For part 37 see: (a) Raban, M.; Craine, L. H.; Greenblatt, J. *Tetrahedron Lett.* **1981**, 807. (b) We are grateful for support of this work by the National Science Foundation (Grant CHE 77-10061).

(2) On sabbatical leave from the Department of Chemistry, Ben Gurion University of the Negev, Beer Sheva, Israel.

(3) Baker, J. W.; Nathan, W. S. *J. Chem. Soc.* **1935**, 1840, 1844.

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(5) Roberts, J. D.; Webb, R. L.; McElhill, E. A. *J. Am. Chem. Soc.* **1950**, *72*, 408.

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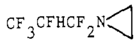
in the absence of hyperconjugation. Secondly, charge delocalization implicit in the canonical structures should result in transfer of electron density from nitrogen to the X group. Finally, VB theory suggests increased stabilization of the molecule with increasing contribution from the minor (i.e., higher energy) canonical structure, in the present case **2b**. This should affect the nitrogen inversion barrier as well as make a contribution to the torsional barrier. Since canonical structure **2b** features a double bond to nitrogen, its contribution should be greater in the transition state for nitrogen inversion than in the ground state. Since hyperconjugation is expected to stabilize the planar transition state, more than the ground state, its effect should be to lower the barrier to nitrogen inversion.[11,12]

Of these three phenomenological criteria, two, the structural and the energy criteria, can in some cases be assessed from experimental data. Indeed, trends in nitrogen inversion barriers as well as experimental geometries determined by X-ray crystallography provide evidence for the importance of hyperconjugation. Thus, the lowered barriers to nitrogen inversion in α-fluoro aziridines, e.g., **3**,[9] and in *N*-((trihalomethyl)sulfenyl)aziridine (**2**)[8a,b] as well as in *N*-(methoxymethyl)isoxazolidine (**4**)[8c] have been attributed to negative hyperconjugation on the basis of the energy criterion. The relatively short N–S bond and long S–C and N–SO_2 bonds in *N*-((1-naphthyl)ethyl)-*N*-(phenylsulfonyl)trichloromethanesulfenamide are examples of the geometric criterion for hyperconjugation.[13] Similar crystallographic evidence was found in phosphonamide (**5**), in which the P–N bond is relatively short and the P–Cl bond is relatively long.[14] The high torsional barriers in sulfenamides bearing inductively withdrawing substituents have been attributed to hyperconjugation.[8d,e] Finally, numerous applications of the energy and geometry criteria of hyperconjugation to other phenomena in organic chemistry have been studied recently.[15-20]



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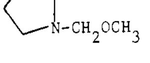

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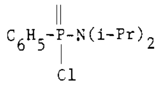


$C_6H_5-P(=O)(Cl)-N(i\text{-}Pr)_2$

5

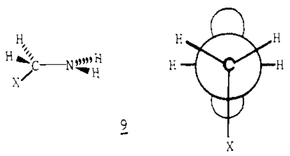
All three probes for hyperconjugation, i.e., geometry, charge distribution and energy, can be applied to the results of SCF-MO calculations. Such calculations can provide a useful supplement to experimental data, especially where the latter are difficult or impossible to obtain. Thus, while ground-state geometries can be obtained from the results of X-ray crystallographic measurements, geometries of the transition state for nitrogen inversion can only be arrived at by SCF-MO calculation. Likewise, changes in charge densities in various parts of a molecule are not amenable to convenient experimental evaluation but are readily obtained from MO calculations. The collection of this kind of data belonging to the three above-mentioned categories was one motivation for carrying out this investigation.

Method

Three molecular models of the form XCH_2NH_2 were chosen: **6**, CH_3NH_2; **7**, FCH_2NH_2; and **8**, $H_3N^+CH_2NH_2$. Geometries with pyramidal nitrogen represent the ground state for nitrogen inversion and are designated GS, those in which the arrangement of ligands at nitrogen is planar correspond to the transition state for nitrogen inversion and are labeled TS. In all three cases the aziridine ring was simulated by constraint of the HNH angle to 60°. This constraint was necessary in order to raise the barrier to nitrogen inversion to the point where the effect of hyperconjugation might be manifest and to allow comparison with experimental barriers in aziridines. Compounds **7** and **8** represent models for aziridines with polar substituents α to nitrogen. While fluorine has often been regarded as the most convenient substituent in such calculations, it is known to present problems in SCF-MO calculations. In our particular case the π-donor properties of fluorine (i.e., the presence of low-lying occupied p orbitals) could complicate the analysis of the eigenfunctions. In addition, it might have been argued that calculations on a fluoro compound could be specific to this substituent and not a general reflection of the effect of inductive electron withdrawal. For these reasons we have chosen the NH_3^+ group in **8** as an additional model for a substituent which is strongly electron withdrawing in the inductive sense (i.e., a σ-withdrawing substituent).

Although our initial experimental observations were based upon sulfenylaziridines,[8a,b] similar observations have also been reported in systems in which other elements (e.g., carbon or phosphorus) are attached to nitrogen.[9,21,22] Since the effect appears to be general, we have carried out this study on model compounds with C–N bonds to eliminate the complications associated with calculations involving second-row elements and lone pairs of electrons.

We have adopted three general strategies in making comparisons which can be relevant in assessing the magnitude of possible hyperconjugation effects. One comparison is that between the nitrogen inversion barriers in **7** and **8** with that calculated for **6** in which hyperconjugation should be at a minimum. Secondly, we have made comparisons between two geometries of the inversion transition state of **8** (and of **7**). These two geometries (**9** and **10**) both feature planar nitrogen (TS) but differ in the relative orientation of the C–X σ bond and the nitrogen lone-pair orbital. They are characterized by torsion angles between the C–X bond and the normal to the HNH plane (i.e., the lone-pair local axis) of 0 and 90°, respectively. In **9** these two orbitals could conceivably interact (overlap) while in **10** the C–X σ bond lies in the nodal plane of the lone-pair p orbital. The difference between the total energies of these two geometries should provide a measure of the importance of hyperconjugation while eliminating possible isotropic (dihedral angle independent) inductive effects. Similar comparisons could also be made for the inversion ground state in which nitrogen is pyramidal. In this case there are three limiting torsional geometries to be considered, **11**, **12**, and **13**, corresponding to torsional angles (between the C–X bond and the bisector of the HNH angle) of 0, 90, and 180°, respectively. We have arbitrarily chosen 0° to represent the anti-periplanar relationship between the lone-pair orbital and X. In both cases (GS and TS) we have examined additional points along the torsional coordinate in order to define more fully the shape of the torsional potential since a substantial rotational barrier could be considered prima facie evidence for hyperconjugation. Indeed, the substantial twofold component of the torsional barrier in fluoromethyl amine was associated with hyperconjugation.[23]



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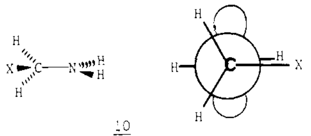

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[11] The importance of the energy criterion and its geometrical consequences in ionic systems at the TS geometry have been studied recently by Hoffman et al.[10]

[12] A refinement of the structural criterion to include "tilt" angles in **3** and analogues has recently been introduced by: Pross, A.; Radom, L.; Riggs, N. V. *J. Am. Chem. Soc.* **1980**, *102*, 2253.

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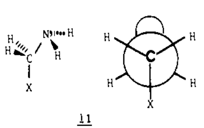
Table I. Calculated (431G) Energies and Geometries for Methylaziridine (6)

6-TS	torsion angle[a] 0° (=60°)	30° (=90°)
C–N, Å	1.4248	1.4248
total energy, au	−94.944329	−94.944329
relative energy,[b] kcal/mol	23.153	23.153
HOMO energy,[d] eV	−9.354	−9.354

6-GS	torstion angle[a] 0° (=120°)	30° (=90°)	60° (=180°)
C–N, Å	1.4769	1.4798	1.4827
pyramidal angle,[c] deg	116.260	116.485	116.693
total energy, au	−94.981226	−94.980173	−94.979142
relative energy,[b] kcal/mol	0.0	0.661	1.308
HOMO energy,[d] eV	−11.089	−11.065	−11.042

[a] The torsion angle is defined as the dihedral angle between the C–X bond and the bisector at the HNH angle. [b] Energies relative to the lowest energy form for 6, i.e., 6-GS, 0°. [c] The pyramidal angle is defined as the angle between the CN bond and the bisector of the HNH angle. [d] Using the conversion factor 1 au = 27.2107 eV.

Finally we make comparisons between the nitrogen inversion barriers at various torsion angles. Thus, if hyperconjugation were important, we might expect a smaller barrier to inversion at 0° and 180° torsion angles than at 90°, where the effect of hyperconjugation is minimal due to the orthogonality of the C–X and lone-pair orbitals. Hyperconjugation should be more important in **9** than in **11** because of better overlap with the C–X σ^* orbital and higher energy of the lone-pair orbital in **9** (which is pure p) relative to that in **11** (a hybrid orbital with substantial s character).



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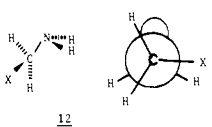

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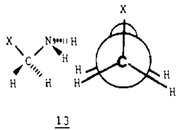

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Computation Section

Single determinant ab initio SCF-MO calculations were carried out by using the Gaussian 70 system of programs[24a] with the standard built in basis set.[24b] Extensive geometry optimizations were made for the molecules in this study, **6**, **7**, and **8**, both at their TS (planar) and GS (pyramidal) conformations and at their different torsional states, 0, 90, and 180°. For all of the optimizations the split valence shell 4-31G basis set was employed. Optimizations of the geometrical parameters were repeated until "self-consistency" was achieved, such that bond lengths in successive runs differed by no more than 0.015 Å and angles by no more than 2°. This required two passes in most cases and three to four in others. The following parameters were optimized: C–N bond length, C–X bond length, and the "pyramidal angle"—the angle between the C–N bond and the H–N–H bisector. The H–N–H angle was kept constant at 60° to simulate an aziridine ring, and N–H bond length was taken as 1.0 Å. The local geometry about carbon was fixed at a tetrahedral arrangement, with C–H bond lengths of 1.085 Å. In **6**, only the C–N bond and the pyramidal angle (at the ground state) were optimized.

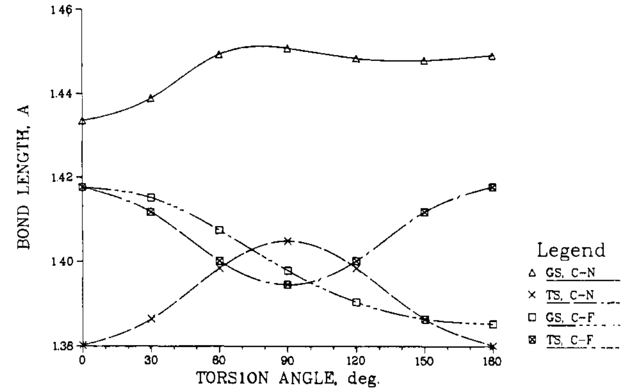

Figure 1. Calculated bond lengths in (fluoromethyl)aziridine (FCH_2NH_2, **4**) as a function of torsion angle: △, 7-GS, C–N bond, pyramidal nitrogen; □, 7-GS C–F bond, pyramidal nitrogen; ×, 7-TS, C–N bond, planar nitrogen; ⊠, 7-TS C–F bond, planar nitrogen.

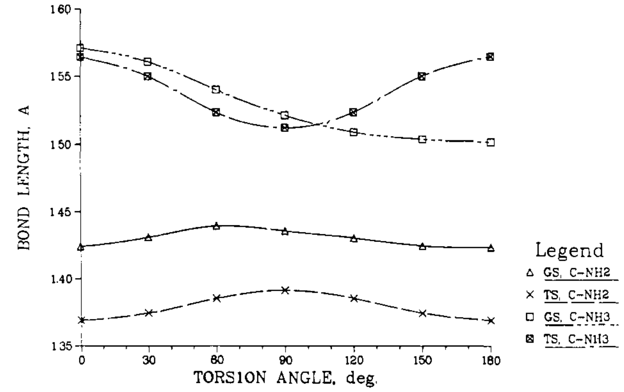

Figure 2. Calculated bond lengths in $H_3N^+CH_2NH_2$ (**8**) as a function of torsion angle: △, **8**-GS, C–NH_2 bond, pyramidal nitrogen; □, **8**-GS, C–X Bond (X = H_3N^+), pyramidal nitrogen; ×, **8**-TS, C–NH_2 bond, planar nitrogen; ⊠, **8**-TS, C–X bond, planar nitrogen.

In order to provide molecular orbitals more amenable to visualization and analysis, we repeated the calculations for the final optimized structures with the minimal STO-3G basis set. These results were also needed as input for plotting three-dimensional contour maps of molecular orbitals, using Jorgensen's program PSI/77.[25]

Results and Discussion

Examination of the results in Table I–III reveals that two of the criteria, the energy criterion and the geometry criterion, are well borne out by our calculations. However, our results do not indicate charge transfer of the magnitude that might have been expected on the basis of significant contribution of canonical structure **2b**.

Figures 1 and 2 illustrate changes in C–X and C–N bond lengths in the ground and transition states for nitrogen inversion as a function of torsion angle. The curves for the transition state in both cases (× and ⊠) provide a vivid picture of the geometric criterion. In both molecules the expected lengthening of the C–X bond and shortening of the C–N bond is observed in the 0° conformation, in which hyperconjugation should be maximal. The two bond lengths exhibit a pronounced anti-phase relationship, suggesting that the changes in these two bond lengths are manifestations of the same phenomenon. The situation in the ground state is more complicated. Between 0 and 90° the bond lengths show the expected trends. However, between 90 and 180° the possible changes due to hyperconjugation are obscured by the superposition of additional effects.

The degree of pyramidality at nitrogen could be assessed by using θ, the optimized angle between the C–N bond an the H–

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(23) (a) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371. (b) A similar Fourier analysis, for which we thank a reviewer, indicated stabilizing twofold components (**4**, 2.0 kcal/mol; **5**, 1.5 kcal/mol) slightly smaller than that reported[13a] for (2-fluoroethyl)amine, along with much larger onefold components. While the angular distortion made to simulate the aziridine system would lessen the validity of such an analysis, the qualitative results are in complete accord with our conclusions.

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(25) Jorgensen, W. L. Program No. 340, QCPE, University of Indiana, Bloomington, IN.

Table II. Calculated (431G) Energies and Geometries of (Fluoromethyl)aziridine (7)

7-TS	torsion angle[a] 0°	30°	60°	90°
C-N, Å	1.3802	1.3864	1.3984	1.4048
C-F, Å	1.4176	1.4117	1.4001	1.3945
μ,[b] D	1.946	1.864	1.706	1.627
total energy, au	−193.68762	−193.68439	−193.67786	−193.674574
relative energy,[c] kcal/mol	21.347	23.376	27.470	29.533

7-GS	torsion angle[a] 0°	30°	60°	90°	120°	150°	180°
C-N, Å	1.4335	1.4388	1.4493	1.4507	1.4483	1.4478	1.4489
C-F, Å	1.4176	1.4151	1.4074	1.3978	1.3904	1.3864	1.3853
pyramidal angle,[d] deg	117.05	116.97	116.41	115.95	116.64	119.55	119.65
μ,[b] D	0.901	1.227	1.816	2.356	2.767	3.031	3.124
total energy, au	−193.72164	−193.71855	−193.71342	−193.71110	−193.71007	−193.70802	−193.70680
relative energy,[c] kcal/mol	0.0	1.936	5.154	6.612	7.261	8.547	9.312

[a] The torsion angle is defined as the dihedral angle between the C-X bond and the bisector at the HNH angle. [b] The dipole moments were taken from 3G (431G) calculations. [c] Energies relative to the lowest energy form for 7, i.e., 7-GS, 0°. [d] The pyramidal angle is defined as the angle between the CN bond and the bisector of the HNH angle.

Table III. Calculated (431G) Energies and Geometries for (Ammoniomethyl)aziridine (8)

8-TS	torsion angle[a] 0°	30°	60°	90°
C-NH_2, Å	1.3690	1.3745	1.3855	1.3914
C-NH_3, Å	1.5641	1.5498	1.5233	1.5118
total energy, au	−150.271132	−150.267334	−150.259855	−150.256169
relative energy,[b] kcal/mol	14.018	16.401	21.094	23.407

8-GS	torsion angle[a] 0°	30°	60°	90°	120°	150°	180°
C-NH_2, Å	1.4240	1.4309	1.4393	1.4355	1.4303	1.4244	1.4233
C-NH_3, Å	1.5709	1.5607	1.5398	1.5400	1.5086	1.5034	1.5011
pyramidal angle,[c] deg	129.03	127.01	122.85	119.51	119.50	121.68	123.21
total energy, au	−150.277493	−150.276523	−150.277392	−150.283277	−150.289776	−150.292805	−150.293470
relative energy, kcal/mol	10.026	10.635	10.089	6.397	2.378	0.418	0.0

[a] The torsion angle is defined as the dihedral angle between the C-X bond and the bisector at the HNH angle. [b] Energies relative to the lowest energy form for 8, i.e., 8-GS, 180°. [c] The pyramidal angle is defined as the angle between the CN bond and the bisector of the HNH angle.

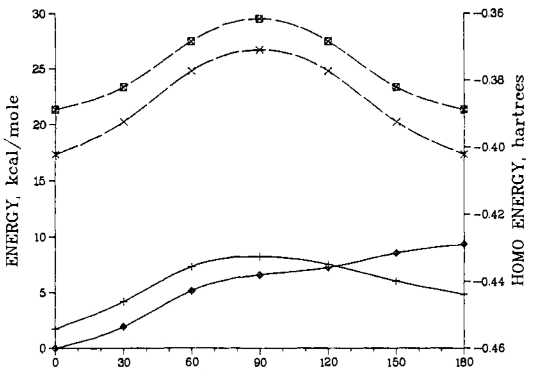

Figure 3. Relative total energies and HOMO energies in FCH_2NH_2 as a function of torsion angle: ⊠, 7-TS relative total energy; ×, 7-TS HOMO energy; ◇, 7-GS relative total energy; +, 7-GS HOMO energy.

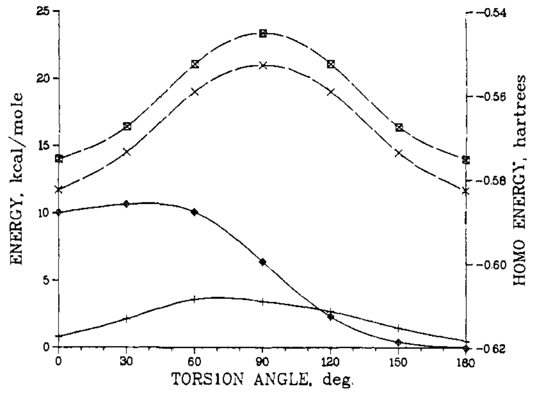

Figure 4. Relative total energies and HOMO energies in $H_3N^+CH_2NH_2$ as a function of torsion angle: ⊠, 8-TS, relative total energy; ×, 8-TS HOMO energy; ◇, 8-GS relative total energy; +, 8-GS HOMO energy.

N–H plane. This angle would correspond to 125° for a tetrahedral geometry and 180° for planar nitrogen. In aziridines this angle is normally around 120°.[26] The planarity of nitrogen in a number of acyclic amines substituted with electron-withdrawing groups vicinal to the lone pair (e.g. **15**) has been attributed to hyperconjugation.[14] In the present study we find that θ changes in the expected direction, it is larger in the 0° geometry than in the 90° geometry. However, the magnitude of this effect is rather small, possibly reflecting the steeper inversion potential in aziridines relative to simple acyclic amines.

The energy criterion is reflected in the barriers to both rotation and inversion. The calculated rotational barriers (Table II and III, Figures 3 and 4) in the transition state for inversion in **7** and **8** are substantial (8.2 and 9.4 kcal/mol, respectively) while that in methylaziridine (Table I) is negligible. This is in full accord with the predictions based on the VB model.

The ground-state energies (symbol ◇ in Figures 3 and 4) are not so simple to interpret since other effects are present.[23b] In compound **7**-GS, the 180° conformation, in which the fluorine and lone-pair orbitals have a syn relationship, exhibits a destabilization, while in **8**-GS this geometry is the torsional ground state.

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[26] Ito, T.; Sakurai, T. *Acta Crystallogr., Sect. B* **1973** *B29*, 1594.

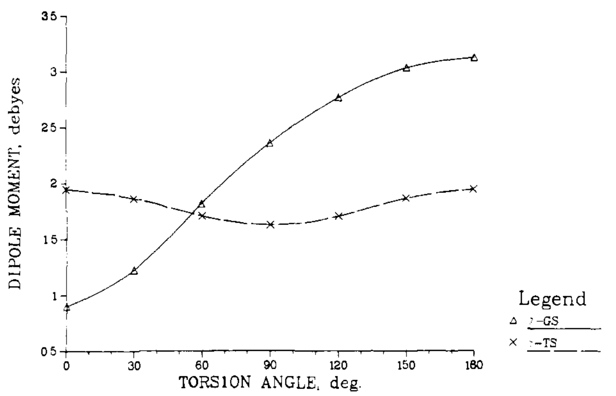

Figure 5. Calculated dipole moments of (fluoromethyl)aziridine as a function of torsion angle: △, 7-GS; ×, 7-TS.

However, the results of the calculations suggest possible explanations. The calculated dipole moments (STO-3G) of **7**-GS and **7**-TS are given in Figure 5 and Table II as a function of torsion angle. It is clear that torsion about the C–N bond in **7**-TS effects only a small change in the dipole moment associated mainly with an in-phase C–F bond length change (Figure 1).

The change in the dipole moment of **7**-GS is more dramatic, and, significantly, comparison of Figures 5 (symbol △) and 1 (symbol □) indicates that the two curves exhibit an out-of-phase relationship. This out-of-phase relationship suggests that the observed changes in the dipole moment do not arise from changes in the C–F bond length but rather that the changes in the bond length may reflect a mechanism for minimization of dipole–dipole destabilization. Thus we suggest that the higher energy and shorter C–F bond in the 180° conformation are associated with dipole–dipole destabilization which is maximized in this conformation. The opposite trend in the energy profile observed for **8**-GS may be attributed to a 1,3 stabilizing interaction between the NH_3 and NH_2 groups. This may be viewed as hydrogen bonding of the ammonium hydrogens with the aziridine nitrogen.[27] This is consistent with the shortening of both C–N bonds and is furthermore supported by the observation of increased positive charge on the ammonium hydrogens nearest the aziridine nitrogen.

In contrast to the energy profiles for **7** and **8** (Figures 3 and 4), the torsional barriers found for **6** are smaller than could be accurately determined at this level of optimization: **6**-GS, 1.31 kcal/mol; **6**-TS, 0.00 kcal/mol. This provides conclusive evidence that the torsional barriers in **7** and **8** are associated with the presence of the electronegative substituents.

The difference between the energies of the TS and GS geometries of **6** provides an estimate of the inversion barrier in a typical alkylaziridine. The calculated value, 23.15 kcal/mol (the difference in energies of **6**-TS and **6**-GS at the 0° torsion angle), is in good agreement with experimental barriers in *N*-alkylaziridines.[28] This indicates that the constrained NH_2 group provides a good model for the aziridine system. This inversion barrier represents a standard for barriers in the absence of significant hyperconjugation.[29]

We now examine the inversion barrier in **7**. The 90° conformations of **7**-GS and **7**-TS also represent a situation in which hyperconjugation is excluded. The barrier for this conformation, 22.92 kcal/mol, is essentially the same as for **6**. The effect of hyperconjugation on the barrier can be assessed by comparison of these values with the calculated barrier for the 0° conformation, where hyperconjugation is possible. The inversion barrier of **7** at 0° torsion angle, 21.35 kcal/mol, is about 1.7 kcal/mol lower. While this effect is small compared to the total barrier, it is of the magnitude expected based on experiments in sulfenyl aziridines **2**.[8a,b] In those experiments hyperconjugation was estimated to lower the inversion barrier by ca. 2 kcal/mol.

It may be noted that the effect of hyperconjugation on the torsional barrier seems much larger than on the inversion barrier. If we assume that a major portion of the torsional barrier derives from hyperconjugation, we may conclude that there is some hyperconjugation in the GS geometry as well as in the TS geometry. While the torsional profile of **8**-TS parallels that of **7**-TS, the profile for **8**-GS is complicated by additional factors, as discussed above. For this reason an analysis of inversion barriers in **8** is not useful although examination of Figure 3 indicates clearly that the smallest barrier is found for the 0° conformation and the maximum is found between 90 and 120° where hyperconjugation is minimized.

The third criterion for hyperconjugation is the transfer of electron density from nitrogen to the substituent X. This can be assessed by following the change in total charge on the NH_2 group and the X group along the torsional coordinate. In both compounds there appears to be a very small transfer of electron density from the NH_2 moiety to X in the 0° geometry as compared to the 90° geometry. This small shift of charge density corresponds to no more than a few percent of an electron in either STO-3G or 4-31G calculations. Furthermore, the magnitude of the shift change is basis set dependent, as discussed recently by Streitwieser.[7]

In summary, we find that the phenomenological picture of hyperconjugation agrees with that suggested by VB canonical structures, as far as the energy and geometry criteria are concerned. We note, however, that no substantial charge transfer occurs, as might have been expected on the basis of canonical structure **2b**. In general, the charges implied by VB canonical structures are rarely borne out in atomic charges obtained by MO calculations. In the present case this charge transfer is reflected in the HOMO orbital, as discussed below. The absence of this charge transfer in the molecule itself indicates the presence of compensating effects in other occupied MO's.

Molecular Orbital Analysis

Besides allowing an assessment of the phenomenological criteria for hyperconjugation, these calculations provide an explanation of these phenomena within the framework of MO theory. In this section we shall translate the simple VB concept of hyperconjugation into the language of perturbational molecular orbital (PMO) theory[30] and trace this effect within the calculated MO's.

We begin the PMO analysis by dissection of the molecule, in a conceptual sense, into two fragments XCH_2– and –NH_2. These fragments will be recombined to reform the molecule in different torsional conformations. We then can analyze the interactions between orbitals in the two fragments in order to determine differences in interactions along the torsional coordinate. Ideally, one would like to consider *all* possible interactions between orbitals on the fragments. However, in many cases, consideration of only one or two such interactions suffices to describe the behavior of the molecule qualitatively. PMO analysis is most successful when the fragment orbitals chosen are those which make the greatest contributions to the HOMO and when the HOMO energy parallels that of the total energy of the molecule.[31]

We choose for our analysis of the major interaction the following fragment orbitals: the –NH_2 lone-pair orbital and the σ^*_{C-X} orbital on the X–CH_2 fragment. These make the largest contributions to the HOMO in **7**-TS and **8**-TS in the 0° conformation which permits hyperconjugation. Furthermore, this molecular system is particularly suitable for a PMO analysis, since the trends in HOMO energies (symbol ×) and total energies (symbol □) exhibit

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[27] Similar 1,3 interactions are considered in ref 10, as well as by: Pross, A.; Radom, L. *Aust. J. Chem.* **1980**, *33*, 241.

[28] Lowenstein, A.; Neumer, J. F.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 3599.

[29] Pross et al. have shown that a small effect of hyperconjugation can be detected even in *N*-methylamine.[12]

[30] For leading references see: (a) ref 15; (b) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley-Interscience: New York, 1976. (c) Klopman, G., Ed. "Chemical Reactivity and Reaction Paths"; Wiley-Interscience: New York, 1974. (d) Hudson, R. F. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 36. (e) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum Press: New York, 1975. (f) Jorgensen, W. J.; Salem, L. "The Organic Chemists Book of Orbitals"; Academic Press: New York, 1973.

[31] Deb, B. M. *J. Am. Chem. Soc.* **1974**, *96*, 2030.

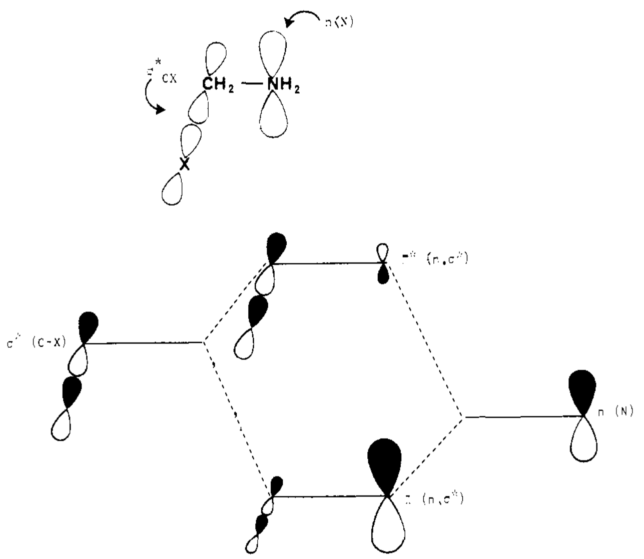

Figure 6. PMO interaction diagram for two-electron interaction of the nitrogen lone pair and σ^* Orbitals.

a remarkable correspondence (Figures 3 and 4). The situation for **7**-GS and **8**-GS is quite different. In both cases, the curve for the HOMO energies (symbol + in Figures 3 and 4) also exhibits a maximum near 90° torsional angle, although the change in HOMO energy is less than for **7**-TS and **8**-TS. This suggests that a similar hyperconjugative effect may be operative but it is of less importance. The curves for the total energies, however, bear no obvious relationship to the HOMO energies, indicating that the hyperconjugation which is apparent in HOMO is no longer the dominant interaction. This is a reflection of the special effects, discussed previously, which destabilize the 180° conformation in **7**-GS and stabilize the 180° conformation of **8**-GS. Because of this lack of correspondence between the HOMO energy and total energy profiles for **7**-GS and **8**-GS, we feel that a PMO analysis based on interactions in the HOMO is no longer fully justified. Accordingly, we have limited our further examination to **7**-TS and **8**-TS.

The interaction between these two orbitals, the n(N) and σ^*_{C-X} orbitals (Figure 6), is a two-electron stabilizing interaction and is the PMO equivalent of hyperconjugation. The two immediate consequences of this interaction are the lowering of the nitrogen n orbital energy and its perturbation by the admixture of some σ^* character, in an in-phase [$\pi(n,\sigma^*)$] manner. The perturbed nitrogen lone-pair orbital is the HOMO in both **7**-TS and **8**-TS at the 0° conformation. The coefficients are shown in Table IV. This perturbation should lead to an increase in C–N bond order and a corresponding decrease in C–X bond order (the geometry criterion).

As we can see, the valence bond concept of hyperconjugation finds its reflection in the HOMO orbital. The consequences of hyperconjugation will be observed in molecular properties to the extent that the properties of HOMO parallel the properties of the total molecule. Of course, molecular properties result from summing of all of the occupied MO's, and, for this reason, we should expect a close correspondence between VB predictions and PMO analysis only when effects in HOMO dominate over effects in other MO's. Indeed, it may be that VB canonical structures predict reactivity so well because they describe mainly the frontier orbitals which become increasingly important during the course of a reaction, near the transition state.

While the first two criteria (geometry and energy) are reflected in both the HOMO and the molecular properties, charge transfer appears in the HOMO but only to a small extent in total atomic charges. Although there is a substantial coefficient on X in the HOMO orbital, which arises from mixing of the σ^* orbital into the nitrogen lone-pair orbital, this charge transfer must be compensated for by effects operative in lower MO's. Hoffmann has noted that the charge transfer associated with methyl substitution in propylene and toluene is similarly small although the effect of the methyl group in polarizing the π system is large.[32] The analysis of the effects of hyperconjugation in the closely related 2-fluoroethyl anion by Streitwieser and co-workers resulted in a comparable picture.[7] There is very little transfer of charge but a substantial polarization effect which can be observed in difference plots of integrated total electron density. While Streitwieser suggested that the concept of hyperconjugation in these systems should be replaced by the concept of polarization, our approach suggests that charge transfer should not be regarded as a criterion for hyperconjugation in this system.

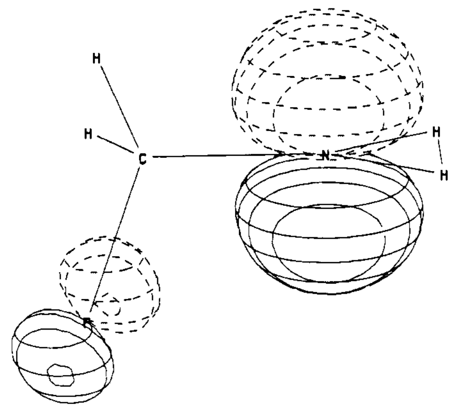

Figure 7. Contour plot of the HOMO orbital of 7-TS, 0° torsion angle.

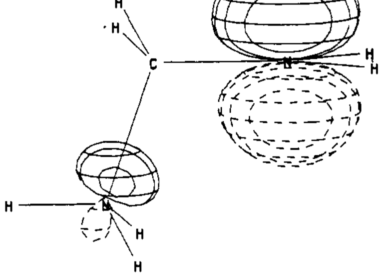

Figure 8. Contour plot of the HOMO orbital of **8**-TS, 0° torsion angle.

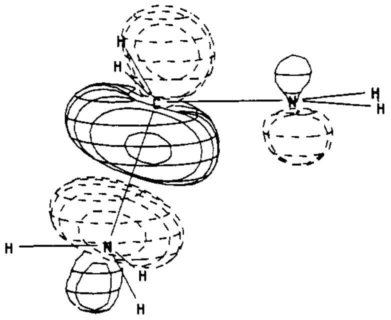

Figure 9. Contour plot of the LUMO orbital of **8**-TS, 0° torsion angle.

The interaction diagram shown in Figure 6 describes the most important perturbation in the system. The mixing in of the σ^* and lone-pair orbitals can be seen in the eigenvectors in Table IV or more visually in Jorgensen plots of the HOMO eigenfunctions (Figures 7 and 8). The perturbed σ^* orbitals correspond to the LUMO orbital of **8** which is shown in Figure 9 and the (LUMO+1) orbital in **7**. The LUMO orbital of **8** clearly shows the mixing in of the nitrogen lone pair in a π anti-bonding manner as indicated in Figure 6 and is close to our expectation.

The appearance of the HOMO orbitals is, however, quantitatively different from our expectation, indicating a second perturbational interaction must be considered. While the $2p_y$ and

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(32) Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370.

Table IV. A Orbital Energies and Coefficients[a,b]

basis function		MO[c]							
		7-TS, 0° HOMO^{13}	8-TS, 0° HOMO^{13}	7-TS, 90° HOMO^{13}	8-TS, 90° HOMO^{13}	7-TS, 0° NLUMO^{15}	8-TS, 0° LUMO^{14}	7-TS, $90^{\circ\,17}$	8-TS, $90^{\circ\,20}$
NH_2	2s		+0.0215			+0.1005	−0.1452		
	2p	−0.9377	+0.9449	+0.9448	−0.9652	−0.2606	+0.3013	+0.2050	−0.2073
	2p		−0.0169			+0.0625	−0.0180		
	1s					−0.0685	+0.0734		
	1s					−0.0685	+0.0734		
CH_2	2s	−0.0207	−0.0740			−0.4414	+0.6625		
	2p	+0.0839	+0.0407	−0.1420	+0.1341	+0.8877	−0.8847	−1.1300	+1.0613
	2p	−0.0161	+0.0692			+0.2694	−0.2927		
	1s	+0.1219	−0.1132	−0.2647	+0.2372		−0.1094	+0.8542	−0.8675
	1s	+0.1219	−0.1132	+0.2647	−0.2372		−0.1094	−0.8542	−0.8075
X (F, NH_3^+)	2s		+0.2097			+0.4509	−0.7426		
	2p	−0.2855	+0.2672	+0.1240		+0.7325	−0.6114	+0.1574	−0.4485
	2p	−0.1994	+0.1142			+0.2536	−0.2255		
	1s		−0.0677				+0.1061		
	1s		−0.0317				+0.1314		+0.3123
	1s		−0.0317				+0.1314		−0.3123
energy, au		−0.2954	−0.5182	−0.2769	−0.4809	+0.5918	+0.2449	+0.7081	0.4912

[a] Eigenvalues and Eigenvectors from STO-3G calculations. [b] Valence shell coefficients greater than 0.01 are included. [c] Superscript numbers refer to the number of the orbital.

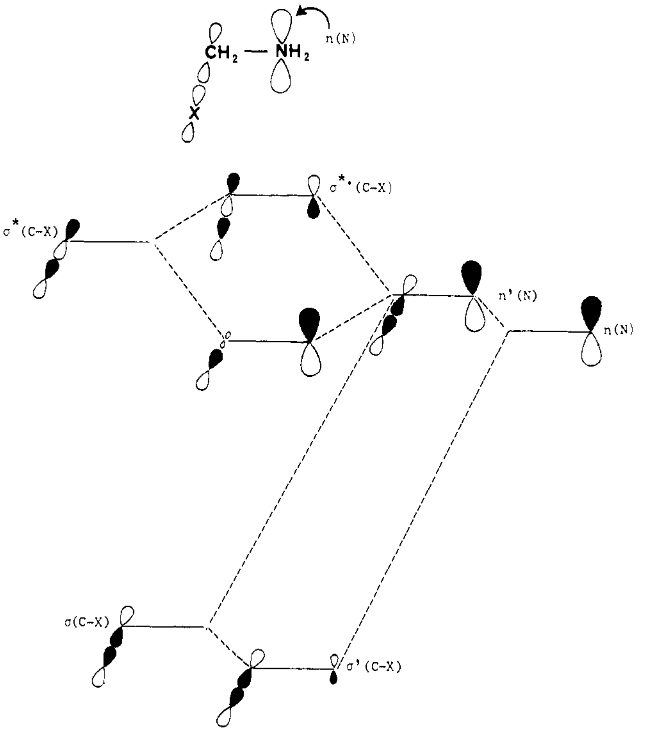

Figure 10. PMO interaction diagram representing the two-electron interaction of the nitrogen lone pair and σ^*_{C-X} orbitals and the four-electron interaction of the nitrogen lone pair and σ_{C-X} orbitals.

$2p_z$ coefficients on carbon are of the correct phase required by the interaction diagram, the magnitudes are very small, so much so that they do not appear in the Jorgensen plots. This is a consequence of the second perturbational interaction, that between the nitrogen lone pair and the *bonding* C–X σ orbital. As indicated in the double perturbation diagram (Figure 10) interaction of n(N) with σ is a four-electron interaction which raises the n level and lowers the energy of the perturbed σ orbital.

The overall effect of interaction of the n level with both σ and σ^* levels is reflected in the calculated HOMO coefficients. The coefficients at X in σ and σ^* mix into HOMO with the same phase, and constructive interference is observed leading to a substantial coefficient at X in HOMO. The coefficients at carbon, however, are of opposite phase, and the destructive interference leads to a drastic decrease in the coefficient calculated for HOMO.[33]

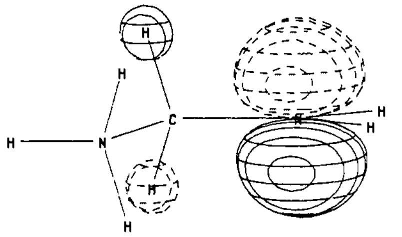

Figure 11. Contour plot of the HOMO orbital of **8**-TS, 90° torsion angle.

As long as the perturbation of the lone-pair orbital by the σ^*_{C-X} orbital is of major importance and the interaction with σ_{C-X} orbital is secondary, the net effect would be a stabilization associated with the observable consequences of hyperconjugation.[10,34] This situation occurs as long as X is an electron withdrawing substituent. When X is replaced by hydrogen, in **6**-TS, hyperconjugation is no longer observed (Table I). Instead, the HOMO now consists of the $n(NH_2)$ fragment orbital which has mixed into it, in an antibonding fashion, some of the π-CH_3 (σ-bonding) orbital. Indeed, the HOMO energy of **6**-TS is higher than in either **7**-TS or **8**-TS (in the 0° conformation), indicating a relative destabilization in **6**-TS (Tables I and IV). Similarly, no torsional dependence of the total energy is observed in **6**-TS as expected in the absence of hyperconjugation.

We now understand why the effect of negative hyperconjugation can only be found in the presence of electron-withdrawing groups X: the balance between the $n \rightarrow \sigma^*$ and n–σ interactions is determined by the electronegativity of X. Hyperconjugation will only be observed when the $n \rightarrow \sigma^*$ interaction is dominant and the n–σ interaction secondary. An electron-withdrawing group X is associated with lower lying σ and σ^* orbitals and hence with greater n–σ^* and weaker n–σ interactions.

The effect of rotation about the N–C bond is similar to that of changing substituents. Examination of the HOMO's of **7**-TS and **8**-TS at their 90° conformations (Table IV, Figure 11) shows

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(33) Libit and Hoffmann[32] discussed polarization of a π system through second order mixing of π and π^* orbitals during interaction with a π-donor substituent. They also mention the opposite polarization in the n (substituent) orbital and conclude that the overall polarization of the π system derives from the HOMO polarization (whether the π or the n orbital is HOMO). Our case is similar, in that we observe the polarization of the n-donor orbital. The π system in the present case is replaced with a pseudo-π orbital (mainly σ_{C-X} and σ^*_{C-X}) system.

(34) The relative importance of such two-electron and four-electron interactions on the "gauche effect" has been discussed: Cutledge, V. *J. Am. Chem. Soc.* **1974**, *96*, 5693.

that they now consist of the $n(NH_2)$ fragment orbital interacting with the π-CH_2 (σ-bonding) orbital. This is a four-electron interaction, and its net result is destabilization. Thus, torsion about the N–C bond gradually decreases the stabilizing effect of hyperconjugation and at the same time increases the repulsive four-electron interaction between the nitrogen lone pair and the π-CH_2 orbital.

Conclusion

We have tested experimental criteria for the definition of negative hyperconjugation in neutral molecular model systems. These criteria are as follows: (a) the stabilization energy (total energy); (b) changes in geometry (bond lengths and angles); and (c) charge transfer. We find the first two criteria to be useful in the definition of hyperconjugation, and the third one, transfer of charge, we find to be of lesser importance.

Analysis of the MO's of hyperconjugated and nonhyperconjugated conformations of **6**, **7**, and **8** provides an insight into the phenomenon: the VB concept of hyperconjugation, as expressed in **2a** and **2b**, is translated into the HOMO orbital. The effects of hyperconjugation in neutral systems such as these can be expected as long as (a) X is sufficiently electronegative and (b) the changes in HOMO dominate the behavior of the molecule.

Registry No. 4, 22524-88-5; **6**, 74-89-5; **7**, 36336-09-1; **8**, 62901-70-6.

An Electrochemical Investigation of the Effect of Macrocycle Ring Size on the Binding of Di- and Trivalent Lanthanide Cations by 12-Crown-4, 15-Crown-5, 4-*tert*-Butylbenzo-15-crown-5, and Dibenzo-30-crown-10 in Propylene Carbonate

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Abstract: The complexation in anhydrous propylene carbonate of the lanthanide ions by various macrocyclic polyethers featuring from four to ten oxygen atoms has been investigated by a competitive potentiometric technique with lead(II) or thallium(I) as auxiliary ions. The stability of the complexes appears to depend primarily on the relative sizes of the metal ions and of the internal cavity of each macrocycle. It depends also on the rigidity of the ligands and is influenced by solvation effects. The small ligands 12-crown-4 (**1**) and 15-crwon-5 (**2**) exhibit a similar behavior: they form 1:2 lanthanide complexes, the stability of which decreases with decreasing ionic radius despite the higher charge density of the metal ions. The presence of an electron-withdrawing phenyl group, as in 4-*tert*-butylbenzo-15-crown-5 (**3**), leads to a strong reduction of the stability constants. A maximum stability of 1:1 complexes of **3** is found at Nd(III) while a marked minimum is observed at Gd(III) in the complexation curve of dibenzo-30-crown-10 (**5**). Divalent samarium and ytterbium are more strongly coordinated than the corresponding trivalent ions by the crown ethers **1**–**5**. The larger divalent ions fit better into the internal cavity of **5** and they form stable 1:2 sandwich complexes with **1** and **3**. The properties of the complexes described in the present work are completely different from those reported so far in the case of noncyclic ligands.

The advantages of using macrocyclic compounds as ligands of the alkali-metal ions are now well documented.[1-2] Much less attention has been focused on the complexes formed between the lanthanide ions and the macrocycles, although it has been demonstrated in several recent reports that the crown ethers[3] and the cryptates[4,5] can also bind the lanthanides by sequestering them within their internal cavity. In a previous communication,[6] we discussed the complexation of the lanthanide cations by 4,4'-(5')-di-*tert*-butylbenzo-18-crown-6 in anhydrous propylene carbonate. The stability constants of 1:1 complexes were found to decrease regularly through the lanthanide series. A similar behavior was noted[7] in the case of 18-crown-6 in partially hydrated methanol. The opposite trend has been reported for all the more familiar, noncyclic complexing agents such as the polyaminopolycarboxylic acids or the β-diketones.[8] Another intriguing feature of the complexing properties of 4,4'(5')-di-*tert*-butylbenzo-18-crown-6 is its ability to bind more strongly divalent samarium and ytterbium than the corresponding trivalent ions.[6] The stabilization of the +2 oxidation state of europium in aqueous solution by various cryptates has also been observed recently.[5] These stabilization effects contrast significantly with the properties of the noncyclic ligands which always complex better with the trivalent lanthanides.[8]

Except for the data cited above, no measurements of the stability constants of crown ether complexes of di- and trivalent lanthanides have been carried out. The aim of the present research work is to rectify this situation. We investigated the complexation of the lanthanide ions in anhydrous propylene carbonate by the small ligand 12-crown-4 (**1**), by the medium size cycle 15-crown-5 (**2**) and its substituted derivative 4-*tert*-butylbenzo-15-crown-5 (**3**),

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