

## On the Origin of the Bohlmann Bands

SAUL WOLFE, H. BERNHARD SCHLEGEL,<sup>1</sup> AND MYUNG-HWAN WHANGBO<sup>2</sup>

*Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6*

AND

FERNANDO BERNARDI

*Laboratorio C.N.R. dei Composti del Carbonio contenenti eteroatomi, Ozzano E., Bologna, Italy*

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SAUL WOLFE, H. BERNHARD SCHLEGEL, MYUNG-HWAN WHANGBO, and FERNANDO BERNARDI.  
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A perturbational molecular orbital analysis has been performed of the strengths of the CH bonds of methylamine and methanol in their staggered conformations. This analysis leads to the prediction that a CH bond *anti*-coplanar to a directed lone pair is stronger than a *gauche* CH bond, and is in disagreement with experimental observation. The origin of the disagreement is to be found in the underestimation of the role of the nuclear-nuclear contribution to the bond strengths. *Ab initio* computation of the *gauche* and *anti* stretching force constants of methylamine provides quantitative theoretical support for the view that these differ because of a nuclear-dominated effect. It is suggested that effects, analogous to those observed in the Bohlmann bands, may be seen even in the absence of nonbonded electron pairs.

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On effectue une analyse orbitale moléculaire, par la méthode des perturbations, des forces des liaisons CH de la méthylamine et du méthanol dans leurs conformations décalées. Cette analyse conduit à la prévision que le lien CH, *anti*-coplanaire par rapport à un doublet libre dirigé, est plus fort qu'une liaison CH *gauche*; cette prévision est en désaccord avec l'observation expérimentale. La sous-estimation du rôle de la contribution noyau-noyau dans les forces des liaisons est à l'origine de ce désaccord. Un calcul *ab initio* des constantes des forces de valence *gauche* et *anti* de la méthylamine fournit un appui théorique quantitatif à l'idée qu'elles diffèrent à cause de l'effet nucléaire dominant. On suggère que des effets analogues à ceux observés dans les bandes Bohlmann, peuvent être observés même en l'absence de doublets électroniques non-liés.

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### Introduction

The Bohlmann bands are found in the 2800–2650 cm<sup>-1</sup> region of the i.r. spectra of amines (1). They have been correlated (2) with the stretching of carbon-hydrogen bonds that are *anti*-coplanar to the nitrogen lone pair and this correlation has been used extensively for the assignment of configuration to the quinolizidine alkaloids (1) and other piperidine derivatives (2, 3). Simple aliphatic alcohols and thiols also exhibit the phenomenon (4).

Because of the nature of the empirical correlation, it has seemed natural to rationalize the existence of the Bohlmann bands in terms of some kind of interaction between an axial

(directed) lone pair and an *anti*-coplanar  $\sigma_{\text{CH}}$  bond. Thus, Hamlow (5) and Krueger (2, 4) and their co-workers have suggested that participation of the lone pair in a  $\sigma_{\text{CH}_{\text{ax}}}$ \* orbital would lead to an electronic weakening of the  $\text{CH}_{\text{ax}}$  bond, and cause its stretching frequency to be shifted away from the normal CH stretching envelope.

Mechanical coupling between the vibrations of two CH bonds *anti* to a nitrogen lone pair, via a pulsating vibration of the nitrogen, has been offered as an alternative mechanism (6). However, such coupling appears to be small (7, 8) and unable to account for the observed shifts. Moreover, primary amines, which can have only one CH bond *anti* to the nitrogen lone pair, and thus cannot display such mechanical coupling, have Bohlmann bands (2).

Recent Raman studies of partially deuterated quinolizidines and piperidines (8) have shown

<sup>1</sup>Holder of a National Research Council of Canada 1967 Science Scholarship, 1972 – present.

<sup>2</sup>Holder of a National Research Council of Canada Studentship, 1972 – present.

that Fermi resonance between the low-lying CH stretching mode and the first overtone of a CH deformation can, in some cases, contribute to the Bohlmann bands. However, from a partial valence force field analysis of their data, Ernstbrunner and Hudec (8) found the CH bond *anti* to the nitrogen lone pair still to be significantly weaker than the corresponding *gauche* CH bond. Consequently it appears that Fermi resonance may serve to amplify the effect of an already weakened CH bond in producing low frequency CH stretching bands but is not the primary cause of these bands.

We have become interested in the origin of the Bohlmann bands because of the implications of two kinds of observations made in the course of theoretical studies related to the *gauche* effect (9). First, lone electron pairs seem to be less important to the understanding of stereochemical observations than bonding electron pairs, because of their quasi-spherical behavior (10). Clearly, if the lone pairs of amines, alcohols, and thiols were to behave as non-directed ligands, it would not be possible to specify the geometric relationship between these lone pairs and vicinal CH bonds as required by the electronic argument of Hamlow *et al.* (5). Secondly, certain stereochemical observations seem to be the result of nuclear-nuclear repulsion effects which override electronic interactions (11). Extension of these two findings to the present problem could be possible if it could be demonstrated that the weakening of the *anti* CH bonds occurs, not in response to the presence of a directed lone pair but rather to the absence of a nucleus.

The purpose of this paper is to show, qualitatively, by a more complete treatment than that employed previously (2, 4, 5) that orbital interaction predicts that the effect of a directed lone pair upon an *anti* CH bond serves to *strengthen* this bond, *i.e.*, that the Bohlmann bands cannot be attributed to interactions of the type depicted in Fig. 1. We then provide, by nonempirical SCF-MO computations, quantitative support for this conclusion and for

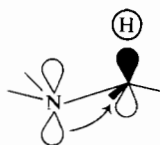


FIG. 1. The model of Hamlow *et al.* (5), showing charge transfer from  $N_{1p}$  to  $\sigma^*_{CH_{ax}}$ .

the view that the Bohlmann bands are the result of a nuclear-dominated effect. Some experimental consequences of this result are also considered.

### Results and Discussion

The treatment of Hamlow *et al.* (5) supposes charge transfer from the nitrogen lone pair ( $N_{1p}$ ) to the antibonding axial CH molecular orbital ( $\sigma^*_{CH_{ax}}$ ) and is depicted schematically in Fig. 1. It predicts partial double bond character in the CN bond, an increase in the charge at the axial hydrogen atom, and a weakening of the axial CH bond. Charge transfer from  $N_{1p}$  to the antibonding CH equatorial molecular orbital ( $\sigma^*_{CH_{eq}}$ ) is not considered, because  $N_{1p}$  and  $\sigma^*_{CH_{eq}}$  do not overlap. This analysis represents a simplified perturbational treatment of the problem. However, it is a well-established consequence of perturbation theory (12) that the interaction between two orbitals depends not only upon their symmetries but also upon the differences in their orbital energies.

We have selected methylamine and methanol as our model systems. Following the usual procedure (13), we treat these molecules in terms of the interactions between the  $CH_3$  and  $NH_2$  ( $CH_3$  and  $OH$ ) groups. The coordinate system for methylamine and the approximate molecular orbitals of  $CH_3$  and  $NH_2$  groups are shown in Fig. 2. The most important interactions are those between HOMO and LUMO. According to perturbation theory, the stabilization of an occupied orbital by an unoccupied orbital means that the occupied orbital has a small contribution from the unoccupied orbital and this may be interpreted in terms of charge transfer from the former to the latter (14).

From the interaction diagram in Fig. 2 it is evident that 1 and 2 are the most important interactions. Interaction 1 corresponds to charge transfer from  $N_{1p}$  to  $\pi_x^*$ . This is a  $\pi$ -type interaction and its effect is to weaken all of the CH bonds. But since the CH bond which is *anti* to  $N_{1p}$  has more antibonding character in the  $\pi_x^*$  orbital than the *gauche* CH bonds, it may reasonably be argued that the weakening of the *anti* CH bond will be greater and that the *anti* hydrogen will have a higher atomic charge than the *gauche* hydrogens. This analysis resembles closely the one given by Hamlow *et al.* Interaction 2 corresponds to charge

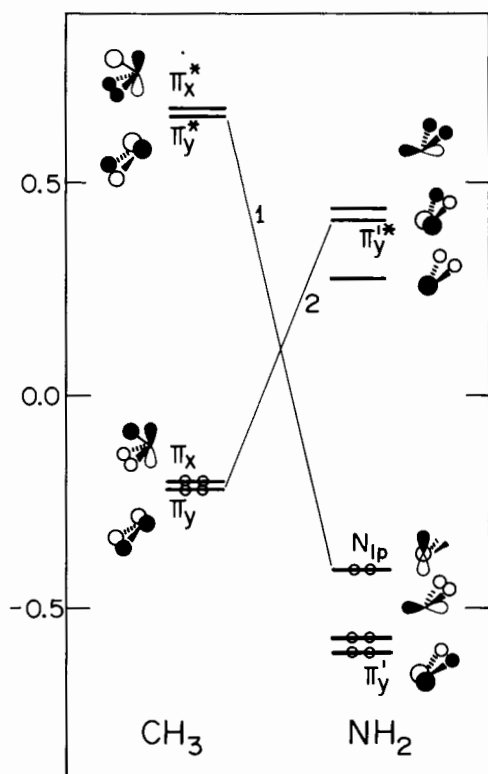


FIG. 2. Orbital interaction model employed to determine the strengths of the *gauche* and *anti* CH bonds of  $\text{CH}_3\text{NH}_2$ . The symmetries and energy levels shown in Figs. 2 and 3 have been taken from *ab initio* wavefunctions computed for  $\text{CH}_3^-$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ . Although the absolute positions of the various orbital levels depend upon the particular choice of wavefunction, the relative orderings remain the same for wavefunctions of the same quality. For the extended Hückel level orderings and symmetries of some simple molecules, see ref. 25.

transfer from  $\pi_y$  to  $\pi_{y^*}$ , and its effect is to decrease the bonding character of the *gauche* CH bonds and, thus, weaken these relative to the *anti* CH bond. Again the *anti* hydrogen is predicted to have a higher atomic charge.

It must now be noted that interaction 2 is more important than interaction 1, because the energy difference between HOMO and LUMO is smaller in the case of 2. Consequently, the effect of this more complete description of the problem is to reverse Hamlow's conclusion. An interesting consequence of the analysis is the finding that the classical conjugative interaction depicted in Fig. 1, which predicts greater charge at the axial hydrogen, is supported; but this is not associated with a weakening of the  $\text{CH}_{\text{ax}}$  bond.

Extension of this model to the treatment of methanol is shown in Fig. 3. Here the dominant interaction is 1, and leads to greater weakening of the CH bond which is *anti* to the OH bond, i.e., that CH bond which is *not anti-coplanar* to an oxygen lone pair.

It is clear that, in both cases, the prediction of the perturbation model is in disagreement with the experimental facts. However, such orbital interaction models can underestimate the effects of nuclear-nuclear repulsion upon the total energy of the system. This can be seen more clearly from the expression of the total energy in a one-determinantal treatment:

$$[1] \quad E_T = 2 \sum_i^{\text{occ}} \varepsilon_i - V_{ee} + V_{nn}$$

where  $\varepsilon_i$ ,  $V_{ee}$ , and  $V_{nn}$  are, respectively, the orbital energy of the *i*th orbital, the electron-electron, and the nuclear-nuclear repulsion energies. The success of the model depends explicitly upon the assumption that there is cancellation of the last two terms of eq. 1 (15).

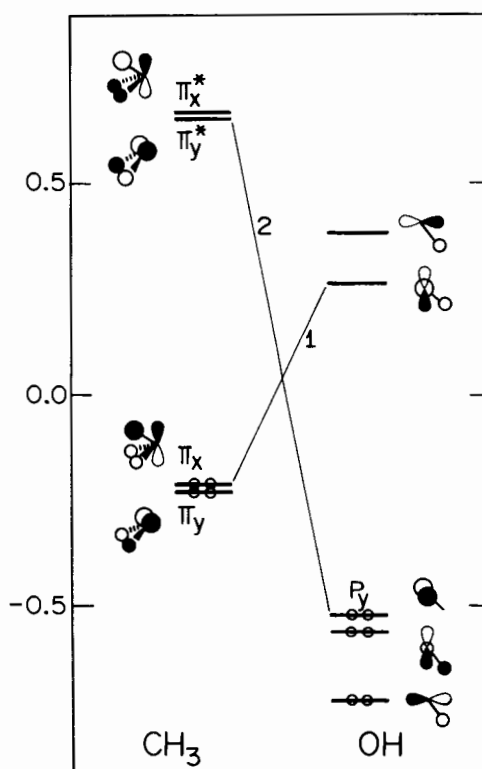


FIG. 3. Orbital interaction model employed to determine the strengths of the *gauche* and *anti* CH bonds of  $\text{CH}_3\text{OH}$ .

TABLE 1. The total energy of methylamine and its nuclear and electronic components at several *anti* and *gauche* CH bond lengths

CH bond length (Å)		Energy (Hartree)		
<i>Anti</i>	<i>Gauche</i>	Electronic	Nuclear	Total
1.09	1.09	-136.977299	41.912882	-95.064416
1.04	1.09	-137.166092	42.103195	-95.062897
1.14	1.09	-136.798767	41.735948	-95.062819
1.09	1.04	-137.166996	42.103590	-95.063406
1.09	1.14	-136.797889	41.735658	-95.062231
1.089*	1.081			-95.064525

\*Optimized geometry and energy as determined from the parabolic fit to the above data.

TABLE 2. The computed and experimental CH stretching force constants of methylamine

C—H Bond	Force constant (mdyn/Å)			
	Total	Electronic	Nuclear	Experimental*
<i>Anti</i>	5.435	-17.895	23.329	4.652 (4.732)†
<i>Gauche</i>	5.572	-17.941	23.512	4.760 (4.939)
<i>Gauche-anti</i>	0.137	-0.046	0.183	0.108 (0.207)

\*See ref. 18.

†Values in parentheses are for the deuterated species.

That such cancellation does not always occur has been noted recently (16). Should this situation exist in the case of the Bohlmann bands it would follow that the weakening of the CH bond *anti* to an adjacent lone pair would be the result of the nuclear contribution to the force constant. It was necessary, therefore, to test the validity of this argument by an *ab initio* computation of the nuclear and electronic components of CH stretching force constants of bonds *gauche* and *anti*-coplanar to a lone pair.<sup>3</sup>

The computations were performed on methylamine in its stable (staggered) conformation, using the CDC version<sup>4</sup> of Gaussian 70 (17), the extended (4-31 G) basis set and, initially, the following geometry: C—N, 1.48 Å; N—H, 1.02 Å;  $\angle$ HNH =  $\angle$ CNH = 106.0°. The force constants of the CH<sub>*anti*</sub> and the two CH<sub>*gauche*</sub> bonds were obtained from eq. 2, where

$$[2] \quad f_{JK} = \partial^2 E / \partial R_J \partial R_K$$

the second derivative of the total energy  $E$  is

<sup>3</sup>It is convenient to employ the traditional notion of a directed lone pair to facilitate the description of the geometry of the system.

<sup>4</sup>We thank Professor W. J. Hehre for this version of the programme.

taken with respect to the nuclear coordinates at equilibrium.

The total energy was calculated at several CH<sub>*anti*</sub> and CH<sub>*gauche*</sub> bond lengths close to the equilibrium values (see Table 1) and two parabolic fits to these values were obtained. The second derivatives of these parabolas were then calculated and these numbers, shown in Table 2, are taken as estimates of the two stretching force constants. Both computed harmonic force constants are within 15% of the experimental values (18), the CH<sub>*anti*</sub> force constant being lower. In addition, the difference between the *gauche* and *anti* force constants is in the range given for the experimental values.

*Ab initio* computations of force constants are well established in the theoretical chemical literature (19) and it is usually found that, at the Hartree-Fock level, stretching force constants are overestimated by 10-15%, as in the present work. The origin of the error is to be found in the neglect of electron pair correlation. A similar situation exists in the *ab initio* computation of conformational energies. Though correlation effects contribute significantly to absolute energies, the contribution to energy differences is small because of the conforma-

tional invariance of the correlation energy term (20). It is generally agreed, therefore, that calculations within the Hartree-Fock framework contain all of the information required for the understanding of conformational problems (20). Since the present computations are performed at geometries close to the energy minimum of the molecule, and differing energetically from the energy minimum by less than the energy difference between the eclipsed and staggered conformations, it seems valid to assume that a similar invariance exists in the computation of force constants, and that the *difference* in the calculated *gauche* and *anti* force constants is significant.

We have, therefore, proceeded with the partitioning of each force constant into its nuclear and electronic components. This partitioning has the form (21)

$$[3] \quad f_{JK} = f_{\text{nuc1}} + f_{\text{elec}}$$

where

$$[4] \quad f_{\text{nuc1}} = \partial^2 \Omega / \partial R_J \partial R_K$$

and  $\Omega$  is the potential energy associated with nuclear repulsion, given by

$$[5] \quad \Omega = \sum_{J>K=1}^N Z_J Z_K R_{JK}^{-1}$$

The contribution of  $f_{\text{nuc1}}$  could thus be computed readily and  $f_{\text{elec}}$  obtained by difference. The results are included in Table 2.

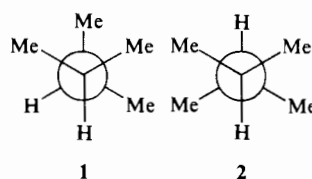
It is evident that the nuclear contribution to the *gauche-anti* difference in force constants is dominant; and it is larger than the total because the electronic component *strengthens* rather than weakens the  $\text{CH}_{\text{anti}}$  bond. A rationalization of this result can be found in the orbital interaction model presented above. Alternatively, the result can be considered to be a natural consequence of the variational principle, which allows electron density to flow into those regions of space in which maximum stabilization (*i.e.*, greatest nuclear-electron attraction) is achieved. Table 3 displays the computed net atomic charges in methylamine and shows higher electron density in the *anti* CH bond, as predicted by the interaction model. This increases the attraction between this bond and the two *gauche* amino hydrogens, and results in an electronic strengthening of the *anti* CH bond.

We conclude that the change from a bond to a

TABLE 3. The computed net atomic charges in methylamine

Atom	Net atomic charge
Carbon	-0.279
Nitrogen	-0.778
Hydrogen	
Amino	0.296
<i>Gauche</i>	0.168
<i>Anti</i>	0.129

lone pair has a less important effect upon the potential hypersurface than the removal of a nucleus. Since the presence of the lone pair is thus not essential to the observed weakening of an *anti* CH bond, it may be speculated that such weakening could also be observable in a hydrocarbon containing a suitably nonsymmetric nuclear-nuclear term. For example, the infrared spectrum of 2,3-dimethylbutane, which exists in both *gauche* and *anti* conformations (22), exhibits a strong band at  $2877 \text{ cm}^{-1}$  (23), which may be assigned to the stretching of the tertiary hydrogens of the *gauche* conformation. As seen in 1, these hydrogens are *anti-coplanar* to methyl groups. In addition, the infrared spectrum has a weak band at  $2810 \text{ cm}^{-1}$ , which might be caused by the antisymmetric stretch of the tertiary hydrogens of the *anti* conformation. As seen in 2, these hydrogens are *anti-coplanar* to each other. If such an interpretation were correct, it would follow that the difference in the effects of H and  $\text{CH}_3$  upon the stretching of an *anti-coplanar* CH bond is of the same order of magnitude as observed for the Bohlmann bands. A more detailed examination of the infrared spectra of 2,3-dimethylbutane and its deuterated analogs would, therefore, seem to be desirable.<sup>5</sup>



Finally, we wish to emphasize that the present results, although highly suggestive, should be regarded as a preliminary analysis of the problem, because only two of the diagonal

<sup>5</sup>The  $2800 \text{ cm}^{-1}$  region of the spectrum is free from overtone bands.

harmonic force constants of methylamine have been computed *ab initio*. What is now needed is a computation of the anharmonic force field of the whole molecule. A prerequisite to this study is the development of an *ab initio* program for the calculation of harmonic and anharmonic force fields. This programming phase of the work has been completed recently (24) and its application to the Bohlmann bands is presently under investigation.

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1. F. BOHLMANN. *Angew. Chem.* **69**, 641 (1957); *Chem. Ber.* **91**, 2157 (1958).
2. J. SKOLIK, P. J. KRUEGER, and M. WIEWOROWSKI. *Tetrahedron*, **24**, 5439 (1968), and references cited therein.
3. (a) J. B. LAMBERT, R. G. KESKE, R. E. CARHART, and A. P. JOVANOVICH. *J. Am. Chem. Soc.* **89**, 3761 (1967); (b) T. A. CRABB and E. R. JONES. *Tetrahedron*, **26**, 1217 (1970).
4. P. J. KRUEGER, J. JAN, and H. WIESER. *J. Mol. Struct.* **5**, 375 (1970).
5. H. P. HAMLLOW, S. OKUDA, and N. NAGAKAWA. *Tetrahedron Lett.* 2553 (1964).
6. J. KONARSKI. *Chem. Phys. Lett.* **12**, 249 (1971); *J. Mol. Struct.* **5**, 389 (1970); *J. Mol. Struct.* **7**, 337 (1971).
7. D. C. MCKEAN. *Chem. Commun.* 1373 (1971).
8. E. E. ERNSTBRUNNER and J. HUDEC. *J. Mol. Struct.* **17**, 249 (1973).
9. S. WOLFE. *Acc. Chem. Res.* **5**, 102 (1972).
10. (a) S. WOLFE, A. RAUK, L. M. TEL, and I. G. CSIZMADIA. *J. Chem. Soc. B*, 136 (1971); (b) S. WOLFE, L. M. TEL, J. H. LIANG, and I. G. CSIZMADIA. *J. Am. Chem. Soc.* **94**, 1361 (1972); (c) S. WOLFE, L. M. TEL, W. J. HAINES, M. A. ROBB, and I. G. CSIZMADIA. *J. Am. Chem. Soc.* **95**, 4863 (1973).
11. (a) S. WOLFE, L. M. TEL, and I. G. CSIZMADIA. *Can. J. Chem.* **51**, 2423 (1973); (b) A. LIBERLES, A. GREENBERG, and J. E. EILERS. *J. Chem. Educ.* **50**, 676 (1973).
12. L. SALEM. *J. Am. Chem. Soc.* **90**, 543 (1968).
13. R. HOFFMANN, L. RADOM, J. A. POPLÉ, P. V. R. SCHLEYER, W. J. HEHRE, and L. SALEM. *J. Am. Chem. Soc.* **94**, 6221 (1972).
14. N. D. EPIOTIS. *J. Am. Chem. Soc.* **94**, 1924 (1972).
15. R. HOFFMANN. *J. Chem. Phys.* **39**, 1397 (1963).
16. N. D. EPIOTIS. *J. Am. Chem. Soc.* **95**, 3087 (1973).
17. (a) W. J. HEHRE, R. F. STEWART, and J. A. POPLÉ. *J. Chem. Phys.* **51**, 2657 (1969); (b) R. DITCHFIELD, W. J. HEHRE, and J. A. POPLÉ. *J. Chem. Phys.* **54**, 724 (1971).
18. A. Y. HIRAKAWA, M. TSUBOI, and T. SHIMANOUCHE. *J. Chem. Phys.* **57**, 1236 (1972).
19. (a) K. F. FREED. *J. Chem. Phys.* **52**, 253 (1970); (b) P. PULAY. *Mol. Phys.* **17**, 197 (1969); (c) P. PULAY. *Mol. Phys.* **18**, 473 (1970); (d) P. PULAY and W. MEYER. *J. Chem. Phys.* **57**, 3337 (1972).
20. L. C. ALLEN. *Ann. Rev. Phys. Chem.* **20**, 315 (1969).
21. J. GERRAT and I. M. MILLS. *J. Chem. Phys.* **49**, 1719, 1730 (1968).
22. (a) G. J. SZASZ and N. SHEPPARD. *J. Chem. Phys.* **17**, 93 (1949); (b) D. W. E. AXFORD and D. H. RANK. *J. Chem. Phys.* **18**, 51 (1950); (c) E. J. JACOB, H. B. THOMPSON, and L. S. BARTELL. *J. Chem. Phys.* **47**, 3736 (1967); (d) A. L. VERMA, W. F. MURPHY, and H. J. BERNSTEIN. *J. Chem. Phys.* **60**, 1540 (1974).
23. Selected infrared spectral data. American Petroleum Institute Research Project 44. Serial No. 811.
24. H. B. SCHLEGEL and S. WOLFE. Unpublished results.
25. B. M. GIMARC. *J. Am. Chem. Soc.* **93**, 593 (1971).