Conformational Analysis of Some Alcohols and Amines: A Comparison of Molecular Orbital Theory, Rotational and Vibrational Spectroscopy

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1 Introduction

While spectroscopists have been remarkably successful in determining general structural features of molecules from their spectra, the assignment of microwave and infrared absorptions or Raman lines relating to detailed shape often cannot be decided uniquely from spectra alone. Corroborative chemical or other physical evidence sometimes may be available, although frequently assumptions regarding conformations and their relative energies have to be made. Recent progress in molecular orbital (MO) methods promises the potential not only for improving our understanding of spectral features and their relationship to molecular conformation but for providing a closer examination of the role of various intramolecular forces governing conformational stability. A number of these include steric hindrance, intramolecular hydrogen bonding, the *gauche* effect, and the *trans* lone-pair effect.

The influence of these factors can be seen experimentally in the conformational analysis of alcohols, amines, and substituted alcohols and amines. Therefore, in this review, we shall stress the mutual interdependence of MO methods and rotational and vibrational spectroscopy in the conformational analyses of these compounds.

2 Methodology

A. Molecular Orbital.—MO methods are usually restricted to calculations within the Hartree–Fock scheme.[1] Examples of these are *ab initio* IBMOL, POLYATOM, or GAUSSIAN-70 programmes,[2] which in principle evaluate all integrals for an all-electron calculation. Alternatively, semi-empirical methods such as CNDO/2[3] perform calculations in which only valence electrons are included,

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[1] See *e.g.*, C. C. J. Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.

[2] A. Veillard, IBMOL: Computation of Wavefunctions for Molecules of General Geometry, Version 4, IBM Research Laboratory, San Jose, California; for POLYATOM (Version 2) ref. 4 No. 199; for GAUSSIAN-70, W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, ref. 4 No. 236.

[3] J. A. Pople and L. Beveridge, 'Approximate Molecular Orbital Theory', McGraw-Hill, New York, 1970.

and many integrals are either neglected or treated parametrically. A number of these programmes are currently available.[4]

The various *ab initio* methods employ either minimal or extended Gaussian-type orbital (GTO) basis sets or a Slater-type orbital (STO) basis set expanded in terms of a set of GTO's. In extended bases, which provide greater flexibility in the MO description with a concomitant lowering of the total energy, E_T, extra functions are added to allow for anisotropic shape and angular distortion of the atom in the molecular environment. For semi-empirical methods, the basis is usually fixed as a minimal STO basis for elements in the second period. Parameterization partly compensates for inadequacies of such a basis.

For each calculation in the Hartree–Fock scheme, E_T is computed for a fixed nuclear configuration. In analysing conformational motion, E_T is obtained as a numerical function of nuclear position. Rather than a full-geometry optimization, often one or more molecular parameters are altered while standard[3] or experimental values are assumed for the remaining bond lengths and angles. From such a potential energy surface, relative stabilities of local minima, or barriers to rotation and inversion can be extracted. Energy barriers have been labelled as repulsive or attractive dominant.[5]

Although the Hartree–Fock method permits adequate evaluation of relative conformational stability and barriers,[5] within the constraints of the basis set, use of standard geometries limits interpretation to general structural features. Electron correlation aside, the relationship of detailed band positions and fine features of conformational structure require a full-geometry optimization. With this in mind, small energy differences of *ca.* 4 kJ mol^{-1} between inequivalent minima of large molecules should be used cautiously. Further, isotope effects are not included because of the Born–Oppenheimer approximation.

Finally we wish to emphasize that MO calculations pertain to the gas-phase molecule. Use of MO results to interpret solution spectra, especially where solvent–solute interaction is appreciable, should be approached with caution.

B. Experimental Methods.—The evaluation of rotational constants and hence molecular geometries from microwave data is generally straightforward, and the necessary procedures are described elsewhere.[6a] When two or more equivalent molecular arrangements are possible either by rotation around a bond or inversion at an atom, the rotational lines are split into several components. The barrier heights to internal rotation or inversion can be determined from the splittings. For rotamers that are not equally stable, the moments of inertia differ sufficiently so that separate rotational spectra can be observed. In such cases the energy of excited torsional states is estimated from relative intensities of corresponding

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[4] See Program Catalogue Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Indiana 47401, U.S.A.

[5] L. C. Allen, *Chem. Phys. Letters*, 1968, **2**, 597.

[6] (*a*) See, for example, W. Gordy and R. L. Cook, 'Microwave Molecular Spectra', in 'Chemical Applications of Spectroscopy', ed. W. West, Interscience, New York, 1970; (*b*) J. R. Durig, S. M. Craven and W. C. Harris in 'Vibrational Spectra and Structure', Vol. 1, ed. J. R. Durig, Dekker, New York, 1972.

rotational lines, from which the potential function governing internal rotation can be evaluated.

Also, the same function can be derived directly from infrared or far-infrared absorptions. The procedures involved have been reviewed recently.[6b] More sophisticated computations are required when the molecular rotation lines are split appreciably as a result of internal rotation or inversion.

Molecular vibrations are analysed usually in terms of the classical GF formalism of Wilson.[7a] Since the kinetic energy elements are governed in part by molecular geometry, certain modes of different conformers in principle should have different vibrational frequencies. If they are observed as isolated absorption bands or Raman lines, their relative intensities may be monitored as a function of temperature, from which the enthalpy difference can be estimated. When it is impossible to make unique frequency assignments, force-field calculations prove helpful. These computations have become common practice, and their methods and applications have been reviewed recently.[7b]

3 Alcohols and Amines

A. Methanol.—The question of a staggered or eclipsed form for methanol does not seem resolvable by i.r. spectroscopy. Günthard and co-workers[8] have attempted to settle the matter by fitting a force field to their i.r. data for eight isotopic species: $CH_3OH(D)$, $CD_3OH(D)$,$CH_2DOH(D)$ and $CHD_2OH(D)$. If an eclipsed structure is postulated, there is a force field which does predict all vibrational frequencies although with greater standard errors in the frequencies than if a staggered form were assumed. On the other hand, MO calculations determine the staggered conformation to have greater stability than the eclipsed.[9,10]

Lees and Baker[11] have obtained, in our opinion, the best structure from microwave data to date with the single assumption of C_{3v} symmetry of the methyl group (Table 1). The methyl tilt, the angle between the local C_3 axis and the C—O bond, of about 3° has been established also by earlier microwave measurements.[11] However, an improvement of the fit of the force-field calculations on methanol[8] was found when the tilt was reduced to zero. The significance of the presence of the tilt in fitting the rotational spectrum, and its absence in the treatment of vibrational data is difficult to extract from the complexities of both calculations. In the latter, it appears that the stretching force constant of a C–H bond *trans* to the O–H bond is greater than those *gauche*.[8] In the asymmetrically deuteriated molecules, *e.g.*, CHD_2OH, there are two rotamers (1a, b) giving rise to two C–H

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[7] (*a*) E. B. Wilson, jun., J. C. Decius, and P. C. Cross, 'Molecular Vibrations', McGraw-Hill, New York, 1955; (*b*) I. W. Levin and R. A. R. Pearce, in 'Vibrational Spectra and Structure', Vol. 4, ed. J. R. Durig, Elsevier Scientific Publishing, Amsterdam, 1975.

[8] A. Serrallach, R. Meyer, and Hs. H. Günthard, *J. Mol. Spectroscopy*, 1974, **52**, 94.

[9] M. S. Gordon, *J. Amer. Chem. Soc.*, 1969, **91**, 3122.

[10] L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 2371.

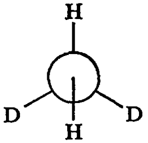
[11] R. M. Lees and J. G. Baker, *J Chem. Phys.*, 1968, **48**, 5299; references therein.

Table 1 *Molecular geometry of methanol*

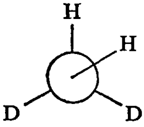
	Microwave[a]	*MO Calculation*[b]
CH_t	1.0936 ± 0.0032 Å	1.082 Å
CH_g		1.075 Å
CO	1.4246 ± 0.0024 Å	1.429 Å
OH	0.9451 ± 0.0034 Å	0.951 Å
∠COH	108° 32′ ± 29′	113.21°
$\angle OCH_t$	111.9°	110.43°
$\angle OCH_g$	107.0°	106.14°
methyl tilt	3.26°	2.89°

[a] Ref. 11. [b] Ref. 13.

stretching frequencies differing by about 60 cm^{-1}.[8] Mallinson and McKean[12] suggest that the C–H bond length changes from 1.094 to 1.100 Å on going from the *trans* to the *gauche* conformer. An *ab initio* calculation[13] with a complete optimization of molecular geometry has shown both a methyl tilt (Table 1) and C_s local symmetry for the methyl group. In agreement with the infrared results,[8,12] the C–H bonds *trans* to the lone pairs are longer and have lower force constants.[13,14]



(Ia) *t*-CHD_2OH



(Ib) *g*-CHD_2OH

It is interesting that the zero-point energies of the two rotamers of CHD_2OH, for example, differ by about 10 cm^{-1}, the *g*-form being more stable (*i.e.* the one with the larger number of CH *trans* lone-pair interactions—see section 5).

The rotational barrier, ΔE_R, is well determined by microwave to be about 373 cm^{-1} (4.46 kJ mol^{-1}), varying slightly with different treatment of data,[11,15] and is highly sinusoidal.[15] It decreases upon deuteriation, by about 3 cm^{-1} upon methyl deuteriation and between 6 to 8 cm^{-1} upon hydroxyl deuteriation. An explanation of this decrease has been given in terms of an electrostatic model which includes the influence of zero-point vibrations on the electronic-charge distributions of the isotopic species.[15] The values of the MO rotational barriers are given in Table 2. In spite of the variety of methods, the spread in the ΔE_R

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[12] P. D. Mallinson and D. C. McKean, *Spectrochim. Acta*, 1974, **30**, *A*, 1133.

[13] H. B. Schlegel, Ph.D. Thesis, Queens University, Ontario, 1975.

[14] S. Wolfe, H. B. Schlegel, and M.-H. Whangbo, *Canad. J. Chem.*, 1974, **52**, 3787.

[15] Y. Y. Kwan and D. M. Dennison, *J. Mol. Spectroscopy*, 1972, **43**, 291.

Table 2 *Methanol rotation barriers* (ΔE_R/kJ mol^{-1})

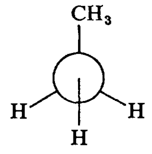
ΔE_R	*Method*
4.46	Experiment[a]
3.26	CNDO/2 (Pople parameters)[b]
4.39	Gaussian lobe expansion (extended)[c]
6.65	Gaussian lobe expansion[d]
4.68	GAUSSIAN-70 (4-31G basis)[e]
6.02	GFT basis (IBMOL IV or POLYATOM2)[f]
5.81	Gaussian lobe expansion[g]
6.02	Gaussian lobe expansion[h]

[a] Ref. 11. [b] Ref. 9. [c] Ref. 16. [d] L. Pedersen and K. Morokuma, *J. Chem. Phys.*, 1967 **46**, 3941. [e] Ref. 10. [f] Ref. 17. [g] S. Rothenberg, *J. Chem. Phys.*, 1969, **51**, 3389. [h] T.-K. Ha, R. Meyer, and Hs. H. Günthard, *Chem. Phys. Letters*, 1973, **22**, 68.

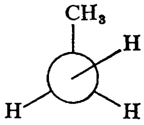
values is small, the better the basis set the better the value obtained. The barrier is repulsive dominant.[16,17]

An alternative mechanism for interconversion of conformation is inversion at oxygen. This is unlikely to enjoy much popularity since the barrier to this process has been calculated in the range 126—146 kJ mol^{-1}, considerably higher than internal rotation.[17]

B. Ethanol.—Microwave spectra show both *t* and *g* conformers (2a, b) in ethanol vapour.[18] While a value for their relative stability is not available from experiment, line intensities suggest that the *t* form is more stable.[19] In agreement with this observation, *ab initio* MO calculations (standard geometry) predict a relative stability of 2.63 kJ mol^{-1}.[10] In the most recent structure determination,[18] an r_0-structure was derived for the *t*-conformer by a best fit of observed moments of inertia of eight isotopic species reported in the literature (Table 3). Only the C–C and C–O distances and the CCO angle were allowed to vary for fitting. Structural parameters for *g*-ethanol were estimated from two sets of rotational constants for the two nonequivalent *g*-conformers of [1-$^2H_1$]ethanol using only the C–O bond length, the CCO angle and the dihedral angle as adjustable variables. The data in Table 3 imply that the C—O bond sweeps out a cone as the



(2a) *t*-CH_3CH_2OH



(2b) *g*-CH_3CH_2OH

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[16] W. H. Fink and L. C. Allen, *J. Chem. Phys.*, 1967, **46**, 2261.

[17] L. M. Tel, S. Wolfe, and I. G. Csizmadia, *J. Chem. Phys.*, 1973, **59**, 4047.

[18] Y. Sasada, M. Takano, and T. Satoh, *J. Mol. Spectroscopy*, 1971, **38**, 33; references therein.

[19] J. Michielsen-Effinger, *Bull. Classe Sci. Acad. Roy. Belg.*, 1964, **50**, 645.

Table 3 *Molecular geometry of ethanol (microwave data)*[a]

			trans
CH(methyl)	1.0936 ± 0.0032 Å		
		CO	1.4247 ± 0.0025 Å
OH	0.9451 ± 0.0034 Å		
		∠CCO	107° 20′ ± 14′
CC	1.5297 ± 0.0020 Å		
		ϕ^b	0°
CH(methylene)	1.0936 ± 0.0050 Å		
			gauche
∠HCH(methyl)	108° 32′ ± 42′		
		CO	1.4273 ± 0.0060 Å
∠HCH(methylene)	109° 5′ ± 33′		
		∠CCO	112° 21′ ± 30′
∠CCH(methylene)	110° 18′ ± 42′		
		ϕ^b	126° ± 6°

Ref. 18. [b] ϕ is the CCOH dihedral angle.

dihedral angle varies through 360° (*cf.*, ethanethiol[20]); this also resembles the methyl tilt in methanol.

Values for the *trans–gauche* and *gauche–gauche* barriers of 5.60 and 8.61 kJ mol^{-1}, respectively were obtained from MO studies.[10] Microwave work on *g*-ethanol gives a *gauche–gauche* barrier of 5.05 kJ mol^{-1}.[21] For methyl torsion, a barrier height of about 3.76 kJ mol^{-1} was estimated by Michielsen-Effinger,[19,22] whereas Sasada *et al.*[18] claimed they were unable to assign CH_3 torsion transitions.

Evidence for two conformers in the condensed phases has been found from the two O–H stretching absorptions seen for ethanol in an argon matrix at 20 K;[23] the more intense, low-frequency component was assigned to *t*-ethanol. Several other modes show doublets, and the *g*-conformer was usually assigned to the weaker component of a pair. A proportion of one *gauche* to two *trans* conformers was estimated from relative optical densities.

Doublet structure of the O–H stretching band is seen also in the i.r. spectra of the vapour and dilute solutions in CCl_4.[24,25] The favoured interpretation is the co-existence of the *trans* and *gauche* conformers. While the shape of the doublet in solution is clearly temperature dependent,[24] overlapping of the bands precludes identification of the more stable component. The C–D stretching bands of CH_3CD_2OH in dilute CCl_4 solution also indicate conformational heterogeneity.[26] The four bands have been interpreted as the asymmetric and

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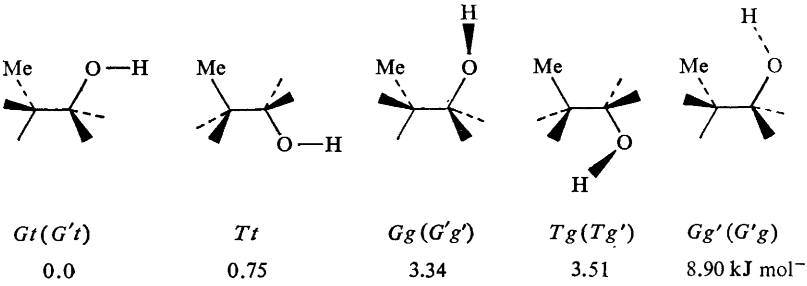
[20] R. E. Schmidt and R. E. Quade, *J. Chem. Phys.*, 1975, **62**, 3864.
[21] R. K. Kakar and P. J. Seibt, *J. Chem. Phys.*, 1972, **57**, 4060.
[22] J. Michielsen-Effinger, *Ann. Soc. sci. Bruxelles Ser. I*, 1964, **78**, 223.
[23] A. J. Barnes and H. E. Hallam, *Trans. Faraday Soc.*, 1970, **66**, 1932.
[24] H. Wieser, Ph.D. Thesis, University of Calgary, Alberta, 1966; references therein.
[25] J.-P. Perchard and M.-L. Josien, *J. Chim. phys.*, 1968, **65**, 1834.
[26] P. J. Krueger, J. Jan, and H. Wieser, *J. Mol. Structure*, 1970, **5**, 375.

symmetric CD_2 stretching modes of the two conformers, the high-frequency components being assigned to the *g*-form.[27] Temperature dependence of the symmetric stretching doublet establishes *t*-ethanol as the more stable form.[26] But it has been suggested from an analysis of solution spectra of CH_3CH_2OH and CD_3CH_2OH that the in-plane COH bending mode is coupled with the CH_2 twisting and out-of-plane methyl rocking modes,[25] implying that it is essentially *g*-ethanol which exists in CCl_4 solution since such an interaction would not be permitted by symmetry for the *t* form. Thus, it appears so far to be impossible to establish conclusively which conformer predominates in CCl_4 solution or which is more stable at lower temperature.

C. **Propanol.**—For 1-propanol, the existence in the vapour of both the *trans* (*T*) and *gauche* (*G*) orientations about the central C–C bond have been confirmed by microwave,[28] *G* being more stable by 1.2 ± 0.6 kJ mol^{-1}. A dihedral angle of about 116° was quoted. This lends credence to the *ab initio* MO results[29] of 0.75 kJ mol^{-1} with *Gt* as the favoured form; the *t* orientation of the OH was calculated for both *G* and *T* isomers (Scheme 1). The lesser stability of the *Gg′* form has been attributed to steric repulsion between the methyl and hydroxyl hydrogens.[29] Conformations arising from OH rotation were not identified from microwave, but barrier heights to methyl rotation of 12.9 and 12.0 kJ mol^{-1} were given for *T* and *G*, respectively.[28]



Scheme 1

In earlier electron diffraction work, only *T*-1-propanol was identified.[30] This skeletal structure was used in a normal-co-ordinate treatment[31] to generate a set of frequencies for the *Tt* and *Tg* conformers by fitting a modified Urey–Bradley

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[27] With one C–D bond *trans* to the O–H bond. This is consistent with the stretching force constant of a C–H bond *trans* to the O–H bond in methanol being greater than those for *gauche*; see ref. 8.

[28] A. A. Abdurahmanova, R. A. Rahimova, and L. M. Ivanov, *Phys. Letters* (*A*), 1970, **32**, 123.

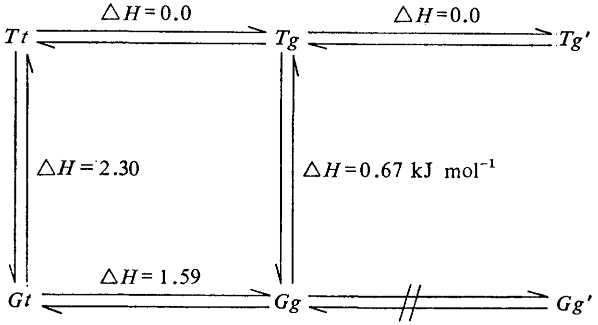
[29] L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1973, **95**, 693.

[30] N. E. Abdel Aziz and F. Rogowski, *Naturwiss.*, 1964, **19**, 967.

[31] K. Fukushima and B. J. Zwolinski, *J. Mol. Spectroscopy*, 1968, **26**, 368.

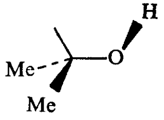
force field to vapour and liquid vibrational spectra for $CH_3CH_2CH_2OH(OD)$ reported in the literature. With this force field, the frequencies for *Gt*, *Gg*, and *Gg′* were also calculated. Since no infrared or Raman lines corresponding to *G* positions were observed, it was assumed that the molecule has the *T* form in the liquid state.

So far, the only experimental work attempting to identify OH orientation is a study of the complicated i.r. O–H stretching band in dilute CCl_4 solution.[32] Three overlapping bands with maxima at 3638.5, 3632.5, and 3626.7 cm^{-1} are assigned to *T*(*t*, *g* and *g′* absorbing at the same position—in all three forms the CH_3 group cannot interfere with *trans* OH), *Gg*, and *Gt*. *Gg′* was rejected on steric grounds,[32] consistent with its lower calculated stability.[29] From the temperature dependence of the band contour, the authors[32] concluded that *Gt* was the most stable form and the *T*'s were the least stable (apart from *Gg′*), giving the equilibria shown in Scheme 2.

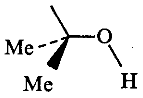


Scheme 2

For 2-propanol, microwave confirms the existence of *trans* and *gauche* conformations (3a, b)[33]; a threefold barrier to OH rotation was assumed, and a height of 7.03 kJ mol^{-1} was calculated. By MO results[34] the *gauche* form was calculated to be 2.88 kJ mol^{-1} more stable than *trans* (*cf.* experimental estimate



(3a) *g*-Me_2CHOH



(3b) *t*-Me_2CHOH

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[32] P. J. Krueger and H. D. Mettee, *Canad. J. Chem.*, 1964, **42**, 347.
[33] S. Kondo and E. Hirota, *J. Mol. Spectroscopy*, 1970, **34**, 97.
[34] W. A. Lathan, L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1973, **95**, 699; references therein.

of 1.17 kJ mol^{-1} [34]). The barrier to methyl rotation was estimated to be 17.5 kJ mol^{-1} from far-i.r. spectra of the vapour.[35]

From an analysis of the infrared and Raman spectra of several isotopic variations Tanaka[36] found both *t* and *g* conformers in the vapour whereas only *g* persisted in the liquid. The temperature dependence of the C–D stretching doublet of Me_2CDOH was studied in dilute CCl_4 solution and attributed to two conformers.[26] It was suggested that *t* most likely predominates at room temperature since the two bands have nearly the same intensity, whereas *g* is more stable by 0.42 kJ mol^{-1} at lower temperatures.

D. Methylamine.—In contrast to methanol, conformations of methylamine can be reached through two mechanisms: rotation about the C—N bond and inversion at nitrogen. These motions, because of low barriers, are coupled with each other and with molecular rotation. Each rotational energy level, specified by the rotational quantum number *K*, is split into three by internal rotation, and these are further split into two by inversion. The extent of splitting varies as *K* so that the resulting pure rotation and rotation–vibration spectra are very complicated.[37–39]

The microwave spectra[37] of CH_3NH_2, CH_3ND_2, and CD_3ND_2 have been interpreted in terms of an r_0-structure in which the CH_3 group has C_{3v} local symmetry but with a methyl tilt of about 2.9° (Table 4). The possibility of a structure with a slightly longer bond distance for the C–H bond *trans* to the nitrogen lone pair (*cf.*, methanol) was not considered. The optimized *ab initio* MO structure is consistent with this proposal and the methyl tilt (Table 4).[13]

Table 4 *Molecular geometry of methylamine*

	Microwave[a]	*MO Calculation*[b]
CH_t	1.0987 Å	1.089 Å
CH_g	1.0987 Å	1.080 Å
CN	1.4714 Å	1.452 Å
NH	1.0096 Å	0.994 Å
$\angle NCH_t$	110.27°	114.56°
$\angle NCH_g$	110.27°	109.40°
methyl tilt	2.9°	3.4°

[a] Ref. 37. [b] Ref. 13.

Values for ΔE_R in CH_3NH_2 and CH_3ND_2 obtained from the pure rotational spectrum[37] as well as the rotation–vibration fine structure of the first torsional excited state[39] are given in Table 5. Similarly, inversion barriers have been

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[35] J. R. Durig, C. M. Player, jun., Y. S. Li, J. Bragin, and C. W. Hawley, *J. Chem. Phys.*, 1972, **57**, 4544.

[36] C. Tanaka, *Nippon Kagaku Zasshi*, 1962, **83**, 661.

[37] K. Takagi and T. Kojima, *J. Phys. Soc. Japan*, 1971, **30**, 1145.

[38] M. Tsuboi, A. Y. Hirakawa, T. Ino, T. Sasaki, and K. Tamagake, *J. Chem. Phys.*, 1964, **41**, 2721.

[39] K. Tamagake, M. Tsuboi, and A. Y. Hirakawa, *J. Chem. Phys.*, 1968, **48**, 5536.

Table 5 *Methylamine rotation barriers, ΔE_R, and inversion barriers, ΔE_I*

(/kJ mol^{-1})

Experiment	CH_3NH_2	CH_3ND_2	CH_3NHD	CD_3NH_2
ΔE_R (microwave)[a]	8.203	8.144	—	—
ΔE_R (infrared)[b]	8.173 ± 0.014	8.034	—	—
ΔE_I	20.19 ± 0.12[c]	20.18[c]	21.11 ± 0.66[d]	22.34 ± 0.36[c] 21.30 ± 0.36[c]

ΔE_R (*calculated*)	*Method*
10.1	Gaussian lobe expansion[e]
8.44	Gaussian lobe expansion[f]
6.56	CNDO/2 (Pople parameters)[g]
8.90	GAUSSIAN-70 (4-31G basis)[h]
ΔE_I (*calculated*)	
16.7	CNDO/2 (Inversion parameters)[i]

[a] Ref. 37. [b] Ref. 39. [c] Ref. 40. [d] Ref. 41. [e] W. H. Fink and L. C. Allen, *J. Chem. Phys.*, 1967, **48**, 2276. [f] L. Pedersen and K. Morokuma, *J. Chem. Phys.*, 1967, **46**, 3941. [g] Ref. 9. [h] Ref. 10. [i] Ref. 42.

estimated from the rotation–vibration spectra of the amino-wagging vibration of CH_3NH_2, CH_3ND_2, CD_3NH_2,[40] and CH_3NHD[41] (Table 5). Normally, barrier heights should be independent of isotopic substitution. For CD_3NH_2 and CH_3NHD, the barrier is significantly higher, and this has been attributed to a change in the normal co-ordinate.[40,41] Barriers to rotation, which are repulsive dominant, and an inversion barrier obtained by MO methods are also given in Table 5. The agreement between experiment and theory is good, although the CNDO/2 version used to calculate the inversion barrier for methylamine specifically employed a set of parameters optimized for inversion at nitrogen rather than the Pople parameters.[42]

The most recent vibrational analysis of methylamine[43] including force-field calculations and the i.r. spectrum of $CH_3{}^{15}NH_2$, used a local-symmetry force field and a geometry determined by an earlier microwave study[44] with the methyl tilt excluded. It is particularly interesting that when transformed to a general-valance force field, the force constant of the C–H *trans* to the lone pair is slightly less than those *gauche* (*i.e.*, 4.700 *versus* 4.736 aJ $Å^{-2}$). The neglect of anharmonicity in the force field calculations obscures the significance of this small difference. However, this decrease also appears in force constants derived recently for methylamine from *ab initio* calculations where the difference is somewhat larger.[13,14]

Evidence for the existence of *trans* and *gauche* CH_2DNH_2 (4a, b) has been

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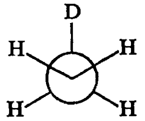
[40] M. Tsuboi, A. Y. Hirakawa, and K. Tamagake, *J. Mol. Spectroscopy*, 1967, **22**, 272.

[41] K. Tamagake and M. Tsuboi, *J. Mol. Spectroscopy*, 1971, **39**, 454.

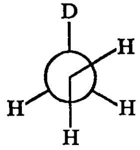
[42] A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6507.

[43] A. Y. Hirakawa, M. Tsuboi, and T. Shimanouchi, *J. Chem. Phys.*, 1972, **57**, 1236.

[44] T. Itoh, *J. Phys. Soc. Japan*, 1956, **11**, 264.



(4a) t-CH_2DNH_2



(4b) g-CH_2DNH_2

found in its i.r. spectrum.[45] A number of modes apparently give rise to two absorptions, one for each conformer. Doubling of several of these absorptions was confirmed by normal-co-ordinate calculations for the two different isomers. The doubling of the CH(D) stretching modes, clearly seen in the spectrum, was not confirmed by the force-field calculation, undoubtedly because of an inadequate force field. The microwave also shows both conformations.[45] An energy difference of 6.7 ± 0.4 cm^{-1} between the two conformers was estimated favouring the *gauche*-form. This is consistent with the more stable structure having a larger number of CH *trans* lone-pair interactions (*cf.* CD_2HOH). Tsuboi *et al.*[46] have analysed the rotation–vibration fine structure of the amino-wagging infrared band of CH_2DNH_2. The first excited state of this mode is about 5 cm^{-1} more stable for the *trans* than the *gauche* conformer. On the other hand, the first excited state of the torsion vibration has been estimated to be 30 cm^{-1} higher for *trans*.[46] One explanation for this variation of relative energies requires the extent of coupling between modes to differ for the two conformers.[46]

E. **Dimethylamine and Trimethylamine.**—A recent microwave study of 12 isotopic species of dimethylamine (5) yielded the most useful structural information (Table 6).[47] It was assumed that the bond lengths C–H′ and C–H″ were equal and the H···H′ and H···H″ distances were identical. While asymmetric methyl groups were indicated, uncertainty in the CNC angle permitted structures with more symmetric methyl groups. Also, it appears that both CH_3 symmetry axes are tilted with respect to the C—N bonds towards the nitrogen lone pair.

Table 6 *Molecular geometry of dimethylamine*[a]

CN	1.462 ± 0.005 Å	∠HCH″	109.0 ± 0.2°
NH	1.019 ± 0.007 Å	∠H′CH″	107.2 ± 0.3°
CH	1.084 ± 0.005 Å	∠HNC	108.9 ± 0.3°
CH′	1.098 ± 0.004 Å	∠NCH	109.7 ± 0.3°
CH″	1.098 ± 0.004 Å	∠NCH′	108.2 ± 0.3°
∠CNC	112.2 ± 0.2°	∠NCH″	113.8 ± 0.3°
∠HCH′	109.0 ± 0.2°		

[a] Ref. 47.

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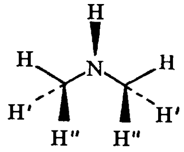
[45] K. Tamagake and M. Tsuboi, *Bull. Chem. Soc. Japan*, 1974, **47**, 73.

[46] M. Tsuboi, K. Tamagake, and A. Y. Hirakawa, *Spectrochim. Acta*, 1975, **31**, *A*, 495; *J. Chem. Phys.*, 1969, **51**, 2592.

[47] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, 1968, **48**, 5058.



(5)

Inversion splittings of the ground-state rotational lines[47] have yielded an inversion barrier of 18.4 ± 4.6 kJ mol^{-1} for $MeNH_2$ (*cf.*, a CNDO/2 value[42] of 21.7 kJ mol^{-1}). A methyl rotation barrier of 13.5 ± 0.1 kJ mol^{-1} was deduced from the splittings of the rotational lines in the first excited state of the methyl torsion of a number of isotopic species including ND and ^{15}N.[48] When a far-i.r. absorption at 257 cm^{-1} was assigned to the a'' combination of the methyl torsions in Me_2NH, a height of 13.7 ± 0.2 kJ mol^{-1} was calculated.[49] These values compare favourably with 15.1 kJ mol^{-1} obtained by the GAUSSIAN-70 method.[10]

Trimethylamine has C_{3v} symmetry such that one C—H bond in each CH_3 group is *trans* to the nitrogen lone pair.[50] The structural parameters derived from the microwave spectra of five isotopic variations are listed in Table 7. The C–H bond *trans* to the lone pair is longer than those *gauche*, consistent with similar findings for methanol and primary methylamine. Also, the methyl symmetry axes are tilted by about 1.3° towards the nitrogen atom.

Table 7 *Molecular geometry of trimethylamine*[a,b]

CN	1.451 ± 0.003 Å	$\angle NCH_a$	110.1 ± 0.5°
CH_s	1.109 ± 0.008 Å	$\angle NCH_s$	111.7 ± 0.4°
CH_a	1.088 ± 0.008 Å	$\angle H_aCH_s$	108.1 ± 0.7°
$\angle CNC$	110.9 ± 0.6°	$\angle H_aCH_a'$	108.6 ± 0.8°

[a] Ref. 50. [b] CH_s *trans* to N lone pair.

The rotational lines are not split by inversion implying a rather high inversion barrier (28.8 kJ mol^{-1} from CNDO/2 calculations[42]). There are, however, several satellite lines which could be attributed to rotational transitions in excited states of the methyl torsions.[51] From the relative intensities of these lines, the a_2 combination of the torsion modes was placed at 263 ± 20 cm^{-1} and the e combination at 290 ± 20 cm^{-1}, resulting in a methyl rotation barrier of 18.4 kJ mol^{-1}. In the far-i.r. spectrum an absorption at 269 cm^{-1} was assigned to the only i.r. active torsional transition (the e combination) from which the barrier was estimated to be 18.5 ± 0.1 kJ mol^{-1}.[49]

F. Ethylamine and Diethylamine.—Whereas no microwave work seems to have

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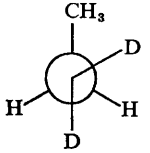
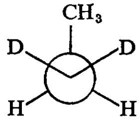
[48] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, 1971, **54**, 532.
[49] W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, 1962, **18**, 977.
[50] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, 1969, **51**, 1580.
[51] D. R. Lide, jun., and D. E. Mann, *J. Chem. Phys.*, 1958, **28**, 572.

been published,[52] a recent far-i.r. study[53] of $CH_3CH_2ND_2$ and $CH_3CD_2ND_2$ established the existence of the two conformers (6a and 6b) in the vapour.



(6a) *g*-$CH_3CH_2ND_2$



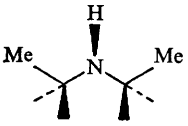
(6b) *t*-$CH_3CH_2ND_2$

A potential function derived from the absorptions shows the *gauche* form to be more stable by 1.24 kJ mol^{-1} with *gauche–gauche* and *gauche–trans* barriers of 6.40 and 9.53 kJ mol^{-1} respectively. *Ab initio* calculations also give the *gauche* as the favoured conformer[10] with the corresponding barrier values of 2.17, 8.07, and 11.5 kJ mol^{-1}, respectively. There is some evidence for coupling between Me and NH_2 torsions;[53] the effect while small for the deuteriated molecules is significant in the parent, $CH_3CH_2NH_2$.

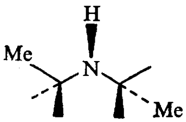
Two rotamers in liquid ethylamine are seen in the Raman spectrum[54] as a temperature-dependent doublet at 880, 890 cm^{-1} assigned to the symmetric CCN stretching vibration. The same Raman doublet was observed in the vapour at room temperature.[55] The lower-frequency component, favoured at lower temperature, has been ascribed to the *trans* form implying its greater stability.

Krueger and Jan[56] have investigated the temperature behaviour of dilute CCl_4 solutions of $CH_3CD_2NH_2$ and $CD_3CH_2NH_2$ in the C–D and C–H stretching regions, respectively. Both the asymmetric and symmetric methylene stretching modes are doubled. The low-frequency components are said to arise from 'perturbed' CD_2 (or CH_2) groups [possessing a CD(CH) bond *trans* to the nitrogen lone pair], and since their intensity increases at lower temperature the *g*-conformer is claimed to be more stable, although no enthalpy values were obtained.

For diethylamine, Verma[57] has interpreted vapour and liquid infrared bands by assuming the presence of only *TT* (7a) and *TG* (7b), the former predominating.



(7a) *TT*-Et_2NH



(7b) *TG*-Et_2NH

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[52] There is a reference to unpublished results by Y. S. Li and V. W. Laurie in V. W. Laurie, *Accounts Chem. Res.*, 1970, **3**, 331 and a private communication from Y. S. Li, ref. 7*b*.

[53] A. S. Manocha, E. C. Tuazon, and W. G. Fateley, *J. Phys. Chem.*, 1974, **78**, 803.

[54] H. Wolff and D. Staschewski, *Ber. Bunsengesellschaft Phys. Chem.*, 1964, **68**, 135.

[55] H. Wolff and H. Ludwig, *Ber. Bunsengesellschaft Phys. Chem.*, 1964, **68**, 143.

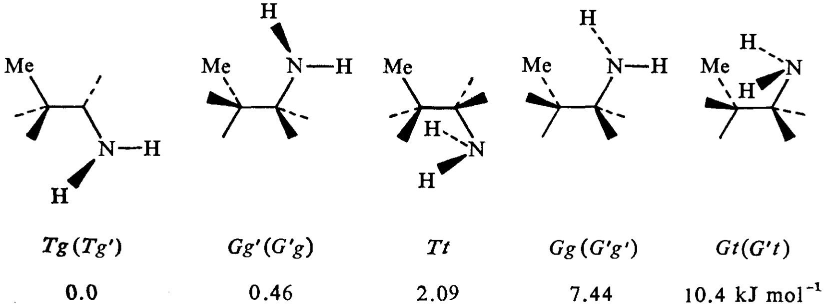
[56] P. J. Krueger and J. Jan, *Canad. J. Chem.*, 1970, **48**, 3229.

[57] A. L. Verma, *Spectrochim. Acta*, 1971, **27**, *A*, 2433.

In the solid *TG* or *TG'* may persist, suggesting that *TT* is less stable. Doubling of the N–H infrared stretching absorption and of its first overtone was investigated at various concentrations (in n-hexane and CCl_4) and temperatures.[58] In dilute n-hexane at 20 °C the fundamentals appear at 3338, 3318 cm^{-1} and the overtone at 6510, 6476 cm^{-1}. Integrated intensities as a function of temperature were calculated for the latter, from which the low-frequency component was attributed to the stable isomer, favoured by a ΔH of 2.98 kJ mol^{-1}. The ΔS evaluated from the same bands suggests further that one or both of *TG* and *TG'* belong to the high-frequency component so that *TT* must be assigned to the lower one.

G. Propylamine.—1-Propylamine vapour shows two Raman triplets at 833, 853, 865 cm^{-1} and 444, 448, 453 cm^{-1} which were assigned to skeletal vibrations.[55] By comparison with n-butane the former is believed to arise from the three possible *gauche* structures while two of the latter are attributed to the two possible *trans* conformers. No estimate of relative stability was given, and no other experimental work has been reported attempting to clarify the problem of rotational isomers.

Ab initio calculations[29] were performed on a selected number of conformations (Scheme 3); *Gg* and *Gt* are less favourable probably because of steric repulsion between the methyl and amine groups.



Scheme 3

For 2-propylamine, the temperature dependence of the two i.r. CD stretching bands of Me_2CDNH_2 (8a, b) in dilute CCl_4, appearing at 2156 and 2081 cm^{-1}, was investigated.[56] The lower-frequency band was assigned to *t*-Me_2CDNH_2, the form which permits a *trans* lone-pair interaction with the C–D bond. An enthalpy difference of 0.50 ± 0.08 kJ mol^{-1} was estimated, the *trans*-conformer being the most stable. Compare this with a value of 2.80 kJ mol^{-1} in favour of the *trans*-form reported for *ab initio* calculations.[34]

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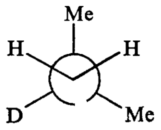
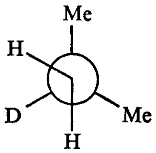
[56] H. Wolff and G. Gamer, *Spectrochim. Acta*, 1972, **28**, *A*, 2121.



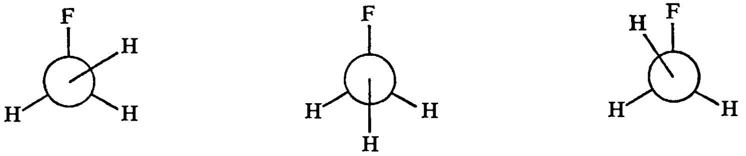
(8a) *g*-Me_2CDNH_2



(8b) *t*-Me_2CDNH_2

4 Substituted Alcohols and Amines

A. Fluoromethanol and 1-Fluoroethanol.—Owing to their low stability no experimental data are available for these molecules. Fluoromethanol (Scheme 4) is the simplest molecule illustrating the *gauche*-effect[59] and has been studied extensively by various MO methods.[10,59,60,61] All predict that the most stable conformation has the O–H bond *gauche* to the C–F. The smaller barrier (O–H and C–F eclipsed) is repulsive dominant whereas the larger barrier (O–H *trans* to C–F) is attractive dominant. The large differences in the rotational barriers are not easily rationalized for the two *ab initio* methods.[10,59] Whereas *ab initio* calculations show the *t* conformer as a maximum,[10,59,62] CNDO/2 actually yields a small local minimum.[60]



g	*t*	
0	52.7	34.5 kJ mol^{-1} [59]
	23.4	5.48 kJ mol^{-1} [10]
	7.94	2.93 kJ mol^{-1} [60]

Scheme 4

A selected number of 1-fluoroethanol conformations were studied by an *ab initio* method and the behaviour is analogous to fluoromethanol.[34]

B. 2-Fluoroethanol.—The five distinguishable rotamers (Scheme 5) with their relative energies from *ab initio* calculations[29] are:

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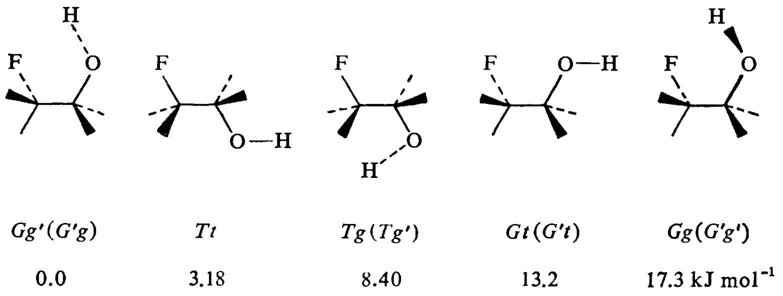
[59] S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc.* (*B*), 1971, 136.

[60] D. R. Truax, H. Wieser, P. N. Lewis, and R. S. Roche, *J. Amer. Chem. Soc.*, 1974, **96**, 2327.

[61] S. Wolfe, L. M. Tel, W. J. Haines, M. A. Robb, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, 1973, **95**, 4863.

[62] S. Wolfe, *Accounts Chem. Res.*, 1972, **5**, 102.



Scheme 5

In dilute CCl_4 solution a distinct asymmetry on the high frequency side of the O–H stretching absorption was detected,[63] implying the existence of at least two conformations. In other halogenoalcohols this asymmetry develops into a well-separated band. The lower-frequency absorption was accepted as evidence of intramolecular hydrogen bonding while the high frequency component was ascribed to a 'free' OH group. Although *Gt*, *G′t*, *Gg*, and *G′g′* could not be excluded as contributing to the 'free' OH band, the competition was thought to be mainly between the *T* and *G* conformations. A ΔH of 8.66 ± 2.22 kJ mol^{-1} favouring *Gg′* was calculated from the temperature dependence of absorbance ratios.

From i.r. data, only the *Gg′* conformation is thought to exist in the vapour with trace amounts of *T* perhaps appearing at higher temperatures (up to 120 °C).[64] Similarly, the i.r. spectrum in dilute solutions has failed to show the doubling of any of the vibrations seen in all other halogenoethanols suggesting that only small amounts of *trans* can be present.[65] Electron diffraction also shows the presence of only the *G* form at ambient temperature in the vapour.[66]

The orientation of the OH group was resolved from the microwave spectra of FCH_2CH_2OH and OD.[67] With structural assumptions about the CCH_2F and CH_2OH fragment the best fitting dihedral angles were 62.2 ± 1° for FCCO and 55.3 ± 3° for CCOH. The F···H distance is then only 2.42 Å (*cf.*, 2.55 Å, the sum of atomic Van der Waals radii).

C. Fluoroamines.—The authors are aware of no vibrational or microwave studies of any of the lower homologues of the monofluoroamines. *Ab initio* calculations have been done on fluoromethylamine,[10] 1-fluoroethylamine,[34] and 2-fluoroethylamine[29] with results paralleling those of the fluoroalcohols.

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[63] P. J. Krueger and H. D. Mettee, *Canad. J. Chem.*, 1964, **42**, 326.

[64] P. Buckley, P. A. Giguère, and D. Yamamoto, *Canad. J. Chem.*, 1968, **46**, 2917.

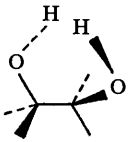
[65] E. Wyn-Jones and W. J. Orville-Thomas, *J. Mol. Structure*, 1967, **1**, 79.

[66] M. Igarshi and M. Yamaka, *Bull. Chem. Soc. Japan*, 1956, **29**, 871; K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, 1973, **95**, 8263.

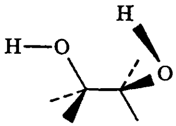
[67] K. S. Buckton and R. G. Azrak, *J. Chem. Phys.*, 1970, **52**, 5652.

D. Ethane-1,2-diol.—According to the i.r. spectra of all phases (vapour up to 125 °C)[68] and of matrix-isolated species[69] only the *gauche* conformer about the C–C bond (*G*) exists. The two *ab initio* methods, although differing on important points, also arrive at the same conclusion.[29,69] The interpretation of the microwave spectrum in terms of this form as a rigid rotor has failed, the complexity probably arising from tunnelling between the two mirror images of the conformer which allows for one 'free' and one 'intramolecular hydrogen bonded' OH.[70] The tunnelling frequency was estimated at 17 GHz (0.6 cm^{-1}).

Two such structures (9a, 9b) were suggested, *gGg′* being more stable.[69]



(9a) *gGg′*



(9b) *tGg′*

A doubly hydrogen-bonded isomer (*gGg* or *g′Gg′*) has also been proposed on the basis of a new 'bonded' OH stretching absorption below 0 °C,[71] and although the double bonding is questionable, this band may well correspond to the more stable *gGg′* form. Neither *gGg* nor *g′Gg′* are low-energy species according to the MO calculations.[29,69]

Neither i.r. nor MO methods favour a *T* conformer, although the two MO calculations differ dramatically on the energy assignment for it. Ha *et al.*[69] show that the *T* form is considerably less stable than at first calculated.[29] These two approaches differ on several points which arise either from a more detailed analysis of the potential surface[69] or differences which may be ascribed to the choice of basis set.

5 Intramolecular Interactions

In this review, we have found that relative stabilities of conformers and barriers may be consistently compared for the various methods in only some cases, where, with few exceptions, the agreement is reasonable, and values are at least the same order of magnitude. Qualitative features are in remarkable agreement, and this has led to a consideration of special effects governing the stability of various conformations.

Intramolecular hydrogen bonding has been construed traditionally as the increased stabilization resulting from the polarization of an atom possessing lone pairs by a nearby acidic proton. More recently, it has been noted that certain *gauche* conformations of molecules bearing polar substituents are particularly

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[68] P. Buckley and P. A. Giguère, *Canad. J. Chem.*, 1967, **45**, 397.

[69] T.-K. Ha, H. Frey, R. Meyer, and Hs. H. Günthard, *Theor. Chim. Acta*, 1974, **34**, 277.

[70] K.-M. Marstokk and H. Møllendal, *J. Mol. Structure*, 1974, **22**, 301.

[71] P. J. Krueger and H. D. Mettee, *J. Mol. Spectroscopy*, 1965, **18**, 131.

stable. This effect, termed the '*gauche* effect', has been defined as the tendency of a molecule to prefer a structure which has the maximum number of *gauche*-interactions between adjacent lone pairs and/or polar bonds.[62] Another effect which has gained prominence is the *trans* lone-pair effect. For unsubstituted alcohols, amines, and thiols, it has been observed experimentally that conformations with the largest number of α-C–H bonds *trans* to oxygen, nitrogen, or sulphur lone pairs are more stable.[26] It is impossible to separate and view these effects in isolation since in many instances more than one of them may be operative, although generally for the most stable or least stable conformers, one of these effects is dominant or totally absent.

I.r. bands originating from the *trans* lone-pair effect may be observed in the C–H stretching region of simple alcohols and amines. In methylamine and methanol, the C–H bonds *trans* to lone pairs are weakened as reflected by their lower force constants and slightly longer bond lengths compared to those *trans* to an N–H or O–H bond.[8,12,13,14] This is consistent with the structures reported for dimethylamine and trimethylamine (Tables 6 and 7) as well as other similar molecules reported by McKean.[72] Two explanations of this effect are current in the literature. The first postulates a flow of charge from a directed N(O) lone pair into a $\sigma^*_{\mathrm{CH}_{trans}}$ orbital with a concomitant weakening of the C—H bond.[73] This mechanism was questioned by Wolfe *et al.*[14] who suggest that in view of the nondirected character of lone pairs and the importance of nuclear–nuclear repulsions neglected in the previous argument that the *trans* lone-pair effect arises from the absence of a nucleus rather than a directed lone pair.

A survey of the most stable conformers of alcohols and amines as determined by MO calculations or experiment clearly illustrates the greater stability of structures with the maximum number of *trans* lone-pair interactions. It is even more remarkable that the preferred structures of CHD_2OH and CH_2DNH_2 have C–H, rather than C–D, bonds *trans* to a lone pair. These observations coupled with the lower stretching frequency for a C–H *trans* to a lone pair provide an important diagnostic tool for elucidating conformational stability by infrared. They also imply for microwave analyses that CH_3 or CH_2 groups adjacent to an O or N atom are asymmetric.

The *gauche* effect has been considered extensively elsewhere.[62] Clearly, in the substituted alcohols and amines considered here, as well as many others, the *gauche* (*G*) configuration about the C–C bond is the preferred one. The evidence for this comes from both experiment and MO results.

Of particular interest are those factors which stabilize the orientation of the hydroxyl or amine groups in substituted alcohols and amines. From the few examples considered here, it is evident that the *gauche* effect, hydrogen bonding, and perhaps the *trans* lone-pair effect contribute although the role of the last is not understood. In fluoromethanol, the *gauche* effect is the dominant factor in stabilizing the *gauche* conformation. The most stable form of 2-fluoroethanol,

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[72] D. C. McKean, *Chem. Comm.*, 1971, 1373.
[73] H. P. Hamlow, S. Okuda, and N. Nagakawa, *Tetrahedron Letters*, 1964, 2553,

Gg′, has an OH–CF hydrogen bond which is precluded in the *Gg* form, destabilized by 17.3 kJ mol^{-1} (MO) and absent in the microwave spectrum. For the stable conformers of ethane-1,2-diol, experimental and theoretical evidence indicate that the orientation of the 'free' OH is governed by first the *gauche* and second the *trans* lone-pair effect, whereas the 'bonded' OH responds to an interplay between the *gauche* effect and hydrogen bonding.

6 Concluding Remarks

From the foregoing discussions, the following remarks seem appropriate:

(*a*) Favoured orientations around C–O or C–N bonds in simple alcohols or amines require a maximum number of *trans* lone-pair interactions. This may also hold for related molecules substituted beyond the β carbon.

(*b*) The *gauche* conformation predominates when the *gauche* and *trans* lone-pair effects compete.

(*c*) Although intramolecular hydrogen bonding may have been overrated in the past as a force determining general conformational features, it is of considerable consequence in stabilizing hydroxyl or amine orientations, the uncertain influence of other factors notwithstanding.

(*d*) Whenever possible, at least a partial optimization involving more than one molecular parameter in MO calculations is desirable. In *ab initio* methods, the influence of basis sets on conformational stability needs further clarification.

(*e*) The influence of the *trans* lone-pair effect on C–H stretching force constants is well established. The same effect could produce changes in other vibrational modes and further investigations of this are necessary.

Finally we would stress that, since MO methods are of considerable value in gaining insight into molecular shape, a more integrated approach with spectroscopy in conformational analysis is indispensable.