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Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XVII. Internal Rotation in 1,2-Disubstituted Ethanes

Leo Radom, William A. Lathan, Warren J. Hehre, and John A. Pople*[1]

Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received June 9, 1972*

Abstract: *Ab initio* molecular orbital theory is used to study internal rotation in the complete set of 1,2-disubstituted ethanes XCH_2CH_2Y (X, Y = CH_3, NH_2, OH, or F). Conformational predictions are in agreement with available experimental data. Factors which are found to influence the conformational preferences include steric, dipolar, and hyperconjugative interactions and intramolecular hydrogen bonding.

It is well known that the most stable conformations of ethane (CH_3CH_3) and monosubstituted ethanes (XCH_2CH_3) are staggered. For these molecules, the three staggered conformations generated in a 360° rotation of the methyl group are equivalent and an energy of approximately 3 kcal mol^{-1} is required for their interconversion. On the other hand for 1,2-disubstituted ethanes (XCH_2CH_2Y) rotation about the central C–C bond leads to nonequivalent staggered arrangements corresponding to a trans and a pair of gauche structures. If the internal rotation potential function has minima near these staggered arrangements, the molecule will have distinct rotational isomeric forms (rotamers). Additional rotational isomers may arise through rotation about C–X and C–Y. Although interconversion of such rotamers in general also requires relatively little energy and is therefore quite rapid at ordinary temperatures, there is substantial evidence for their separate existence. Information on the structures and relative energies of the separate rotamers and the potential barriers between them has been obtained by numerous experimental techniques including infrared, Raman, nuclear magnetic resonance and microwave spectroscopy, dipole moments, electron diffraction, electrical birefringence, ultrasonic absorption, and calorimetry.[2]

Molecular orbital theory has not yet been extensively applied to 1,2-disubstituted ethanes. The only such molecule studied by *ab initio* methods has been *n*-butane.[3,4] For monosubstituted ethanes, on the other hand, a general theoretical study has had some success in describing internal rotation.[5,6] We are therefore encouraged to apply the same method to the disubstituted systems. In this paper we give results for all the distinguishable staggered conformations of the set of saturated molecules XCH_2CH_2Y (X, Y = CH_3, NH_2, OH, F) and compare the calculated energies with experimental results where possible. This corresponds to a complete mapping of the internal rotation potential hypersurface at a 120° grid. This is too coarse to determine positions and numbers of local minima precisely, but it does indicate some of the broad features of the surfaces. For *n*-butane, *n*-propyl fluoride, and 1,2-difluoroethane, a more complete study is made. In addition, for all the molecules we consider the energy of interaction between substituents in terms of bond separation energy concepts developed earlier.[7,8]

Method

Standard LCAO–SCF molecular orbital theory[9] with the extended 4-31G basis set[10] is used. Ideally, complete optimization of bond lengths and bond angles would be desirable. However, for the relatively large set of molecules discussed here, the computation time required to do this would be too great. For one molecule (*n*-butane), we use partially optimized geometries, but in all other cases, bond lengths and angles are given the standard values listed by Pople and Gordon.[11] The results we obtain are clearly subject to the errors inherent to this approximation. All staggered conformations of the molecules XCH_2CH_2Y have been considered. The notation used to specify the rotational

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[1] Author to whom correspondence should be addressed.

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Table I. Calculated and Experimental Energies for Disubstituted Ethanes

Molecule	Formula	Conformation	Total energy, hartrees	Relative energy, kcal mol^{-1}	Bond separation energy,[a] kcal mol^{-1} Calcd	Bond separation energy,[a] kcal mol^{-1} Exptl[c]	1,3-Interaction energy,[b] kcal mol^{-1} Calcd	1,3-Interaction energy,[b] kcal mol^{-1} Exptl[c]
n-Butane	$CH_3CH_2CH_2CH_3$	*T* (I)	−157.06892	0	2.2	5.2	−0.3	0.7
		G (II)	−157.06440	2.84	−0.6		−3.1	
n-Propyl fluoride	$CH_3CH_2CH_2F$	*G* (III)	−216.81947	0	7.7	6.3[d]	0.3	−0.1[d]
		T (IV)	−216.81932	0.09	7.8		0.4	
1,2-Difluoroethane	FCH_2CH_2F	*T* (V)	−276.56407	0	9.6		−2.7	
		G (VI)	−276.56173	1.47	8.2		−4.1	
n-Propylamine	$CH_3CH_2CH_2NH_2$	*Tg* (VIII)	−173.02601	0	4.6	6.6	−0.2	0.9
		Gg' (IX)	−173.02583	0.11	4.5		−0.3	
		Tt	−173.02522	0.50	4.2		−0.1	
		Gg	−173.02318	1.78	2.9		−1.9	
		Gt	−173.02202	2.50	2.1		−2.2	
1-Propanol	$CH_3CH_2CH_2OH$	*Gt* (X)	−192.83173	0	6.9	8.6	0.3	0.5
		Tt (XI)	−192.83145	0.18	6.7		0.1	
		Gg	−192.83045	0.80	6.1		0.1	
		Tg	−192.83039	0.84	6.0		0.0	
		Gg'	−192.82834	2.13	4.7		−1.3	
2-Fluoroethylamine	$FCH_2CH_2NH_2$	*Gg* (XII)	−232.77692	0	10.5		0.8	
		Gt (XIII)	−232.77591	0.63	9.8		0.6	
		Tg	−232.77523	1.06	9.4		−0.3	
		Tt	−232.77436	1.61	8.8		−0.4	
		Gg'	−232.77052	4.02	6.4		−3.3	
2-Fluoroethanol	FCH_2CH_2OH	*Gg'* (XIV)	−252.58044	0	11.3		0.4	
		Tt	−252.57923	0.76	10.6		−0.9	
		Tg	−252.57723	2.01	9.3		−1.6	
		Gt	−252.57542	3.15	8.2		−3.3	
		Gg	−252.57386	4.13	7.2		−3.7	
Ethylenediamine	$NH_2CH_2CH_2NH_2$	*tGg'* (XV)	−188.98480	0	8.2		1.5	
		gGg' (XVI)	−188.98438	0.26	7.9		0.7	
		gTg'	−188.98299	1.14	7.0		−0.2	
		gTg	−188.98273	1.30	6.9		−0.3	
		tTg	−188.98219	1.64	6.5		−0.2	
		gGg	−188.98158	2.02	6.1		−1.1	
		tTt	−188.98130	2.20	6.0		−0.2	
		tGg	−188.97984	3.11	5.0		−1.7	
		tGt	−188.97853	3.93	4.2		−2.0	
		g'Gg'	−188.97545	5.87	2.3		−4.9	
2-Aminoethanol	$NH_2CH_2CH_2OH$	*g'Gg'* (XVII)	−208.79095	0	10.6		2.3	
		gGt (XVIII)	−208.79051	0.28	10.4		1.4	
		tGt (XIX)	−208.78985	0.69	10.0		1.5	
		gTt	−208.78801	1.84	8.8		−0.2	
		tGg	−208.78793	1.90	8.8		1.0	
		gGg	−208.78771	2.03	8.6		0.3	
		tTt	−208.78739	2.23	8.4		−0.1	
		gTg	−208.78691	2.54	8.1		−0.2	
		gTg'	−208.78663	2.71	7.9		−0.4	
		tTg	−208.78598	3.12	7.5		−0.3	
		gGg'	−208.78564	3.33	7.3		−1.0	
		tGg'	−208.78354	4.65	6.0		−1.8	
		g'Gg	−208.78182	5.73	4.9		−3.4	
		g'Gt	−208.78088	6.32	4.3		−4.7	
Ethane-1,2-diol	$HOCH_2CH_2OH$	*tGg'* (XX)	−228.59605	0	12.5	12.0	2.3	0.2
		tTt	−228.59285	2.01	10.5		−0.3	
		gGg'	−228.59245	2.26	10.2		0.7	
		tTg	−228.59130	2.98	9.5		−0.7	
		gTg'	−228.58986	3.88	8.6		−0.9	
		gTg	−228.58949	4.12	8.4		−1.1	
		g'Gg'	−228.58792	5.10	7.4		−2.1	
		tGt	−228.58698	5.69	6.8		−4.0	
		gGg	−228.58648	6.01	6.5		−3.0	
		tGg	−228.58613	6.22	6.3		−3.9	

[a] The energy change in the reaction $XCH_2CH_2Y + 2CH_4 \rightarrow XCH_3 + CH_3CH_3 + CH_3Y$. [b] The energy change in the reaction $XCH_2CH_2Y + CH_3CH_3 \rightarrow XCH_2CH_3 + CH_3CH_2Y$. [c] Experimental values calculated using $\Delta H_f°$ (298°) values from S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 69, 279 (1969), unless otherwise noted. The theoretical energies should strictly be compared with experimental values at 0°K corrected for zero-point vibration but in the absence of sufficient data to do this we simply use $\Delta H_f°$ (298°) values. [d] $\Delta H_f°$ values for CH_3CH_2F and CH_3CH_2F taken from D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969, and J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034 (1968), respectively.

isomers is shown in Figure 1. Firstly, we use the symbols *T* (trans) and *G* (gauche) to describe the arrangement of X and Y about the central C–C bond. When X or Y are NH_2 or OH, we also have to specify orientations about the C–X and C–Y bonds. These are defined by CCOH and CCN: dihedral angles for

Table II. Calculated Total Energies for Conformations of *n*-Butane, *n*-Propyl Fluoride, and 1,2-Difluoroethane

XCH_2CH_2Y	XCCY dihedral angle, deg	Total energy
$CH_3CH_2CH_2CH_3$[a]	0	−157.05921
	60	−157.06834
	68.5	−157.06870
	120	−157.06473
	180	−157.07044
$CH_3CH_2CH_2F$	0	−216.81111
	60	−216.81947
	61.5	−216.81946[b]
	120	−216.81241
	180	−216.81932
FCH_2CH_2F	0	−276.55009
	60	−276.56173
	72.7	−276.56242
	120	−276.55894
	180	−276.56407

[a] Calculated using optimized CCC angles from ref 3. [b] The energy for the interpolated minimum at $\phi = 61.5°$ is very slightly higher than for $\phi = 60°$ reflecting the limitations of the three-term Fourier expansion (3).

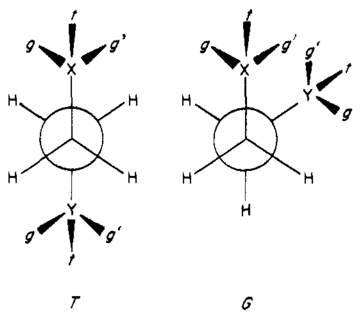


Figure 1. Notation used to specify rotational isomers.

Table III. Quantities Describing the Internal Rotation in *n*-Butane, *n*-Propyl Fluoride, and 1,2-Difluoroethane

	$CH_3CH_2CH_2CH_3$		$CH_3CH_2CH_2F$		FCH_2CH_2F	
	Calcd	Exptl	Calcd	Exptl[f]	Calcd	Exptl[g]
V_1, kcal mol^{-1}	−3.19		−0.48	−3.22 ± 2.02	−4.68	−3.23
V_2, kcal mol^{-1}	−1.43		−0.61	−3.05 ± 1.72	−2.72	−2.66
V_3, kcal mol^{-1}	−3.86		−4.67	−6.48 ± 2.15	−4.09	−2.90
ϕ(gauche), deg	68.5	67.5[a]	61.5	63	72.7	73
E(gauche) − *E*(trans), kcal mol^{-1}	1.09	0.77[b]	−0.09	−0.47 ± 0.31	1.04	0 ± 0.2[h]
Trans → gauche barrier, kcal mol^{-1}	3.58	3.6–4.2[c–e]	4.34	4.2 ± 1.5	3.22	2.0
Gauche → gauche barrier, kcal mol^{-1}	5.95	5.3–6.7[d,e]	5.24	10.1 ± 4.4	7.74	4.6

[a] Reference 12. [b] Reference 13. [c] K. S. Pitzer, *J. Chem. Phys.*, 8, 711 (1940). [d] K. Ito, *J. Amer. Chem. Soc.*, **75**, 2430 (1953). [e] J. E Piercy and M. G. S. Rao, *J. Chem. Phys.*, **46**, 3951 (1967). [f] Reference 14. [g] Except where noted, from reference 15. [h] Reference 16.

OH and NH_2 groups, respectively (: signifies the tetrahedral lone pair direction). The symbols *t*, *g*, and *g'* in Figure 1 then refer to the positions of the H or : (of the OH or NH_2 groups, respectively). The appropriate (CCOH or CCN:) dihedral angles are 180, +60, and −60° for *t*, *g*, and *g'*, respectively.

Results and Discussion

A complete set of total and relative energies calculated with the 4-31G basis set for staggered conformations of molecules XCH_2CH_2Y is given in Table I. In addition, we give the corresponding theoretical and experimental bond separation energies,[7,8] *i.e.*, energies of the formal reactions 1. These energies are mea-

$$XCH_2CH_2Y + 2CH_4 \longrightarrow CH_3CH_3 + CH_3X + CH_3Y \qquad (1)$$

sures of the stabilization of XCH_2CH_2Y relative to products in which the bonds between heavy atoms are separated into different molecules. Finally, we present calculated and experimental values of the energy change for the formal reaction 2. These energies measure the

$$XCH_2CH_2Y + CH_3CH_3 \longrightarrow CH_3CH_2X + CH_3CH_2Y \qquad (2)$$

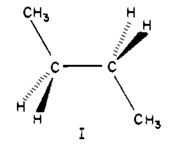
1,3 interaction between the bonds.

For the three molecules *n*-butane, *n*-propyl fluoride, and 1,2 difluoroethane, a more complete study has been made. The methyl groups are held in staggered arrangements and only rotation about the central C–C bond is then considered. In addition to the staggered trans and gauche forms (corresponding to XCCY dihedral angles (ϕ) of 180 and 60°), we have performed calculations for eclipsed conformations with $\phi = 0$ and 120°. This enables the determination of the potential constants V_i in the truncated Fourier expansion 3 of the potential function $V(\phi)$. From the potential function

$$V(\phi) = {}^1/_2V_1(1 - \cos \phi) + {}^1/_2V_2(1 - \cos 2\phi) + {}^1/_2V_3(1 - \cos 3\phi) \qquad (3)$$

3, the optimum dihedral angles for the gauche potential minima may be obtained. These additional results are summarized in Tables II and III. We now discuss individual molecules in detail.

***n*-Butane.** In agreement with experiment,[12] the most stable form of *n*-butane is found to be the trans conformation (I). Both calculated and experimental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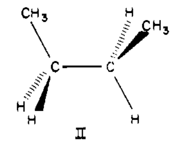
II

bond separation energies are approximately twice the propane values indicating that the 1,3 interaction of the two C–CH_3 bonds is very small in this conformation. When standard values of bond lengths, bond angles, and dihedral angles are used, the gauche rotamer (II) is found to have an energy 2.8 kcal mol^{-1} higher than the trans, somewhat larger than the experimental value[13] of 0.77 kcal mol^{-1}.

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(12) K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **32**, 748 (1959).

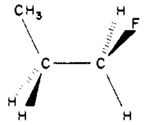
(13) G. J. Szasz, N. Sheppard, and D. H. Rank *J. Chem. Phys.*, **16**, 704 (1948).

In a previous study[4] of *n*-butane using the minimal STO-3G basis set, it was found that the internal rotation potential function is poorly described if rigid rotation is assumed. However, substantial improvement was obtained using a flexible rotor model in which the CCC angles were optimized for each conformation. The optimized CCC angles show considerable widening from the tetrahedral angle, particularly for low values of ϕ, *e.g.*, CCC = 115.3° in the cis (ϕ = 0°) form. The results for *n*-butane in Tables II and III refer to calculations with these optimized angles.

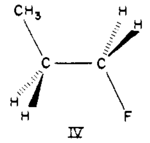
Evaluation of the potential constants V_i in (3) from the calculated energies (Table II) at ϕ = 0, 60, 120, and 180° allows the determination of the minimum in $V(\phi)$ in the vicinity of ϕ = 60° which, of course, corresponds to the gauche rotamer. The calculated dihedral angle (ϕ = 68.5°) again shows widening from the standard value (60°) in close agreement with experiment[12] (ϕ = 67.5°). The gauche–trans energy difference becomes 1.09 kcal mol^{-1} which is much closer to the experimental value than the standard model estimate. Calculated gauche → gauche and trans → gauche barriers (Table III) are also in reasonable agreement with experimental information.

The V_3 for *n*-butane (3.86 kcal mol^{-1}) is slightly larger than values obtained from similar calculations for propane (3.70 kcal mol^{-1}) and ethane (3.26 kcal mol^{-1}) confirming that methyl substitution increases the V_3 for substituted ethanes.[6] The large V_1 term shows that the cis form is much less favored than the trans, clearly because of steric effects. This, in turn, leads to the observed distortions both in dihedral angle and in CCC bond angles to relieve the steric interaction in the gauche form which is consequently less stable than the trans rotamer. These results are very similar to those of the two previous *ab initio* studies[3,4] of internal rotation in *n*-butane.

***n*-Propyl Fluoride.** The gauche rotamer (III, ϕ_{calcd} = 61.5°, ϕ_{exptl} = 63°) of *n*-propyl fluoride is calculated to be slightly more stable than trans (IV) in agreement with experiment.[14] However, the calculated potential constants (Table III) are not in good agreement with experimental values.[14] This difference arises largely from a disagreement between the calculated and experimental estimates of the gauche → gauche barrier (5.24 and 10.1 ± 4.4 kcal mol^{-1}, respectively) where the experimental value has a large uncertainty; the other barriers and energy differences are in reasonable agreement. The calculated and experimental 1,3-interaction energies indicate that there is little interaction between the C–CH$_3$ and C–F bonds in the most stable form.

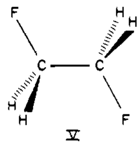


III

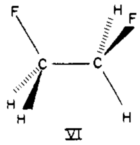


IV

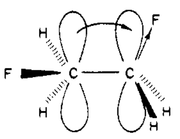
1,2-Difluoroethane. The lowest energy for this molecule is obtained for the trans conformation (V). When the optimum dihedral angle is used for the other stable form, the gauche conformation (VI, ϕ_{calcd} = 72.7°; *cf.* ϕ_{exptl} = 73°[15]), the theoretical gauche–trans energy difference is 1.0 kcal mol^{-1} compared to an experimental gas-phase result[16] of 0 ± 0.2 kcal mol^{-1}. Nuclear magnetic resonance studies in the liquid state and in solution suggest that the gauche conformation is preferred.[17]



V



VI



VII

The calculated potential constants (Table III) are only in moderate agreement with experimental values but show some interesting features. The large negative V_1 shows the preference for the trans conformation over the cis, probably because of dipole interactions. On the other hand, the negative V_2 indicates a contribution to the potential function in which the orthogonal conformation is preferred to either cis or trans forms. Withdrawal of electrons in the C–F bond partially empties the 2p orbital on carbon and thus facilitates hyperconjugative electron delocalization from the pseudo π system of the adjacent CH$_2$ group (see VII). This is likely to be more effective when the two CCF planes are orthogonal to one another (VII) rather than in a uniplanar arrangement. Calculated π-overlap populations for the C–C bond (which reflect the π character of this bond) are more positive for the (FCCF) orthogonal conformation than for either of the periplanar arrangements and therefore support this idea. Superimposed on the V_1 and V_2 contributions to the potential function is a sizable V_3 term favoring staggered conformations. The large calculated V_3 (4.09 kcal mol^{-1}) is consistent with the increase in V_3 observed both experimentally and theoretically with monofluorosubstitution in ethane.[6] Thus the theoretical (4-31G) V_3 values for ethane and fluoroethane are 3.26 and 3.63 kcal mol^{-1}, respectively. However, whereas the experimental V_3's also increase in going from ethane[18] (2.93 kcal mol^{-1}) to fluoroethane (3.30 kcal mol^{-1}),[19] the value for 1,2-difluoroethane (2.90 kcal mol^{-1}) is lower.

The relative energies of the gauche and trans conformations depend on the delicate balance between large V_1 and V_2 terms. It is possible that the theoretical estimate of V_1 is too large since the 4-31G basis set is known to overestimate dipole moments.[9] This would lead to a preference for the trans over the gauche conformation and may be the reason for the disagreement for the gauche–trans energy difference.

The calculated bond separation energies for both trans and gauche conformations of 1,2-difluoroethane are less than twice the value for ethyl fluoride. Thus

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[16] P. Klaboe and J. R. Nielsen, *ibid.*, **33**, 1764 (1960).

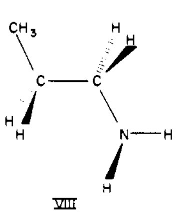
[17] (a) R. J. Abraham and R. H. Kemp, *J. Chem. Soc. B*, 1240 (1971); (b) A. A. Bothner-By and D. Vitus, unpublished data.

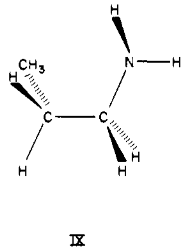
[18] S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968).

[19] D. R. Herschbach, *ibid.*, **25**, 358 (1956).

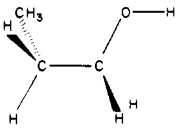
the 1,3 interaction of the two C–F bonds is predicted to be destabilizing. In the absence of special effects such as steric interaction or hydrogen bonding, a destabilizing interaction between vicinal, electron-withdrawing polar bonds is found for the other molecules examined in this paper and thus seems to be a general phenomenon. Experimental heats of formation required to test this hypothesis are not currently available.

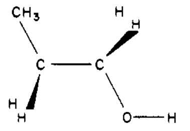
n-Propylamine. We find that the most stable conformation (VIII, *Tg*) of this molecule has a trans arrangement about the C–C bond and a gauche arrangement about the C–N bond. Other low energy forms are *Gg′* (IX), 0.11 kcal mol^{-1} higher) and *Tt* (0.50 kcal mol^{-1} higher than *Tg*). The low energies for the *Tg* and *Gg′* conformations are consistent with the preferred gauche (*g*) conformation of ethylamine.[5,6,20,21] A recent analysis of the vibrational spectrum of n-propylamine has shown[21] that the observed vibrational frequencies can be accounted for in terms of two conformations, *Tg* and *Gg* or *Gg′*. Most of the conformations of n-propylamine have small 1,3-interaction energies. Destabilizing interactions in the *Gg* and *Gt* conformations are probably due to steric effects.


VIII

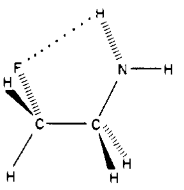

IX

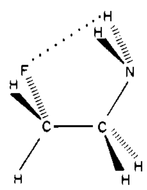
1-Propanol. The two most stable rotamers of this molecule are found to have CCOH trans as in the favored conformation of ethanol.[5,6,20,22] These are the *Gt* (X) and *Tt* (XI) forms, the former being 0.18 kcal mol^{-1} lower in energy. A microwave study[23] of 1-propanol has indicated the presence of two isomers corresponding to gauche (*G*) and trans (*T*) arrangements about the C–C bond. The gauche form is found to be more stable by 0.29 ± 0.15 kcal mol^{-1} in close agreement with the theoretical result. The 1,3-interaction energies are small for most of the conformations of 1-propanol. A destabilizing interaction found for the *Gg′* form is probably a steric effect.


X

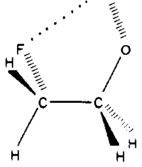

XI

2-Fluoroethylamine. In the *Gg* (XII) and *Gt* (XIII) conformations of 2-fluoroethylamine, intramolecular N–H···F hydrogen bonding is possible and these two forms have lowest calculated energy. The stabilization of these two structures is reflected in the positive 1,3-interaction energies. The *Gg* form is 0.63 kcal mol^{-1} more stable than *Gt* because of the gauche arrangement about the C–N bond (which is preferred in ethylamine). Interaction energies for the *Tg* and *Tt* conformations are small but there is a large destabilizing interaction for the *Gg′* form. In this structure, the C–F bond and the nitrogen lone pair are nearly parallel leading to unfavorable dipole interactions. No experimental information on the structure is available.


XII

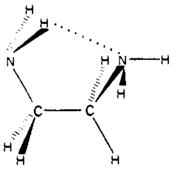

XIII

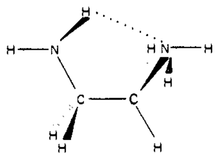
2-Fluoroethanol. The lowest energy form of this molecule is *Gg′* (XIV) which involves an intramolecular O–H···F hydrogen bond. This structure has a small positive 1,3-interaction energy; all the remaining conformations have destabilizing 1,3 interactions. This supports the suggestion (*vide supra*) that in the absence of intramolecular hydrogen bonding, the interaction of vicinal polar bonds is destabilizing.


XIV

Our results are in agreement with several experimental studies[24–29] which indicate that the intramolecularly hydrogen bonded structure of 2-fluoroethanol with a gauche arrangement about the C–C bond is predominant. In particular, analysis of the microwave spectrum[29] has shown that the most stable rotamer is *Gg′* (XIV). The trans–gauche (*T–G*) energy difference has been estimated from infrared studies[25,27] to be greater than 2 kcal mol^{-1}. This is somewhat larger than our theoretical estimate (0.76 kcal mol^{-1}); however, it should be kept in mind that we have made no attempt to optimize dihedral angles but have assumed exactly staggered structures throughout. The microwave study of 2-fluoroethanol shows that there are distortions in the *Gg′* conformation because of the intramolecular hydrogen bond. It is therefore likely that the relative energy of XIV would be lowered by such effects.

Ethylenediamine. The most stable conformations of this molecule (*tGg′*, XV and *gGg′*, XVI) are again


XV


XVI

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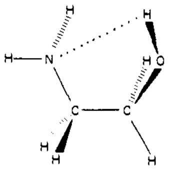
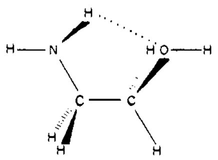
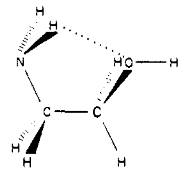
stabilized by intramolecular hydrogen bonding (N–H···N). The 1,3-interaction energies for these conformations are stabilizing while all remaining conformations have negative interaction energies. An electron diffraction study[30,31] has shown that ethylenediamine has a gauche (*G*) arrangement about the C–C bond in agreement with the theory. The fraction of any other isomer (if present) was calculated to be less than 5%. No definite conclusions were reached in the electron diffraction work regarding the orientation of the NH_2 groups.

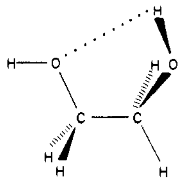
2-Aminoethanol. There are several conformations of this molecule in which intramolecular hydrogen bonding is possible and these are found to have the lowest energies. The most stable form is *g'Gg'* (XVII) with an N···H–O hydrogen bond. The *gGt* (XVIII) and *tGt* (XIX) forms both have N–H···O bonds and are respectively 0.28 and 0.69 kcal mol^{-1} higher in energy than XVII. The intramolecular hydrogen bonds in these conformations and in the *tGg* form are reflected in positive 1,3-interaction energies; most of the other conformations have destabilizing 1,3-interactions. The calculated interaction energies suggest that the N···H–O hydrogen bond is stronger than the N–H···O bond. Both microwave[32] and infrared[33] studies of 2-aminoethanol agree that the most stable conformation is XVII. However, in contrast to the theory, the infrared analysis[33] indicates that a nonhydrogen bonding trans (*T*) conformation is lower in energy than the N–H···O bonded structures (XVIII and XIX).


XVII


XVIII


XIX

Ethane-1,2-diol. We predict that the most stable conformation of this molecule is *tGg'* (XX) in which there is an intramolecular O–H···O hydrogen bond. No other low-energy conformations are indicated by the theory. Positive interaction energies are only found for XX and for the *gGg'* rotamer, another hydrogen-bonded form. Both electron diffraction[34] and infrared studies[35,36] indicate that ethane-1,2-diol exists only in this gauche (*G*) arrangement. An nmr study[28] has suggested some contribution from the trans (*T*) conformations in solution.


XX

Conclusions

Several points should be noted from this study of 1,2-disubstituted ethanes. (1) In all cases, where data are available, the lowest energy conformation predicted by the theory agrees with that determined experimentally. (2) The conformational preferences and stabilities of molecules XCH_2CH_2Y are influenced both by 1,2 interactions, *i.e.*, the conformational preferences and stabilities of the monosubstituted ethanes XCH_2CH_3 and CH_3CH_2Y *and* by 1,3 interactions. (3) The 1,3 interactions include steric and dipolar effects, electron delocalization effects and hydrogen bonding and have important conformational consequences. The steric and dipolar interactions often affect the V_1 term of the potential function for rotation about the C–C bond. When both X and Y are either bulky or electronegative groups, these effects contribute a preference for trans conformations. Charge delocalization is facilitated when the two electron-withdrawing polar bonds C–X and C–Y are perpendicular to each other rather than coplanar; this effect influences the V_2 term in the potential function. An additional factor which contributes to the conformational preference is the tendency for bonds to be staggered; this enters the potential function as a V_3 term. Intramolecular hydrogen bonding is possible for many of the disubstituted ethanes and in these cases, the hydrogen-bonded structures are generally favored. (4) Both positive (stabilizing) and negative (destabilizing) values of 1,3-interaction energies are obtained. Steric interactions are destabilizing while hydrogen bonding is stabilizing. In the absence of hydrogen bonding, the interaction of two vicinal electron-withdrawing polar bonds is found to be destabilizing.

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