for other large ion systems.[16] The entropy for the addition of the first phosphine to PH_4^+ can be calculated. The translational entropy change is calculated from the Sackur–Tetrode equation $\Delta S_{trans} = -34.5$ eu. The rotational entropy can be calculated[17] from the equation

$$\Delta S_{rot} = {}^1\!/_2 R \ln (I_A I_B I_C)_2/(I_A I_B I_C)_1 = 6.4 \text{ eu} \quad (20)$$

The vibrational entropy can be estimated from the six new modes of vibration in the $PH_4^+ \cdot PH_3$ complex. One would expect one new stretching frequency of the P–P bond formed and two bending frequencies of the P–PH_3 bond. The three additional modes would be either deformation of hydrogen rocking. To approximate the magnitude of these frequencies, we use the spectroscopic results for diphosphine.[18] The stretching frequency for the P–P bond in this compound is $v_s' \sim 450$ cm^{-1} and the bending frequency $v_b' \sim 400$ cm^{-1}. The remaining three modes would be expected to have frequencies of at least 800 cm^{-1} and at the temperature of these studies would make no significant contribution to the entropy. From Benson's correlation table for vibration entropy and frequency,[19] we estimate the $\Delta S_{vib} \sim 3$ eu. The calculated total entropy change is $\Delta S_{total} = -25.1$ eu. This is in good agreement with the observed $\Delta S_{0,1} = -25.9$ eu.

(16) P. Kebarle in "Ion-Molecule Reactions," Vol. 1, J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1972, Chapter 7.

(17) The moments of inertia of phosphine are known from spectroscopic data: $I_A = 7.16$, $I_B = I_C = 6.29 \times 10^{-40}$ g cm^2: C. A. Burrus, Jr., A. Jache, and W. Gordy, *Phys. Rev.*, **95**, 706 (1954); A. P. Altshuller, *J. Amer. Chem. Soc.*, **77**, 4220 (1955). The moments of inertia for $PH_4^+ \cdot PH_3$ can be calculated using a symmetrical top model for the complex (E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, London, 1957, p 496): $I_A = 7.16 \times 10^{-40}$ g cm^2, $I_B = I_C = 160 \times 10^{-40}$ g cm^2.

(18) (a) M. Baudler and L. Schmidt, *Z. Anorg. Allg. Chem.*, **289**, 219 (1957); (b) see D. E. C. Corbridge, "Topics in Phosphorus Chemistry," Vol. 6, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1969, p 235.

(19) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

There is a constant decrease in entropy with successive solvation steps as shown in Table I. This trend suggests a very loose complex is formed as larger numbers of PH_3 molecules are joined to the central ion. From the electrostatic considerations, this is what one might expect. Since the diameter of the phosphine neutral is quite large and the electrostatic bonding forces small, the entropy change with solvation decreases as molecules are bound further away from the central ion. This result is in contrast to the ammonia results where no decrease in entropy is observed within the first solvation shell.[16]

Conclusion

The ion–solvent reactions of phosphine with its major product ions are reported. These reactions have not been observed previously. A study of the equilibrium constants for the solvation of PH_4^+ gives thermochemical values for the solvation of a large ion in a nonpolar gas. A better understanding of the contributions the neutral gas makes to the total interaction potential of ion solvation in the gas phase is obtained by studying the difference in thermochemical data between phosphine and ammonia. The differences in these results reflect the increase in solvation efficiency of a small polar molecule over a large nonpolar one. From the total solvation energies calculated for the two congeners, one can see that a major contribution to the total solvation energy of any ion is the energy required to form the first solvation shell. Hopefully, future work with different ions in both polar and nonpolar solvent gases may shed further light on the individual energy contributions to the total ion-solvation energy in both the gas phase and the solution phase.

Conformational Analysis of Some Fluoro Alcohols. CNDO/2 Calculations, Infrared Evidence, and Dipole Moments[1]

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Abstract: A conformational analysis was carried out on hexafluoropropan-2,2-diol, fluoral hydrate, and hexafluoropropan-2-ol using the semiempirical CNDO/2 method. The more stable structures found for these molecules conform to those predicted from the dominance of one, or some combination of the gauche effect, trans lone-pair effect and intramolecular hydrogen bonding. The results are shown to be consistent with the experimental dipole moments and infrared evidence.

Since the earliest observations of splitting and asymmetry of the infrared bands associated with the hydroxyl stretching mode in alcohols, it has been recognized that rotational isomerism about the CO

bond is the origin of the observed effects.[3–5] With the development of *ab initio* and semiempirical molecular orbital methods for the calculation of the potential energy of a molecule as a function of molecular geom-

(1) Contribution No. 73-02 from the Biopolymer Research Group, University of Calgary.

(2) Biophysics Laboratories, Portsmouth Polytechnic, Portsmouth, England.

(3) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, 4, 711 (1936).

(4) R. Piccolini and S. Winstein, *Tetrahedron Lett.*, 4 (1959).

(5) F. Dalton, G. P. Meakins, J. H. Robinson, and W. Zaharia, *J. Chem. Soc.*, 1566 (1962).

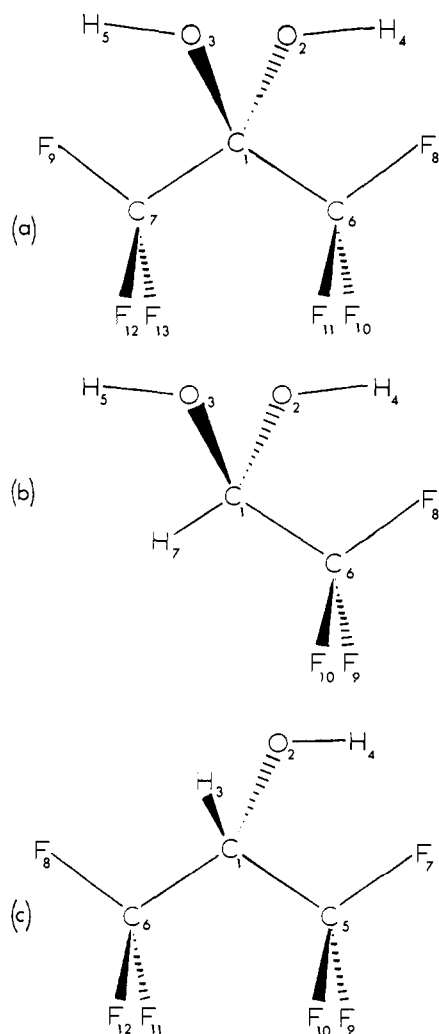Figure 1. Geometry and atomic numbering scheme for (a) hexafluoropropane-2,2-diol, (b) fluoral hydrate, and (c) hexafluoropropan-2-ol.

etry,[6,7] the rotational isomeric model can be subjected to closer theoretical scrutiny. As a result, it is now possible to assign relative energies, at least in a semiquantitative way, to the accessible rotamers of fairly complex molecules. This permits a more complete conformational analysis in terms of the relative populations of isomeric species and the barriers for rotation around individual bonds.

Hitherto, conformational analysis of alcohols in terms of the rotational isomeric model has usually been based largely on an empirical assessment of the relative magnitudes of the interactions thought to contribute to the conformational energy of each species. Interactions which are believed to contribute to the stabilization of certain rotamers in polar molecules such as alcohols include the trans lone-pair effect,[8] the gauche effect,[9] and, in the case of halo alcohols, intramolecular hydrogen bonding between halogen and the hydroxyl

proton.[10] In some cases, the dominance of one of the above interactions is clear, and an empirical correlation of conformation with observed spectral features is unequivocal. For example, conformations associated with the maximum number of trans lone-pair interactions between α-CH bonds trans to the lone-pair on N, O, and S have been shown[6] to have higher stability and to have characteristic frequencies both in the OH and CH stretching regions of the infrared spectra of alkanols, alkane thiols, and primary and secondary alkylamines.[11] In these molecules, the trans lone-pair effect seems to be the dominant conformational determinant.[6] However, in fluoromethanol, an alcohol with a more polar substituent, molecular orbital calculations have shown that the minimum energy conformation is the one in which the polar OH and CF bonds are gauche. This preference for the gauche conformation has been termed the gauche effect.[9,12,13] In the gauche conformer of fluoromethanol, there is also one trans lone-pair interaction whereas the anticoplanar conformation, which is the least stable conformer, has two trans lone-pair interactions. Clearly, in this molecule, the gauche interaction dominates the trans lone-pair effect. The role of the gauche effect as a conformational determinant in the other fluoro alcohols remains largely unexplored.

In higher fluoro alcohols, for example, 2-fluoroethanol, intramolecular hydrogen bonding between fluorine and the hydroxyl proton was considered to be the dominant interaction.[10,14-16] If the CF and CO bonds are gauche, then a fluorine–hydroxyl proton interaction is possible. In this case, since both the gauche effect and hydrogen bonding are cooperative, it would be prudent to leave open the question as to which effect is dominant.

Which of these intramolecular interactions dominates in the highly fluorinated gem diols, hexafluoropropane-2,2-diol and fluoral hydrate, and the alcohol hexafluoropropan-2-ol is not clear from a cursory examination of their structures. Since we have an interest in these molecules because of their unusual solvent properties toward biopolymers,[17] we have undertaken dipole moment and CNDO/2 studies of these fluoro alcohols. Our objective is to clarify the empirical conformational analyses of these molecules based on an interpretation of their infrared spectra[18,19] and the possible intramolecular interactions discussed above.

Experimental Section

CNDO/2 Calculations. The semiempirical, all valence electron CNDO/2 method[7] was used to study the relative stabilities of various conformations of hexafluoropropane-2,2-diol, fluoral hydrate, and hexafluoropropan-2-ol. The conformational analysis for each alcohol was carried out by examining the changes in total

(6) For example, see (a) W. H. Fink and L. C. Allen, J. Chem. Phys., 46, 2261 (1967); (b) W. R. Oegerle and J. R. Sabin, J. Mol. Struct., 15, 131 (1973); (c) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Amer. Chem. Soc., 95, 693 (1973); (d) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, ibid., 95, 699 (1973).

(7) J. A. Pople and L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(8) P. J. Krueger, J. Jan, and H. Wieser, J. Mol. Struct., 5, 375 (1970).

(9) S. Wolfe, Accounts Chem. Res., 5, 102 (1972).

(10) P. J. Krueger and H. D. Mettee, Can. J. Chem., 42, 326 (1964).

(11) J. Jan and P. J. Krueger, Can. J. Chem., 48, 3236 (1970).

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

(13) S. Wolfe, L. M. Tel, W. J. Haines, M. A. Robb, and I. G. Csizmadia, J. Amer. Chem. Soc., 95, 4863 (1973).

(14) P. J. Krueger and H. D. Mettee, Can. J. Chem., 42, 340 (1964).

(15) E. Wyn-Jones and W. J. Orville-Thomas, J. Mol. Struct., 1, 79 (1967).

(16) K. G. R. Pachler and P. L. Wessels, J. Mol. Struct., 6, 471 (1970).

(17) D. Balasubramanian and R. S. Roche, Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem., 11, 127, 132 (1970).

(18) J. Murto and A. Kivinen, Suom. Kemistilehti B, 40, 6, 14 (1967).

(19) A. J. Barnes and J. Murto, J. Chem. Soc., Faraday Trans. 2, 68, 1642 (1972).

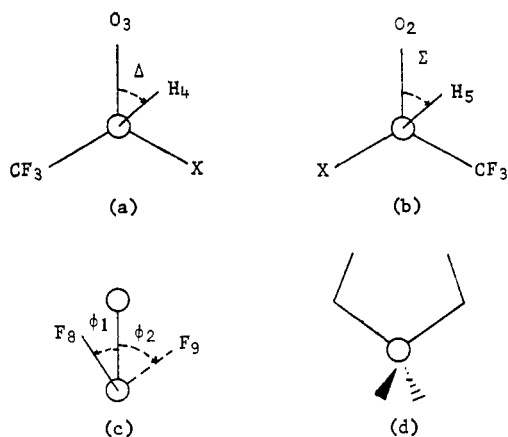Figure 2. Definition of the dihedral angles (a) Δ, (b) Σ, and (c) ϕ_1 and ϕ_2. Part d shows the hydroxyl group orientation for $\Delta = 0°$ and $\Sigma = 0°$.

energy as a function of molecular geometry. The dipole moment for each conformer was also calculated.

The molecular parameters and atomic numbering schemes for these molecules are shown in Figure 1. The CF and CC bond distances as well as the CCF bond angles were fixed at the values obtained for hexafluoroacetone by Hilderbrandt, et al.[20] The CO, OH, and CH distances were assumed to have standard values. The magnitudes of these parameters are given in Table I.

Table I. Fixed Molecular Parameters for $(CF_3)_2C(OH)_2$, $CF_3CH(OH)_2$, and $(CF_3)_2CHOH$

CF	1.335 Å
CC	1.549 Å
CO	1.450 Å
OH	1.000 Å
CH	1.091 Å
$\angle CCF$	110.3°

The total energy of hexafluoropropane-2,2-diol was optimized with respect to the angles {Δ, Σ, ϕ, COH, CCC, OCO}. The dihedral angles Δ, Σ, and $\phi = \phi_1 = \phi_2$ specify the orientations of the O_2H_4, O_3H_5, and CF_3 groups, respectively. These angles are defined more clearly in Figure 2. The orientation of the hydroxyl groups for $\Delta = 0°$ and $\Sigma = 0°$ is shown in Figure 2. For $\phi = 0°$, F_8 and F_9 lie in the CCC plane. The remaining three angles, COH, CCC, and OCO, specify the corresponding bond angles.

The total energy of fluoral hydrate was optimized with respect to the molecular parameters {Δ, Σ, ϕ = α_1, COH, CCH, OCO}. The CCH angle is the $C_6C_1H_7$ angle.

For hexafluoropropan-2-ol, the COH, CCC, and HCO angles were fixed at 105, 113.4, and 109.1°, respectively.[21] The total energy was then calculated as a function of Δ, ϕ_1, and ϕ_2.

To demonstrate the applicability of the CNDO/2 method to a conformational analysis of these polar molecules, we have performed calibrating calculations on fluoromethanol and 1,2-difluoroethane and compared them to available experimental or ab initio results.

For fluoromethanol,[22] the potential energy curves generated by ab initio calculations[12,13] and our CNDO/2 results as a function of the rotation about the CO bond show qualitative agreement in that they predict the gauche conformer to be more stable than the anticoplanar structure (see Figure 3a). The energy difference between these conformations was predicted by CNDO to be about 1.9 kcal/mol compared with 12.60 kcal/mol from ab initio results.[12,13]
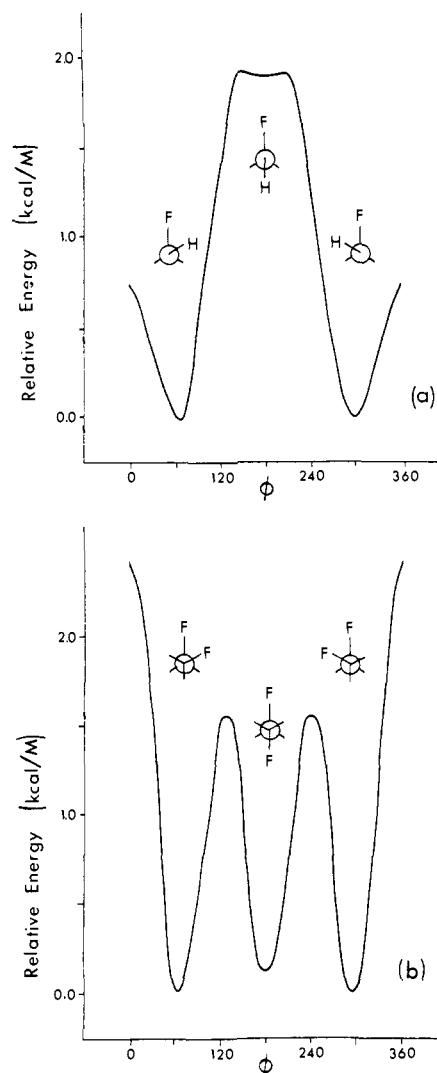

Figure 3. Potential energy curves for (a) fluoromethanol as a function of rotation about the CO bond and (b) 1,2-difluorethane as a function of rotation about the CC bond.

No experimental value is available because the molecule is unstable.[23]

The rotational energy curve for 1,2-difluoroethane[22] is shown in Figure 3b. Our CNDO/2 results predict the gauche conformation to be more stable than the anticoplanar conformer by ~100 cal/mol. Klaboe and Nielsen[24] have observed that these conformers have about the same energy (0 ± 200 cal/mol) in the gas phase while the gauche conformation is preferred in the liquid. An ab initio calculation[6c] suggests that the anticoplanar structure is more stable than the gauche conformer by about 1.0 kcal/mol. Another point of interest is that we predict a barrier of ~2.4 kcal/mol between equivalent gauche conformers and a barrier of ~1.5 kcal/mol between the gauche and anticoplanar conformers. The corresponding experimental values[25] are 4.6 and 2.0 kcal/mol, respectively. It should be pointed out that other CNDO/2 calculations[26] show that the method is useful in giving good rotational barriers although, consistently, it underestimates experimental values. On the basis of the calibrating calculations on fluoromethanol and 1,2-difluoroethane reported above, we conclude that the application of the CNDO/2 method to a conformational analysis of the fluoro alcohols is sound.

(20) R. L. Hilderbrandt, A. L. Andreassen, and S. H. Bauer, J. Phys. Chem., 74, 1586 (1970).

(21) The calculations described here used the optimum values found for hexafluoropropane-2,2-diol.

(22) The geometry used for fluoromethanol was that specified in ref 13. For 1,2-difluoroethane, all carbon atoms were assumed to be tetrahedral and standard bond distances were used for CH and CF bonds.[7]

(23) G. A. Olah and G. D. Mateescu, J. Amer. Chem. Soc., 93, 781 (1971).

(24) P. Klaboe and J. R. Nielsen, J. Chem. Phys., 33, 1764 (1960).

(25) S. S. Butcher, R. A. Cohen, and T. C. Rounds, J. Chem. Phys., 54, 4123 (1971).

(26) For example, see (a) M. S. Gordon, J. Amer. Chem. Soc., 91, 3122 (1969); (b) R. B. Davidson, W. L. Jorgensen, and L. C. Allen, ibid., 92, 749 (1970).

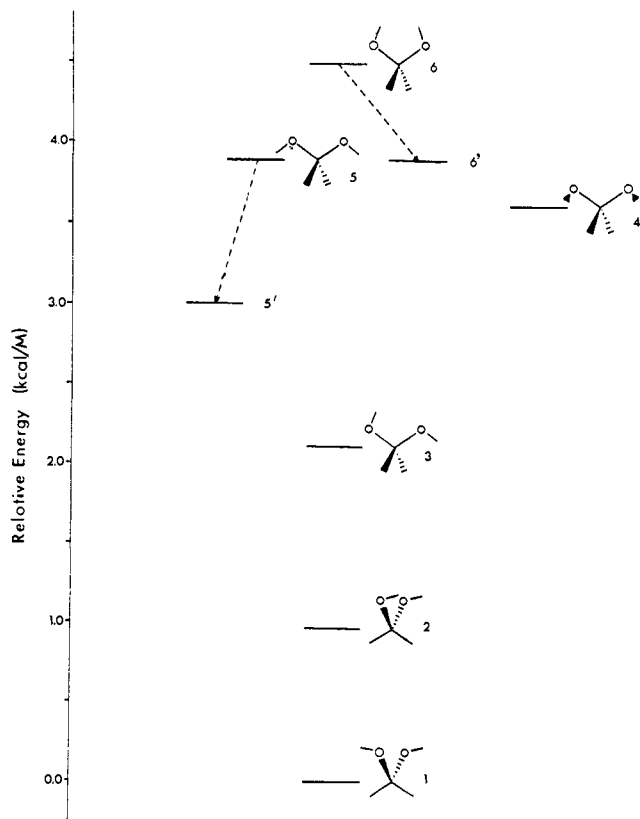**Figure 4.** Relative energies of selected conformations of hexafluoropropane-2,2-diol.

Figure 5. A potential energy surface for hexafluoropropane-2,2-diol as a function of the dihedral angles Δ and Σ. Selected minima are labeled and reference contour values are in units of kilocalories per mole. The difference between contour values is $\sim$0.4 kcal/mole.

Dipole Moments. The dipole moments of hexafluoropropane-2,2-diol, fluoral hydrate, and hexafluoropropan-2-ol were calculated as a function of Δ and Σ (Δ only in the case of hexafluoropropan-2-ol) from standard bond moments.[27] Values of the bond moments are given in Table II.

Table II. Bond Moment Data for the Fluoro Alcohols

$C+\rightarrow CF_3$	2.30 D	$O+\rightarrow H$	-1.50 D
$C+\rightarrow O$	1.15 D	$C+\rightarrow H$	-0.4 D

The dipole moments of hexafluoropropane-2,2-diol and hexafluoropropan-2-ol dissolved in CCl_4 were evaluated from

$$\frac{\epsilon - n^2}{(\epsilon + 2)(n^2 + 2)} = \frac{\epsilon_0 - n_0^2}{(\epsilon_0 + 2)(n_0^2 + 2)} + \frac{4\pi N}{27kT}\mu^2 C$$

by the method of Guggenheim.[28] The parameters ϵ and ϵ_0 are respectively the dielectric constant of a sample solution of concentration C and the pure solvent, n and n_0 are the corresponding refractive indices, N is Avogadro's number, k is Boltzmann's constant, and μ is the molecular dipole moment of the solute.

The dielectric constant of dilute solutions of the two fluoro alcohols in CCl_4 was measured at 2 MHz with a WTW Dipolemeter (type DM01) using the DFL1 cell. The refractive index, n_D, was measured on a Bausch and Lomb precision sugar refractometer using a sodium vapor lamp. The dipolemeter cell and the refractometer were connected in series to a Haake circulating thermostat bath and thermostated at 20.0 ± 0.1°. The dipolemeter was calibrated using pure, dried (Linde 4A molecular sieve) CCl_4 (ϵ 2.2363), benzene (ϵ 2.2825) and cyclohexane (ϵ 2.0228). A polynomial relating scale reading to dielectric constant was evaluated algebraically. All samples were prepared in a nitrogen-filled Dry Box. A precision of 0.1% in the determination of dielectric constant was obtained and of 0.1 D for the dipole moment determination.

(27) C. P. Smyth, "Dielectric Behaviour and Structure," McGraw-Hill, New York, N. Y., 1955.

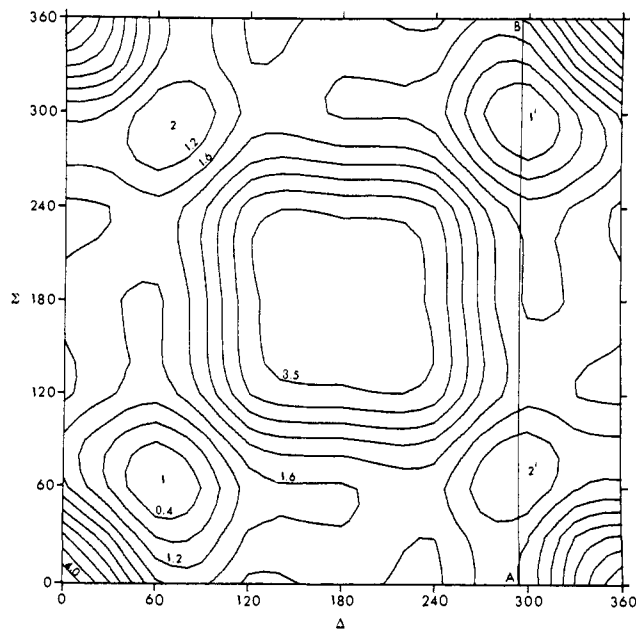(28) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

Results and Discussion

CNDO Calculations. The total energy of a molecule is a function of both its average electron distribution and the nuclear positions. An alteration of the nuclear framework will not only induce changes in the electronic component of the total energy but will also change the nuclear–nuclear repulsion contribution as well. In general, then, continuous deformations of the molecular structure produce continuous changes in the total energy. Different conformations have different total energies, the most stable conformer having the lowest value. In our analysis, the stability of a number of conformations of hexafluoropropane-2,2-diol, fluoral hydrate, and hexafluoropropan-2-ol have been examined relative to the most stable conformer of each compound within the constraints placed upon the molecular parameters we have chosen to vary.

(i) Hexafluoropropane-2,2-diol. In Figure 4, a number of selected conformations of this gem diol and their energies are shown. Each conformer corresponds either to a local minimum or relative maximum in the potential energy surface shown in Figure 5 or to a related conformation. Table III contains the pertinent structural data.

Conformation **1** can occur in two ways $\{69°, 69°, 11°, 105°, 113.4°, 109.1°\}$ and $\{291°, 291°, 349°, 105°,$

Table III. Molecular Parameters for the Structures in Figure 4

Conformer	Δ	Σ	ϕ	COH	CCC	OCO
1	69.0	69.0	11.0	105.0	113.4	109.1
2	68.8	291.2	0.0	105.6	113.5	109.5
3	180.0	0.0	0.0	105.6	113.5	109.5
4	240.0	120.0	0.0	105.6	113.5	109.5
5	180.0	180.0	0.0	105.6	113.5	109.5
5'	180.0	180.0	0.0	105.0	113.0	104.0
6	0.0	0.0	0.0	105.6	113.5	109.5
6'	0.0	0.0	0.0	107.3	112.8	113.0

113.4°, 109.1°}, where we have used the notation {Δ, Σ, φ, COH, CCC, OCO}. These two conformers **1** and **1′**, respectively, are enantiomorphs, possessing

1   **1′**
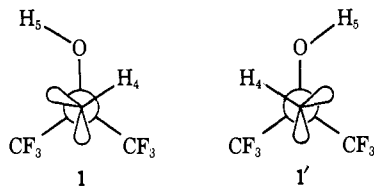
only C_2 symmetry and separated by an energy barrier of approximately 1.8 kcal/mol.[29] One further point of interest is that our predictions for the lowest energy conformation of the diols are essentially in agreement with the *ab initio* calculations of Pople, *et al.*,[6] on ethane-1,1-diol. Conformation **2**, which is about 1 kcal/mol less stable than **1**, also exists in two geometrically identical forms. The two equivalent conformations are specified by the parameters {68.8°, 291.2°, 0°, 105.6° 113.5°, 109.5°} and ({291.2°, 68.8°, 0°, 105.6°, 113.5°, 109.5°}. These two conformers, **2** and **2′**, respectively,

2   **2′**
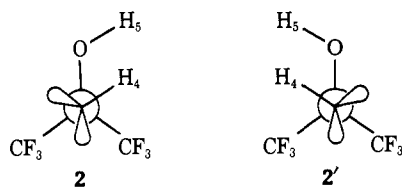
which possess only C_s symmetry are separated by an energy barrier of 0.8 kcal/mol.[30]

Of particular interest is the potential energy surface generated by varying only {Δ, Σ} and fixing the remaining molecular parameters. The contour diagram in Figure 5 is one such surface with φ = 0°, COH = 105.6°, CCC = 113.5°, and OCO = 109.5°. The contour values are in units of kilocalories per mole and have been assigned relative to the equivalent minima at {69°, 69°, 0°, 105.6°, 113.5°, 109.5°} and {291°, 291°, 0°, 105.6°, 113.5°, 109.5°} which lie 0.2 kcal/mol above **1** and **1′**. The remaining two local minima correspond to structures **2** and **2′**. The least stable conformer on this surface is **6**, which is some 4.5 kcal/mol less stable than **1**. The over-all features of this surface are essentially independent of the COH, CCC, and OCO bond angles. This is not unexpected since any changes in these parameters do not alter the symmetry of the intramolecular interactions for any given Δ, Σ, or φ.

Variation of the COH, CCC, and OCO bond angles produces only small changes in the total energy. Even for a large alteration of these angles, the concomitant energy change is only a few hundred calories per mole. For example, if the constraints on these angles are relaxed for structures **5** and **6**, some stabilization of these conformers is achieved. Structure **5′** is about 0.9 kcal/mol more stable than **5**. Similarly, conformer **6′** is stabilized by some 0.7 kcal/mol. Apparently, then, energy changes of the order of 2 or 3 kcal/mol only occur for changes in those parameters which control the symmetry of the intramolecular

(29) This is the lowest such barrier between these two conformers given the molecular parameters we have chosen to vary. Crossing the barrier is a two-step process which involves conformer 2, or its equivalent 2′, as an intermediate stage.

(30) This is the lowest such barrier and crossing it involves a two-step process with 1 (or 1′) as an intermediate stage.
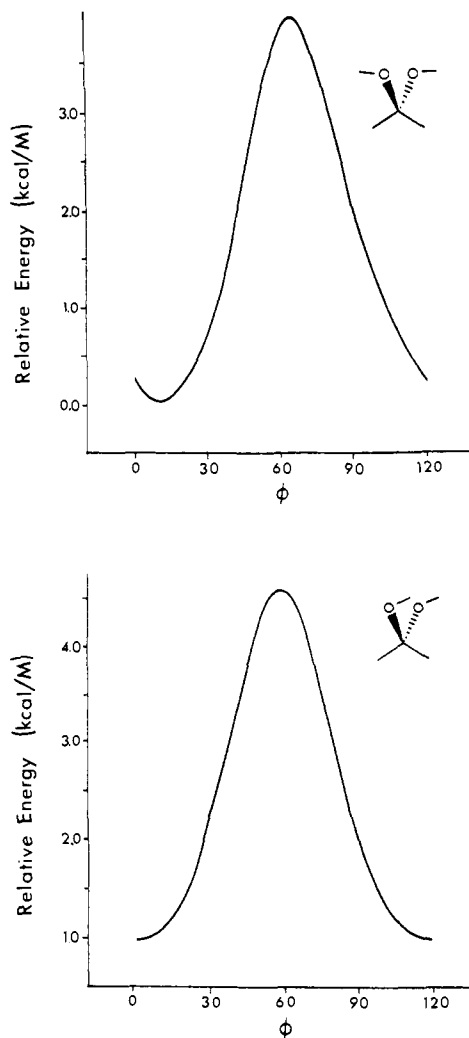

Figure 6. Energy barriers to rotation of the CF_3 groups of hexafluoropropane-2,2-diol as a function of the dihedral angle φ = $φ_1 = φ_2$. The upper plot corresponds to conformation **1** and the lower one to conformation **2**.

interactions, namely, the dihedral angles Δ, Σ, and φ. This fact is readily seen from Figure 4, where the largest energy changes arise for variations in Δ and Σ.

We have calculated the CF_3 rotational barriers as a function of φ for conformations **1** and **2** (Figure 6). The corresponding barriers for **5′** and **6′** are identical in form with that for conformation **2**. The barriers have the same magnitude for all four of these conformers: **1** is 3.9 kcal/mol, **2** is 3.6 kcal/mol, **5′** is 3.7 kcal/mol, and **6′** is 3.8 kcal/mol. All the barriers, except for **1**, are symmetrical about φ = 60°; for **1**, the curve is skewed about φ ≃ 63°. Why this is so can be appreciated from the symmetry of the hydroxyl group interactions. For **1**, a small twist (φ = 11°) of the CF_3 groups is sufficient to increase its stability by ∼0.2 kcal/mol. This is probably indicative of intramolecular O–H···F hydrogen bonding. For structures **2**, **5′**, and **6′** minima in the CF_3 rotational curve occur at φ = 0°

Figure 7 shows an energy profile taken along the path AB in Figure 5. The solid line corresponds to a similar profile from the surface {Δ, Σ, 11°, 105°, 113.4°, 109.1°}, which corresponds to the parameters of conformer **1**. For both curves, Δ = 291° and each is a
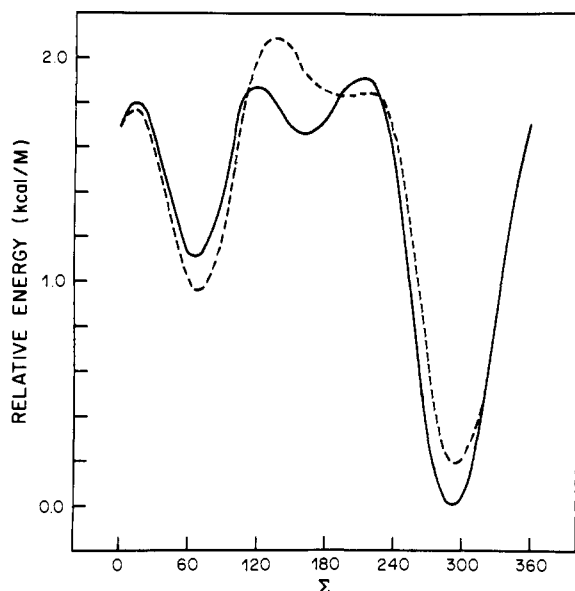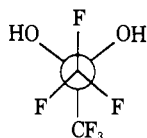
Figure 7. A potential energy profile taken along the path AB of Figure 5. The solid curve is a function of {291°, Σ, 11°, 105°, 113.4°, 109.1°} while the dashed line corresponds to {291°, Σ, 0°, 105.6°, 113.5°, 109.5°}.

function of Σ only. The lowest barrier between 1 and 2 is 1.8 kcal/mol.

The stability of conformations 1 and 2 can be understood in terms of the gauche effect[9] and intramolecular hydrogen bonding. Since there are no CH groups α to the hydroxyl group, no trans lone-pair effect is possible. Three gauche interactions can be distinguished for this molecule. In the first case, a CF bond is gauche to the two CO bonds. If we ignore the small CF_3 twist of $\phi = 11°$ in conformers 1 and 1', this gauche interaction accounts for the preferred orientation of the CF_3 groups with $\phi = 0°$ (see Figure 6) and is always present. It should be noted that this gauche interaction is also found in fluoral hydrate and hexa-

fluoropropan-2-ol as well. The second gauche effect, the OH–CO interaction, the one we are primarily concerned with here, stabilizes the hydroxyl group orientations. The latter effect is dominant while intramolecular hydrogen bonding plays a lesser role in stabilizing these structures, as revealed by the observation that the potential energy surface obtained for propane-2,2-diol[31] has the same qualitative features as that for hexafluoropropane-2,2-diol which is shown in Figure 5. Both structures 1 and 2 show the latter gauche effect, but the repulsive interaction between the hydroxyl groups in 2 decreases its stability by ~1 kcal/mol. Less stable conformations such as 4 and 6' show no gauche interactions and are eclipsed structures. Structures 1, 2, 3, and 5' show a third gauche interaction between the OH and CCF_3 groups, although its presence in the high energy conformer 5' would indicate it is less significant than the OH–CO gauche interaction.

(31) D. R. Truax, unpublished results.

3, 5'   4   6'
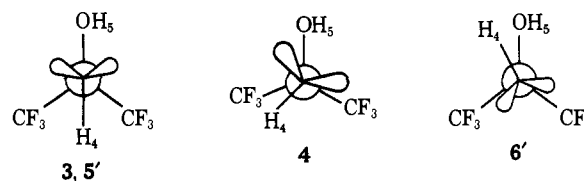
Although we believe that intramolecular hydrogen bonding plays a less important function in stabilizing 1 and 2, its influence can be seen from the perturbation of the CF_3 groups away from the gauche position, $\phi = 0°$ to $\phi = 11°$ in conformer 1. In addition, a $H\cdots F$ interaction is indicated in both 1 and 2 where the closest H–F distances are 2.20 and 2.32 Å, respectively; both of these values are well within the sum of the van der Waals radii,[32] 2.55 Å, for hydrogen and fluorine. However, structures such as 3, 4, and 5' which show "bifurcated" hydrogen bonding interactions are not stable conformations.

Therefore, in the more stable conformers 1 and 2, both the gauche effect and intramolecular hydrogen bonding are cooperating. However, of the two forces, the gauche interactions are the more important stabilizing factors. The least stable conformers lack the gauche interactions and have eclipsed bonds.

(ii) Fluoral Hydrate. In this molecule, all three interactions can be expected to play an important role in stabilizing certain conformations. In Figure 8, a number of selected conformations are shown illustrating the role of these factors. These conformations correspond either to local minima or relative maxima in the contour surface in Figure 9. Table IV contains the relevant structural information.

Table IV. Molecular Parameters for the Structures of Figure 8

Conformer	Δ	Σ	ϕ	COH	CCH	OCO
7	63.0	63.0	6.2	104.5	112.5	109.5
8	65.5	294.5	0.0	105.0	111.9	110.0
9	180.0	300.0				
10	60.0	240.0				
11	180.0	0.0				
12	300.0	60.0		Same as conformer 8		
13	180.0	180.0				
14	240.0	120.0				
15	0.0	0.0				

Conformation 7 has two equivalent geometrical forms. The two conformations can be specified by the molecular parameters {63°, 63°, 6.2°, 104.5°, 112.5°, 109.5°} and {297°, 297°, 353.8°, 104.5°, 112.5°, 109.5°}. These are structures 7 and 7', respectively, and they

7   7'
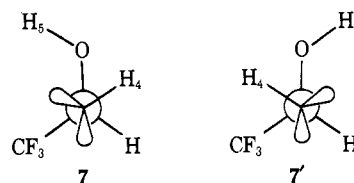
are separated by a potential energy barrier of 1.2 kcal/mol. The remaining low-energy conformation, 8, exists in one structural form.

(32) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.
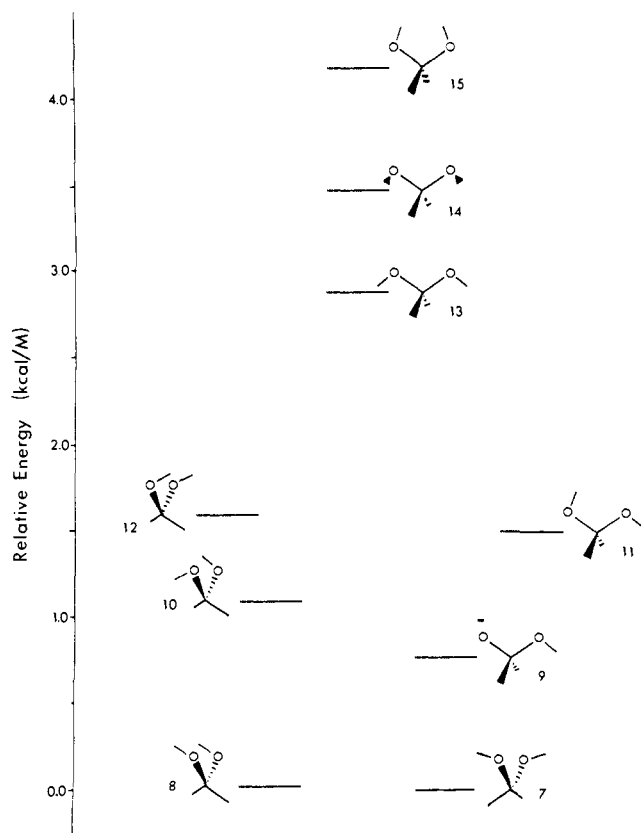
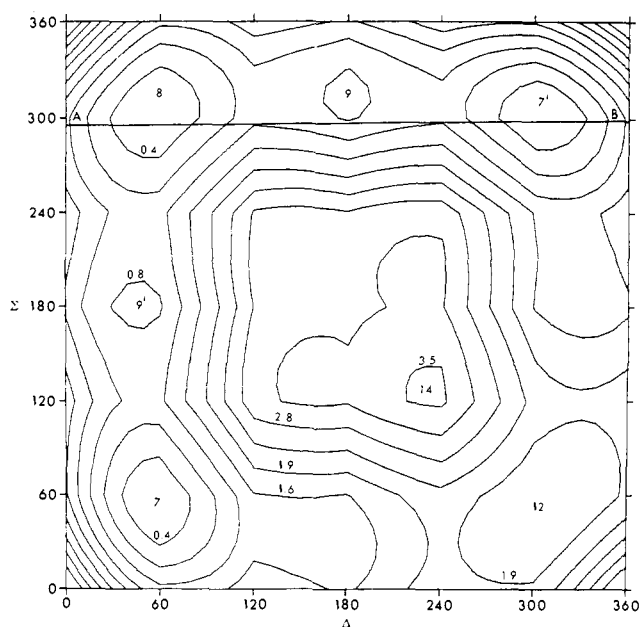Figure 8. Relative energies of selected conformations of fluoral hydrate.

Figure 9. A potential energy surface for fluoral hydrate as a function of the dihedral angles Δ and Σ. Selected minima are labeled and reference contour values are in units of kilocalories per mole. The difference between contour values is $\sim$0.4 kcal/mol.

Of the structures specified in Table IV, only the geometries of conformers **7** and **8** were optimized. As in the case of hexafluoropropane-2,2-diol, the total energy was found to be insensitive to variations of the COH, CCH, and OCO bond angles. No attempt was made to relax the constraints on the angles {ϕ, COH, CCH, OCO} for conformers **9** to **15**.
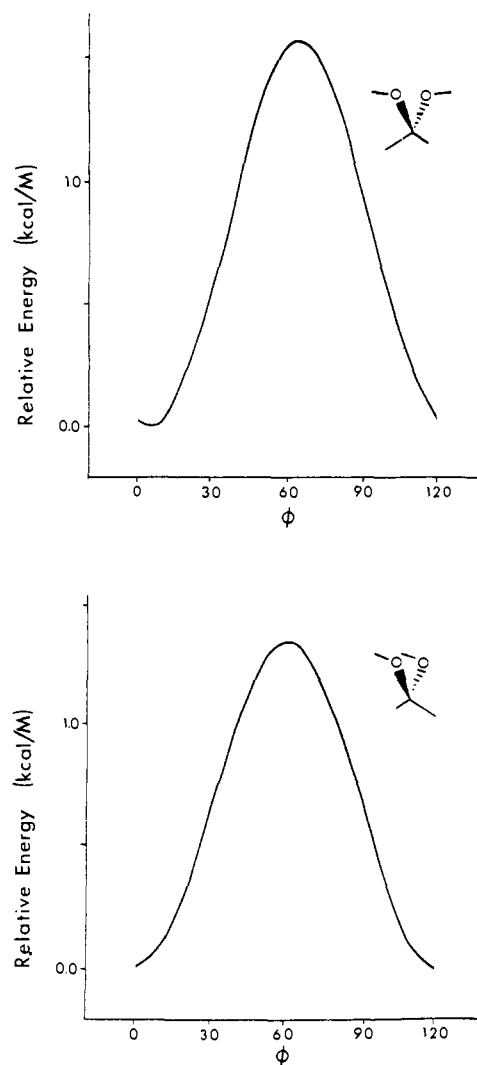
Figure 10. Energy barriers for the rotation of the CF_3 group in fluoral hydrate as a function of the dihedral angle $\phi = \phi_1$. The upper plot corresponds to conformation **7** and the lower one to conformation **8**.

The contour surface in Figure 9 is generated by varying only {Δ, Σ} and holding the remaining variables fixed at $\phi = 0°$, COH $= 105°$, CCH $= 111.9°$ and OCO $= 110.0°$. The surface shows three minima of approximately equal depth corresponding to **7**, its equivalent **7'** and **8**. A number of other local minima also occur, and several of these are shown in Figure 9, namely **9**, its equivalent **9'**, and **12**. The high-energy conformations are **13, 14,** and **15**. When Figures 4 and 8 are compared we note a striking resemblance between the low- and high-energy conformers of the two gem diols. Even their respective potential energy surfaces show marked similarities. The latter observations are consistent with the fact that the OH–CO gauche effect is the dominant conformational determinant in the gem diol structure and that the remaining interactions play a less significant role.

The barriers to rotation of the CF_3 group are 1.6 and 1.3 kcal/mol for conformers **7** and **8**, respectively. Figure 10 shows the potential energy curves as a function of ϕ for **7** and **8**. As might be expected, the curve for **8** is symmetrical about $\phi = 60°$, but the corresponding curve for **7** is slightly skewed. We believe this is
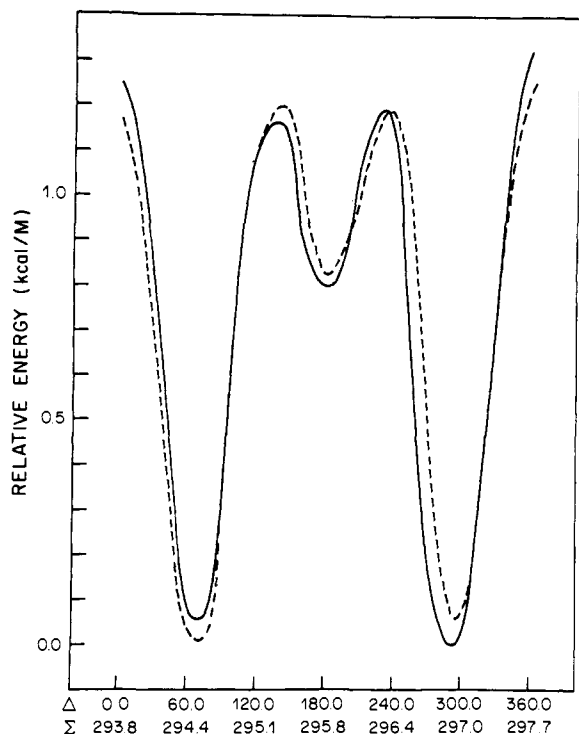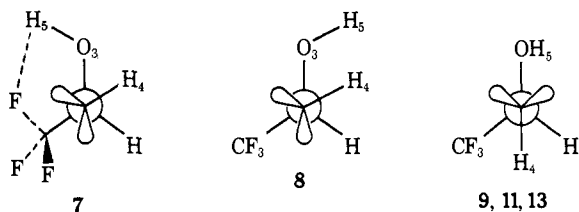
Figure 11. A potential energy profile taken along the path AB of Figure 9. The solid curve is a function of $\{\Delta, \Sigma, 6.2°, 104.5°, 109.5°\}$ and the dashed line corresponds to $\{\Delta, \Sigma, 0°, 105°, 111.0°, 110.0°\}$.

Figure 12. Relative energies of selected conformations of hexafluoropropan-2-ol.

the result of intramolecular hydrogen bonding, as in the case of conformer 1 of hexafluoropropane-2,2-diol.

Figure 11 shows two potential energy profiles. The dashed line is generated by varying Δ and Σ along the path AB in Figure 9. The solid curve corresponds to the curve $\{\Delta, \Sigma, 6.2°, 104.5°, 112°, 109.5°\}$. The local minimum at $\Delta = 180°$ and $\Sigma = 295.8°$ should be identified with conformation 9.

In fluoral hydrate, we expect that some combination of the gauche effect, trans lone-pair effect, and intramolecular hydrogen bonding will participate in stabilizing the low-energy conformations. In 7 and 7′, all three interactions are possible. The $O_2H_4-C_1O_3$ gauche effect is present, and because of the orientation

of the O_2H_4 group a trans lone-pair interaction can occur. The $O_3H_5-C_1O_2$ gauche interaction is also possible and an H_5-F_8 intramolecular hydrogen bonding interaction is indicated by the twist of the CF_3 group away from the gauche position by some 6° (cf. hexafluoropropane-2,2-diol). Only the OH–CO gauche effects and trans lone-pair effects appear to contribute to the stabilization of conformation 8. As can be seen from Figure 8, both conformers 7 and 8 have about the same energy. Although the approximations used in the CNDO/2 method preclude a precise designation of 7 or 8 as the more stable conformer, the former was calculated to be slightly more stable. Conforma-

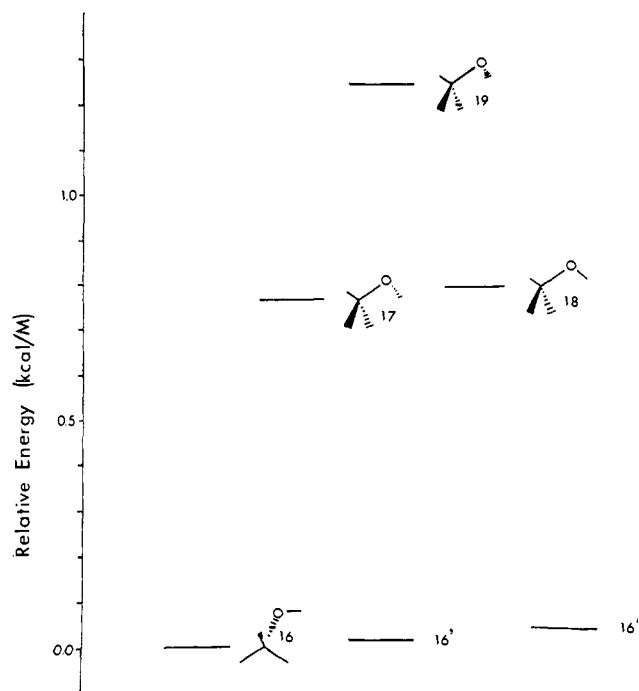tion 11 has no OH–CO gauche interactions, but both a trans lone-pair effect and intramolecular hydrogen bonding are possible. Structures 13 and 15 show no OH–CO gauche effects and intramolecular hydrogen bonding interactions are possible only for 13. Structure 15 also shows no trans lone-pair effects, but conformation 13 does show two such interactions. Conformer 14, which is analogous to structure 4 of hexafluoropropane-2,2-diol and which shows possible "bifurcated" hydrogen bonding interactions, is not a stable conformation.
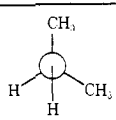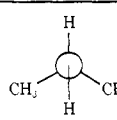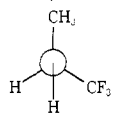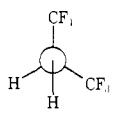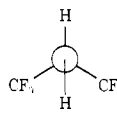
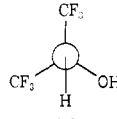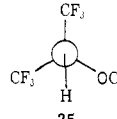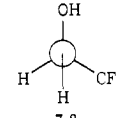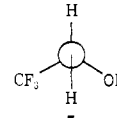In summary then, we find that the most stable conformer, 7, has all three factors, the OH–CO gauche effect, the trans lone-pair effect, and intramolecular hydrogen bonding, cooperating to stabilize that conformation. The other local minima combine one or two of these interactions. Again, those conformations which exhibit none of these stabilizing influences such as 14 and 15 have the highest energy. The OH–CO gauche interaction appears to be the dominant one in this molecule, as in hexafluoropropane-2,2-diol, since those structures which exhibit no such interaction but do show trans lone-pair effects or intramolecular hydrogen bonding are usually of higher energy.

(iii) Hexafluoropropan-2-ol. This compound has no OH–CO gauche interaction; only the trans lone-pair effect and intramolecular hydrogen bonding are important as conformational determinants.

Table V. Molecular Parameters for the Structures of Figure 12

	Δ	ϕ_1	ϕ_2
16	296.9	293.5	0.0
16′	296.9	296.5	296.5
16″	296.9	0.0	0.0
17	186.3	6.3	0.0
18	180.0	0.0	0.0
19	240.0	0.0	0.0

Table VI. OH Stretching Frequencies (cm^{-1}) and Conformations of Several Fluoro Alcohols

	Conformation and infrared absorption						
	One lone-pair interaction			No lone-pair interaction			
		Band max			Band max		
Compd	Conformation	Vapor	Dil CCl₄ soln	Conformation	Vapor	Dil CCl₄ soln	Reference
Propan-2-ol	CH₃ / H–CH₃ / H **20, 20'**		3627.1	H / CH₃–CH₃ / H **21**		3617	8
Trifluoropropan-2-ol	CH₃ / H–CF₃ / H **22**	3651	3614				18, 33
Hexafluoropropan-2-ol	CF₃ / H–CF₃ / H **16**	3666	3615	H / CF₃–CF₃ / H **18**	3626	3578	18, 33
Hexafluoropropane-2,2-diol				CF₃ / CF₃–OH / H **1,2**		3580	18
2-Methoxyhexafluoro-propane-2,2-diol				CF₃ / CF₃–OCH₃ / H **25**		3580	18
Fluoral hydrate	OH / H–CF₃ / H **7,8**		3613	H / CF₃–OH / H **7**		3578	35

A number of conformations of hexafluoropropan-2-ol are illustrated in Figure 12. Only the angles $\{\Delta, \phi_1, \phi_2\}$ were varied while the COH, CCC, and OCH bond angles were fixed at 105°, 113.4° and 109.1°, respectively. The structural data for the conformations of Figure 12 can be found in Table V.

The energy dependence on Δ can be seen in Figure 13 where the three curves have been obtained for three different values of ϕ_1. Small changes in this parameter produce only qualitative changes in the form of the energy dependence. In all cases, minima or local minima occur with $\Delta \sim 60°$, $\Delta \sim 300°$, and $\Delta \sim 180°$. Maxima or relative maxima are obtained for $\Delta \sim 120°$, $\Delta \sim 240°$, and $\Delta \sim 0°$. Both structures with $\Delta \sim 60°$ and $\Delta \sim 300°$ **(16)** show trans lone-pair effects as well as intramolecular O–H—F hydrogen bonding and correspond to the global minimum obtained within the constraints of the fixed geometrical parameters used in the calculations. Those structures which show no trans lone-pair effect or have "bifurcated" hydrogen

16   **17**   **18**
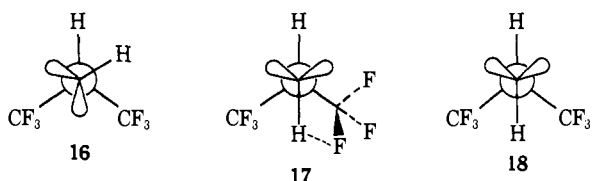
bonding interactions[18] are the least stable conformations.
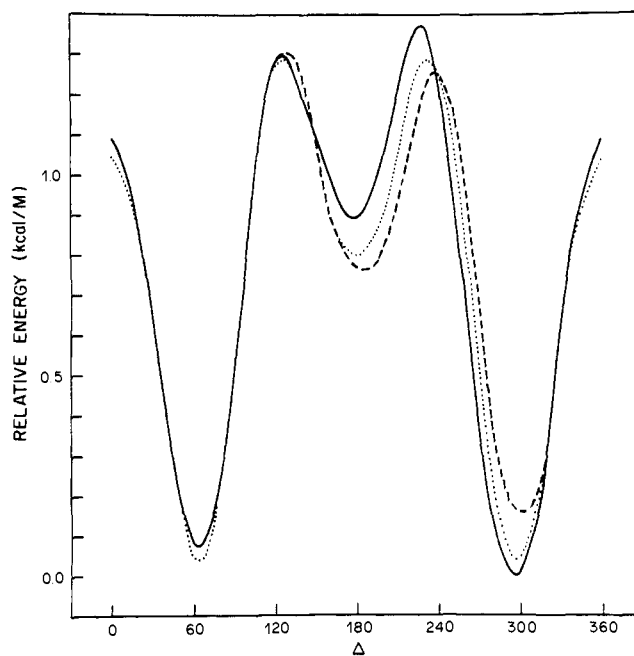**Infrared Evidence.** The conformational evidence

Figure 13. Relative energy of hexafluoropropan-2-ol as a function of the dihedral angle Δ. The dotted curve corresponds to $\{\Delta, 0°, 0°\}$, the dashed curve to $\{\Delta, 6.3°, 0°\}$, and the solid curve to $\{\Delta, 293.5°, 0°\}$.

provided by the infrared absorption spectra of fluorinated alcohols is readily correlated with the above

conclusions since, as mentioned earlier, it has been demonstrated[8] that the OH (and the CH) stretching vibrations are often characteristic of conformational states and much corresponding experimental data are available in the chemical literature.[18,19,33] For example, propan-2-ol, which exists in two distinguishable

20 (20')   21
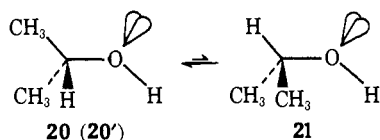
conformations (20 and 21) in dynamic equilibrium, shows doublet OH and CH stretching absorptions.[8] The higher frequency component of the OH bonds and the lower frequency component of the CH bonds correspond to the rotamer that permits one trans lone-pair interaction (20). The same conformer apparently is also the more stable one by about 0.1 kcal/mol in dilute CCl_4 solution[8] and 0.28 kcal/mol in the vapor phase.[34] These spectroscopic results have recently been confirmed by *ab initio* molecular orbital calculations[6d] which yield an energy difference of 0.69 kcal/mol between the two conformers. Associated with the infrared spectral features, one finds that the trans lone-pair interactions appear to enhance the acidity of the hydroxyl proton.[8]

For 1,1,1-trifluoropropan-2-ol, again two distinguishable conformers are possible, one with a trans lone-pair interaction and one with none. However, only one infrared absorption band has been observed in the OH stretching region[18,33] (see Table VI). On this basis, it seems reasonable to conclude that rotamer 22, corresponding to 20, probably is the most stable. Indeed, it is in this conformer that one should be able to observe the additional influence of an intramolecular H···F interaction; with the presence of a trans lone-pair interaction as well as the possibility of intramolecu-

22   23   24
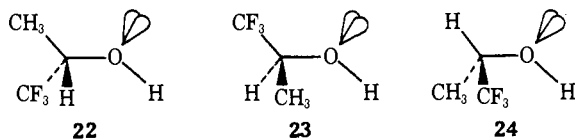
lar hydrogen bonding between the CF_3 and OH groups, this structure probably predominates to the exclusion of conformer 23 and 24.

Infrared evidence for hexafluoropropan-2-ol, on the other hand, suggests the presence of at least two conformers (see Table VI). Our molecular orbital calculations show quite clearly that rotamer 16 which allows for a trans lone-pair interaction should be more stable by about 1 kcal/mol than 18 with no trans lone-pair interaction. Murto and his coworkers[19,33] have assigned the OH and CH stretching absorptions in a fashion consistent with the requirements of the trans lone-pair effect. However, we disagree with their conclusions as to the relative stability of the conformers. From the empirical point of view of the trans lone-pair effect alone, one would predict that conformer 16 should be lower in energy, in agreement with the CNDO/2 calculations, while Murto and his coworkers have

come to the opposite conclusion from their infrared data.

For hexafluoropropane-2,2-diol, we would expect to find an OH stretching absorption characteristic of a rotamer with no trans lone-pair interaction. In fact, only one infrared absorption band is observed;[18] the band position in CCl_4 solution is nearly the same as that of the corresponding conformer of hexafluoropropan-2-ol (see Table VI). In disagreement with Murto and Kivinen,[18] who have proposed the bifurcated hydrogen bonded structure 5 (or 5') (Figure 4), our CNDO/2 calculations suggest that conformers 1 and 2 are the most stable. Apparently, then, the frequency of the OH stretching vibration is governed largely by the existence of trans lone-pair interactions.
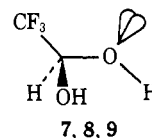

1, 2   3, 5
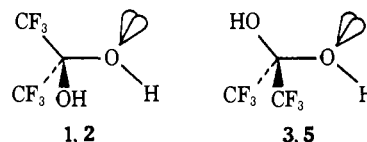
The two most stable conformations of hexafluoropropane-2,2-diol are separated by about 1 kcal/mol, which normally is an energy difference readily distinguished spectroscopically. However, only one OH absorption band has been observed, suggesting that the OH stretching vibration in the two conformers must have very nearly the same frequency since neither has a trans lone-pair interaction.

As we have pointed out earlier, the relative stability of conformers 1 and 2 of the diol is determined by the gauche effect. By comparison, one would predict that the related compound, 2-methoxyhexafluoropropan-2-ol, would exist in a conformational state similar to 1. While there presently are insufficient data confirming this suggestion, it is significant that this com-

25
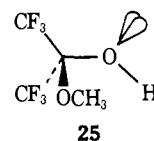
pound displays its OH stretching absorption at the same frequency as the diol and as conformer 18 of hexafluoropropan-2-ol, *i.e.*, at a position apparently characteristic of the absence of trans lone-pair interactions (*cf.* Table VI). We should point out that Murto and Kivinen in their original publication[18] were unable to explain the single OH stretching band of 2-methoxyhexafluoropropan-2-ol. Thus, we find that the scheme, based on a classification of trans lone-pair interactions, is at least consistent with the molecular orbital calculations.

The conformers of fluoral hydrate may be stabilized by all three factors considered here, namely the gauche effect, trans lone-pair effect, and intramolecular hydrogen bonding. With respect to the infrared features, we note specifically that conformers 7 and 7' (Figure 8)

7, 8, 9

(33) J. Murto, A. Kivinven, R. Viitala, and J. Hyomaki, *Spectrochim. Acta, Part A,* 29, 1121 (1973).
(34) S. Kondo and E. Hirota, *J. Mol. Spectrosc.,* 34, 97 (1970).

incorporate one OH bond perturbed and one unperturbed by trans lone-pair interaction. Moreover, the
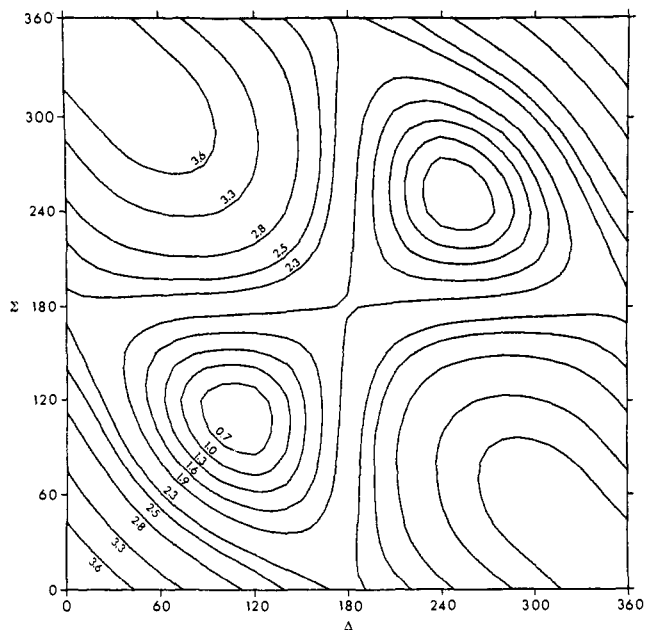
Figure 14. Dipole moment map for hexafluoropropane-2,2-diol as a function of the dihedral angles Δ and Σ. Contour values are in Debye units.

Figure 15. Dipole moment map for fluoral hydrate as a function of the dihedral angles Δ and Σ. Contour values are in Debye units.

structures **8, 9,** and **9'** which, according to the CNDO/2 calculations, correspond to local minima (Figure 9), feature two perturbed OH bonds. The doublet OH stretching absorption observed in dilute CCl₄ solution[35] is therefore readily explained (Table VI). However, the relative stability of the conformers cannot be easily established by means of infrared spectroscopy. It is curious that only one absorption corresponding to a perturbed OH bond has been reported in the vapor phase.[35] This would suggest that conformers **8** or perhaps even **9** and **9'** predominate in the gaseous state, apparently in disagreement with the molecular orbital calculations.

Dipole Moments. The CNDO/2 dipole moment maps calculated as a function of the conformational variables {Δ, Σ} (Figures 14 and 15) reproduce the main features of the corresponding maps calculated from the vector sum of bond moments. A further indication of the reliability of the molecular orbital calculations is provided by the calculated average molecular dipole moment. We have used the rotational isomeric approximation in calculating the latter quantity for hexafluoropropane-2,2-diol, fluoral hydrate, and hexafluoropropan-2-ol (Table VII). In each case, we used a two- or three-state model considering only the conformation corresponding to the global minimum and local

minima of the next highest energy including an appropriate statistical weighting factor when more than one minimum of the same energy appears on the energy surface.

In the case of hexafluoropropane-2,2-diol, conformations (**1, 1'**) and (**2, 2'**) were included in the averaging process. For fluoral hydrate, it was found that (**7, 7'**), **8,** and (**9, 9'**) gave essentially the same result as (**7, 7'**) and **8.** Similarly, hexafluoropropan-2-ol was treated on the basis of a two-state model including only conformation **16,** its equivalent, and **17.** Although the calculated and experimental moments in Table VII are not consistent, it is not surprising that the discrepancies arise in view of the limitations of the rotational isomeric approximation used in the molecular averaging process[36] and within the molecular constraints under which the calculations have been performed.

Conclusion

We have demonstrated in this study that the gem diols, hexafluoropropane-2,2-diol and fluoral hydrate, are useful molecules for the investigation of the relative importance of the gauche effect, trans lone-pair interaction, and intramolecular hydrogen bonding in the stabilization of certain conformations of these molecules. While the OH–CO gauche effect is the dominant interaction, the relative importance of the trans lone-pair effect and hydrogen bonding remains somewhat unclear. However, we can reach a number of general conclusions on the basis of our calculations. (1) The most stable conformation of each molecule is the one in which the number of stabilizing interactions is a maximum. (2) Local minima are associated with conformations having less than the maximum number of stabilizing interactions. (3) Relative maxima show none of these effects. (4) Bifurcated hydrogen bonding, in each case, was associated with conformations of low stability. These general conclusions should serve as a

Table VII. Conformer Dipole Moment, Boltzmann Factor, Average Dipole Moment, and Experimental Dipole Moment

Compd	Conformer (dipole moment, Boltzmann factor)	μ_{calcd}, D	μ_{exptl}, D
Hexafluoropropane-2,2-diol	**1** (1.89 D, 0.83); **2** (3.73 D, 0.17)	2.2	2.5
Fluoral hydrate	**7** (2.03 D, 0.57); **8** (4.88 D, 0.23); **9** (3.60 D, 0.20)	2.9	2.3
Hexafluoropropan-2-ol	**16** (3.08 D, 0.88); **17** (0.26 D, 0.12)	2.7	2.0

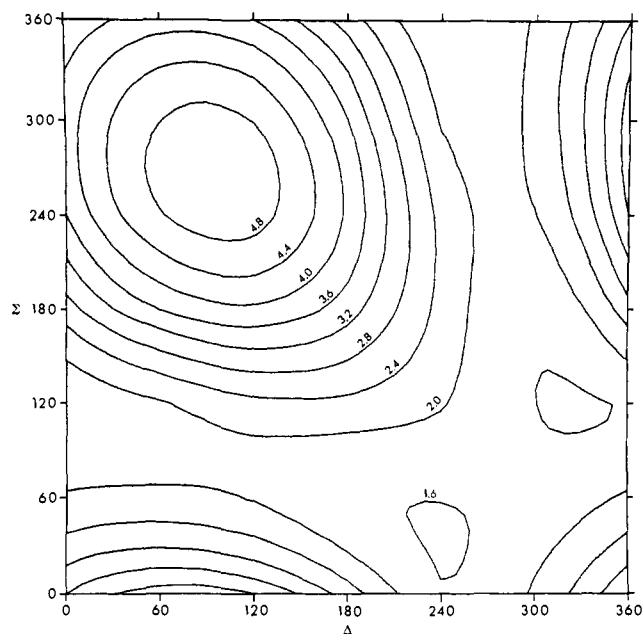(35) A. Novak and E. Whalley, *Spectrochim. Acta,* **16,** 521 (1960).

(36) P. J. Flory, *J. Polym. Sci., Part A-2,* **11,** 624 (1973).

set of useful empirical rules to guide conformational assignments for molecules of this type.

While the trans lone-pair effect may not be the dominant interaction with respect to conformational stability, it appears to be the most useful feature for identifying rotational isomers by means of infrared spectroscopy. Namely, the frequencies of the OH and CH stretching vibrations are governed largely by the existence of a trans lone-pair interaction, although the band separation may vary. On the other hand, the OH stretching vibration apparently is insensitive to the gauche effect, as exemplified by the single, sharp OH absorption band arising from the two most stable conformers of hexafluoropropane-2,2-diol. Since this insight has been gained largely by CNDO/2 calculations, we believe that this method can be used as a reliable tool by the spectroscopist for the purpose of conformational analysis.
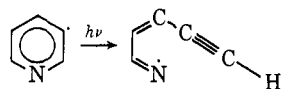
2-Hydroxyphenyl and 2-Methoxyphenyl Radicals. Matrix-Isolation Electron Spin Resonance Study

Paul H. Kasai* and D. McLeod, Jr.

Contribution from the Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591. Received August 23, 1973

Abstract: 2-Hydroxyphenyl and 2-methoxyphenyl radicals generated in argon matrices were examined by electron spin resonance spectroscopy. Both radicals were found to be σ radicals and were found to isomerize under thermal or photoexcitation to phenoxy and phenoxymethyl radicals as the result of intramolecular hydrogen abstraction from the respective substituent group.

An electron spin resonance (esr) study of phenyl radicals isolated in argon matrix revealed that the radical is stable against uv ($\lambda > 250$ nm) irradiation.[1] The radical must also possess substantial thermal stability, since it is the only radical observed when produced by pyrolysis (500 $\approx$ 700°) of phenyl iodide. Pyridyl radicals,[2] on the other hand, have been found to undergo readily a ring-rupture rearrangement when irradiated with uv light, *e.g.*

We report here the results of a matrix-isolation esr study of 2-hydroxyphenyl and 2-methoxyphenyl produced from 2-iodophenol and 2-iodoanisole, respectively. Both radicals were found to be σ radicals despite the essentially nonbonding lone-pair electrons at the oxygen p_π orbital. Most interestingly, it was found that thermal or photoexcitation of these radicals leads to intramolecular hydrogen abstraction by the radical center from the substituent group.

Experimental Section

The cryostat-spectrometer assembly that would permit isolation of reactive species in rare-gas matrices and observation of their esr spectra has been detailed earlier.[3] The matrix is formed upon a cold finger (a sapphire rod) which is attached to the bottom of the inner liquid helium dewar. The design was such that the entire inner dewar can be rotated about and moved along its vertical axis. During the course of the present study, the lower section of the inner dewar was extensively modified in order to achieve a variable temperature capability. The essential features of the modification are depicted in Figure 1. The cold finger is now attached to the bottom of the lower can which is cooled by a liquid-helium flow from the upper reservoir and heated by a resistant coil wound around it. With this arrangement it was possible to vary and maintain the temperature of the lower can from 4.6°K up with the accuracy of ± 0.5°K. The temperature is monitored by a Chromel *vs.* gold (0.07 at. % Fe) thermocouple,[4] the cold junction of which is imbedded in the wall of the upper reservoir. From the change in the intensity of an esr signal related to the Boltzmann distribution, it was concluded that, when the temperature of the lower can is changed (within the range covered, 4.6–20°K), the matrix comes to thermal equilibrium with the can in less than 0.5 min.

In the case of pyrolysis the precursor (2-iodophenol or 2-iodoanisole) was passed through a resistively heated quartz tube and trapped in an argon matrix being formed upon the cold finger. In the case of photolysis, an argon matrix containing the precursor was prepared and then irradiated with uv through the side quartz window. In the case of the dissociative photoelectron transfer process,[5] an argon matrix containing the precursor molecules and Na atoms (the atomic ratio Ar:precursor:Na being roughly 1000:10:1) was prepared and then irradiated with red light ($\lambda > 580$ nm). A high-pressure mercury arc (GE, AH-6) equipped with appropriate filters (Corning 7–54 for uv, and 2–62 for $\lambda > 580$ nm) was used for these experiments. Unless mentioned otherwise, all the spectra were obtained while the matrix was maintained at 4.6°K. The frequency of the spectrometer locked to the sample cavity was 9.430 GHz. 2-Iodophenol and 2-iodoanisole were obtained from Aldrich Chemicals and purified further by sublimation.

2-Hydroxyphenyl Radicals

Figure 2 shows the esr spectrum obtained when an argon matrix containing 2-iodophenol was irradiated

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