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by

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ABSTRACT

Ab initio calculations on a series of alcohol dimers including $(CH_3OH)_2$, $(CH_3CH_2OH)_2$, and $(CF_3CH_2OH)_2$ have been carried out to compare the effects of various substituents on the hydrogen bond energies and structures and to correlate the results with the wealth of new experimental data on them. Calculations were done with the minimal STO-3G basis set. The methanol and ethanol dimers both have nearly linear hydrogen bonds. The ethanol dimer is also similar in energy to the methanol dimer. Dimers involving both the *g*-staggered and *t*-staggered isomers of 2,2,2 trifluoroethanol were considered. The *g*-staggered isomer is more stable than the *t*-staggered isomer by 0.7 kcal/mole and has an intramolecular bond. The dimer of the *t*-staggered isomer was found to have a linear hydrogen bond as in the methanol and ethanol dimers with a similar hydrogen bond energy. In contrast, the dimer of the *g*-staggered isomer has a cyclic structure which is more stable by about 0.5 kcal/mole. The results are consistent with experimental measurements of the gas phase enthalpies of association of alcohols.

I. Introduction

Ab initio calculations have been carried out on methanol, ethanol, and trifluoroethanol dimers. The purpose of these calculations is to provide a basis for comparison with experimental measurements of the enthalpies of association of these alcohol dimers.

Studies of molecular association in alcohol vapors have been made using a variety of different experimental techniques. Among these are analysis of PVT, heat capacity, and thermal conductivity measurements to determine which polymers are present in the vapor and their enthalpies and entropies of association.[1] The thermal conductivity technique developed in this laboratory has proved successful in a study of association in methanol vapor.[2] This technique is currently being used to measure the enthalpies and entropies of association of a number of other alcohols including ethanol, isopropanol, 2,2,2 trifluoroethanol,[3] and 1,1,1,3,3,3 hexafluoropropanol. The goal of these measurements is to sort out the differences in the hydrogen bonding of a series of alcohols and provide consistent data for comparison with quantum mechanical calculations.

In this paper, results on the structures and binding energies of the methanol, ethanol, and trifluoroethanol dimers obtained with a minimal basis set are presented. In the case of trifluoroethanol, dimers involving two of its isomers are considered. The results are analyzed in terms of the effect of the substituents $-CF_3$ and $-CH_3$ and compared to the experimental results.

II. Computational Methods

In this study, self-consistent molecular orbital theory is used to calculate total energies. Each molecular orbital is written in the form

$$\psi_i = \sum_\mu c_{\mu i} \phi_\mu \qquad (1)$$

where the ϕ_μ are basis functions and $c_{\mu i}$ are variational coefficients. The dimer is considered as one molecule in these calculations. The intermolecular energy (binding energy) of each dimer is obtained by subtracting the sum of the monomer energies from the total energy computed for the equilibrium dimer. The basis set used is the minimal STO-3G[4] basis which has been found to give reasonable results for other hydrogen-bonded complexes.[5]

It has been noted previously that the binding energy and structures of complexes obtained from these types of theoretical calculations are dependent on the geometry of the monomer.[6] Use of an optimized geometry for the monomer gives a different binding energy for the dimer than if the experimental geometry is used for the monomer. Since it is not feasible to optimize the geometries of the various trifluoroethanol isomers that are considered in this study, we have decided to use a standard experimental model[7] for all of the molecules in order to have a better basis for comparison of the binding energies and structures. The intermolecular angles have been optimized to ±2° and the hydrogen bond length to ±.01 Å in all the results which are reported.

III. Equilibrium Structures of Methanol and Ethanol Dimers

Optimization of the methanol dimer having standard geometries[7] for the monomers was carried out in terms of two intermolecular parameters. They are illustrated in fig. 1: R is the distance between the oxygen centers and Θ is the angle that the bisector of the COH angle of the proton acceptor molecule makes with the OO axis. The hydrogen bond is assumed linear and the bisector is taken to lie in the same plane as the COH of the proton

donor. This should be a good approximation based on a more complete optimization of the methanol dimer by Del Bene[8] using the STO-3G basis set. The optimized R and Θ values which we obtain are given in Table I. The binding energy of -6.15 kcal/mole compares with the -5.57 kcal/mole obtained by Del Bene[8] using the optimized geometries for the monomers.

For the ethanol dimer, R and Θ were also optimized with the resulting values given in Table I. Rotation of each of the ethanol molecules about the bisectors of their COH angles, χ_1 and χ_2, was tested to see if they would have a tendency to change position because of the $-CH_3$ substituent. Their positions were found to be nearly the same as the methanols in $(CH_3OH)_2$. Also, the hydrogen bond was tested and found to be linear within 1°. A binding energy of -6.00 kcal/mole for the dimer was obtained.

IV. Equilibrium Structures of the Trifluoroethanol Dimer

The CF_3CH_2OH molecule has a number of possible rotational isomers. Rotation of the CF_3 group about the C-C bonds leads to staggered and eclipsed forms, while rotation about the C-O bond generates configurations which are described by the CCOH dihedral angle. Calculations with the STO-3G basis set were carried out on five of the most likely configurations illustrated in fig. 2 to determine the most stable isomers for consideration in forming the dimer structures. Three staggered forms were considered with CCOH dihedral angles of 0°, 60° (designated as *g* for gauche), and 180° (designated as *t* for trans). Two eclipsed forms were considered with CCOH dihedral angles of 60° (*g*) and 180° (*t*). The relative energies of these structures are given in Table II.

The two lowest energy structures are the gauche-staggered and trans-staggered isomers. The theoretical prediction that the gauche form is lower in energy by 0.70 kcal/mole over the trans form is in agreement

with an infrared study[9] which found that the gauche form was predominant. In the same study, the gauche-trans energy difference was estimated to be 3.3 kcal/mole. This is somewhat larger than our theoretical prediction; however, it should be kept in mind that no attempt was made to optimize the structures and a small basis set was used. Stabilization of the gauche isomer is apparently due to an internal hydrogen bond of the type H···F.

We first considered complexes involving the trans isomer. Hydrogen bonding is possible at the lone pairs of either the oxygen or fluorine and is illustrated in fig. 3. The structure for the dimer having an O-H···F bond was constructed with a linear hydrogen bond similar to the HOH···FH complex in a different study.[5] The structure having the oxygen as the lone pair donor, O-H···O, was constructed similar to the methanol dimer. For both dimers, the R and Θ parameters shown in fig. 3 were optimized. The results are given in the figure. The angle ϕ describing the relative orientations of the two molecules was also tested and found to be nearly 180° in both cases. Structure II having the O-H···O hydrogen bond was found to be more stable with a binding energy of -5.84 kcal/mole as compared to -2.62 kcal/mole for the O-H···F dimer (I).

Two structures were then considered for dimers involving the gauche form of trifluoroethanol which has an intramolecular hydrogen bond. The structures were initially constructed with O-H···F and O-H···H hydrogen bonds similar to the trans dimers and are illustrated in fig. 4. In the case of structure III, the fluorine (F') involved in the intramolecular hydrogen bond was chosen to be the lone pair donor so as to allow for interaction between the fluorines (of the proton donor) and the hydroxyl hydrogen (of the proton acceptor). The parameters (see fig. 4a) which were allowed to vary were R, the hydrogen bond length; Θ, the angle OHF'; and ϕ, rotation of the proton

acceptor molecule about the C'F' axis ($\phi \approx 0°$ corresponds to the CCO and C'CO planes being parallel). The results of optimization of these parameters are shown in fig. 4a. The binding energy of this dimer is -3.15 kcal/mole.

For the dimer involving the O-H···O bond, a similar type of initial structure allowing for the additional H···F interaction was set up with the six intermolecular parameters indicated in fig. 4b. These are R, the hydrogen bond distance; Θ_1 and Θ_2, the hydrogen bond angles; χ_1 and χ_2, the rotation of each molecule about an axis bisecting the COH angle; and ϕ, the orientation of each molecule with respect to each other. The results shown in fig. 4b indicate that a cyclic hydrogen bond is formed with the proton acceptor being rotated about ϕ and χ_2 such that the hydroxyl hydrogen interacts with the F. The resulting structure has two F···H internal hydrogen bonds having distances of 2.46 Å, an O-H···O bond with an H···O distance of 1.71 Å, and an external hydrogen bond F···H having a distance of 2.21 Å involving the same F that is taking part in the intramolecular bond. This structure is the most stable of the four structures investigated with a binding energy of -6.46 kcal/mole. The energies are summarized in Table III.

It is of interest to approximate the various contributions to the hydrogen bond energy of this cyclic structure. The O-H···O bond contributes about 5.8 kcal/mole based on the binding energy of the trans dimer (II) with the same type of bond. The external F···H interaction probably contributes about 0.7 kcal/mole on the basis of the intramolecular F···H bond in the gauche isomer. Hence, these two bonds add up to 6.5 kcal/mole which is close to the hydrogen bond energy of 6.46 kcal/mole of the cyclic structure (IV).

V. Comparison of Energies and Structures

The methanol and ethanol dimers are very similar in binding energy and structure (see Table I). The Mulliken gross populations[10] for methanol and

ethanol are given in Table IV. The addition of the $-CH_3$ group tends to slightly increase the electron population on the OH group, but not enough to affect the hydrogen bond substantially. Experimentally the enthalpies of association of the methanol and ethanol dimers have been found to be similar. From PVT measurements, Kretchmer and Wiebe[11] obtain a ΔH of approximately -4.0 kcal/mole for both dimers. From vapor heat capacity measurements and prior PVT measurements, Weltner and Pitzer[12] obtain a ΔH of -3.22 kcal/mole for the methanol dimer and Barrow[13] finds a ΔH of -3.4 kcal/mole for the ethanol dimer. The experimentally measured ΔH differs from the theoretical binding energy in that it includes the difference in vibrational, rotational, and translational energies of the monomers from the complex.

The trifluoroethanol trans dimer with the O-H···O bond (II) is similar in structure to the methanol and ethanol dimers, but is slightly less stable (-5.84 kcal/mole). The Mulliken populations (Table IV) indicate that the $-CF_3$ group is slightly electron withdrawing. The positive charge on the hydroxyl hydrogen increases (0.015 compared to ethanol) only slightly more than the negative charge on the oxygen decreases (0.012). The hydrogen bond energy is apparently not affected significantly by the $-CF_3$ group. In contrast, in the case of the gauche dimer of trifluoroethanol (IV) the intramolecular bond results in an extra external hydrogen bond being formed, H···F, which increases the stability to -6.46 kcal/mole. The resulting structure has a cyclic hydrogen bond. The external hydrogen bond apparently contributes about 0.6 kcal/mole extra stability to the dimer. This is very similar to the stabilizing effect of the internal hydrogen bond in the gauche isomer. The cyclic hydrogen bond in structure IV is similar to those found by Del Bene[14] in alcohols with $-NH_2$ substituents.

Experimentally, the trifluoroethanol dimer has a larger negative enthalpy of association than the ethanol dimer. Thermal conductivity measurements[3,15] find it to be more stable by 1.4 kcal/mole. This is to be compared to the theoretical prediction of a difference in the binding energies of about 0.5 kcal/mole. Optimization of the monomer units as well as use of a larger basis set could change the theoretical value.

The cyclic structure determined for the trifluoroethanol dimer provides a possible explanation for the fact that only dimers are detected in trifluoroethanol vapor in thermal conductivity measurements[3] as opposed to methanol and ethanol vapors where higher polymers such as tetramers are detected.[2,11-13,15] The formation of higher polymers in these cases are apparently facilitated by linear hydrogen bonds.[16] However, in the case of trifluoroethanol, the most stable rotational isomer is the gauche form with an internal hydrogen bond and it forms a cyclic hydrogen bonded dimer. Conversion of the gauche isomer to the trans isomer that forms a linear hydrogen bond (which is present in the higher polymers) requires energy to break the internal hydrogen bond. This extra energy presumably reduces the relative stability of the higher polymers in the trifluoroethanol vapor. Thus, the intramolecular hydrogen bond in monomeric trifluoroethanol and the cyclic structure it stabilizes in the dimer are a possible explanation for only dimers being detected in thermal conductivity measurements on the vapor.

VI. Conclusions

The following conclusions can be drawn from this comparative study of methanol, ethanol, and trifluoroethanol dimers:

(1) The methanol and ethanol dimers are very similar in structure and binding energy.

(2) The dimer of trans-staggered trifluoroethanol with a linear hydrogen bond is only slightly less stable than the ethanol and methanol dimers. The dimer of the gauche-staggered isomer is stabilized by about 0.6 kcal/mole over the trans dimer by an extra external hydrogen bond between the hydroxyl hydrogen of the proton acceptor and a fluorine of the proton donor. This is consistent with experimental results on ethanol and trifluoroethanol vapors.

(3) The presence of an intramolecular bond in the trifluoroethanol monomer could be the reason that higher polymers are not observed in trifluoroethanol vapor as they are in methanol and ethanol vapors.

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Table I. Optimized geometries and binding energies for $(CH_3OH)_2$ and $(CH_3CH_2OH)_2$ with standard geometries for the monomers[a]

Dimer	R,Å	Θ	B.E., kcal/mole
$(CH_3OH)_2$[b]	2.71(2.74)	137°(132°)	-6.15(-5.57)
$(CH_3CH_2OH)_2$	2.70	138°	-6.00

[a] Energies of the monomers are: CH_3OH, E = -113.54551; CH_3CH_2OH, E = -152.12951 a.u.

[b] The numbers in parentheses are from an optimization of the dimer using optimized monomer geometries in ref. 8.

Table II. Energies of various rotational isomers of 2,2,2 trifluoroethanol (STO-3G)

Isomer[a]	Energy, a.u.	Relative Energy, kcal/mole
I	-444.50884	0
III	-444.50773	0.70
II	-444.50575	1.94
V	-444.50549	2.10
IV	-444.50524	2.26

[a]Structures illustrated in fig. 2.

Table III. Energies of 2,2,2 trifluoroethanol dimers (STO-3G)

Structure[a]	Energy, a.u.	Binding Energy, kcal/mole
I (*t*-staggered; OH···F)	-889.01963	-2.55
II (*t*-staggered; OH···H)	-889.02476	-5.84
III (*g*-staggered; OH···F)	-889.02270	-3.15
IV (*g*-staggered; OH···H)	-889.02798	-6.46

[a]Structures in fig. 3 and fig. 4.

Table IV. Mulliken gross atomic populations for monomers with standard geometries (see ref. 7)

Species	O	H[a]	C[b]
CH_3OH	8.307	0.811	6.066
CH_3CH_2OH	8.314	0.814	6.177
CF_3CH_2OH[c]	8.302	0.799	6.028
CF_3CH_2OH[d]	8.301	0.799	6.027

[a] The hydroxyl hydrogen.

[b] Carbon nearest the oxygen.

[c] *t*-staggered isomer.

[d] *g*-staggered isomer.

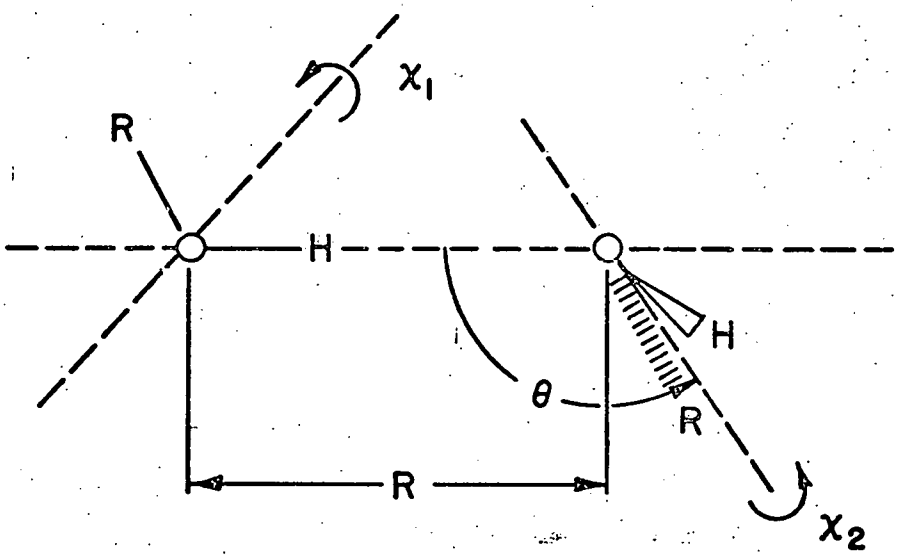


Fig. 1. Geometrical parameters for $(ROH)_2$ structures (χ_1 and χ_2 bisect the ROH angles).

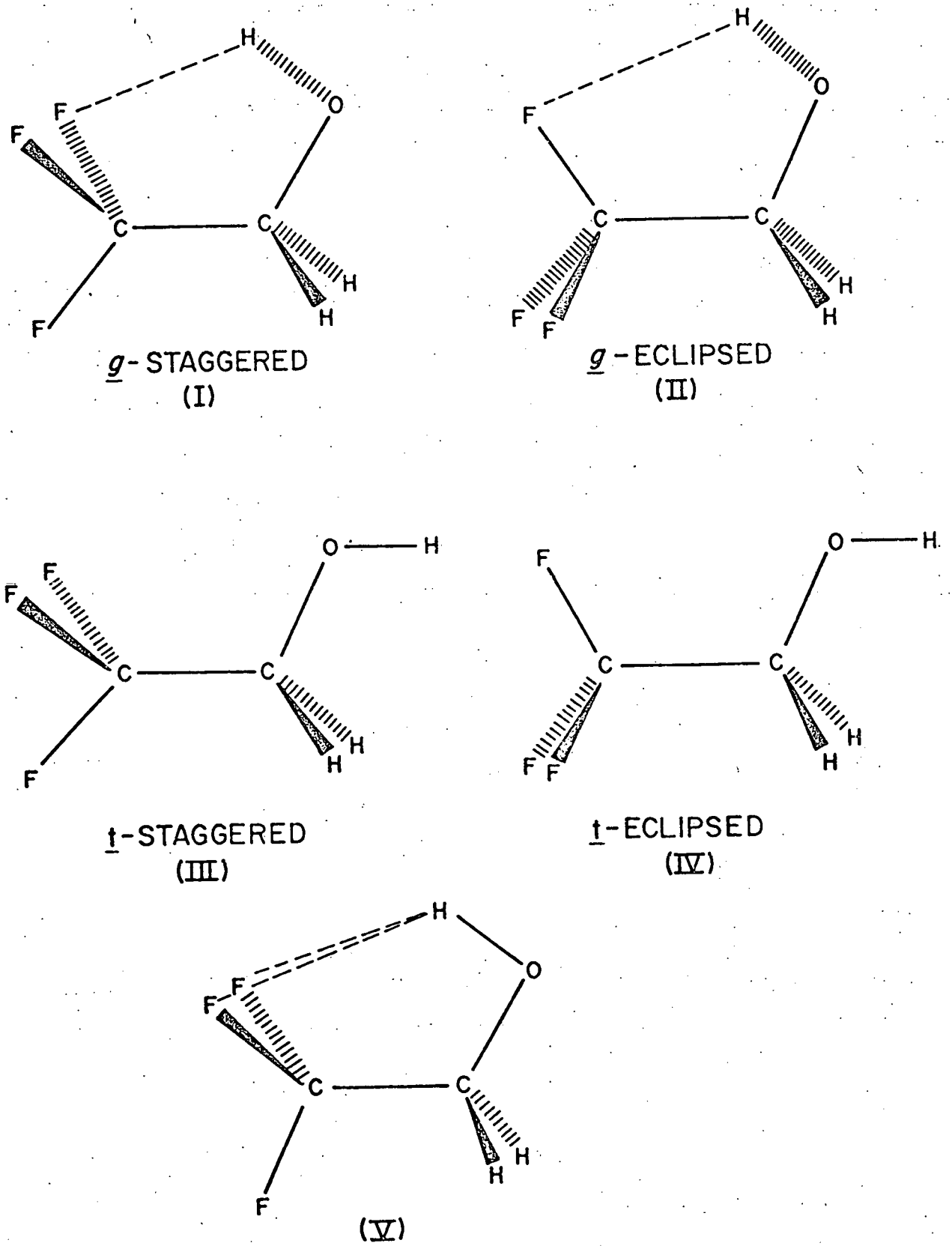
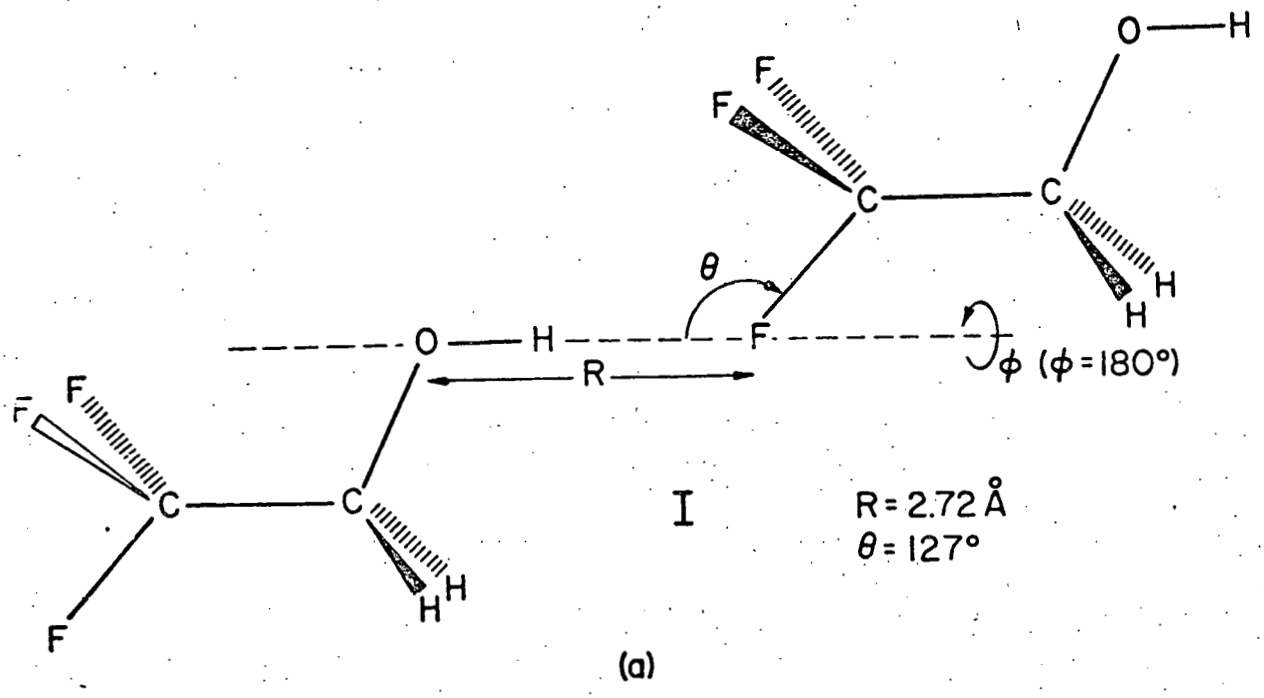


Fig. 2. Various rotational isomers of trifluoroethanol.



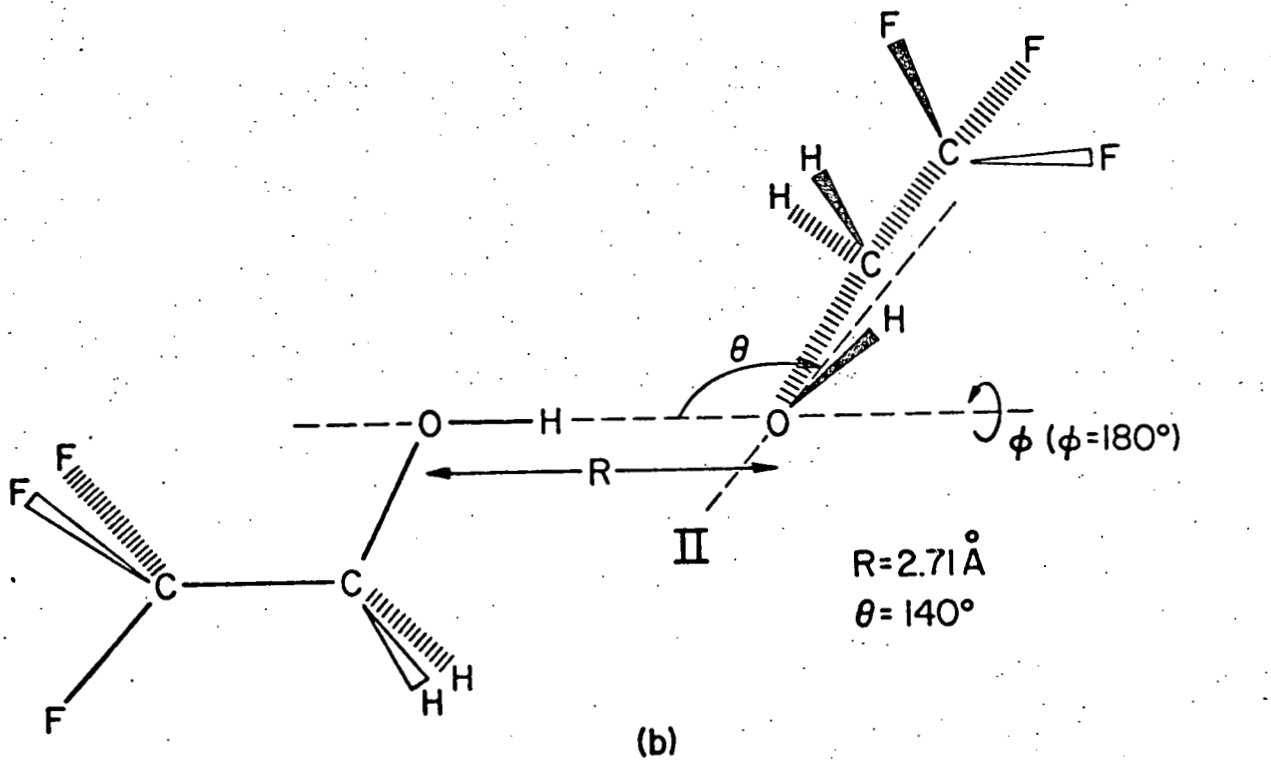


Fig. 3. Dimers between trans-staggered isomers of trifluoroethanol. (The values of the parameters in parentheses correspond to the positions in the diagrams.)

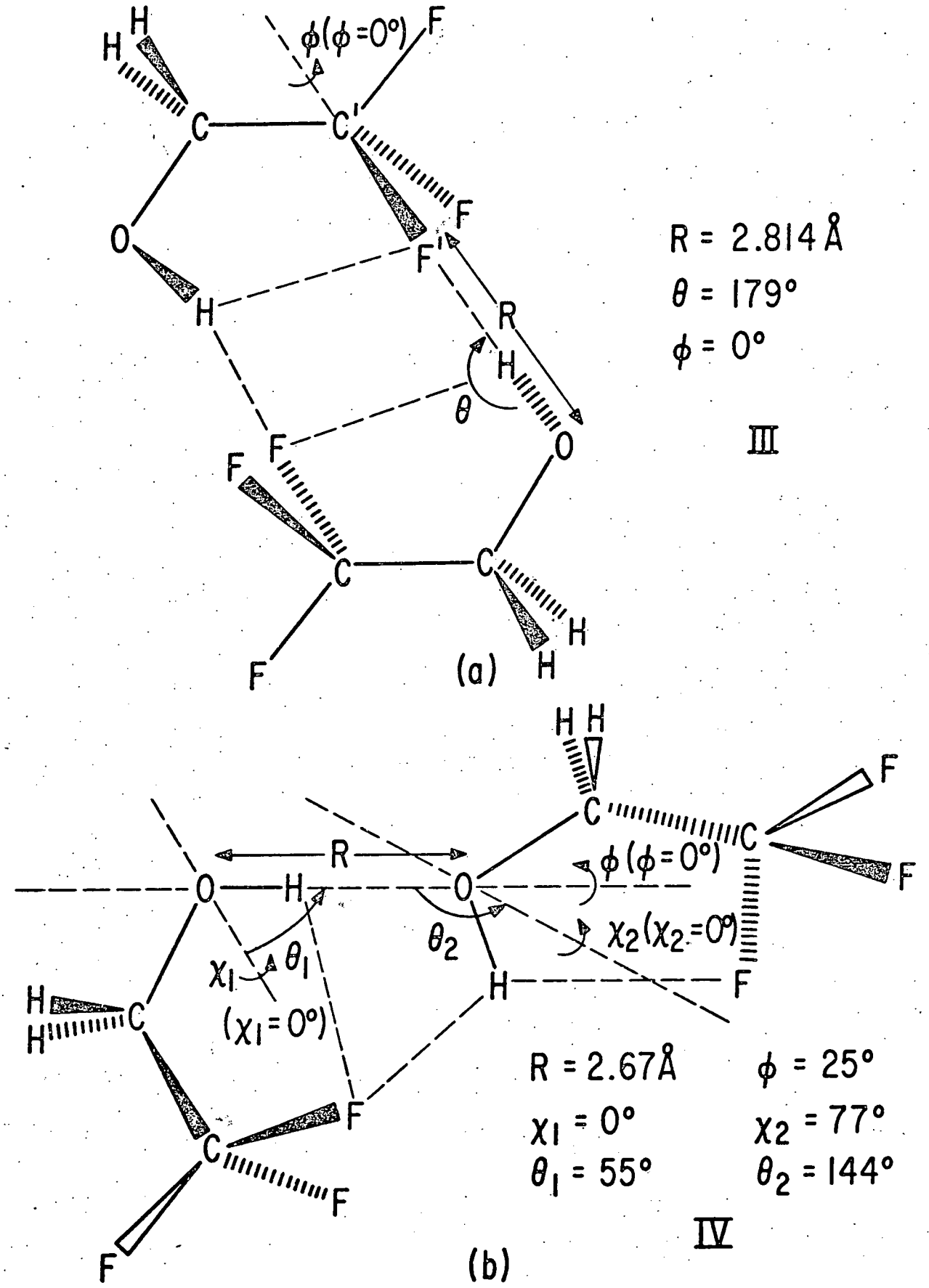


Fig. 4. Dimers between gauche-staggered isomers of trifluoroethanol. (The values of the parameters in parentheses correspond to the positions in the diagrams.)