

Intrinsic Acidity and Basicity of 2,2,2-Trifluoroethanethiol. The First Experimental and Theoretical Study[†]

M. T. Molina

Instituto de Química Médica, C.S.I.C. c/Juan de la Cierva 3, E-28006 Madrid, Spain

W. Bouab and M. Esseffar

Département de Chimie, Faculté des Sciences (Semlalia), Marrakesh, Morocco

M. Herreros, R. Notario, and J.-L. M. Abboud*

Instituto de Química Física "Rocasolano", C.S.I.C. c/Serrano 119, E-28006 Madrid, Spain

O. Mó and M. Yáñez*

Departamento de Química, C-IX, Universidad Autónoma de Madrid, E-28049, Cantoblanco (Madrid), Spain

Received March 19, 1996[®]

The gas phase acidity and basicity of 2,2,2-trifluoroethanethiol (TFET), i.e., the standard Gibbs energy changes for the following two reactions have been determined by means of Fourier transform ion cyclotron resonance spectroscopy: $\text{CF}_3\text{CH}_2\text{SH}(\text{g}) \rightarrow \text{CF}_3\text{CH}_2\text{S}^-(\text{g}) + \text{H}^+(\text{g})$ and $\text{CF}_3\text{CH}_2\text{SH}_2^+(\text{g}) \rightarrow \text{CF}_3\text{CH}_2\text{SH}(\text{g}) + \text{H}^+(\text{g})$. Also determined were the equilibrium constants for the 1:1 associations in dilute solution between TFET and pyridine *N*-oxide, 3,4-dinitrophenol (both in cyclohexane), and molecular iodine (in tetrachloromethane). Quantum-mechanical treatments at the G2(MP2) level were carried out on TFET, 2,2,2-trifluoroethanol, ethanethiol, and ethanol as neutral, protonated, and deprotonated species. Topological analyses of the charge densities and the Laplacians thereof were performed on all of them. This combination of experimental and theoretical information leads to a vastly enlarged view of structural effects on the reactivity of alcohols and thiols as well as to a satisfactory rationalization of the reactivity of TFET.

Introduction

We have been involved for several years in the quantitative study of the basicities and acidities of homologous series of oxygen and sulfur compounds, using both theoretical and experimental methods. Following are the basicity and acidity criteria¹ most frequently investigated:

(1) The proton affinities (PAs) and gas phase basicities (GBs) of these compounds. For a given base B in the gas phase, PA(B) and GB(B) respectively stand for the standard enthalpy and Gibbs energy changes for reaction 1.² Extensive sets of PA and GB values for thiocarbonyl³



and carbonyl^{2,4,5} compounds have been determined. Values are also available for several alkanols and alkanethiols.^{2,4}

In a similar vein, the gas phase acidity of neutral species AH is defined as the standard Gibbs energy change for reaction 2. Values of gas phase acidities for



alcohols and a few alkanethiols are presently available.^{6,7}

(2) The equilibrium constants, K_c , for the formation of the 1:1 hydrogen-bonded complexes between selected hydrogen bond (HB) donors, AH, and oxygen (e.g., ethers⁸ and alcohols^{9,10}) and sulfur *n*-bases (e.g., thiols and thioethers¹¹ and thiocarbonyl compounds^{11,12}) in highly dilute solutions in cyclohexane or tetrachloromethane solvents S (reaction 3).

Also established was a preliminary quantitative ranking of HB acidities of monomeric alcohols and a few alkanethiols through the determination of the equilibri-

(4) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl. 1* **1988**, *17*, 1–861.

(5) Homan, H.; Herreros, M.; Notario, R.; Abboud, J.-L. M.; Esseffar, M.; Mó, O.; Yáñez, M.; Foces-Foces, C.; Ramos-Gallardo, A.; Martínez-Ripoll, M.; Vegas, A.; Molina, M. T.; Casanovas, J.; Jiménez, P.; Roux, M. V.; Turrión, C. Submitted for publication.

(6) NIST Standard Reference Database 19B, NIST Negative Ion Energetics Database, Computerized Version 3.01; National Institute of Standards and Technology, Gaithersburg, MD 20899; 1993.

(7) (a) Taft, R. W.; Taagepera, M.; Abboud, J.-L. M.; Wolf, J. F.; De Frees, D. J.; Hehre, W. J.; Bartmess, J. E.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7765–7767. (b) Abboud, J.-L. M.; Elguero, J.; Liotard, D.; Esseffar, M.; El Mouhtadi, M.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1990**, 565–571; 1279.

(8) Abboud, J.-L. M.; Bellon, L. *Ann. Chim. (Paris)* **1970**, *5*, 63–74.

(9) Abboud, J.-L. M.; Sraidi, K.; Guihéneuf, G.; Negro, A.; Kamlet, M. J.; Taft, R. W. *J. Org. Chem.* **1985**, *50*, 2870–2873.

(10) Laurence, C.; Berthelot, M.; Helbert, M.; Sraidi, K. *J. Phys. Chem.* **1989**, *93*, 3799–3802.

(11) Abboud, J.-L. M.; Roussel, C.; Gentric, E.; Sraidi, K.; Lauransan, J.; Guihéneuf, G.; Kamlet, M. J.; Taft, R. W. *J. Org. Chem.* **1988**, *53*, 1545–1550.

(12) Laurence, C.; Berthelot, M.; Le Questel, J.-Y.; El Ghomari, M. *J. J. Chem. Soc., Perkin Trans. 2* **1995**, 2075–2079.

[†] This work is dedicated in memoriam to Professor Robert W. Taft.

[®] Abstract published in *Advance ACS Abstracts*, July 15, 1996.

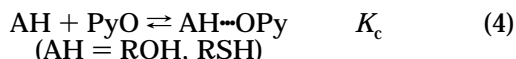
(1) (a) Gal, J.-F.; Maria, P.-C. *Prog. Phys. Org. Chem.* **1990**, *17*, 159–238. (b) Maria, P.-C.; Gal, J.-F.; de Franceschi, J.; Fargin, E. *J. Am. Chem. Soc.* **1987**, *109*, 483–492.

(2) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695–808.

(3) (a) Abboud, J.-L. M.; Mó, O.; de Paz, J. L. G.; Yáñez, M.; Bouab, W.; Mokhlisse, R.; Ballesteros, E.; Herreros, M.; Homan, H.; López-Mardomingo, C.; Notario, R. *J. Am. Chem. Soc.* **1993**, *115*, 12668–12676. (b) Decouzon, M.; Exner, O.; Gal, J.-F.; Maria, P.-C. *J. Phys. Org. Chem.* **1994**, *71*, 511–517.



um constants, K_c , for the formation of the 1:1 complexes between these compounds in pyridine *N*-oxide (PyO) in dilute solution in cyclohexane at 23.3 °C, (reaction 4).^{13,14}



Our interest in the title compound originates in the fact that this is one of the simplest thiols in which the sulfhydryl group is close to a substituent exerting a large positive field effect. This opens up the possibility of vastly enlarging the experimentally accessible range of intrinsic acidities and basicities for thiols.

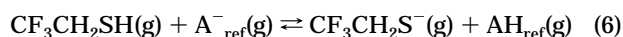
A more comprehensive appraisal of structural effects on the acidities and basicities of sp^3 oxygen and sulfur acids and *n*-bases is thus possible. $\text{CF}_3\text{CH}_2\text{SH}$ has recently become commercially available. Hence, information on its HB acidity and basicity is likely to be quite interesting for its potential use as a *solvent*.

In this work, the intrinsic (gas phase) acidity and basicity of $\text{CF}_3\text{CH}_2\text{SH}$ were determined by means of Fourier transform ion cyclotron resonance (FTICR) spectroscopy. The HB acidity and basicity of this compound were probed through the experimental determination of the equilibrium constants, K_c , for its associations with 3,4-dinitrophenol (HB donor) and PyO (HB acceptor). Also determined was the equilibrium constant pertaining to the formation of the 1:1 charge-transfer complex^{15–18} with molecular iodine in tetrachloromethane solvent at 25.0 °C. This is intended to provide an estimate of its electron-donating ability.

Using the gas phase data as a vantage point, an ab initio study of ethanol (**1**), 2,2,2-trifluoroethanol (**2**), ethanethiol (**3**), and 2,2,2-trifluoroethanethiol (**4**) as neutral, protonated, and deprotonated species was performed at the G2(MP2) level.

Experimental Section

The gas phase basicity and acidity were determined from equilibrium proton-transfer reactions conducted in a modified Bruker CMS-47 FT ICR mass spectrometer.¹⁹ Working conditions were similar to those already described.^{3a} The average cell temperature is ~ 333 K. These FTICR measurements provide the standard Gibbs energy change, $\delta\Delta G_{\text{H}^+}(\text{g})$, for the proton-exchange reactions 5 and 6:



AH_{ref} and B_{ref} are reference acids and bases, respectively. For each of these equilibria,

(13) Frange, B.; Abboud, J.-L. M.; Benamou, C.; Bellon, L. *J. Org. Chem.* **1982**, *47*, 4553–4557.

(14) Abboud, J.-L. M.; Sraidi, K.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1990**, *55*, 2230–2232.

(15) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600–608.

(16) Mulliken, R. S.; Person, W. B. *Molecular Complexes—A Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969.

(17) Briegleb, G. *Elektronen-Donator-Acceptor Komplexe*; Springer: Berlin, 1961.

(18) Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: London, 1969.

(19) *Fourier Transform Mass Spectrometry, Evolution, Innovation and Applications*; Buchanan, M. V., Ed.; ACS Symposium Series 359; American Chemical Society: Washington, DC, 1987.

$$\delta\Delta G_{\text{H}^+}(\text{g}) = -RT \ln K_p \quad (7)$$

In every case, the reversibility of reactions 5 and 6 was confirmed by means of double resonance experiments.

In the case of equilibrium 6, AH_{ref} and $\text{CF}_3\text{CH}_2\text{SH}$ were initially deprotonated by $\text{iso-C}_5\text{H}_{11}\text{O}^-$, generated in situ by electron ionization of isoamyl nitrite.

The pressure readings for the various neutral reagents, as determined by the Bayard–Alpert gauge of the FTICR spectrometer, were corrected by means of the appropriate calibration coefficients obtained for each reagent by plotting the readings of the ion gauge against the absolute pressures provided by a capacitance manometer (Baratron, MKS). Routinely, three calibration runs were performed on each gas. The reproducibility of the calibration can be estimated at $\sim 3\%$. The formal relative sensitivity of the ion gauge is $\sim 10\%$.

K_c values for the 1:1 associations between TFET and 3,4-dinitrophenol, PyO, and I_2 in solution were determined by means of UV–visible spectroscopy. Experiments were performed on a Cary 219 spectrophotometer using matched 1-cm silica window cells in the case of the charge-transfer complexes with iodine. For the associations with 3,4-dinitrophenol and PyO, 10-cm matched silica window cells were used. The experimental methods have already been described in detail: for reactions 3 and 4, see refs 9 and 13. For charge-transfer complexation, Drago's method^{20,21} was used. The equilibrium constants we report are the averages of four independent measurements. Relative uncertainties are reasonably large, $\sim 15\%$. This is not surprising, on account of the very small values of the various constants.

The purifications of 3,4-dinitrophenol and PyO have already been described in refs 9 and 13, respectively. Solvents of spectrograde quality were refluxed over and distilled from a sodium–potassium alloy (cyclohexane) or $\text{P}_{4}\text{O}_{10}$ (CCl_4). TFET (Aldrich) was carefully distilled immediately prior to use.

To our knowledge, no precise information is available so far on the physiological effects of **4**. Thus, appropriate care should be exercised when handling this compound.

Computational Details

To obtain the most reliable energetics possible, the proton affinities and the deprotonation energies of the neutrals under investigation were obtained in the framework of the G2 theory.²² Since in its original formulation this theoretical scheme would be prohibitively expensive for systems of this size, we shall use the more economic G2(MP2) formalism, which has proved to yield proton affinities not significantly different from those obtained at the G2 level.²³ Although in the G2 formalism the geometries are obtained at the MP2/6-31G* level, in the present study we shall employ MP2/6-311+G(d,p) optimized geometries, since it is well established that, to properly reproduce anionic systems, the inclusion of diffuse functions in the basis set is crucial.^{24a} Although this requirement does not apply to protonated species, for the sake of consistency we have used the same scheme for neutrals, cations, and anions. The calculations were performed using the Gaussian 94 package of programs.^{24b}

The geometries were initially optimized at the HF/6-311+G(d,p) level. The corresponding harmonic vibrational frequencies were evaluated at the same level of accuracy by means of analytical second derivatives techniques and used to characterize the stationary points

(20) Rose, N. J.; Drago, R. S. *J. Am. Chem. Soc.* **1959**, *81*, 6138–6141.

(21) Guihéneuf, G.; Abboud, J.-L. M.; Bouab, W. *Can. J. Chem.* **1987**, *65*, 2106–2108.

(22) (a) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221–7226. (b) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293–1298.

(23) Smith, B. J.; Radom, L. *Chem. Phys. Lett.* **1994**, *231*, 345–351.

of the potential energy as local minima and to evaluate the zero-point energies, which were scaled by the empirical factor 0.893 298.^{24c} These geometries were then refined at the MP2/6-311+G(d,p) level.

To investigate the charge redistributions undergone by the neutral systems upon protonation and deprotonation, we have carried out a topological analysis of the electronic charge density, ρ , and its Laplacian, $\nabla^2\rho$.²⁵ In general, bond reinforcements and bond activations imply significant changes of the charge density and its Laplacian at the corresponding bond critical points, defined as points where the charge density is minimum along the bond path and maximum in the other two directions. Bader and co-workers have shown that the existence of these critical points is associated with the existence of a bond. More importantly, the values of ρ and $\nabla^2\rho$ at the bond critical points (bcps) permit classification of the nature of the interaction as covalent, ionic, etc. and may be used as a quantitative measure of the strength of the bond, since negative values of the Laplacian indicate that charge density increases in that region, while positive values are generally associated with charge depletion. Hence, an increase (decrease in the absolute value) of the (negative) Laplacian indicates^{26a} that the bond is somewhat activated, while an increase is associated with a bond reinforcement process. Another index of interest which may be defined in this topological analysis is the ellipticity of the bond, defined as $\epsilon = 1 - \lambda_1/\lambda_2$, where λ_1 and λ_2 are the two negative values of the Hessian of ρ , evaluated at the bcp. Obviously, these two values will be identical only for those bonds which, as the single and the triple bonds, have cylindrical symmetry, for which the ellipticity will be zero.

This topological analysis is carried out on the wave function correct to first order, to take explicitly into account the electron correlation effects. For this purpose, we have used the AIM-PAC²⁷ series of programs.

Since predicted structural variations can be qualitatively rationalized in terms of the bonding indexes, such as hybridization parameters, we have also carried out a natural bond order analysis²⁸ at both the HF and MP2 levels. Values derived in this way are compatible with the classical notion of hybridization, as introduced by Pauling.

(24) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*. John Wiley & Sons: New York, 1986; pp 86–88. (b) Frisch, M. J.; Trucks, C. W.; Schlegel, H. B.; Cill, D. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andrés, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; González, C.; Pople, J. A. *Gaussian 94*, Revision B.3; Gaussian Inc.: Pittsburgh, PA, 1995. (c) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; Defrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whitesode, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, 15, 269.

(25) (a) Bader, R. W. F.; Essén, H. *J. Chem. Phys.* **1984**, 80, 1943–1960. (b) Bader, R. W. F.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, 106, 1594–1605. (c) Bader, R. W. F. *Atoms in Molecules. A Quantum Theory*, Oxford University Press: New York, 1990.

(26) (a) Alcami, M.; Mó, O.; Yáñez, M.; Abboud, J.-L. M.; Elguero, J. *J. Chem. Phys. Lett.* **1990**, 172, 471–477. (b) Tipping, A. E.; Jiménez, P.; Ballesteros, E.; Abboud, J.-L. M.; Yáñez, M.; Essefar, M.; Elguero, J. *J. Org. Chem.* **1994**, 59, 1039–1046. (c) Esseffar, M.; El Mouhtadi, M.; López, V.; Yáñez, M. *J. Mol. Struct. (Theochem)* **1992**, 255, 393.

(27) The AIM-PAC program was kindly provided by J. R. Cheseman and R. W. F. Bader.

(28) (a) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (Theochem)* **1988**, 169, 41–62. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, 78, 4066–4073. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899–926.

Table 1. Experimental Determination of the Gas Phase Basicity of CF₃CH₂SH

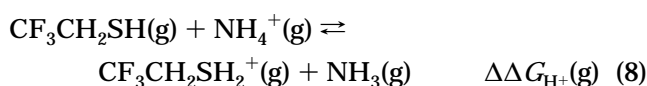
reference	$\Delta\Delta G_{\text{H}^+}(\text{std})^a$	$\delta\Delta G_{\text{H}^+}(\text{g})^a$	$\Delta\Delta G_{\text{H}^+}^a$	ΔGB^a
Cl ₃ CCN	27.5 ^b	−0.82	26.6(8)	
Cl ₃ CCH ₂ OH	26.0 ^c	1.11	27.1(1)	26.9
CF ₃ CO ₂ CH ₃	23.8 ^b	3.22	27.0(2)	(SD = 0.2)

^a All values in kcal/mol (1 cal = 4.184 J). ^b See text. ^c Determined in this work. Cl₃CCH₂OH was found to be 1.50 kcal/mol more basic than Cl₃CCN and 2.20 kcal/mol less basic than CF₃CO₂CH₃.

Experimental Results

(1) Gas Phase Basicities. Table 1 presents the results of proton-transfer equilibria (5) between **4** and a series of standard reference bases. The values of $\delta\Delta G_{\text{H}^+}(\text{g})$ given in this table are defined by means of eq 7.

All gas phase basicities, ΔGB , are referred to ammonia. Thus, with respect to this reference, $\Delta\text{GB}(\mathbf{4}) = -\Delta\Delta G_{\text{H}^+}(\text{g})$ for reaction 8:



$\Delta\Delta G_{\text{H}^+}(\text{g})$ is the average of the $\Delta\Delta G$ values obtained through eq 9:

$$\Delta\Delta G = \delta\Delta G_{\text{H}^+}(\text{g}) + \Delta\Delta G_{\text{H}^+}(\text{std}) \quad (9)$$

where $\Delta\Delta G_{\text{H}^+}(\text{std})$ pertains to reaction 10:



The values of $\Delta\Delta G_{\text{H}^+}(\text{std})$ used in this work have been determined in Prof. Taft's laboratory and are given in refs 2 and 4.

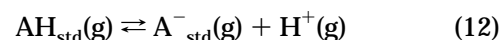
Inasmuch as the entropy change for reaction 1 cannot be obtained directly from the FTICR experiments, we have used the value computed at the 6-31G**//6-31G** level, 24.2 cal mol^{−1} K^{−1}. This value combines the contribution from $S(\text{H}^+)$ as determined from the Sackur–Tetrode equation with those from $\Delta S(\text{rot})$ and $\Delta S(\text{vib})$ for the molecules and ions as determined by means of the partition functions calculated at the 6-31G**//6-31G** level. The standard state is 298 K and 1 atm (0.1 MPa).

Combining these values with the most recent values of $\text{GB}(\text{NH}_3)$ and $\text{PA}(\text{NH}_3)$, 195.3 and 203.5 kcal mol^{−1}, respectively,²⁹ we obtain $\text{GB}(\mathbf{4}) = 168.4 \pm 0.2$ and $\text{PA}(\mathbf{4}) = 175.6 \pm 0.2$ kcal mol^{−1}.

(2) Gas Phase Acidity. The Gibbs energy change for reaction 3, $\Delta G_{\text{acid}}(\text{g})(\text{av})$, is the average of the $\Delta G_{\text{acid}}(\text{g})$ values obtained through eq 11:

$$\Delta G_{\text{acid}}(\text{g}) = \delta\Delta G_{\text{acid}}(\text{g}) + \Delta G_{\text{acid}}(\text{std}) \quad (11)$$

wherein $\Delta G_{\text{acid}}(\text{std})$ pertains to reaction 12:



Experimental results are summarized in Table 2. From these results, we obtain $\Delta G_{\text{acid}}(\mathbf{4}) = 335.6 \pm 0.3$ kcal mol^{−1}. The corresponding standard enthalpy change is $\Delta H_{\text{acid}}(\mathbf{4}) = 342.4 \pm 0.3$ kcal mol^{−1} using the computed (see above) entropy change (22.8 cal mol^{−1} K^{−1}).

(29) Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, 115, 7839–7847.

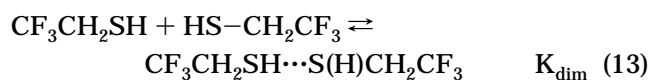
Table 2. Experimental Determination of the Gas Phase Acidity of CF₃CH₂SH

reference	ΔG_{acid}^- (std) ^{a,b}	$\delta\Delta G_{\text{acid}}^-$ (g) ^a	ΔG_{acid}^- (g) ^a	$\Delta G_{\text{acid}}(\text{g})$ (av) ^a
β -naphthol	336.5	-0.54	335.9(6)	
4-nitroaniline	336.2	-0.68	335.5(2)	335.6
C ₆ H ₅ CO ₂ H	333.1	2.35	335.4(4)	(SD = 0.3)

^a All values in kcal/mol. ^b From ref 6.

Notice that the uncertainties reported for acidities and basicities are rather small, as far as the overlaps with the reference compounds are concerned. The "absolute" values are obviously less precise, perhaps by as much as 1 or 2 kcal mol⁻¹. The quality is most certainly not significantly worse than this, because of the multiple overlaps involved in the construction of the acidity and basicity scales.

(3) Hydrogen-Bonding Acidity and Basicity. The equilibrium constants K_c for the formation of the 1:1 complexes in *c*-C₆H₁₂ solution at 23.3 °C between **4** and 3,4-dinitrophenol and PyO are respectively equal to 1.11 ± 0.17 and 1.52 ± 0.23 dm³ mol⁻¹. These are rather small values and, thus, are somewhat uncertain. The experimental study of reaction 4 also provides the value of K_{dim} , the dimerization constant of **4** in *c*-C₆H₁₂ solution at 23.3 °C:



This value is quite small, 0.10 ± 0.05 dm³ mol⁻¹.

(4) Charge Transfer Basicity. The equilibrium constant K_c for reaction 14 in tetrachloromethane solution at 25.0 °C, as determined in this work, equals 1.20 ± 0.18 dm³ mol⁻¹:



Discussion

Structures and Bonding Characteristics. The MP2/6-311+G(d,p) geometries of the four species under investigation and their protonated and deprotonated forms **1H**⁺, **2H**⁺, **3H**⁺, **4H**⁺, **1**⁻, **2**⁻, **3**⁻, and **4**⁻ have been schematized in Figure 1 and are also given as supporting information. Their bonding characteristics are summarized in Table 3. Since a detailed discussion of geometries is not the aim of this paper, we shall concentrate our attention on the structural differences between species **2** and **4** and on the effects associated with their protonation and deprotonation processes. The most important difference between **2** and **4** is that, in the

latter, the SH hydrogen is *gauche* with respect to the substituted carbon atom, while in the former it is *anti*. This seems to point to the existence of an intramolecular hydrogen bond in **4** that does not appear in **2**. However, no bcp was found between the SH hydrogen and the closest fluorine atom. Hence, very likely the preference for a *gauche* conformation in **4** is simply the result of the attractive electrostatic interaction between the positively charged H(S) hydrogen and the closest negatively charged fluorine atom. This will be particularly favored in **4** due to the small value of the CSH bond angle and the large S-H bond length.

Due to the charge transfer that takes place from the neutral to the incoming proton, protonation of ethanol implies a significant lengthening of the C-O bond and a shortening of the C-C linkage.^{26b} However, when the methyl group is substituted by a trifluoromethyl group, the C-C bond slightly lengthens. This simply reflects the greater ability of the methyl group to accommodate a positive charge.

Since sulfur is less electronegative and more polarizable than oxygen, the aforementioned geometrical changes are smaller for the corresponding sulfur-containing systems.

It is worth noting that, although the F \cdots H distances in **2H**⁺ and **4H**⁺ are about 2.5 Å (1 Å = 100 pm), no bcps were found in the corresponding interatomic regions. Hence, as for the neutrals, we must conclude that, strictly speaking, no intramolecular hydrogen bonds are present.

Upon deprotonation, the changes are also important, in particular for the oxygen-containing species. Deprotonation implies that the σ orbital involved in the O-H bond becomes a lone pair, with a concomitant decrease of the electronegativity of the oxygen atom. Accordingly, the s character of the carbon hybrid orbital involved in the C-O bond increases, and the bond becomes shorter. By orthogonality, the other three hybrids increase their p character, and the C-C and C-H bonds become longer. Consistent with this, the CCO bond angle increases, while the CCH bond angles decrease. These hybridization changes are well reproduced by the corresponding NBO analysis (see Table 3). A similar behavior is found for the sulfur-containing derivatives.

CF₃ substitution has almost negligible effects on the O-H and S-H bonds. This seems to be consistent with previous findings,^{26b,c} which showed that CF₃ substitution in pyrazole has small effects on the azolic system.

It is also interesting to realize that, upon deprotonation, the charge density at the most electronegative atoms becomes larger than that in the neutral, since the system becomes electron-excessive. This favors the π back-

Table 3. Bonding Characteristics of the Systems (Y₃C-CH-XH; X = O, S; Y = H, F) Included in This Study^a

bond		1	1 ⁻	1H ⁺	2	2 ⁻	2H ⁺	3	3 ⁻	3H ⁺	4	4 ⁻	4H ⁺
C-C	ρ	0.253	0.231	0.357	0.273	0.253	0.278	0.243	0.240	0.244	0.268	0.267	0.268
	$\nabla^2\rho$	-0.625	-0.510	-0.650	-0.752	-0.642	-0.773	-0.566	-0.548	-0.576	-0.710	-0.707	-0.705
	ϵ	0.037	0.045	0.010	0.060	0.056	0.004	0.004	0.011	0.004	0.018	0.006	0.021
C-X	ρ	0.249	0.315	0.167	0.261	0.324	0.189	0.178	0.172	0.172	0.181	0.170	0.179
	$\nabla^2\rho$	-0.409	-0.714	0.003	-0.459	-0.770	-0.412	-0.285	-0.258	-0.257	-0.303	-0.254	-0.292
	ϵ	0.024	0.010	0.118	0.039	0.013	0.028	0.102	0.002	0.003	0.122	0.013	0.014
C-Y	ρ	0.271	0.261	0.271	0.267	0.246	0.274	0.272	0.263	0.274	0.274	0.266	0.290
	$\nabla^2\rho$	-0.903	-0.837	-0.915	-0.151	-0.137	-0.276	-0.910	-0.851	-0.933	-0.140	-0.121	-0.233
	ϵ	0.006	0.005	0.007	0.146	0.256	0.128	0.009	0.005	0.011	0.132	0.163	0.113
X-H	ρ	0.365		0.341	0.363		0.336	0.217		0.225	0.219		0.229
	$\nabla^2\rho$	-2.500		-2.525	-0.253		-0.219	-0.666		-0.709	-0.674		-0.718
	ϵ	0.027		0.021	0.027		0.022	0.153		0.038	0.146		0.229

^a Charge densities (ρ in e \cdot au⁻³), Laplacians of the charge density ($\nabla^2\rho$ in e \cdot au⁻⁵), ellipticities (ϵ), and percentage of s character (s/c). The natural atomic charges (q_N) of the atoms involved in the bonds are also given.

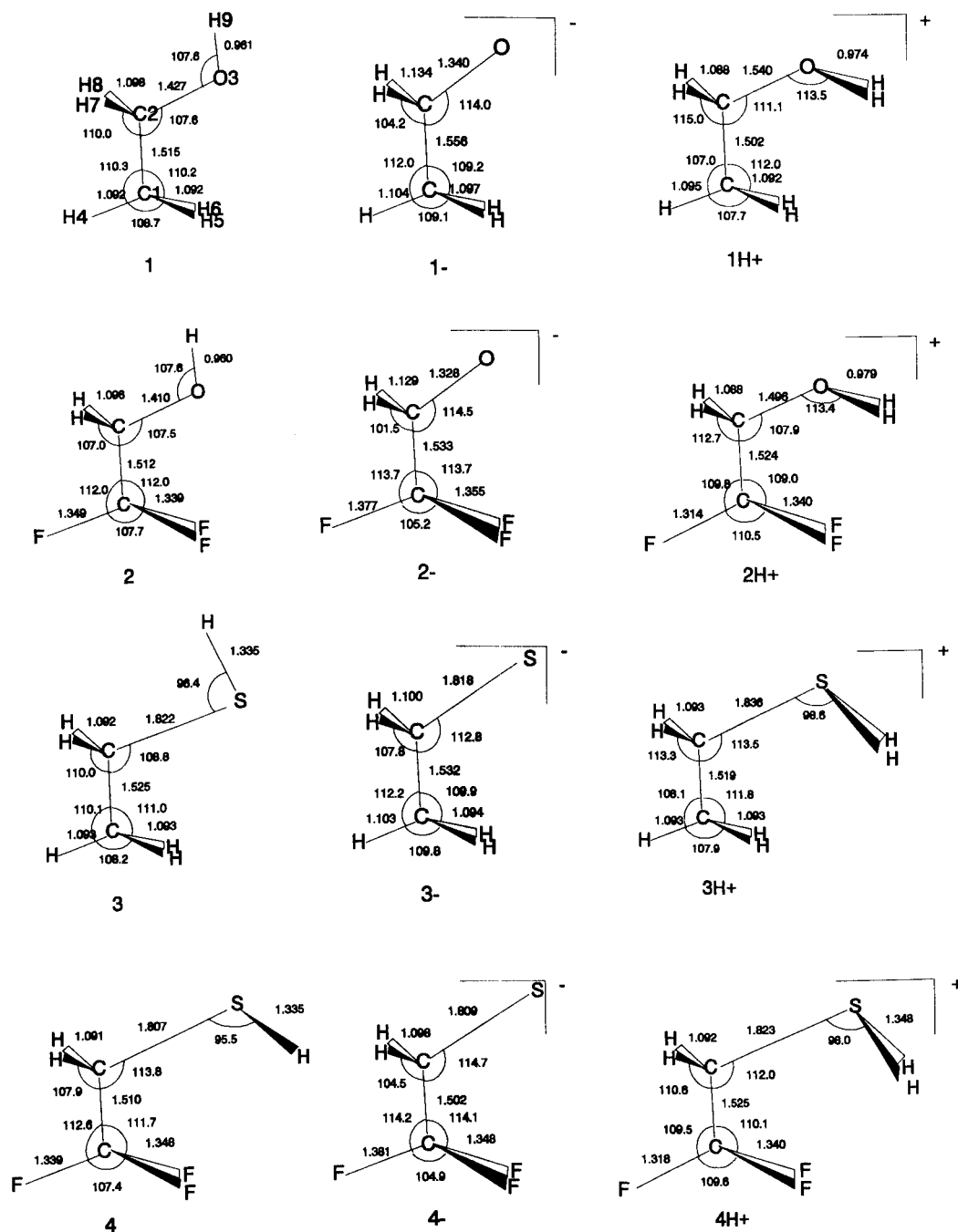


Figure 1. Optimized structures for 1–4 and their corresponding protonated and deprotonated forms. Bond lengths are in angstroms, and bond angles are in degrees.

donation from the fluorine atoms to the carbon atom, which is reflected in an increase of the ellipticity of the C–F bonds (see Table 3).

As for protonation, the effects of the deprotonation processes on sulfur-containing systems are smaller than those described above for oxygen-containing compounds. As we will discuss later, this dampening of the charge redistributions undergone by sulfur derivatives may be also related to the fact that trifluoromethyl substitution effects on the intrinsic basicities and acidities are also slightly smaller for sulfur- than for oxygen-containing compounds.

Acidities and Basicities. For comparison purposes, we have gathered in Table 4 the proton affinities and deprotonation enthalpies in the gas phase of sets of representative alkanols and alkanethiols. From these results, it is clear that, in all cases, the substitution of

an alkyl group by a trifluoroethyl group brings about an important increase in acidity and a substantial decrease in basicity. Both acidity and basicity are seen to increase with the size of the alkyl groups, largely as a consequence of polarizability effects.⁷

Theoretically calculated proton affinities and deprotonation enthalpies for compounds 1–4 are presented in Table 5. It can be seen that the quantitative agreement with our results is excellent. Furthermore, these calculations reproduce well the fact that 3 is slightly more basic than 1, while it is significantly more acidic.

Figures 2 and 3 present the relationships between the proton affinities and deprotonation enthalpies of alcohols and thiols. Some relevant features of these plots are as follows:

(1) Structural effects on the proton affinities and deprotonation enthalpies of thiols and alcohols are lin-

Table 4. Experimental Ionization Enthalpies, ΔH_{acid} , and Proton Affinities, PA, of Selected Alcohols (R-OH) and Thiols (R-SH)

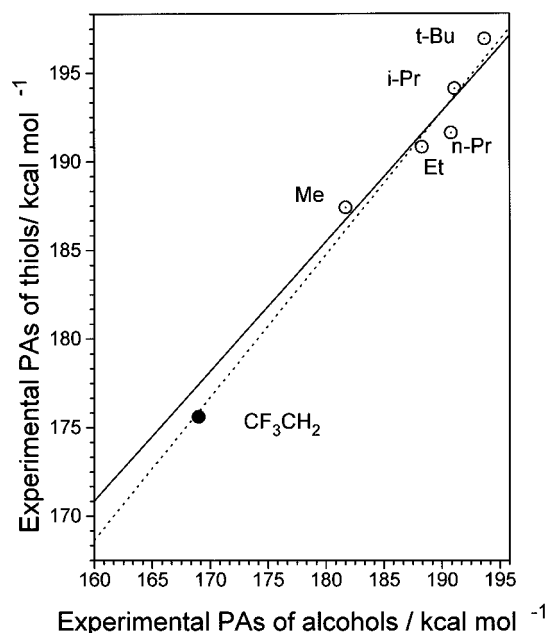
R	alcohols		thiols	
	$\Delta H_{\text{acid}}^{a,b}$	PA ^{a,c}	$\Delta H_{\text{acid}}^{a,b}$	PA ^{a,c}
Me	380.6	181.7 ^d	356.9	187.4
Et	377.4	188.3	355.2	190.8
<i>n</i> -Pr	376.0	190.8	354.2	191.6
<i>i</i> -Pr	375.4	191.1	353.4	194.1
<i>n</i> -Bu	375.4	191.1	353.7	
<i>i</i> -Bu	374.7	192.4	353.1	
<i>t</i> -Bu	374.6	193.7	352.5	196.9
<i>t</i> -BuCH ₂	372.6	193.6	351.7	
CF ₃ CH ₂	361.8	169.0	342.4	175.6

^a All values in kcal/mol. ^b From ref 6. ^c From ref 4. ^d From ref 29.

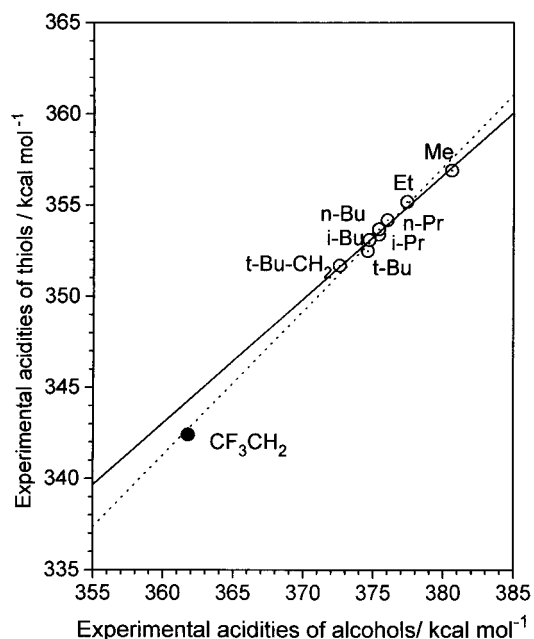
Table 5. G2-Calculated Total Energies (*E*), Proton Affinities (PA), Acidities (ΔH_{acid}), and Dipole Moments (μ)

compd	<i>E</i> (Hartrees)	PA (kcal/mol) ^a	AA (kcal/mol) ^a	μ (D)
1	-154.753 3284	186.4	378.4	1.79
1 ⁻	-154.152 1926			4.27
1H ⁺	-155.048 2019			2.46
2	-452.251 6636	169.5	360.2	3.59
2 ⁻	-451.679 3357			5.83
2H ⁺	-452.519 6033			7.46
3	-477.359 4227	189.6	355.7	1.66
3 ⁻	-476.794 2003			5.07
3H ⁺	-477.659 4959			
4	-774.842 0471	174.1	343.8	1.87
4 ⁻	-774.295 7616			6.50
4H ⁺	-775.117 3293			7.16

^a These values include the corresponding thermal corrections evaluated at 298.15 K.

**Figure 2.** Experimental proton affinities of thiols versus experimental proton affinities of homologous alcohols.

early related to a high degree of precision. The correlation involving PAs is of slightly lower quality. This likely reflects the fact that the experimental determination of the PAs of secondary and tertiary alcohols is somewhat less precise because of the competing dehydration of the protonated species. In these plots, the data for the **2/4** couple were not included in the correlations represented as solid lines. We see that the corresponding point is either on the line or very close to it (in plots 2 and 3, we

**Figure 3.** Experimental deprotonation enthalpies of thiols versus experimental deprotonation enthalpies of homologous alcohols.

have portrayed as a dotted line the correlation obtained upon inclusion of the **2/4** data). These results show for the first time the pattern of similarity between alcohols and thiols to be quite broad.

(2) In both cases, the introduction of the trifluoromethyl group more than doubles the range of structural effects.

(3) In every case, thiols are both more acidic and more basic than the corresponding alcohols. This reflects the fact that the polarizability of sulfur is larger than that of oxygen. On the other hand, the slopes are significantly less than 1. Thus, substituent effects are appreciably attenuated in thiols with respect to alcohols, possibly as a consequence of the S-C bonds being longer than the O-C ones. It is noteworthy that this is exactly the same pattern of sensitivity to substituent effects on the intrinsic basicities of carbonyl and thiocarbonyl compounds.³

The much greater acidity of **3** relative to **1** is in clear contrast with their behavior in aqueous solution.³⁰ This may be rationalized in terms of the differences between the electronic structures of both neutrals. On the one hand, due to the larger size of sulfur, the S-H linkage is weaker than the O-H bond, as reflected by a much smaller charge density at the corresponding bcp (see Table 3). On the other hand, since oxygen is more electronegative than sulfur, the O-H⁺ polarity of the hydroxylic bond is much higher than that of the S-H linkage of ethanethiol, which also contributes to enhance the stability of the former. As a consequence, the O-H bond fission for the alcohol is energetically less favorable than the S-H bond fission in the thiol. In aqueous solution, the situation is different. The great polarity of the O-H linkage of ethanol strongly favors the interactions with the solvent and the heterolytic fission of the bond to yield an ethoxide anion, which is more stabilized by the interactions with the solvent than the thioethoxide anion. Hence, the gap between the acidities of both

(30) (a) Fehrst, A. R. *J. Am. Chem. Soc.* **1971**, *93*, 3504-3515. (b) Pohl, E. R.; Hupe, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 8130-8133.

systems decreases considerably, and **3** is only about 7 kcal/mol more acidic than **1**.

Hydrogen-Bonding Acidity and Basicity. The equilibrium constant for the complexation between **4** and PyO^{14} can be linked to the α^{H_2} scale of hydrogen-bonding acidity of monomeric species.^{31,32} The computed value, 0.08, is very small and ranks **4** significantly below dichloromethane ($\alpha^{\text{H}_2} = 0.13$).

Regarding the hydrogen-bonding basicity, the equilibrium constant for the association between **4** and 3,4-dinitrophenol can be linked to the β^{H_2} scale of hydrogen-bonding basicity of monomeric species.^{31,33} The equilibrium constant is about one-half of the value for $\text{C}_2\text{H}_5\text{-SH}^{11}$ and some 240 times smaller⁹ than that for $\text{C}_2\text{H}_5\text{-OH}$ ($\beta^{\text{H}_2} = 0.44$). The β^{H_2} value for **4** equals 0.12 and is substantially smaller than that for $\text{CF}_3\text{CH}_2\text{OH}$ (0.18).^{10,33}

It is clear that **4** is an extremely weak hydrogen-bonding base and also a very weak hydrogen-bonding acid. Consideration of the self-association process (eq 14) is appropriate at this point.

As indicated earlier, the equilibrium constant K_{dim} for this reaction is of the order of $0.1 \text{ dm}^3 \text{ mol}^{-1}$. Now, it has been shown that, for thousands of 1:1 HB complexes in solution in CCl_4 or $c\text{-C}_6\text{H}_{12}$ solvents, eq 15 holds to a very satisfactory degree of precision.^{31,34} Using the values

$$\log K_c = 7.354\alpha^{\text{H}}_2\beta^{\text{H}}_2 - 1.094 \quad (15)$$

$\alpha^{\text{H}_2}(\mathbf{4}) = 0.08$ and $\beta^{\text{H}_2}(\mathbf{4}) = 0.12$, this equation predicts a value for the dimerization constant of $0.095 \text{ dm}^3 \text{ mol}^{-1}$, in excellent (and perhaps somewhat fortuitous) agreement with the experimental value. It is remarkable that equilibrium constants of this order of magnitude are considered to define the onset³⁴ of "true" HB interactions. **4** seems to be precisely at this onset and is, therefore, very feebly self-associated.

(31) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Morris, J. J.; Taft, R. W.; Morris, J. J.; Taylor, P. J.; Laurence, C.; Berthelot, C.; Doherty, R. M.; Kamlet, M. J.; Abboud, J.-L. M.; Sraïdi, K.; Guihéneuf, G. *J. Am. Chem. Soc.* **1988**, *110*, 8534–8535.

(32) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Duce, P.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 699–712.

(33) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2* **1990**, 521–530.

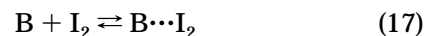
(34) Abboud, J.-L. M.; Notario, R.; Botella, V. In *Quantitative Treatments of Solvent/Solute Interactions, Theoretical and Computational Chemistry, Vol. 1*; Politzer, P., Murray, J. S., Eds.; Elsevier: Amsterdam, 1994.

Charge-Transfer Basicity. We showed a few years ago³⁵ that there is a good linear relationship between the proton affinities in the gas phase and the Gibbs energy changes pertaining to the 1:1 charge-transfer complexation between $\text{S}(\text{sp}^3)$ *n*-bases and molecular iodine in $\text{CH}_2\text{-Cl}_2$ solution at 298 K.

The correlation equation was eq 16,

$$\Delta G^\circ_{\text{I}_2}(\text{CH}_2\text{Cl}_2) = (-3.67 \pm 0.09) - (0.113 \pm 0.007)\Delta\text{PA} \quad (16)$$

wherein $\Delta G^\circ_{\text{I}_2}(\text{CH}_2\text{Cl}_2)$ is the Gibbs energy change for reaction 17 and ΔPA is the proton affinity relative to ammonia of the base B, an $\text{S}(\text{sp}^3)$ *n*-donor base.



$\Delta G^\circ_{\text{I}_2}$ values determined in CCl_4 solution were linked to values in CH_2Cl_2 solution through eq 18,

$$\Delta G^\circ_{\text{I}_2}(\text{CH}_2\text{Cl}_2) = (-0.46 \pm 0.14) + (1.04 \pm 0.05)\Delta G^\circ_{\text{I}_2}(\text{CCl}_4) \quad (18)$$

If we apply eq 18 to our data for **4**, we get $\Delta G^\circ_{\text{I}_2}(\text{CH}_2\text{Cl}_2) = -0.57 \text{ kcal mol}^{-1}$. The $\Delta G^\circ_{\text{I}_2}(\text{CH}_2\text{Cl}_2)$ value one would predict on the basis of eq 16 and using the experimental ΔPA (-27.9 kcal/mol) is $-0.52 \text{ kcal mol}^{-1}$. On account of the combined uncertainties of these correlations, the agreement is remarkably good and provides strong support for the contention that, in selected cases, charge-transfer complexation with molecular iodine in solution displays a pattern of structural effects similar to that of gas phase basicity.³⁵

Acknowledgment. This work was supported by Grants PB 93-0289-C02 and PB 93-0142-C03 of the Spanish D.G.I.C.Y.T.

Supporting Information Available: MP2/6-311+G(d,p) geometries and G2 total energies of **1–4**, **1H**⁺, **2H**⁺, **3H**⁺, **4H**⁺, **1**⁻, **2**⁻, **3**⁻, and **4**⁻ (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version on the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960524A

(35) Abboud, J.-L. M.; Notario, R.; Berthelot, M.; Claramunt, R. M.; Cabildo, P.; Elguero, J.; El Ghomari, M. J.; Bouab, W.; Mokhlisse, R.; Guihéneuf, G. *J. Am. Chem. Soc.* **1991**, *113*, 7489–7493.