A Theoretical Study of the Proton Affinities of Water, Alcohols, and Ethers: Absolute *versus* Relative Basicities

José-Luis M. Abboud
Instituto de Química Física, 'Rocasolano', C/Serrano, 119 E-28006 Madrid, Spain
José Elguero
Instituto de Química Médica, C/Juan de la Cierva, 3 E-28006 Madrid, Spain
Daniel Liotard
Université de Pau et des Pays de l'Adour 64000 Pau, France
**M'Hammed Essefar and Mohammed El Mouhtadi ***
Laboratoire de Chimie Théorique, Départment de Chimie, Université Cadi Ayyad, Marrakech, Morocco
Robert W. Taft
Department of Chemistry, University of California, Irvine, CA 92717

In this work we report the proton affinities (E_{pa}) of water, seven alcohols, and seventeen cyclic and acyclic ethers, as measured by ion cyclotron resonance spectroscopy (ICR) with respect to the same 'basicity ladder.' The E_{pa} for selected compounds have been calculated by MNDO, AM1, and *ab initio* (3-21G and, in some cases, 4-31G*//4-31G and 6-31G*//6-31G) methods. These results are used for a comparison of the various computational techniques and for the analysis of structural effects on the neutral and protonated species. Methyl and other alkyl affinities of aliphatic alcohols are determined and discussed. The experimental E_{pa} are treated by correlation analysis methods.

Alcohols and ethers are common and useful compounds bridging the structural gap between water and cyclic[1] or acyclic polyethers. The gas-phase proton affinity (E_{pa}), of a base B is defined as the standard enthalpy change for reaction (1) in the

$$BH^+ \longrightarrow B + H^+ \qquad (1)$$
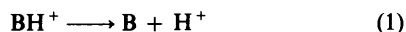
gas-phase. In this work the E_{pa} for water and a variety of alcohols and ethers are reported. These experimental results are then analysed in terms of structure–reactivity relationships using both quantum mechanical and correlation analysis techniques. This study is aimed at (*i*) providing a better understanding of structural effects on the basicity of these compounds, and (*ii*) assessing the ability of advanced semi-empirical techniques to describe these effects. This should facilitate future insights in the field of crown ethers.

Results

Experimental values.—These values were obtained with the same instrument, namely, the U.C. Irvine Ion Cyclotron Resonance Spectrometer and have been anchored to the same 'basicity ladder'.[2] Full experimental details are given elsewhere.[3] Unless stated otherwise, relative proton affinities, $\delta E_{pa}(B)$ defined as $\delta E_{pa}(B) = E_{pa}(B) - E_{pa}(H_2O)$ are believed to be accurate to within 0.2 kcal mol⁻¹.†

Computational Methods and Results.—(*a*) *ab initio*.‡ The choice of the basis set was severely limited by the size of many of the molecules studied herein. Thus, we selected the 3-21G split-valence basis set[4] as a compromise between flexibility and computational tractability. In a few instances, calculations were also performed at higher levels.[5] In all cases, the MONSTER-GAUSS 80[6] package was used.

(*b*) *Semiempirical.* Two of the most advanced NDDO[7] techniques were applied, namely Dewar's MNDO[8] and AM1[9] as implemented in Thiele's[10] and Stewart's[11] computer program. Complete optimization of the geometries for the

neutral and protonated species is necessary if meaningful E_{pa} are to be obtained.[13] Thus, full geometry optimizations have been performed on all the species and by the three methods. The corresponding E_{pa} are given in Table 1. Although we shall not deal here with a detailed, case-by-case comparison of the experimental and calculated geometries, we report in Table 2 results for (2), (2)H⁺, (11), and (11)H⁺ that are useful for the next discussion.

Discussion

Molecular Geometries.—It has been reported[15] that the 3-21G method leads to optimized geometries that compare quite favourably with the experimental structures. This is indeed the case for the neutral forms of the compounds studied herein. In general, bond lengths agree within 0.02 Å, or better, and planar and dihedral bond angles are reproduced to within 3 and 4°, respectively.

Although conformational barriers have not been calculated in this work, the majority of the most stable conformations have been correctly assessed. Of particular interest are the cases of: (*a*) 2,2,2-trifluoroethanol (8) for which the *gauche* (defined by

---

† 1 cal = 4.184 J.

‡ *ab initio* E_{pa} values are obtained as the negative differences between the energies at the potential-energy minima for the protonated (BH⁺) and neutral (B) species, as in equation (2). Because of the

$$E_{pa}(B) = -\Delta E = \Delta E(B) - \Delta E(BH^+) \qquad (2)$$

parametrization features built into the NDDO methods, MNDO and AM1 E_{pa} were calculated according to equation (3) where ΔH_f is the

$$E_{pa}(B) = -\Delta H = -\Delta H_f(BH^+) - \Delta H_f(B) - \Delta H_f(H^+) \qquad (3)$$

enthalpy of formation for the various species in the gas-phase at 298 K. In this formalism the value of $\Delta H_f(H^+)$ is determined by the one-centre core-electron attraction integral, U_{ss}. Its empirical value is quite different from that appropriate to an isolated hydrogen atom. Thus, following previous workers[12] we used the experimental value, $\Delta H_f(H^+) = 367.2$ kcal mol⁻¹.

Table 1. Experimental and calculated proton affinities for water and selected alcohols and ethers.

ROR'			E_{pa}/kcal mol^{-1}			
R	R'	Number	Experimental	STO 3-21G	MNDO	AM1
H	H	(1)	167.3	191.6	172.1	164.5
	H	(2)	182.5	204.8	175.0	171.9
	H	(3)	187.8	208.7	177.1	178.8
	H	(4)	189.6	210.3	178.2	179.0
	H	(5)	190.2	211.8	178.8	179.5
	H	(6)	192.0ᵃ	214.0	180.2	182.8
	H	(7)	193.4ᵃ	215.5	181.8	186.5
CF$_3$CH$_2$	H	(8)	169.3	186.8	155.8	157.9
		(9)	191.1	213.1	177.4	177.4
		(10)	195.2	216.7	179.4	183.4
		(11)	196.1			
		(12)	197.3			
		(13)	198.6	220.4	181.1	187.8
		(14)	201.1	223.0	183.6	190.9
1-Adamantyl		(15)	206.0			
		(16)	198.5	219.8	181.0	188.7
		(17)	202.3			
		(18)	205.1			
		(19)	201.1			
		(20)	204.8			
		(21)	212.0	232.8ᵇ	188.7	200.9
–(CH$_2$)$_2$–		(22)	186.4	203.8	179.4	177.2
–(CH$_2$)$_3$–		(23)	193.2	220.4	183.3	187.0
–(CH$_2$)$_4$–		(24)	197.6	221.3	182.0	185.9
–(CH$_2$)$_5$–		(25)	198.5	219.1	182.9	186.5

ᵃ From ref. 3(c). ᵇ See the text. ᶜ Experimental proton affinities based on $E_{pa}(NH_3) = 204.0$ kcal mol^{-1} (ref. 2).

Table 2. Experimental and calculated geometries for (2), (2)H$^+$, (11), and (11) H$^+$.ᵃ

	Parameter^f	Experimental	3-21G (Base)	3-21G (Base H$^+$)	AM1 (Base)	AM1 (Base H$^+$)
	l(CO)	1.4244ᵇ	1.440	1.532	1.4104	1.496
	l(OH)	0.9630	0.967	0.974	0.964	0.999
	l(CH$_t$)	1.0937	1.083	1.074	1.119	1.120
	$\angle$(COH)	108.53	110.25	119.98	107.16	109.95
	$\angle$(H$_g$CH$_t$)	108.63	108.53	124.44	105.11	112.43
	δ[CO]	3.20ᶜ	3.7	3.3	3.9	3.5
	φ[H$_t$COH]		180.0	180.0	179.9	179.9
	φ[H$_g$COH]		62.1	61.5	61.5	62.5
	l[C(1)O]	1.415ᵉ	1.425	1.504	1.416	1.478
	l[C(2)O]	1.404	1.428	1.527	1.427	1.517
	l[C(2)C(3)]	1.520	1.528	1.519	1.511	1.494
	l(O$^+$H)	—	—	0.971	—	0.995
	l[C(1)H$_g$]	1.084	1.085	1.076	1.118	1.119
	l[C(1)H$_t$]	1.100	1.085	1.076	1.119	1.120
	l[C(2)H$_g$]	1.101	1.087	1.076	1.123	1.123
	l[C(3)H$_g$]	1.092	1.082	1.083	1.116	1.119
	l[C(3)H$_t$]	1.089	1.082	1.083	1.116	1.122
	$\angle$[C(1)OC(2)]	111.49	114.86	121.28	112.57	113.22
	$\angle$[OC(2)C(3)]	108.15	106.75	108.07	106.99	106.69
	$\angle$[H$_t$C(1)H$_g$]	109.33	108.97	111.78	110.50	111.92
	$\angle$[H$_g$C(2)C(3)]	110.95	110.47	113.14	111.12	114.12
	$\angle$[H$_g$C(3)C(2)]	110.10	110.87	108.59	109.31	108.10
	φ[C(1)OC(2)C(3)]	180.0	180.0	178.9	179.9	178.3
	δ[OC(1)]ᶜ	2.24	2.6	1.5	2.2	0.8
	γ[OC(1)]ᵈ	109.90	107.23	105.78	104.55	104.59

ᵃ Bond lengths in Å, angles in degrees. ᵇ All experimental values for (2) are from ref. 14(a). ᶜ Methyl tilt angle as defined in ref. 14(b). ᵈ Corrected OC(methyl)H angle as defined in ref. 14(b). ᵉ All experimental values for (11) are from ref. 14(b). ^{f} l = bond length; $\angle$ = bond angle; φ = torsion angle; δ, γ = methyl tilt angles.

the orientation of the O–H bond) conformer, G, is found to be the most stable form, as a consequence of the lone pair–lone pair repulsion existing in the *trans* conformation and the weak chelation (O–H $\cdots$ F) present in G. This agrees with IR data[16]

and other *ab initio* (4-31G) calculations;[17] (b) (24) and (25), predicted to have puckered (C_2) and chair (C_s) structures, in qualitative and quantitative agreement with the experimental evidence[18] as well as, for (24), with very thorough *ab initio* (4-

31G) calculations.[19] More subtle features, such as the tilt angles of the alkyl groups relative to the C(α)–O bonds in alcohols and acyclic ethers[14] are nicely reproduced.

As expected, the description of the smallest cycles is somewhat poorer. For (22), the calculated (1.465 Å) and experimental (1.436 Å) C–O bond lengths differ substantially (a study at the 6-31G** level[20] also falls short of reproducing this value); (23) is slightly puckered[21] but the calculated potential-energy minimum pertains to a planar structure. Other relevant structural features deduced from this study are as follows.

For alcohols (2) *to* (7). (*i*) The calculated C–O, O–H, and C(α)–C(β) bond lengths are nearly constant and, respectively, equal to 1.437 ± 0.003, 0.965 ± 0.002 and 1.531 ± 0.004 Å (the corresponding averages of the available experimental values are 1.430 ± 0.005, 0.954 ± 0.006 and 1.526 ± 0.003 Å). (*ii*) The COH angles are practically constant with an average value of $110.9 \pm 0.5°$ (appreciably larger than the experimental average, $107.4 \pm 1.6°$).

For acyclic ethers. (*i*) In the ROCH$_3$ series (R = CH$_3$, C$_2$H$_5$, i-C$_3$H$_7$, t-C$_4$H$_9$), the H$_3$C–O bond length is essentially constant, the average value being 1.429 ± 0.004 Å (0.013 Å longer than the experimental values). The O–C(H)(CH$_3$)$_2$ and O–C(CH$_3$)$_3$ bond lengths are calculated to be slightly longer (1.443 Å). The average of the C(α)–C(β) bond distances for (9), (10), (13), (14), and (16) is 1.530 ± 0.004 Å *i.e.* practically the same as for the alcohols. (*ii*) In the same series, $\angle$ COC increases with the bulk of the R moiety, possibly as a consequence of increasing back-strain.

Except for H$_3$O$^+$ in crystals,[14b] no experimental geometries are available for the protonated bases studied here. Our calculations on this ion (an admittedly unique oxonium compound) confirm[15b] that the predicted structure at the 3-21G level has a D_{3h} symmetry. Much more elaborate calculations are needed[22,23a] in order to find its 'floppy' (inversion barrier of 1.4–1.5 kcal mol^{-1}) pyramidal structure.[23b] However, in the light of the results obtained for the neutral bases and on account of the fact that the differences between the experimental and calculated bond lengths and bond angles are quite systematic, we feel that, at least, the general structural trends and the comparisons thereof are likely to be correct. These trends are as follows.

For protonated (2) *to* (7). (*i*) The average R(H)Ö–H and C(α)–C(β) bond lengths are, respectively, equal to 0.974 ± 0.001 and 1.516 ± 0.003 Å. (*ii*) The C–ÖH$_2$ bond distance steadily increases along the series. [1.532 Å for (2), 1.589 Å for (7)]. (*iii*) The average COH bond angle is $120 \pm 1°$.

For the protonated ROCH$_3$ *series.* (*i*) The average R(CH$_3$)-Ö–H and C(α)–C(β) bond lengths are respectively, equal to 0.970 ± 0.001 and 1.521 ± 0.004 Å. (*ii*) Along the series, the R(H)Ö–CH$_3$ and CH$_3$(H)Ö–R bond lengths, respectively, decrease from 1.504 Å (9) to 1.494 Å (14) and increase from 1.504 Å (9) to 1.557 Å (14). (*iii*) The average COC angle is $123.5 \pm 1.6°$.

For protonated (22) *to* (25). In all cases, the C(α)O bond is stretched by 0.07–0.08 Å, while the C(α)–C(β) bonds are shortened by some 0.015 Å. The torsional angles of (24) and (25) are little affected by protonation.

These results lead to the following conclusions. (*a*) The OH bond length is essentially the same for protonated alcohols and ethers and is very slightly longer in the protonated than in the neutral forms. It follows that Ö–H bonds are strong and have largely covalent character.[15b]

(*b*) Upon protonation, all C–O bonds are appreciably stretched[15b,23] while all the C(α)–C(β) bonds are shortened. This implies that mesomeric structures (I'), (II'), and (II'') are significant.

This contention is supported by the fact that bond stretching

$$\overset{+}{\text{ROH}}_2 \longleftrightarrow \text{RO}\overset{+}{\text{H}}_2$$

$$\text{(I)} \qquad \text{(I')}$$

$$\text{R}\overset{+}{\text{O}}(\text{H})\text{R}' \longleftrightarrow \text{RO}(\text{H})\text{R}'^+ \longleftrightarrow \overset{+}{\text{R}}\text{HOR}'$$

$$\text{(II)} \qquad \text{(II')} \qquad \text{(II'')}$$
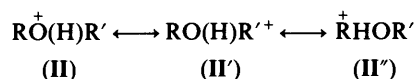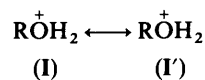
increases with the σ-hyperconjugative[24] ability of R: CH$_3$ < C$_2$H$_5$ < i-C$_3$H$_7$ < t-C$_4$H$_9$. This is related to the finding by Meot-Ner,[25] and Hiraoka and Kebarle,[26] that ΔH for reaction (4) in the gas-phase increases by some 60 kcal mol^{-1} on going

$$\overset{+}{\text{R}} + \text{H}_2\text{O} \longrightarrow (\text{ROH}_2)^+ \qquad (4)$$

from R = CH$_3$ to R = t-C$_4$H$_9$. The same structural criteria indicate that differential σ-hyperconjugative effects are much smaller in the neutral forms.

(*c*) When comparing the series ROH and ROCH$_3$ we found that $\angle$ COC is consistently larger than $\angle$ COH. The same holds for their protonated forms although, for the latter, both sets of angles are wider *i.e.* 120° or more, possibly as a consequence of enhanced electrostatic repulsions between the substituents on the oxygen. In the case of the protonated cycles (22) to (24), the release of *I*-strain by this mechanism is severely restricted and this is likely to be one of the reasons for (22), (23), and (24) being respectively less basic than (9), (10), and (16).[27] As with acyclic ethers, however, protonation leads to a considerable stretching of the C–O bonds.

(*d*) Following protonation, the average increase of the R–O bond length is some 0.03 Å larger for the ROH than for the ROCH$_3$ series. The shortening of the C(α)–C(β) bonds is also more important in the former case. This indicates that, relative to hydrogen, a methyl group reduces the σ-hyperconjugative contribution from R. Although much smaller, the alkyl substituent effect on the Ö–CH$_3$ distance suggests that the weight of contribution of structure (III') decreases as the bulk of R increases.

$$\text{R}\overset{+}{\text{O}}(\text{H})\text{CH}_3 \longleftrightarrow \text{ROH}\overset{+}{\text{CH}}_3$$

$$\text{(III)} \qquad \text{(III')}$$
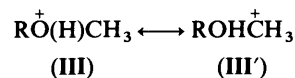
In general, the AM1 method provides a satisfactory description of the geometries of the neutral species.[28] Here we find that the C–C and C–O bond lengths are, at most, to within 0.02 Å of the experimental values and bond angles agree to within 2° or better.[29] This method even out-performs the 3-21G model in the calculation of many COH and COC bond angles. The same holds for the C–O bond length in (23) (calc. 1.436 Å). Also, the most stable conformations of the acyclic molecules are generally well predicted. The main weakness of the method lies in the determination of the torsional angles for (24) and (25); the former is predicted to be planar and while the chair structure of the latter is correctly established, the calculated torsional angles (31.9°) are too small.

For the protonated species, significant differences exist between the AM1 and STO 3-21G geometries. Taking as a reference the optimized geometries for CH$_3$ÖH$_2$ and C$_2$H$_5$ÖH$_2$ determined by means of high level *ab initio* calculations,[23,30] the STO 3-21G results are superior. Nevertheless, the AM1 calculations are able to reproduce the main structural features described in the previous section. This lends support to the finding that the Bu^t–O bond lengths in protonated (7), (14), and (21) decrease following the order (7) > (14) > (21).

MNDO tends to overestimate core–core repulsions.[9] As a consequence we find that for neutral species both the C(α)–C(β) bond lengths and the COC bond angles are too large by *ca.* 0.03

Table 3. Influence of the basis set on the calculated E_{pa} values.

Base	3-21G[b]	3-21G*[b]	4-31G[b]	4-31G*[c]	6-31G[b]	6-31G*[d]	$E_{pa,exp}$[a]
(1)	191.6	182.2	183.2	174.7	182.6	173.7	167.3
(2)	204.8	195.0	199.9	190.3	199.2	189.6	182.5
(6)	214.0	203.2	208.9	198.9	208.4		192.0
(9)	213.1	200.5	209.6	199.2	208.8	198.5	191.1

[a] In kcal mol^{-1}. [b] Fully optimized geometries. [c] 4-31G optimized geometries. [d] 6-31G optimized geometries.
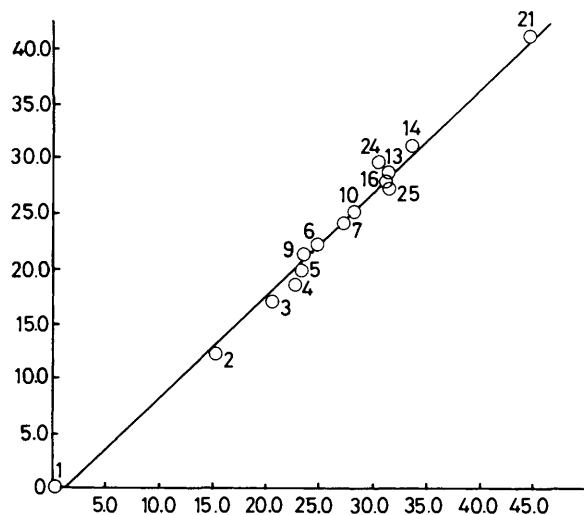
Figure 1. Experimental $E_{pa,exp}$ vs. calculated E_{pa}(3-21G) differential proton affinities. Compounds numbered as in Table 1.

Å [0.1 and 0.05 Å for (8) and (22)]. Again, (24) is found to be planar; for (25), the bond angles are overestimated by up to 11° and the torsional angles underestimated by up to 47°. Even so, most of the trends revealed by the other methods can still be recognized and the correct conformation for alkyl alcohols[31] obtained.

Proton Affinities

Theoretical Calculations.—(*a*) *ab initio.* 'Theoretical E_{pa} values at the STO 3-21G level, E_{pa}(3-21G)s, are defined by equation (2). Let ΔE_{ZP}, ΔE_{ter}, ΔE_{HF}, and ΔE_{corr}, respectively, stand for the difference in zero-point vibrational energy $\Delta E_{ZP} = E_{0,vib}$ (BH$^+$) $- E_{0,vib}$ (B), the thermal energy correction (ΔE_{ter}), the energy difference at the Hartree–Fock (ΔE_{HF}) limit and the electron correlation energy (ΔE_{con}). The E_{pa} at 0 K, $E_{pa,0}$ is given by[23,32] equation (5). From previous work on water[32]

$$E_{pa,0} = -\Delta E_{HF} + \Delta E_{corr} + \Delta E_{ter} + \Delta E_{ZP} \quad (5)$$

and alcohols,[23] the ($\Delta E_{ZP} + \Delta E_{ter}$) contribution is estimated at 7.0 kcal mol^{-1}. It follows that the E_{pa}(3-21G) values are some 16 kcal mol^{-1} too large (the uncorrected values being so by an average of 23 kcal mol^{-1}). This difference has three components,[23,32,33] *i.e.* ΔE(BSE), ΔE(BSSE), and ΔE_{corr}, the first two originating in the basis-set effect and in the basis-set superposition error, respectively. A direct evaluation of these terms for all the bases studied herein was not feasible, but higher level calculations have been carried out on (1), (2), (6), and (9) (calculations at the 4-31G* and 6-31G* levels, respectively). The results are displayed in Table 3. These values show, as expected, a substantial decrease in the calculated E_{pa} values with an increase in the size of the basis set, the effect being largest for (1).[34]

The most remarkable feature is the large effect brought about by the inclusion of the polarization functions. Thus, in every case, E_{pa}(3-21G*) ⩽ E_{pa}(6-31G). In fact, if we recall that (Δ_{ZP} + ΔE_{ter}) *ca.* 7.0 kcal mol^{-1}, the corrected E_{pa}(4-31G*) values are close, within the limits of experimental error, to the experimental E_{pa} values. This explains why the difference between E_{pa}(4-31G*) and E_{pa}(6-31G*) is less than 1 kcal mol^{-1}. These results agree with recent findings[33] regarding the influence of polarization functions on calculated E_{pa} values: (*i*) they reduce the size of the BSSE by a factor of 2–4 and (*ii*) for systems wherein the basic centre is first-row atom, singly polarized basis sets provide a reasonably good description of electron correlation in protonation processes. Recent work[33] on (22) has shown that at the 3-21G level, ΔE(BSSE) is *ca.* −3.3 kcal mol^{-1}. Hence, ΔE(BSE) + ΔE_{corr} *ca.* −13 kcal mol^{-1}. This term is too large for the straightforward use of E_{pa}(3-21G) to be of chemical interest. Fortunately, these errors, as well as ΔE_{ter} and most of the ΔE_{ZP} term largely cancel out when comparing a series of isodesmic reactions such as reaction (6).[34]

$$ROR' + H_3O^+ \longrightarrow RO(H)R'^+ + H_2O \quad (6)$$

Indeed, Figure 1 is a plot of $\delta E_{pa,exp}$ vs. δE_{pa}(3-21G). [$\delta E_{pa} = E_{pa}$(ROR') $- E_{pa}$(H$_2$O)] and it portrays an excellent linear relationship spanning a range of 45 kcal mol^{-1} (equation 7).

$$\delta E_{pa}(3\text{-}21G) = (-0.9 \pm 1.3) + (0.941 \pm 0.050)\delta E_{pa,exp} \quad (7)$$

{In kcal mol^{-1}; $n = 14$ [excluding (8), (22), and (23)]; $r^2 = 0.993$; sd $= 0.9$ kcal mol^{-1}}.

This equation does not apply to (8), (22), or (23), which reflects the inadequacy of a small basis set for the treatment of small cycles and hydrogen-bonded systems.

The E_{pa}(MNDO)s given in Table 1 are seen to be too small (by 7–15 kcal mol^{-1}). A plot of $\delta E_{pa,exp}$ vs. δE_{pa}(MNDO) shows that alcohols and aliphatic ethers define two separate, parallel lines with very high slopes (*ca.* 1.77). This is a consequence of the range of variation of the δE_{pa}(MNDO)s being greatly reduced by the overestimated core–core repulsions. This effect, together with the poor description of hydrogen-bonding provided by this method[9] account for the δE_{pa}(MNDO) of (8) being 19.5 kcal mol^{-1} off the line for aliphatic ethers. The results reported in Table 1 indicate that the E_{pa}(AM1) are too low by 3–12 kcal mol^{-1}. The plot of $\delta E_{pa,exp}$ vs. δE_{pa}(AM1) (Figure 3) however, shows a great improvement with respect to the MNDO results. Thus, a single correlation equation applies to both alcohols and ethers [equation (8)]. (1) and (23) are off the line but (8) and (22)

$$\delta E_{pa}(AM1) = (0.66 \pm 0.23) + (0.960 \pm 0.086)\delta E_{pa,exp} \quad (8)$$

[In kcal mol^{-1}; $n = 15$, $r^2 = 0.974$; sd $= 1.6$ kcal mol^{-1}]

are quite well behaved.

From equations (7) and (8), a linear relationship between δE_{pa}(3-21G) and δE_{pa}(AM1) is derived. It allows the estimation
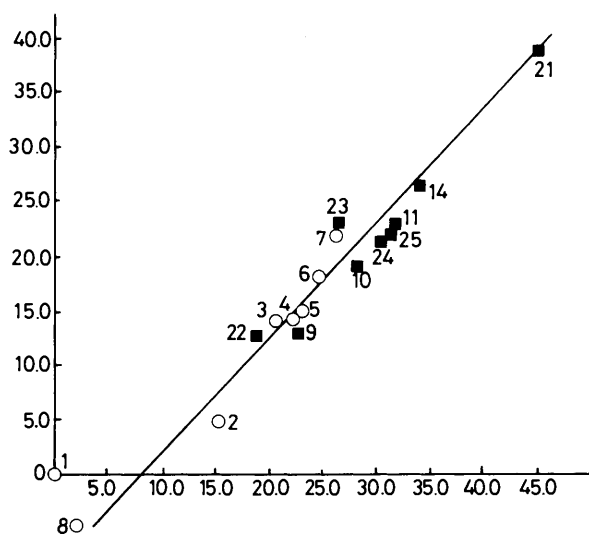
569

Figure 3. Experimental $E_{pa,exp}$ vs. calculated δE_{pa}(AM1) differential proton affinities. Compounds numbered as in Table 1. ○, ROH; ■, ROR'.
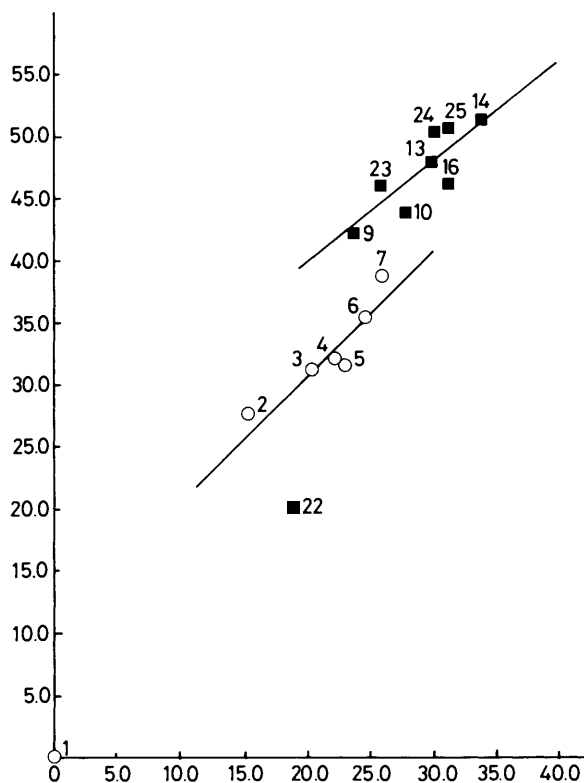

Figure 2. Calculated differential energies of the highest-occupied MOs, δE_{HOMO} vs. experimental differential proton affinities, $\delta E_{pa,exp}$. Compounds numbered as in Table 1. ○, ROH; ■, ROR'.

of δE_{pa}(3-21G) for (21) at 41.2 kcal mol⁻¹. This value has been used to obtain the corresponding E_{pa}(3-21G) given in Table 1.

Empirical Correlations.—(a) Proton charges. Protonation of an n-base leads to a substantial build-up of positive charge on the hydrogen(s) attached to the donor atom. Empirical correlations have been established between the electron populations[35] on these hydrogens, q_{H+}, and the E_{pa} values of the bases.[36] We find a reasonable linear correlation between $\delta E_{pa,exp}$ and q_{H+}(3-21G) $n = 14$ [excluding (8), (22), and (23), $r^2 = 0.968$, sd $= 2.0$ kcal mol⁻¹. It is remarkable that q_{H+}(3-

21G) is essentially the same within the couples (6)/(7) and (13)/(14).

The correlations between the $\delta E_{pa,exp}$ values and the q_{H+} values determined by the NDDO methods are too crude to be useful.[37]

(b) Energies of the highest-occupied molecular orbitals (HOMO). The E_{pa} values of n-bases such as alcohols and ethers can be related to the ionization potential of the lone pairs or the donor atom through equation (9)[38] where HA(BH⁺) is the

$$E_{pa}(B) = HA(BH^+) - E_i(B) + E_i(H) \qquad (9)$$

homolytic bond dissociation energy of the O–H bond. If this term remains constant within these families, the E_{pa} values must then match exactly the adiabatic ionization potentials of the neutral bases. In the absence of all the pertinent experimental data, the energies of the HOMOs, E_{HOMO}, can be used. Figure 2 is a plot of δE_{HOMO} [$\delta E_{HOMO} = E_{HOMO}(B) - E_{HOMO}(H_2O)$] vs. $\delta E_{pa,exp}$. It shows that a crude linear relationship does indeed exist, but its slope (1.6) is much higher than unity. Closer inspection of this plot reveals that two limited correlations pertaining respectively to alcohols [excluding (8)] and alkyl ethers are generated; their slopes (1.00 ± 0.34) and (0.82 ± 0.43) being much closer to the expected value. These results are consistent with the known sensitivity of these correlations to changes in the hybridization and geometry at the basic centre.[38,39] No useful relationships can be obtained by using the AM1 or MNDO values.

O_{1s} *Orbital Energies.*—It has long been established[40] that, within families of bases, good linear relationships exist between E_{pa} and the 1s core binding energies of their basic centres. Thus, McMahon and Kebarle have recently reported[41] a remarkably good linear relationship between E_{pm} and the experimental (ESCA) O_{1s} binding energies for a variety of oxygen bases with E_{pa} values spanning a range of 100 kcal mol⁻¹ (from O_2 to Me_2CO). Since experimental values are lacking for most of the compounds studied herein, we have compared the E_{pa} with the O_{1s} orbital energies calculated at the 3-21G level. In a plot of $E_{pa,exp}$ vs. $\delta E_{O_{1s}} = E_{O_{1s}}(B) - E_{O_{1s}}(H_2O)$, alcohols [excluding (8)] and alkyl ethers define separate lines with slopes much higher than that found experimentally. Thus $E_{O_{1s}}$ values at the 3-21G level are not sufficiently reliable for these purposes.

Correlation Analysis Approach.—This section is restricted to the analysis of E_{pa} for compounds (1–7) and (9)–(21).

The main structural changes to be expected on going from water to alcohols and then to ethers, are those associated with (*i*) polarizability,[42] (*ii*) σ-hyperconjugation, and (*iii*) rehybridization of the oxygen atom.

Polarizability effects are measured by the σ_α parameters.[42] Figure 4 is a plot of $\delta E_{pa,exp}$ vs. $\Sigma\sigma_\alpha = \sigma_\alpha(R) + \sigma_\alpha(R')$ for compounds having the general formula ROR'. From this plot, two highly precise (sd < 0.4 kcal mol⁻¹) linear relationships are obtained, pertaining, respectively, to alcohols [A, $\sigma_\alpha(H) = 0$] and ethers (B). The corresponding correlation equations[43] are given by equations (10) and (11). The additivity of alkyl

$$\delta E_{pa,exp} = (3.0 \pm 2.2) + (36.7 \pm 1.4)\Sigma\sigma_\alpha \qquad (10)$$

$$\delta E_{pa,exp} = (6.4 \pm 1.7) + (26.8 \pm 1.5)\Sigma\sigma_\alpha \qquad (11)$$

polarizability effects in the ether series holds all the way from (CH_3) to $(t-C_4H_9)_2O$.

The slope in equation (10) is smaller than that in equation (11) indicating that $E_{pa}(ROR') < E_{pa}(ROH) + E_{pa}(R'OH) - E_{pa}(H_2O)$. This difference reaches 16.6 kcal mol⁻¹ in the case of (9). It follows that on going from the alcohol to the ether series,
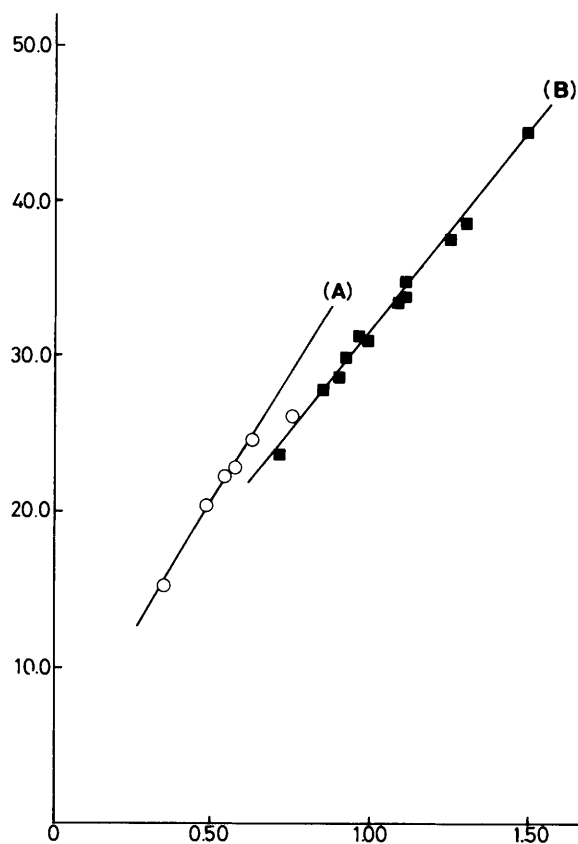
Figure 4. Experimental differential proton affinities $\delta E_{pa,exp}$ vs. polarizability parameters, $\Sigma\sigma_\alpha$. Compounds numbered as in Table 1. $\bigcirc$, ROH; ■, ROR'.

Table 4. Differential methyl-cation and proton affinities $\delta_R E_{mca}$ and $\delta_R E_{pa}$ for selected aliphatic alcohols in the gas-phase at 298 K.

Alcohol	$\delta_R E_{pa}{}^{a,b}$	$\delta_R E_{mca}{}^{a,b,c}$
(2)	0	0
(3)	5.3	3.8
(4)	7.1	5.1
(5)	7.7	6.3
(6)	9.5	6.7
(7)	10.9	7.3

^{a} In kcal mol^{-1}. ^{b} Defined in the text. ^{c} The enthalpies of formation of the neutral species are taken from ref. 44.

and along the latter, increasing polarizability is counterbalanced by some effects(s) varying in a proportional way. Saturation of the σ-hyperconjugation fits this requirement (this follows from the discussion in the section *Molecular Geometries*). Furthermore, an analysis at the 3-21G level of the positive charge transferred to the R groups in the protonated ROCH$_3$ series shows it to be smaller than that transferred to the same groups in the protonated alcohol series. Also, the charge transferred to the CH$_3$ group decreases in the order CH$_3$ > C$_2$H$_5$ > i-C$_3$H$_7$ > t-C$_4$H$_9$.

The methyl cation affinity of an alcohol, E_{mca}(ROH) is defined as E_{mca}(ROH) = $-\Delta H$ for reaction (12) in the gas-

$$ROH + CH_3{}^+ \longrightarrow RO(H)CH_3{}^+ \qquad (12)$$

$$ROCH_3 + H^+ \longrightarrow RO(H)CH_3{}^+ - E_{pa}(ROCH_3) \qquad (13)$$

phase. Taking into account reaction (13) it follows that E_{mca}(ROH) = E_{pa}(ROCH$_3$) + ΔH_f(ROH) − ΔH_f(ROCH$_3$) + ΔH_f(H$^+$) − ΔH_f(CH$_3{}^+$) Differential structural effects on a property X, δ_R(X), are defined as δ_R(X) = X(R) − X(CH$_3$) and from which we obtain equation (14). Using the data given in

$$\delta_R E_{mca}(ROH) = \delta E_{pa}(ROCH_3) + \\ \delta_R[\Delta H_f(ROH) - \Delta H_f(ROCH_3)] \qquad (14)$$

Table 1, the differential methyl-cation affinities collected in Table 4 are obtained. These data also allow the determination (or a very good estimation) of other alkyl affinities.

We notice that:

$$\delta_R E_{mca}(ROH) - \delta_R E_{pa}(ROH) = \\ \delta_R\{\Delta H_f(RO\overset{+}{H}_2) - \Delta H_f[RO(H)CH_3{}^+]\}$$

This indicates that the difference between E_{mca} and E_{pa} is only determined by the stability of the ionic forms.[45]

From the results given in Table 3 we obtain equation (15).

$$\delta_R E_{mca}(ROH) \\ = (0.0 \pm 0.7) + (0.70 \pm 0.10)\delta_R E_{pa}(ROH) \qquad (15)$$

$$(\text{in kcal mol}^{-1}, n = 6, r^2 = 0.971, sd = 0.4 \text{ kcal mol}^{-1})$$

It can be shown[46] that, because of equations (10) and (11), all differential alkyl-cation affinities, $\delta_R E_{aca}$(ROH) are the same, irrespective of the size of the alkyl cation (in the absence of appreciable steric effects). This is confirmed and the average ratio $\delta_R E_{aca}$(ROH)/$\delta_R E_{pa}$(ROH) is found to be equal to 0.73 ± 0.09.[47]

The differential Bu^t cation affinity for Bu^{t}OH is 3.1 kcal mol^{-1}, while the calculated value is 7.5 kcal mol^{-1}. We take this difference as indicating a back-strain effect. Figure 4 shows no abnormal behaviour for Bu$^t{}_2$O, therefore, a strain effect of *ca.* $4.4/0.73 = 6.0$ kcal mol^{-1} is also to be found in the neutral form. Indeed, $\Delta H = 7.8$ kcal mol^{-1} for reaction (16) in the gas phase.

$$t\text{-}C_4H_9OH + t\text{-}C_4H_9OCH_3 \longrightarrow \\ (t\text{-}C_4H_9)_2O + CH_3OH \qquad (16)$$
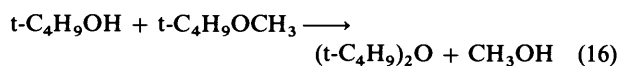
Finally, we notice that differential lithium-cation affinities, E_{la}, are available for a variety of alcohols.[48] Their δE_{la} and E_{pa} are proportional, but the slope of the line is 0.42. In the light of previous analyses,[15b] this is related to the O–Li bond having a smaller covalent character. We have performed calculations at the 4-31G level on the species RO(H)Li$^+$ and CH$_3$O(Li)R$^+$. They show that the stretching of the C–O bond and the amount of positive charge transferred to the alkyl groups are smaller for these ions than for the corresponding protonated forms.[49]

Conclusions

From a computational point of view, to obtain 'absolute' E_{pa} values it is necessary to reach, at least, the 4-31G*//4-31G level. In this case, the calculated E_{pa} values are to within 1 or 2 kcal mol^{-1} of the experimental values (upon the appropriate corrections). *ab initio* 3-21G and semiempirical AM1 calculations are comparable in providing correct 'differential' E_{pa} and geometries of the neutral forms (in the absence of chelation or severe *I*-strain). The MNDO method gives less satisfactory results.

An important conclusion of this study is that σ-hyperconjugative effects play a significant role in both protonated alcohols and ethers.

Regarding structure–reactivity relationships, those existing

between E_{pa}, and O_{1s} orbital energy or HOMO, range from non-existent to poor (3-21G calculations), contrary to literature statements. Within families, E_{pa} is a linear function of the polarizability of the substituent on the oxygen atom (as measured by the σ_α parameter). Moreover in the acyclic ether series, polarizability effects are additive.

Finally, this work leads to new insights regarding alkyl-cation affinities of alcohols.

References

1 (a) H. E. Schroeder and C. J. Pedersen, *Pure Appl. Chem.*, 1988, **60**, 445 and references therein; (b) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017; (c) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 2495; (d) J. R. Damewood, W. P. Anderson, and J. J. Urban, *J. Comput. Chem.*, 1988, **9**, 111, and references therein; (e) J. M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2303, ibid., 1978, **50**, 871; (f) D. J. Cram and J. M. Cram, *Science*, 1974, **183**, 801; (g) G. Dotseni, Y. Sogal, and D. J. Cram, *J. Am. Chem. Soc.*, 1975, **97**, 1259; (h) R. C. Hegelson, K. Koga, J. M. Tinko, and D. J. Cram, ibid., 1973, **95**, 3021, 3023.

2 This is particularly important if uncertainties of up to 1 or 2 kcal mol⁻¹ in the *relative* proton affinities of two compounds are to be avoided. See e.g., S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695.

3 (a) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. Molver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 5417. A temperature correction has been applied as given in, J. Bromilow, J.-L. Abboud, C. B. Lebrilla, R. W. Taft, G. Scorrano, and V. Lucchini, *J. Am. Chem. Soc.*, 1981, **103**, 5448; (b) For a general description of the experimental technique, see, e.g. T. A. Lehman and M. Bursey, 'Ion Cyclotron Resonance Spectrometry,' Wiley, New York, 1976; R. T. McIver, Jr., *Rev. Sci. Instrum.*, 1978, **49**, 111; (c) R. W. Taft, M. Taagepera, J.-L. M. Abboud, J. F. Wolf, D. J. De Fress, W. J. Hehre, J. E. Bartmess, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, 1978, **100**, 7765.

4 J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.

5 D. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **56**, 5255.

6 MONSTERGAUSS 80; M. R. Patersson and R. A. Poirier, Department of Chemistry, University of Toronto, Ontario, Canada.

7 J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, S 129.

8 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.

9 M. J. S. Dewar, E. G. Zoebish, E. F. Healy, and J. J. B. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

10 W. Thiel, in 'Quantum Chemistry Program Exchange Catalog,' Indiana University, Bloomington, Indiana, 1978, QCPE, program 353.

11 M. J. S. Dewar's Research Group and J. J. P. Stewart, QCPE Bull., 1986, **6**, 24; QCPE, program 506.

12 (a) S. Olivella, F. Urpi, and J. Vilarrasa, *J. Comput. Chem.*, 1984, **5**, 230; (b) G. P. and J. D. Scribner, ibid., 1983, **4**, 594; (c) M. J. S. Dewar and K. M. Dieter, *J. Am. Chem. Soc.*, 1986, **108**, 8075.

13 (a) M. J. S. Dewar, *J. Phys. Chem.*, 1985, **89**, 2145; (b) J. A. Del Bene, *J. Am. Chem. Soc.*, 1978, **100**, 1673; (c) J. A. Del Bene and A. Vaccaro, ibid., 1976, **98**, 7526.

14 (a) M. C. L. Gerry, R. M. Lees, and G. Winnewisser, *J. Mol. Spectrosc.*, 1976, **61**, 231; (b) M. Hayashi and K. Kuwada, *J. Mol. Struct.*, 1975, **28**, 147.

15 (a) C. Glidewell and C. Thomson, *J. Comput. Chem.*, 1982, **3**, 495; (b) S. F. Smith, J. Chandrasekhar, and W. L. Jorgensen, *J. Phys. Chem.*, 1982, **82**, 3308.

16 P. J. Krueger and H. D. Mettee, *Can. J. Chem.*, 1964, **42**, 340.

17 J. Murto, M. Räsänen, A. Aspiala, and T. Lotta, *J. Mol. Struct.* (Theochem), 1984, **108**, 99.

18 (a) H. J. Geise, W. J. Adams, and L. S. Bartell, *Tetrahedron*, 1969, **25**, 3045; (b) H. M. Almenningen, R. Seip, and T. Willadsen, *Acta Chem. Scand.*, 1969, **23**, 2748; (c) Gas-phase data suggest almost free pseudorotation but in the crystal (at −170 and −125 °C, the molecule has a single structure with C_2 symmetry: P. Luger and J. Buschman, *Angew. Chem., Int. Ed. Engl.* 1983, **5**, 410); (d) H. E.

Breedm, G. Gundersen, and R. Seip, *Acta Chem. Scand., Ser. A*, 1979, **33**, 225.

19 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1358.

20 O. O. Mó, J. L. G. de Paz, and M. Yáñez, *J. Phys. Chem.*, 1987, **91**, 6484.

21 P. Luger and J. Buschmann, *J. Am. Chem. Soc.*, 1984, **106**, 7119.

22 (a) W. I. Ferguson and N. C. Handy, *Chem. Phys. Lett.*, 1980, **71**; (b) R. Ahlrichs, F. Driessler, H. Lischka, V. Stammler, and W. Kutzelnigg, *J. Chem. Phys.*, 1975, **62**, 1225.

23 (a) H. Huber and Vogt, *J. Chem. Phys.*, 1982, **62**, 399; (b) gas-phase microwave studies of hydrogen-bond complexes between HF and oxygen bases [(1), (22), and (23)] show a pyramidal arrangement of bonds at the oxygen. (See, e.g. C. Legon, *Chem. Soc. Rev.*, 1987, **16**, 467).

24 e.g., Y. K. Sirkin and M. E. Dyatkina, 'Structure of Molecules and the Chemical Bond,' Butterworths, London, 1950. ch. 6.

25 M. Meot-Ner (Mautner), M. M. Ross, and J. E. Campana, *J. Am. Chem. Soc.*, 1985, **107**, 4839.

26 K. Hiraoka and P. Kebarle, *J. Am. Chem. Soc.*, 1977, **99**, 360.

27 Differences in polarizability may also be important (J. Gasteiger and M. J. Hutchings, *J. Am. Chem. Soc.*, 1984, **106**, 6489).

28 e.g., M. Masamura, *J. Mol. Struct.* (Theochem), 1988, **164**, 299 and references therein.

29 For comparison, the average errors in equilibrium bond lengths and bond angles determined by ab initio calculations at the 4-31G level are 0.02 Å and 5°: S. Iwata, 'Reliability of ab initio Calculations' in 'Quantum Chemistry Literature for 1978–1980,' eds. K. Ohno and K. Morokuma, Elsevier, Amsterdam, 1982, p. 427.

30 DZP + electronic correlation.

31 S. Romanowski, T. M. Pietrzak, L. Wojtczak, and S. Tariwska-Osinska, *J. Mol. Struct.* (Theochem), 1986, **137**, 217. This reference also provides a wealth of information on the structures of aliphatic alcohols.

32 J. E. Del Bene, H. D. Mettee, M. J. Frisch, B. T. Luke, and J. A. Pople, *J. Phys. Chem.*, 1983, **87**, 3279.

33 O. Mó, J. L. G. de Paz, and M. Yáñez, *Theor. Chim. Acta*, 1988, **73**, 307.

34 I. A. Koppel, U. H. Mölder, and V. A. Palm, *Org. React.* (Tartu), 1985, **22**, 3.

35 R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833, 1841, 2338, and 2343.

36 W. J. Hehre, M. Taagepera, R. W. Taft, and R. D. Topsom, *J. Am. Chem. Soc.*, 1981, **103**, 1344.

37 q_{H+}(3-21G) and q_{H+}(NDDO) values cannot be directly compared, see ref. 12(b).

38 D. H. Aue and M. T. Bowers in 'Gas-phase Ion Chemistry,' ed. M. T. Bowers, Academic Press, New York, 1978, ch. 2.

39 (a) J. Catalán, O. Mó, J. L. G. de Paz, P. Pérez, M. Yáñez, and J. Elguero, *J. Org. Chem.*, 1984, **49**, 4379; (b) D. Christen, J. H. Griffiths, and J. Sheridan, *Z. Naturforsch., Teil A*, 1982, **37**, 1378.

40 (a) R. L. Martin and D. A. Shirley, *J. Am. Chem. Soc.*, 1974, **96**, 5299; (b) D. W. Davis and J. W. Rabalais, *J. Am. Chem. Soc.*, 1974, **96**, 5305.

41 (a) T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, 1985, **107**, 2612; (b) T. X. Carrol, S. R. Smith, and T. D. Thomas, *J. Am. Chem. Soc.*, 1975, **97**, 659.

42 R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.*, 1987, **16**, 1, and references therein.

43 The value for (7) has not been included in the correlation.

44 J. B. Pedley, R. D. Naylor, and S. P. Kirby, 'Thermochemical Data of Organic Compounds,' 2nd edn. Chapman and Hall, London, 1986.

45 J. I. Brauman and C. Chan, *J. Am. Chem. Soc.*, 1988, **110**, 5611.

46 J.-L. M. Abboud, R. W. Taft, and J. Elguero, manuscript in preparation.

47 T. B. Mc Mahon, T. Heinis, G. Nicol, J. K. Hovey, and P. Kebarle, *J. Am. Chem. Soc.*, 1988, **110**, 7591.

48 R. W. Taft, F. Anvia, J.-F. Gal, S. Walsh, M. Capon, M. C. Holmes, K. Hosn, G. Oloumi, R. Vasanwala, and S. Yazdani, *Pure Appl. Chem.*, in the press.

49 J.-L. M. Abboud, J. Elguero, M. El Mouhtadi, M. Essefar, D. Liotard, R. W. Taft, M. Yáñez, manuscript in preparation.