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The Gas-Phase Acidities of Very Strong Neutral Brønsted Acids

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Abstract: An interlocking ladder of relative gas-phase acidities of a large number of very strong CH (substituted phenylmalononitriles, 2,4,6-$(CF_3SO_2)_3C_6H_2CH_3$, CF_3SO_2- and FSO_2-substituted methanes, TNT, etc.), NH (bis(perfluoroalkyl)sulfonyl imides, 2,4,6-$(CF_3SO_2)_3C_6H_2NH_2$, etc.), OH (triflic acid, picric acid, 2,4,6-$(CF_3SO_2)_3C_6H_2OH$, CH_3SO_3H, etc.) and SH (CF_3COSH) Brønsted acids has been obtained using the pulsed FT ion cyclotron resonance (ICR) equilibrium constant method. The new intrinsic acidity scale covers a wide range from $(CF_3)_2NH$ (ΔG_{acid} = 324.3 kcal/mol) to $(C_4F_9SO_2)_2NH$ (ΔG_{acid} = 284.1 kcal/mol) and is anchored to the thermodynamic ΔG_{acid} value (318.1 kcal/mol) of HBr. In several cases, the gas-phase acidity of compounds which make up the scale exceeds the acidity of such traditionally strong mineral acids as HCl, HBr, HI, or H_2SO_4 by more than 30 powers of 10. The roles of the acidity sites (CH, NH, OH, SH) and the structural factors (i) field/inductive effects (F), (ii) π-electron-acceptor resonance effects (R), and (iii) substituent polarizability (P) effects on increasing the gas-phase acidity of Brønsted acids are discussed. The effects of multiple substitution in families of Brønsted acids have been measured and discussed. The strong and extensive chains of conjugation in the resonance-stabilized planar conjugate anion of (*p*-nitrophenyl)malononitrile lead to the same gas-phase CH acidity (ΔG_{acid} = 299.5 kcal/mol) as for OH superacid CF_3SO_3H. A single *para* substituent in aniline has been found that exerts such a powerful "electron-withdrawing" effect that this aniline has a stronger gas-phase acidity than CH_3SO_3H. The substituent is $-S(O)(=NSO_2CF_3)CF_3$, one of the family of Yagupolskii superacceptor substituents that is generated by replacing $=O$ by $=NSO_2CF_3$ at a bonded S, P, or I (including in addition to the above $-S(=NSO_2CF_3)_2CF_3$, $-P(=NSO_2CF_3)(C_3F_7)_2$ and $-I=NSO_2CF_3$). Perfluoroaromatic acids have been identified as well-behaved compounds for gas-phase acidity determinations. Their moderately strong inherent acidifying effects are illustrated by the fact that a ΔG_{acid} value of 302 ± 1 kcal/mol applies to all of the following: $(4\text{-}C_5F_4N)_2CHCN$, $(p\text{-}CF_3C_6F_4)_2CHCN$, β-$C_{10}F_7CH(CN)_2$, and $(CF_3SO_2)_2CH_2$. The introduction of more bulky strong electron-acceptor substituents in CH_4 or NH_3 has been found to be accompanied by an especially strong nonadditive increase in gas-phase acidity. The nonadditivity is least in CN-substituted compounds, such as for the above compounds. These results are discussed as being associated with saturation and particularly with steric repulsion in the anions. In spite of the nonadditivity of the acidities for disubstituted NH_3 and CH_4 (as well as X_3CH), the acidifying R, F, and P effects tend still to be quite significant for strongly electron-withdrawing substituents. It will be noted that the acid $(C_4F_9SO_2)_2NH$ presently holds the record as the strongest measured gas-phase superacid. Extensive ab initio calculations are reported for several basis sets which have been found useful for the study of structures and electronic and vibrational energies, as well as entropy effects. A major tool is provided for the prediction of new extremely acidic compounds. The present experimental and theoretical results set the grounds for preparation and measurement of new even stronger gas-phase superacids. Such results hold promise not only for extending basic knowledge but also in providing many new practical applications for condensed-phase chemistry, including those that utilize the acidic substructures.

Introduction

Over 60 years ago, J. B. Conant[1] pioneered in using the name "superacid" by calling attention to acid systems more acidic than the conventional mineral acids. Subsequently, R. J. Gillespie[2] introduced an arbitrary but widespread definition according to which superacids are systems whose acidity, as characterized by Hammett acidity function H_o, exceeds that of 100% sulfuric acid ($H_o = -12$). Significant progress in developing new superacid systems and studying their chemistry has been made by G. A. Olah and his group.[3] Brønsted/Lewis acid mixtures of HF–SbF_5, HF–HSO_3F, HSO_3F–SbF_5, etc., with superacidities up to

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10^{15}–10^{18} times stronger ($H_o \leq -30$) than 100% H_2SO_4, have been developed.

Unfortunately, due to substantial experimental and theoretical difficulties, definitive pK_a values have not been available for strong Brønsted acids, e.g., H_2SO_4, $C_6H_5SO_3H$, and CF_3SO_3H, referred to their solutions in water, nonaqueous solvents, or the gas phase as the standard states. This situation is so confusing that large uncertainties remain as to relative acidities in a given solvent and to the nature and magnitudes of solvent effects.[3–6] For example, the pK_a for $HClO_4$ has been given values ranging from −1.6 to −14 by various extrapolation techniques (cf. ref 5). In anhydrous acetic acid, the following acidity order was reported:[6] $TeF_5OH < HCl < H_2SO_4 < FSO_3H < HI < HBr < HClO_4 < CF_3SO_3H$. Measurements by one of us (D.D.D.)[7] by the same method[6a] gave additional results: $CF_3CO_2H < HNO_3 < TeF_5OH < (CF_3SO_2)_2NH < FSO_3H < CF_3SO_3H$. A gas-phase acidity order where $HI < HPO_3 < H_2SO_4 < FSO_3H < CF_3SO_3H$ has been recently reported.[8] These results, in light of present results (and the known specific effects of dimethyl sulfoxide and water on the acidities of weak to moderately strong neutral acids),[9,10] suggest that gas- and solution-phase relative acidities (even within families) can also in many instances be significantly different for the very strong acids.

The intrinsic gas-phase acidities, ΔG_{acid}, refer to the thermodynamic heterolysis equilibrium:

$$AH \overset{K_a}{\rightleftharpoons} A^- + H^+ \qquad (1)$$

A scale has been provided by process 1 for more than 700 weak to moderately strong Brønsted acids whose ΔG_{acid} values vary from 410 to 310 kcal/mol, i.e., by more than 70 pK_a units[11] (recall that as the acidity of HA increases both ΔG and $pK_a \equiv -\log K_a$ values decrease).

We report here new ΔG_{acid} values for intrinsic gas-phase acidities of very strong neutral Brønsted CH, NH, OH, and SH acids that extend the scale to ca. 284 kcal/mol. These results are based upon the gas-phase proton-transfer equilibrium:

$$A_1H + A_0^- \overset{K}{\rightleftharpoons} A_0H + A_1^-; \quad \delta\Delta G = -RT \ln K \qquad (2)$$

where K refers to the transfer of a proton between a given (A_1H) and a reference base (A_0^-). These measurements utilize the pulsed FT-ICR spectroscopy method previously described[9c] or the modifications given in the Experimental Section.

Previous results[9,12–16] provided evidence that three kinds of major substituent effects contribute to the increasing inherent acidity of a given neutral acid functional group: (i) correctly oriented dipolar substituent/anion interactions (F effects), (ii) polarizable substituent/anion interactions (P effects), and (iii) substituent π-electron-acceptor interactions (R effects) which preferentially stabilize the strong electron-pair donor anion forms compared to the corresponding weaker π-donor conjugate acid forms. The interplay and variable contributions from these three kinds of effects, as well as tautomeric equilibria which may sometimes be involved, lead to no simple general pattern of acidity behavior as a function of molecular structure.[4,9c,14,15] The present results not only offer further evidence for the correctness of some of the earlier conclusions but more firmly establish the structural features that optimize inherent acidities. Indeed, the new experimental results and the ab initio theoretical calculations of this paper set the grounds for achieving new structures of inherently very great acidity.

Results

Table 1 presents ΔG_{acid} values (in kcal/mol) for 90 gas-phase acidities obtained from $\delta\Delta G$ values for numerous individual proton-transfer equilibria between the unknown and a standard acid. The results give the multiple overlaps that are involved. These results demonstrate the consistency that is the basis for the ΔG_{acid} values. With a few exceptions, the entire range from $(CF_3)_2NH$ to $(C_4F_9SO_2)_2NH$ will be seen to involve at least two independent paths in the overlaps. It is noted that the results of Table 1 have been tied to the "marker" thermodynamic value for HBr. Further, 3,5-bis(trifluoromethyl)pyrazole, octafluorofluorene, di- and trifluoroacetic acids, 2-chloro-4-nitrophenol, p-((trifluoromethyl)sulfonyl)phenol, and p-methyl- and unsubstituted phenylmalononitriles, the strongest acids for which ICR acidities had previously been determined,[11] are also satisfactorily fit into the present scale, serving as reference compounds.

Table 2 gives ΔG_{acid} values for additional acids of interest for comparisons. The gas-phase acidity order previously known for elemental hydrides or for alkyl derivatives,[11] CH < NH < OH < SH, is found to hold with the CF_3CO derivatives; for example: CF_3COCH_3 (343.1) < CF_3CONH_2 (336.7) < CF_3CO_2H (316.3) < CF_3COSH (312.5). The acidities of CF_3SO_2 (trifyl) derivatives for the first three members have been completed and also display this same order: $CF_3SO_2CH_3$ (339.8) < $CF_3SO_2NH_2$ (321.3) < CF_3SO_3H (299.5). Both the CF_3CO and CF_3SO_2 substituents in m- and p-substituted toluenes, anilines, and phenols were previously shown to give gas-phase acidities in this order.[12,13] We show here that, although further diminished in their differences, 2,4,6-tris(trifyl)toluene, -aniline, and -phenol (305.7, 304.8, and 291.8, respectively) also obey this order. However, the multiple substitutions we have investigated in NH_3 and CH_4 have been found to lead to a reversal in this intrinsic acidity order, as is illustrated by the following results: CF_3SO_3H (299.5) < $(CF_3SO_2)_2NH$ (291.8) < $(CF_3SO_3)_3CH$ (289.0). The present ΔG_{acid} value for CF_3SO_3H has also been confirmed by flowing afterglow spectroscopic results.[8b]

Our results also show that (p-nitrophenyl)malononitrile (299.5) is inherently more acidic than picric acid (302.8) and is of equal acidity to that of triflic acid (CF_3SO_3H, 299.5). The most acidic of the very strong neutral acids that are reported herein is $(C_4F_9SO_2)_2NH$ (284.1), which is 19.8 pK_a units (27.0 kcal/mol) more acidic than HI.

Discussion

Our systematic studies provide new knowledge of the inherent effects of molecular structure on the acidities of organic functional groups (above) as well as of substituent effects. These latter include a result for the superacceptor substituent $-S(O)({=}NSO_2CF_3)CF_3$.[17] The substituent effect results are discussed below in

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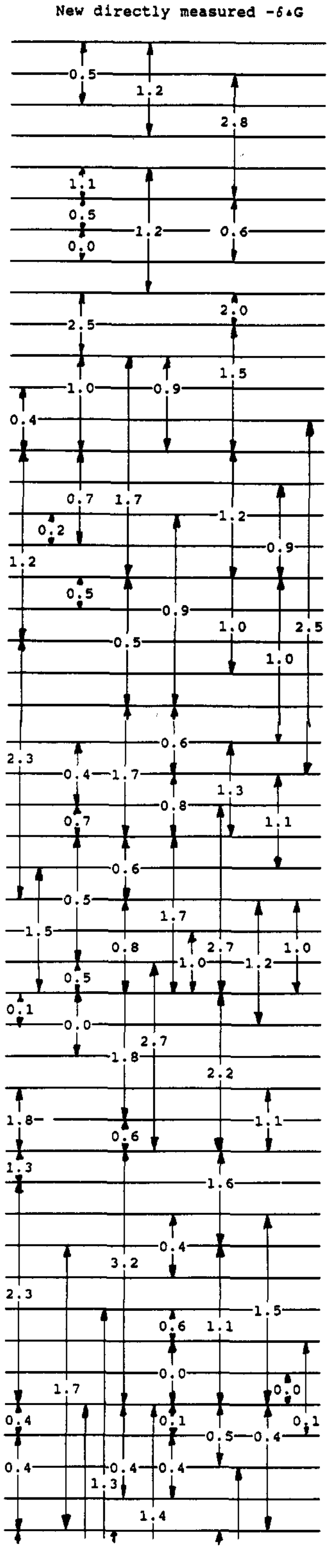
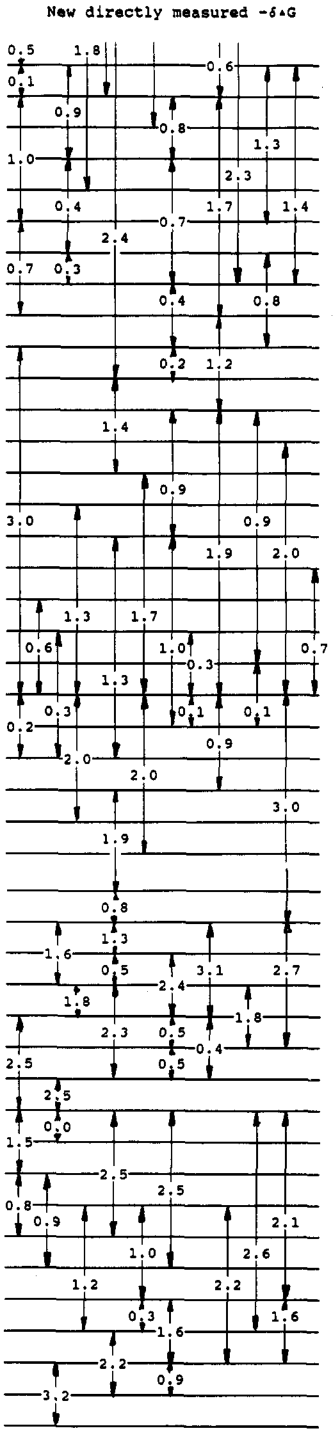
Table 1. ΔG_{acid} Values (kcal/mol) Derived from $\delta\Delta G$ Values for the Proton-Transfer Equilibria between the Indicated Acid–Conjugate Base Pairs



	ΔG_{acid}
$(CF_3)_2NH$	324.3
$(CF_3)_3COH$	324.0[a]
CHF_2CO_2H	323.8[b]
3,5-$(CF_3)_2C_6H_3OH$	322.9[b]
$CF_3COCH_2COCH_3$	322.0[b,c]
$CF_3SO_2NH_2$	321.3
p-$NO_2C_6H_4OH$	320.9[b]
C_6F_5OH	320.8
$CHCl_2CO_2H$	320.8[b]
$CF_3SO_2NHCH_2C_6H_5$	318.8
HBr	318.3[b]
p-$HC_6F_4NHC_6F_5$	317.7
$(C_6F_5)_3CH$	317.6
3,5-$(CF_3)_2$-pyrazole	317.3[b]
Octafluorofluorene	317.3[b]
$C_6F_5CO_2H$	316.6
$(C_6F_5)_2NH$	316.5
CF_3CO_2H	316.3[b]
2-Cl-4-$NO_2C_6H_3OH$	316.1[b]
p-$NO_2C_6H_4NHC_6F_5$	316.0
p-$CF_3SO_2C_6H_4OH$	315.7
p-$CH_3C_6H_4CH(CN)_2$	315.7[b]
p-$CH_3OC_6H_4CH(CN)_2$	315.4
$C_4F_9SO_2NH_2$	315.1
CH_3SO_3H	315.0
$C_6H_5CH(CN)_2$	314.3[b]
α-$OHC_{10}F_7$	314.0
$CF_3SO_2NHC_6H_5$	313.5
$C_6F_5CH(CN)CO_2C_2H_5$	313.5
p-$CF_3(O)(=NSO_2CF_3)SC_6H_4NH_2$	313.4
CF_3COSH	312.5
$(C_6F_5)_2CHCN$	312.4
β-$OHC_{10}F_7$	312.4
4-OHC_5F_4N	311.3
$(4\text{-}C_5F_4N)NHC_6F_5$	310.9
$(CF_3CO)_2CH_2$	310.3
p-$ClC_6H_4CH(CN)_2$	309.0
2,4,6-$(NO_2)_3C_6H_2CH_3$	309.0
m-$ClC_6H_4CH(CN)_2$	308.8
2,4-$(NO_2)_2C_6H_3OH$	308.6
p-$CH_3C_6F_4CH(CN)_2$	308.0
2,4,6-$(FSO_2)_3C_6H_2NH_2$	307.5
p-$CF_3C_6F_4CH(CN)C_6F_5$	307.5
$(CF_3CO)_2NH$	307.5
$(FSO_2)_2CH_2$	307.3
p-$CNC_6F_4NHC_6F_5$	307.0
$C_6H_5CH(SO_2F)_2$	307.0
m-$CF_3C_6H_4CH(CN)_2$	307.0



	ΔG_{acid}
2,4,6-$(CF_3SO_2)_3C_6H_2COCH_3$	306.6
$(CF_3CO)_2CHCO_2CH_3$	306.5
$(4\text{-}C_5F_4N)_2NH$	306.1
2,4,6-$(CF_3SO_2)_3C_6H_2CH_3$	305.7
$(4\text{-}C_5F_4N)CH(CN)C_6F_5$	305.7
p-$HC_6F_4CH(CN)_2$	305.5
2,4,6-$(CF_3SO_2)_3C_6H_2CH_2NO_2$	305.3
$(CF_3CO)_2CHCF_3$	305.0
2,4,6-$(CF_3SO_2)_3C_6H_2NH_2$	304.8
2,4,6-$(CF_3SO_2)_3C_6H_2CH_2CHO$	304.6
m-$CNC_6H_4CH(CN)_2$	304.4
$C_6F_5CH(CN)_2$	303.6
$(4\text{-}C_5F_4N)CH(CN)CO_2C_2H_5$	303.5
m-$NO_2C_6H_4CH(CN)_2$	303.0
2,4,6-$(NO_2)_3C_6H_2OH$	302.8
$(C_3F_7CO)_2CHCF_3$	302.7
$(4\text{-}C_5F_4N)_2CHCN$	302.2
(p-$CF_3C_6F_4)_2CHCN$	302.1
9-C_6F_5-*octafluorofluorene*	301.8
β-$C_{10}F_7CH(CN)_2$	301.8
$(CF_3SO_2)_2CH_2$	301.5
p-$CF_3C_6F_4CH(CN)_2$	301.5
$(CF_3SO_2)_2CHC_6H_5$	301.3
$(CF_3CO)_3CH$	300.6
p-$NO_2C_6H_4CH(CN)_2$	299.5
CF_3SO_3H	299.5
$(C_3F_7CO)_3CH$	298.8
$CF_3CONHSO_2CF_3$	298.2
$CF_3CONHSO_2C_4F_9$	296.9
$C_3F_7CONHSO_2CF_3$	296.5
$C_7F_{15}CONHSO_2CF_3$	295.0
$C_3F_7CONHSO_2C_2F_5$	294.8
$C_3F_7CONHSO_2C_4F_9$	294.3
$(CF_3SO_2)_2NH$	291.8
2,4,6-$(CF_3SO_2)_3C_6H_2OH$	291.8
$CF_3SO_2NHSO_2C_2F_5$	290.3
$CF_2(CF_2SO_2)_2NH$	289.6
$(C_2F_5SO_2)_2NH$	289.4
$CF_3SO_2NHSO_2C_3F_7$	289.3
$(CF_3SO_2)_3CH$	289.0
$(C_4F_9SO_2)_2CH_2$	288.7
$CF_3SO_2NHSO_2C_4F_9$	287.3
$CF_3SO_2NHSO_2C_6F_{13}$	286.5
$(C_4F_9SO_2)_2NH$	284.1

[a] See also ref 9c. [b] See also ref 11. [c] See also ref 28.

the following sequence:(a) the effects of single substituents in H_2O, NH_3, and CH_4, (b) the effects of multiple substitution in NH_3 and CH_4, and (c) the effects of substituents in aromatic acids.

(a) Effects of Single Substituents on Gas-Phase Acidities of Water, Ammonia, and Methane. Table 3 lists typical earlier results[11] together with the new data obtained in this study. Table 3 contains data for 16 measured XOH acids of diverse structures and is arranged in the order of increasing acidities as one proceeds downward in the table. For the 15 measured XNH_2 acids, the substituent acidity order frequently, but not always, parallels that for the XOH acids. For example, $(CF_3)_3C$ is more acidifying than p-$CF_3C_6H_4$ in the XOH family, but it is much less acidifying in the XNH_2 series. Other reversals are to be noted in Table 3. The squared correlation coefficient and standard deviation are 0.975 and 3.0 kcal/mol, respectively, for eq 3 for the 14 substituents of Table 3 that are common to both the XOH and XNH_2 series. Without exception, the acidifying substituent

Table 2. Gas-Phase Acidities, ΔG_{acid} (kcal/mol), of Additional Acids Considered in This Paper

acid	ΔG_{acid}	acid	ΔG_{acid}	acid	ΔG_{acid}
CH_4	408.5^{a}	CH_3NO_2	349.7^{a}	$(CH_3CO)_2CH_2$	336.7^{a}
NH_3	396.1^{a}	*o*-$NO_2C_6H_4CH_3$	348.6^{a}	CF_3CONH_2	336.7^{a}
$Si(CH_3)_4$	390.7^{a}	$PhCONH_2$	347.0^{a}	*p*-$NO_2C_6H_4NH_2$	336.2^{a}
H_2O	384.1^{a}	*p*-$CF_3C_6H_4NH_2$	346.0^{a}	$PhSO_2NH_2$	333.2^{b}
$PhCH_3$	373.7^{a}	*p*-$(CF_3)_3CC_6H_4NH_2$	345.9^{b}	$PhCO_2H$	333.0^{a}
$(CH_3)_3SiNH_2$	371.0^{a}	*p*-$NO_2C_6H_4CH_3$	345.3^{a}	4-$NH_2C_5F_4N$	332.7^{b}
CH_3CN	364.0^{b}	$PhCH_2CN$	344.1^{b}	*p*-$CF_3SO_2C_6H_4NH_2$	331.3^{a}
F_2NH	363.3^{b}	H_2NCN	344.1^{b}	*p*-$CF_3C_6H_4OH$	330.1^{a}
CH_3COCH_3	361.9^{a}	$(CF_3)_2CH_2$	343.9^{b}	$(CH_3CO)_3CH$	328.9^{b}
p-$CF_3C_6H_4CH_3$	359.8^{a}	Ph_2NH	343.8^{a}	$(C_6F_5)_2CHPh$	328.4^{b}
$PhNH_2$	359.1^{a}	*p*-$HCOC_6H_4NH_2$	342.3^{a}	$CH_2(CN)_2$	328.3^{a}
CH_3CHO	359.0^{a}	PhOH	342.3^{a}	$C_6F_5CH_2CN$	327.6^{b}
Ph_2CH_2	358.2^{a}	CF_3COCH_3	342.1^{a}	$(CF_3)_3CH$	326.6^{b}
$CH_3SO_2CH_3$	358.2^{a}	*p*-$CNC_6H_4NH_2$	341.5^{a}	*p*-$CNC_6F_4NH_2$	326.2^{b}
$(CH_3)_3SiOH$	356.0^{a}	$C_6F_5NH_2$	341.3^{b}	*p*-$HCOC_6H_4OH$	326.1^{a}
CH_3CONH_2	355.1^{a}	CH_3CO_2H	341.1^{a}	*p*-CNC_6H_4OH	325.3^{a}
$C_6F_5CH_3$	354.7^{b}	*p*-$CF_3SO_2C_6H_4CH_3$	340.7^{b}	HNO_3	317.8^{a}
$PhCOCH_3$	354.5^{a}	CF_3OH	340.7^{c}	H	312.5^{a}
p-$CNC_6H_4CH_3$	353.6^{a}	$(CH_3CO)_2NH$	339.8^{a}	HI	309.2^{a}
$HCONH_2$	353.0^{a}	$CF_3SO_2CH_3$	339.8^{a}	HPO_3	303.3^{d}
$((CH_3)_3Si)_2NH$	352.9^{a}	*p*-$COCNC_6H_4CH_3$	339.1^{a}	H_2SO_4	302.2^{d}
Ph_3CH	352.8^{a}	$CH_3SO_2NH_2$	338.8^{b}	FSO_3H	299.8^{d}
p-$HCOC_6H_4CH_3$	352.6^{a}	HCO_2H	338.4^{a}	$HClO_4$	285 [illegible] 8^{e}
$(CF_3)_3CNH_2$	350.1^{b}	CH_3COCN	337.7^{a}		

[a] Reference 11. [b] This work, cf. the Experimental Section. [c] Reference 9c. [d] Reference 8b. [e] Reference 16b.

Table 3. Acidifying Effects, $-\delta\Delta G$ (kcal/mol), of Single Substituents on Gas-Phase Acidities of H_2O, NH_3, and CH_4[a]

substituent, X	XOH	XNH_2	XCH_3
H	0.0^{b}	0.0^{c}	0.0^{d}
$(CH_3)_3Si$	28.1	25.1	17.8
C_6H_5	41.8	37.0	34.8
CH_3CO	43.0	41.0	46.6
CF_3	43.4		38.1^{e}
HCO	45.7	43.1	49.5
C_6H_5CO	51.1	49.1	54.0
p-$CF_3C_6H_4$	54.0	50.1	48.7
p-$(CF_3)_3CC_6H_4$		50.2	
CN		52.0	44.5
C_6F_5	63.3	54.8	53.8
4-C_5F_4N	72.8	63.3	
p-$HCOC_6H_4$	58.0	53.8	55.9
p-CNC_6H_4	58.8	54.6	54.9
$(CF_3)_3C$	60.1	46.0	
p-$NO_2C_6H_4$	63.2	59.9	63.2
NO_2	66.3		58.8
CF_3CO	67.8	59.4	66.4
p-$CF_3SO_2C_6H_4$	68.4	64.8	67.8
CH_3SO_2	69.1	57.3	50.3
CF_3SO_2	84.6	74.8	68.7
p-$COCNC_6H_4$			69.4
COCN			70.8
$C_4F_9SO_2$		81.0	
p-$CF_3(O)({=}NSO_2CF_3)SC_6H_4$		82.7	

[a] Based upon data in Tables 1 and 2. [b] $\Delta G_{acid} = 384.1$ kcal/mol. [c] $\Delta G_{acid} = 396.1$ kcal/mol. [d] $\Delta G_{acid} = 408.5$ kcal/mol. [e] Calculated value cf. Table 2.

$$\delta\Delta G_{(g)}(XNH_2) = (0.90 \pm 0.04)\delta\Delta G_{(g)}(XOH) + (0.8 \pm 2.3) \tag{3}$$

effects are seen in Table 3 to be less for corresponding XNH_2 than XOH acids. This is consistent with the less than unit value of coefficient (0.90) in the above equation.

For the 18 substituents in Table 3 common to both XCH_3 and XOH series, the following correlation is obtained:

$$\delta\Delta G_{(g)}(XCH_3) = (0.89 \pm 0.08)\delta\Delta G_{(g)}(XOH) + (1.7 \pm 4.6) \tag{4}$$

The squared correlation coefficient and standard deviation are 0.891 and 6.3 kcal/mol, respectively, for eq 4. The poor quality of this relationship results from the following: in 10 of these cases the acidifying effects are smaller for XCH_3 than XOH, in three cases there are essentially equal substituent effects in the two series, and in three cases (CH_3CO, HCO, and C_6H_5CO) a significantly greater acidifying effect is to be noted in the XCH_3 compared to the corresponding XOH acids. For these carbonyl substituents, π-electron-acceptor effects dominate over electrostatic field/inductive effects. This is quantified by substituent σ_R and σ_F values.[18] The ratio σ_R/σ_F is uniquely large (0.63 ± 0.02) for the CH_3CO, HCO, and C_6H_5CO substituents. On the other hand, for example, the NO_2, CH_3SO_2, and CF_3SO_2 substituents have $\sigma_R/\sigma_F = 0.25 \pm 0.03$, the CF_3 and CN substituents have $\sigma_R/\sigma_F = 0.16$, and for $(CF_3)_3C$ this ratio is 0.

The relationship of substituent structural effects within the three acid series of Table 3 involves, largely, changes in the relative importance of substituent field/inductive, polarizability, and π-electron delocalization effects. The latter effects are dependent upon anion coplanarity (and certain conformational considerations) as well as upon the electron donor properties of the centers. Major changes in π-electron delocalization can in turn produce secondary changes of importance in the field/inductive and polarizability effects. The lower electron affinity of $NH_2^{\cdot}$ and particularly of $CH_3^{\cdot}$ compared to $OH^{\cdot}$ produces a major difference in π-electron-donor delocalization to acceptor substituents in the corresponding anions. This has been well established by the ρ_R reaction constants for *para*-π-electron-acceptor substituents in the gas-phase acidities of anilines, toluenes, and phenols.[12,13] With substituents directly located at the anionic centers, there are even greater differences in this anion π-delocalization order, i.e., $O^- < NH^- < CH_2^-$.[19]

The simplified eq 5 has been found to describe very well the gas phase acidities for most XOH acids:[9c]

$$-\delta\Delta G = P + F + R = \rho_\alpha\sigma_\alpha + \rho_F\sigma_F + \rho_R\sigma_R \tag{5}$$

The three reaction constants for polarizability ($-\rho_\alpha$), field/inductive (ρ_F) and π-electron delocalization (ρ_R) effects are all very much larger than the corresponding values for *p*-XC_6H_4OH gas-phase acidities. For XNH_2 and XCH_3 acidities, deviations from this treatment are much greater, particularly for XCH_3. Applying eq 5 to the XNH_2 and XCH_3 families gives rough correlational results and shows clearly that the approximate ρ_R values tend to markedly increase in the acid order XOH (72.8 ± 2.0) < XNH_2 (80 ± 5) < XCH_3 (151 ± 19). The relatively

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(18) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991,** *91,* 165.
(19) Dahle, G. D.; Kass, S. R. *J. Am. Chem. Soc.* **1991,** *113,* 5566.

large acidifying effects of CH_3CO, CHO, and C_6H_5CO for the XCH_3 series can be attributed to this sequence of ρ_R values and (as noted above) the uniquely large ratio σ_R/σ_F for these substituents. The greater acidity of CH_3COCN than $CH_3SO_2CF_3$ provides a further similar example.

The approximate values of the reaction constants, ρ_F and $-\rho_\alpha$, for the XNH_2 and XCH_3 field/inductive and polarizability effects, respectively, are in the opposite direction to that for the ρ_R value. The values of ρ_F and $-\rho_\alpha$ are in the sequence $XOH > XNH_2 > XCH_3$; for the former, $72.7 \pm 1.4 > 57.4 \pm 1.8 > 32 \pm 5$, and for latter, $24.1 \pm 1.5 > 18. \pm 2. > 3. \pm 8.$

The major cause of this sequence of ρ_F and $-\rho_\alpha$ values is indicated to be the decreasing localization of the charge for effective anion stabilization by substituent dipolar and polarizability interactions. The increasing π-electron delocalization, which goes in the reverse sequence, can make some contribution to the decreasing ρ_F and $-\rho_\alpha$ values. However, the major cause (above) is indicated by the results for the t-C_4F_9 substituent with $\sigma_R = 0$. This substituent consequently has little or no π-electron-acceptor effects.[9c,18] Its observed acidifying effect for the XNH_2 relative to that in the XOH family is only 0.77, reflecting the fact that there are smaller field/inductive and polarizability effects for XNH_2 than XOH acidities even in the absence of R effects. The expected still smaller field/inductive and polarizability effects for t-$C_4F_9CH_3$ acidity could not be confirmed by a direct acidity determination (cf. Experimental Section). Unpublished MOPAC (PM3) and ab initio calculations[20] of this acidity relative to that for CH_4 are consistent with the expectation of still smaller F and P effects.

In Table 3, the results for corresponding X and p-XC_6H_4 substituents are surprisingly similar. Further, for CF_3, CN, and CHO, for example, larger acidifying effects are found in all p-XC_6H_4 families. For CF_3SO_2, however, larger effects are found in all of the X (compared to p-XC_6H_4) families. For NO_2 effects, $XOH > p$-XC_6H_4OH, whereas p-$XC_6H_4CH_3 > XCH_3$. The general behavior of p-XC_6H_4 substituent effects relative to each of their parents, C_6H_5OH, $C_6H_5NH_2$, or $C_6H_5CH_3$, have been well established and discussed.[12,13] These results, which must not be confused with the p-XC_6H_4 substituent results given in Table 3, are relative to the very different kinds of family parents: H_2O, NH_3, or CH_4, respectively.

The interesting specific behavior of p-XC_6H_4 substituents relative to their conventional C_6H_5OH, $C_6H_5NH_2$, or $C_6H_5CH_3$ parents is that $\rho_F = 19 \pm 1$ and $\rho_\alpha \simeq 0$ for all three of these families even though (as already noted) the ρ_R values ($50 < 55 < 78$) significantly increase in the order p-$XC_6H_4OH < p$-$XC_6H_4NH_2 < p$-$XC_6H_4CH_3$. These results show that, at the relatively large substituent distances involved with the p-XC_6H_4OH, p-$XC_6H_4NH_2$, and p-$XC_6H_4CH_3$ acids, the different degrees of charge localizations in the $-O^-$, $-NH^-$, and $-CH_2^-$ anionic centers lead to no significant differentiations in the distant substituent dipolar and polarizability interactions.

(b) Effects of Multiple Substitution on the Inherent Acidities of Ammonia and Methane. For NH_3, the results are given in Table 4. In general, the results display notable nonadditive substitution effects. In this connection, the multiple substituent effects in both NH_3 and CH_4 (Table 5) are in marked contrast with the effects of first and second substitution of groups in the *meta* positions of benzene derivatives. Essentially perfect additive behavior has been observed for such substituents in benzoic acids, phenols, anilines, and toluenes in their gas-phase acidities.[13] These additive effects involve largely electrostatic field/inductive effects. The nonadditive behavior shown in Table 4 can be attributed to two principal causes: (i) there is a significant lessening (saturation) of the donor anionic charge distribution at the deprotonation site with successive introduction of increasingly strong π-acceptor substituents; (ii) there are repulsive steric interactions between the nonbonded charge-enriched substituents of the polysubstituted anions. The resulting anionic destabilization involves some combination of this and the concomitant decrease in stabilizing π-electron delocalization that results from twisting from coplanarity.

Table 4. Effect of the Second Substitution Compared to the First in Ammonia, $-\delta\Delta G$ (kcal/mol)[a]

substituent, X	XNH_2	X_2NH	diff.[b]	ratio[b]
H	0.0[c]	0.0[c]		
F		32.8		
$(CH_3)_3Si$	25.1	43.2	18.1	1.72
C_6H_5	37.0	52.3	15.3	1.41
CH_3CO	41.0	56.3	15.3	1.37
C_6F_5	54.8	79.7	24.9	1.45
CF_3CO	59.4	88.6	29.2	1.49
4-C_5F_4N	63.3	90.0	26.7	1.42
CF_3SO_2	74.8	104.3	29.5	1.32
$C_4F_9SO_2$	81.0	112.0	31.0	1.38

[a] Based upon data in Tables 1 and 2. [b] Difference = $\delta\Delta G(X_2NH) - \delta\Delta G(XNH_2)$; Ratio = $\delta\Delta G(X_2NH)/\delta\Delta G(XNH_2)$. [c] For NH_3, ΔG_{acid} = 396.1 kcal/mol.

Table 5. Nonadditive Effects of Second and Third Substitutions on Gas-Phase Acidities of Methanes, $-\delta\Delta G$ (kcal/mol)

substituent	XCH_3	X_2CH_2	diff.[b]	ratio[b]	X_3CH	diff.[c]	ratio[c]
H	0.0[d]	0.0[d]			0.0[d]		
F	≤18[e]	27.0	≥9	≥1.5	39.3	12.3	≥2.1
C_6H_5	34.8	50.3	15.5	1.45	55.7	5.4	1.60
CF_3	38.0[f]	64.6	26.6	1.70	81.7	17.1	2.15
CN	44.5	80.2	35.7	1.80	115.0[f]	34.8	2.6
CH_3CO	46.6	71.8	25.2	1.54	79.6	7.8	1.71
C_6F_5	53.8				90.9		1.69
CF_3CO	66.4	97.8	31.4	1.47	107.6	9.8	1.62
CF_3SO_2	68.7	106.7	38.0	1.55	117.0	10.3	1.70
$C_4F_9SO_2$		119.8					

[a] Based upon data in Tables 1 and 2. [b] Difference = $\delta\Delta G(X_2CH_2) - \delta\Delta G(XCH_3)$; ratio = $\delta\Delta G(X_2CH_2)/\delta\Delta G(XCH_3)$. [c] Difference = $\delta\Delta G(X_3CH) - \delta\Delta G(X_2CH_2)$; ratio = $\delta\Delta G(X_3CH)/\delta\Delta G(XCH_3)$. [d] For CH_4, ΔG_{acid} = 408.5 kcal/mol. [e] Estimated assuming that $\Delta G_{acid}(CH_3F) \geq \Delta G_{acid}(CH_3Cl)$. [f] Calculated values, cf. Tables 6, 9, and 11.

For CH_4, bis- and tris-substitutional effects on inherent acidities are similar to those for NH_3, as shown by the results summarized in Table 5. Tris-substitutional effects can be seen, as expected, to be even less additive than for bis-substitution. The most additive behavior observed is for $CH_2(CN)_2$, and this can be attributed to the coplanarity of the anion and the weak steric interaction (poorer proximity) of the two CN substituents.

The ratios of $\delta\Delta G(X_2CH_2)/\delta\Delta G(XCH_3)$ and $\delta\Delta G(X_2NH)/\delta\Delta G(XNH_2)$ are approximately equal for corresponding substituents. The values of these ratios (1.5 ± 0.1) are all quite similar for the C_6H_5, CH_3CO, CF_3CO, and CF_3SO_2 substituents. For these same substituents, the ratios $\delta\Delta G(X_3CH)/\delta\Delta G(XCH_3)$ are also of similar value, 1.7 ± 0.1. For the CF_3 substituents, the ratios of $\delta\Delta G(X_2CH_2)/\delta\Delta G(XCH_3)$ and of $\delta\Delta G(X_3CH)/\delta\Delta G(XCH_3)$ are both larger (better additivity) but all effects of successive substitutions are distinctly short of that expected from additivity. Nonetheless, the effects observed are relatively large and significant. It is unfortunate that the $CH(CN)_3$ gas-phase acidity has not yielded to determination in spite of our various attempts. However, an apparently reasonable value has been calculated (cf. Table 9).

Table 6 considers the inherent acidifying effects of differently polysubstituted ammonias and methanes. The observed acidities for 25 such compounds are given together with the additive acidifying effects calculated on the basis of the sum of the separate single substituent effects. Some of the results in Tables 4 and 5 are included in this form in Table 6 for the purposes of comparison. The entries in Table 6 are made according to the

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(20) (a) Koppel, I. A.; Anvia, F.; Taft, R. W.; Burk, P. Unpublished results. (b) Burk, P.; Koppel, I. A. *J. Mol. Struct. (THEOCHEM)* **1993**, *282*, 277 and references therein.

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Table 6. Fractional Additivity for ΔG_{acid} Values of Polysubstituted Derivatives of Ammonia[a] and Methane[b]

acid	ΔG_{acid} (kcal/mol)	$\delta\Delta G$[c] (kcal/mol)	$\Sigma\delta\Delta G$[d] (kcal/mol)	fractional additivity[g]
$(C_6H_5)_3CH$	352.8	55.7	104.4	0.53
$(CF_3CO)_3CH$	300.9	107.6	195.9	0.55
$(C_6F_5)_2CHC_6H_5$	328.4	80.1	142.4	0.56
$(C_6F_5)_3CH$	317.6	90.9	161.4	0.56
$(CH_3CO)_3CH$	328.9	79.6	139.8	0.57
$(CF_3SO_2)_3CH$	289.0	119.5	206.1	0.58
$(CF_3SO_2)_2CHC_6H_5$	301.3	107.2	172.2	0.62
$(C_6F_5)_2CHCN$	312.4	96.1	152.1	0.63
2,4,6-$(CF_3SO_2)_3C_6H_2CH_2CHO$	304.8	103.7	152.2	0.68
$(CF_3SO_2)_2NH$	291.8	104.3	150.2	0.69
$(C_4F_9SO_2)_2NH$	284.1	112.0	162.0	0.70
(4-$C_5F_4N)_2NH$	306.1	90.0	126.6	0.71
p-$NO_2C_6H_4CH(CN)_2$	299.8	108.7	152.2	0.71
$(CF_3)_3CH$	326.8	81.7	114[e]	0.72
$CH_3CONHC_6H_5$	340.6	55.5	78.0	0.72
$CH_3COCH_2COCH_3$	343.3	65.2	90.0	0.72
$CF_3CONHC_6H_5$	326.4	69.7	96.0	0.72
$(CF_3CO)_2NH$	307.5	88.6	118.8	0.74
$C_6H_5COCH_2COCH_3$	333.0	75.5	100.8	0.75
$C_6H_5CH(CN)_2$	314.3	94.2	123.8	0.76
$CF_3COCH_2COCH_3$	322.0	86.5	111.9	0.77
p-$NO_2C_6H_4CH_2CN$	322.7	85.8	107.7	0.80
$C_6H_5CH_2CN$	344.1	64.4	79.3	0.81
$C_6H_5COCH_2CN$	326.3	82.2	98.7	0.83
$(CF_3)_2CH_2$	343.9	64.6	(76)[e]	0.85
$CH_3SO_2CH_2CN$	328.6	79.9	94.1	0.85
$NCCH_2CO_2C_2H_5$	333.6	74.9	87.9	0.85
$CH(CN)_3$	(293)[f]	(115)	133.5	0.86
$[(CH_3)_3Si]_2NH$	352.9	43.2	50.2	0.86
$CH_2(CN)_2$	328.3	80.2	89.0	0.90

[a] For NH_3, ΔG_{acid} = 396.1 kcal/mol. [b] For CH_4, ΔG_{acid} = 408.5 kcal/mol. [c] ΔG for NH_3 or CH_4 minus ΔG for the given acid. [d] Sum of the single substituent $\delta\Delta G$ values for each substitution for H in the acid structure. [e] Based upon calculated value of 38 kcal/mol for CF_3CH_3, cf. Tables 5 and 9. [f] Based upon calculated value of 115 kcal/mol for $CH(CN)_3$, cf. Tables 5 and 9. [g] $\delta\Delta G/\Sigma\delta\Delta G$.

increasing ratio (called the fractional additivity) of the total observed substituent effect $\delta\Delta G$ divided by the corresponding calculated additive value, $\Sigma\delta\Delta G$. The new results in Table 6 follow the same pattern as that discussed for the results of Tables 4 and 5. Namely, CN or CN with another substituent gives the most additive behavior. The $(C_6H_5)_3CH$ acid gives the lowest fractional additivity. The CF_3 and $(CH_3)_3Si$ substituents give the next best additivity to that for CN.

On the basis of results in Table 5, we may estimate that $HC(CN)_3$ would have $\Delta G_{acid} = 408.5 - 2.6(44.5) = 293$. Further, fractional additivities for XCH_2CN and $XCH(CN)_2$ are indicated in Table 6 to be relatively large (although not as good as for $CH_2(CN)_2$ or $CH(CN)_3$)). Thus, compounds like $CF_3SO_2CH(CN)_2$ may be predicted to be superstrong acids, with ΔG_{acid} (in this case) probably ca. 281 kcal/mol (cf. Table 10).

Although the values of fractional additivity in Table 6 appear to be largely determined by the thermodynamic stabilities of the anions, there may be contributions from certain specific interactions in the neutral acids, e.g., chelated enol forms, or from statistical and other entropy factors (no corrections have been made for these, cf. the Experimental Section). The extensive formation of a cyclic chelated enol form can decrease the observed acidity by as much as 8–10 kcal/mol. Hexafluoroacetylacetone in the gas phase is known to be in the cyclic chelated enol form.[20b] A similar situation probably prevails for $(CF_3CO)_2NH$. A FT-IR spectral investigation was performed for us by M. Berthelot on gas-phase samples of $(CF_3SO_2)_2NH$, $CF_3SO_2NHCOCF_3$, and $C_4F_9SO_2NHCOCF_3$. There was no detectable amount of enol observed in their spectra. Only NH vibrations at 3344, 3424, and 3422 cm^{-1}, respectively, were observed. The latter two compounds have CO vibrations at 1814–1815 cm^{-1}. A much more extensively fluorinated mixed imide $C_4F_9SO_2NHCOC_7F_{15}$, however, showed a gas-phase spectrum with significant amounts of free enol (ca. 10%) and bonded enol (ca. 40%).

Table 7. Effect of *Meta*- and *Para*-Substituents on the Gas-Phase Acidities, $-\delta\Delta G^a$ (kcal/mol), of Substituted Phenylacetonitriles (PhAN) and Phenylmalononitriles (PhMN)

substituent	PhAN[b]	PhMN[c]	substituent	PhAN[b]	PhMN[c]
p-OCH_3	–0.9	–1.1	*m*-CF_3	8.8	7.3
p-CH_3	–0.9	–1.4	*m*-CN	11.9	9.9
H	0.0[d]	0.0[d]	*m*-NO_2	13.2	11.3
p-Cl	5.6	5.3	*p*-NO_2	21.4	14.8
m-Cl	6.6	5.5			

[a] A positive sign denotes greater acidity than that of the parent acid. [b] From refs 12 and 13. [c] From this work. [d] ΔG_{acid} = 344.1 kcal/mol for PhAN and 314.3 kcal/mol for PhMN.

In view of the foregoing results, the smaller observed difference (2.0 kcal/mol, Table 1) in the gas-phase acidity of $CF_3CONHSO_2CF_3$ and $CF_3CONHSO_2C_4F_9$ compared with the larger difference (4.5 kcal/mol) between the pair $CF_3SO_2NHSO_2CF_3$ and $CF_3SO_2NHSO_2C_4F_9$ appears not to be explained by enol formation. It has been suggested[24] that enolization of a different kind may increase (not decrease) gas-phase acidity:

$$(CF_3SO_2)_2NH \rightleftharpoons CF_3(O)({=}NSO_2CF_3)SOH$$

where the latter enol form can be derived from CF_3SO_3H by replacement of =O by $=NSO_2CF_3$. Our results showing that $(CF_3SO_2)_2NH$ is only ca. 8 kcal/mol more acidic than triflic acid leave this suggestion in an uncertain state.

(c) Effects of Substitution in Aromatic Acids. The *m*- and *p*-substituted phenylmalononitriles (PhMNs) of Table 7 give an informative linear free energy relationship (LFER) with corresponding gas-phase acidities of phenylacetonitriles (PhANs) that had been determined at UCI previously.[13,14] The linear regression equation for the unsubstituted and eight substituted derivatives (Table 7) is the following:

$$-\delta\Delta G_{acid}(\mathrm{PhMN}) = (0.76 \pm 0.05)[(-\delta\Delta G_{acid}(\mathrm{PhAN})] + (0.2 \pm 0.5) \quad (6)$$

where $n = 9$, $R = 0.988$, and SD = 1.0 kcal/mol. A rational deviation occurs for the *p*-NO_2 substituent, as is shown by the much more precise LFER (eq 7) that is based upon the eight nonconjugated substituents (p-OCH$_3$, p-CH$_3$, H, p-Cl, m-Cl, m-CF$_3$, m-CN, and m-NO$_2$):

$$-\delta\Delta G_{\text{acid}}(\text{PhMN}) = (0.87 \pm 0.02)[(-\delta\Delta G_{\text{acid}}(\text{PhAN})] - (0.2 \pm 0.2) \quad (7)$$

where $n = 8$, $R = 0.998$, and SD = 0.3 kcal/mol.

The p-NO$_2$PhMN acid is measured to be 3.0 kcal/mol less acidic than predicated by eq 7. This deviation provides a further example of reduced acidity (electronic "saturation") when two or more strong conjugated π-electron-acceptor substituents are competing for the carbanion charge. That is, considered as a substituted methane, the PhMN anion has p-NO$_2$C$_6$H$_4$ and two CN's that are competing, whereas in the corresponding PhAN anion, p-NO$_2$C$_6$H$_4$ competes with only one CN group. The result is a greater p-NO$_2$ substituent effect for p-NO$_2$C$_6$H$_4$CH$_2$CN. The additivity approach, $\Sigma\delta\Delta G$, for the above substituents in methane gives (in kcal/mol) 107.7 for p-NO$_2$C$_6$H$_4$CH$_2$CN and 152.2 for p-NO$_2$C$_6$H$_4$CH(CN)$_2$ from which one obtains fractional additivities of 0.80 and 0.71, respectively.

The acidity of 2,4,6-trinitrotoluene (TNT) relative to toluene is not additive, but the fractional additivity of 0.83 is relatively large. The 2,4,6-trinitro effect is 65.3 kcal/mol, and the separate individual effects of o-NO$_2$ and p-NO$_2$ in toluene are 25.1 and 28.4 kcal/mol, respectively, giving 0.83 (65.3/78.6). Unfortunately, the o-CF$_3$SO$_2$C$_6$H$_4$CH$_3$ acidity is not available to use for a similar analysis of the ΔG_{acid} value for 2,4,6-(CF$_3$SO$_2$)$_3$C$_6$H$_2$CH$_3$. It will be noted that there is a larger difference in acidity between TNT and p-NO$_2$C$_6$H$_4$CH$_3$ ($-\delta\Delta G_{\text{acid}}$ = 36.3 kcal/mol) than between 2,4,6-(CF$_3$SO$_2$)$_3$C$_6$H$_2$CH$_3$ and p-CF$_3$SO$_2$C$_6$H$_4$CH$_3$ ($-\delta\Delta G_{\text{acid}}$ = 35.0 kcal/mol).

The enhancement in acidity in the nitrophenols (between 2,4,6-(NO$_2$)$_3$C$_6$H$_2$OH and p-NO$_2$C$_6$H$_4$OH) is much smaller (18.4 kcal/mol). These results indicate a major steric repulsive interaction between the o-NO$_2$ substituent and the phenoxide center as compared to that in the benzyl anions. Although chelation in the free acid form (internal H-bonding, OH···ONO) contributes to the acid weakening effects, it must be secondary in importance to the anion destabilization effect. This conclusion is supported by the smaller increase in acidity between 2,4,6-(NO$_2$)$_3$C$_6$H$_2$OH and 2,4-(NO$_2$)$_2$C$_6$H$_3$OH (5.5 kcal/mol) than between 2,4-(NO$_2$)$_2$C$_6$H$_3$OH and p-NO$_2$C$_6$H$_4$OH (12.9 kcal/mol).

The greater effects of two o-NO$_2$ groups in p-NO$_2$C$_6$H$_4$CH$_3$ (the 36.3 kcal/mol effect above) compared to the corresponding effect of 35.0 kcal/mol (above) for two *ortho* CF$_3$SO$_2$ groups in p-CF$_3$SO$_2$C$_6$H$_4$CH$_3$ indicate (because the p-CF$_3$SO$_2$ effect on toluene acidity is 4.6 kcal/mol greater than the p-NO$_2$ effect) that there is greater steric destabilization in the bis(o-trifyl)-substituted benzyl carbanion.

We have observed an ultimate for anionic repulsive electronic "saturation" and accompanying effects of twisting from planarity in the 2,4,6-(CF$_3$SO$_2$)$_3$C$_6$H$_2$CH$_2$X family of acids. The gas-phase acidity order is X = CH$_3$CO < H < NO$_2$ < HCO. Further, from Table 1, it will be seen that the overall acidity increase for this family covers the scant range of only 1.9 kcal/mol! This is very remarkable compared to the effects of these same substituents in the XCH$_3$ family, where the order of increasing acidities is H < CH$_3$CO < HCO < NO$_2$ and the overall range is 58.8 kcal/mol.

Perfluorophenyl Acids. Perfluorophenyl groups are of frequent use in the chemistry of organometallic and other compounds. The effects on inherent gas-phase acidities of C$_6$F$_5$ compared to corresponding C$_6$H$_5$ substituted compounds are of interest. The following results are included in this report (in kcal/mol): $-\delta\Delta G_{\text{acid}}$(C$_6F_5CH_3$ − C$_6$H$_5$CH$_3$), 19.0; $-\delta\Delta G_{\text{acid}}$(C$_6F_5NH_2$ − C$_6$H$_5$NH$_2$), 17.8; $-\delta\Delta G_{\text{acid}}$(C$_6F_5CO_2$H − C$_6H_5CO_2$H), 17.8; $-\delta\Delta G_{\text{acid}}$((C$_6F_5$)$_2$NH − (C$_6H_5$)$_2$NH), 27.4; $-\delta\Delta G_{\text{acid}}$(C$_6F_5$OH − C$_6H_5$OH), 21.5; $-\delta\Delta G_{\text{acid}}$(C$_6F_5CH_2$CN − C$_6H_5CH_2$CN), 16.5; $-\delta\Delta G_{\text{acid}}$(C$_6F_5$CH(CN)$_2$ − C$_6$H$_5$CH(CN)$_2$), 10.5. McMahon and Kebarle have reported[21] the following substituent effects on the gas-phase benzoic acid acidities: o-F, 2.3; m-F, 7.6; p-F, 5.8 kcal/mol (giving 25.6 kcal/mol as the additive effect for C$_6$F$_5$ relative to C$_6$H$_5$). The above observed effect in benzoic acid is therefore of 0.70 fractional additivity. There are insufficient data to do a similar analysis for the other C$_6$F$_5$ substituted CH acids. There appears to be a crude trend for fractional additivity to decrease as more anionic charge is delocalized from the phenyl ring by side chain substituents.

Para-substituted X-C$_6$F$_4$CH(CN)$_2$ compounds given in Table 1 are in the expected acidity order CH$_3$ < H < F < CF$_3$, but quantitative comparisons with the corresponding substituted C$_6$H$_5$CH(CN)$_2$ acids are not possible. The overall range of acidities appears to be larger for the latter series of acids.

4-Perfluoropyridyl Acids. The replacement of a *para*-CF fragment of the C$_6$F$_5$ group by a nitrogen atom leads to substantially stronger acidity. Tables 1 and 2 show greater acidities for 4-OH-C$_5$F$_4$N compared to HOC$_6$F$_5$ and for 4-NH$_2$-C$_5$F$_4$N compared to H$_2$NC$_6$F$_5$ by 9.5 and 8.5 kcal/mol, respectively. An acidifying effect of 10.0 kcal/mol accompanies the substitution of the 4-C$_5$F$_4$N group for C$_6$F$_5$ in C$_6$F$_5$CH(CN)CO$_2$C$_2$H$_5$. The replacement of a C$_6$F$_5$ group by a 4-C$_5$F$_4$N group in (C$_6$F$_5$)$_2$CHCN and in (C$_6$F$_5$)$_2$NH increases the acidity of these compounds by 6.6 and 5.6 kcal/mol, respectively. Replacement of the second C$_6$F$_5$ group by 4-C$_5$F$_4$N in the same compounds results in further increases (by 3.5 and 4.8 kcal/mol, respectively) in their intrinsic acidities. The comparison of acidity (Table 1) of (4-C$_5$F$_4$N)$_2$CHCN and (p-CF$_3$C$_6$F$_4$)$_2$CHCN shows that the acidifying effects of 4-C$_5$F$_4$N and p-CF$_3$C$_6$F$_4$ groups are practically equal.

Superacceptor Substituents. Yagupolskii and co-workers[17,22] have demonstrated through the use of the substituent F-NMR chemical shift method[23] that replacement by the =NSO$_2$CF$_3$ group of an oxygen doubly bonded to S, P, and I systems yields superstrong electron-acceptor substituents. These specifically include –S(O)(=NSO$_2$CF$_3$)CF$_3$, –P(=NSO$_2$CF$_3$)(C$_3$H$_7$)$_2$, and –I=NSO$_2$CF$_3$.

We report here that the determination of the gas-phase acidity of the p-CF$_3$(O)(=NSO$_2$CF$_3$)SC$_6$H$_4$NH$_2$ (**I**) has confirmed the superacceptor ability of the first substituent above. The value of ΔG_{acid} is found to be 313.4 ± 0.4 kcal/mol, or 34 pK_a units stronger than aniline.[24] **I** is very much more acidic (by 13.1 pK_a units) than the most acidic previously measured substituted aniline, p-CF$_3$SO$_2$C$_6$H$_4$NH$_2$. The remarkably great acidity of **I** is further shown by its stronger gas-phase acidity than that of any of the following acids (ΔG_{acid} value is given in parentheses in kcal/mol): p-nitrophenol (320.9), HBr (318.2), CF$_3$CO$_2$H (316.3), p-trifylphenol (315.7), and CH$_3$SO$_3$H (315.0) (see Table 1).

It is impressive that the measured acidity of **I** is well predicted by the σ_F and σ_R parameters (1.17 and 0.38, respectively) obtained[18] from the F-NMR shifts for the corresponding m- and p-substituted fluorobenzenes in CH$_2$Cl$_2$ solution. Equation 8 was obtained[12,13] previously from the gas-phase acidities of nine *para*- (+R) substituted anilines relative to aniline:

$$-\delta\Delta G_{\text{acid}} = (0.4 \pm 0.2) + (19.4 \pm 0.4)\sigma_F + (54.9 \pm 1.7)\sigma_R \quad (8)$$

Substitution of the above values for σ_F and σ_R into eq 8 gives for **I** $-\delta\Delta G_{\text{acid}}$ = 44.0 ± 1.5 kcal/mol compared to the experimental value of 45.7 ± 0.4 kcal/mol. It is of interest also that the

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electrostatic field effect term for the acidity of I is estimated from the σ_F value to be 22.7 kcal/mol, slightly more than the resonance effect term (54.9)(0.38) = 20.9 kcal/mol. A similar situation prevails for the gas-phase acidities estimated in this manner (with σ_F and σ_R values from ref 17) for aniline substituted with p-P(=NSO_2CF_3)(C_3H_7)$_2$ [ΔG_{acid}(calcd) = 322.9 ± 1.5 kcal/mol] and with p-I=NSO_2CF_3 [ΔG_{acid}(calcd) = 328.6 ± 1.5 kcal/mol], although in both of these cases the field effects are quite predominant.

While this work was in progress, the following additional compounds were prepared in the laboratories of L.M.Y. and Yu.L.Y. (see ref 34) which contained superacceptor substituents of the aforementioned type: ($C_6H_5S(O)(=NSO_2CF_3)NH_2$, p-$CH_3C_6H_4S(O)(=NSO_2CF_3)NH_2$, p-$CH_3C_6H_4S(=NSO_2CF_3)_2NH_2$, and p-$NO_2C_6H_4S(=NSO_2CF_3)NHSO_2CF_3$. Unfortunately all our attempts to measure their gas-phase acidities have failed because under low energy (2–3 eV) electron impact the conjugate anions did not form (only fragment ions), in either the absence or presence of *iso*-amyl nitrite in the ICR cell. However, experiments in DMSO[25] indicate that p-$CH_3C_6H_4S(=NSO_2CF_3)_2NH_2$ is more acidic than $C_6H_5SO_2NH_2$ by about 13 powers of 10.

Theoretical Calculations. Ab initio calculations[26] have been carried out to determine their usefulness in interpretation and prediction of experimental gas-phase acidities of very strong acids. These acids involve large molecules, frequently with perfluoroalkyl groups in combination with second row element substituent, as in the CF_3SO_2 substituent. Machine time is consequently very large. Great concern for any usefulness is also apparent in the report[26] that gas-phase acidities of seven monosubstituted methanes *relative to* methane are only reproduced by 3-21G//3-21G calculations of $\delta\Delta E$ to a mean deviation of 22 kcal/mol and by 3-21+G//3-21+G calculations to a mean of 10 kcal/mol. Even in the latter, the acidity of nitromethane relative to methane is calculated to be too strong by 31 kcal/mol. A further uncertainty in the comparison of theoretical $\delta\Delta E$ values with corresponding $\delta\Delta G_{acid}$ values is the role of $\delta\Delta E_{1/2h\nu o}$ and $T\Delta S$ contributions to the latter.

For the simple molecules CH_4, HCN, NH_3, H_2, and HF, DeFrees and McLean[27] obtained successful high-level calculations of (absolute) ΔG_{acid} values. The agreement with experimental values is to within ±0.7 kcal/mol for the MP4/6-311++G(3df,3pd) calculated values using a CID/6-31(d) level of theory to obtain optimized structures. These authors suggested that MP2/6-311++G(d,p) calculations might be particularly useful for large molecules. Our objective was to see if useful calculations of absolute acidities (those in agreement with experimental ΔG_{acid} values to within ±2 pK_a units) can be achieved for very strong large acids.

ΔG_{acid} calculations were first carried out using 3-21G//3-21G (or 3-21G*//3-21G* used for the S-containing acids) with the Gaussian 88, 90, and 92 programs on UCI Convex C240 computer. A series of 14 CH acids ranging from CH_4 to $C_6H_5CH(CN)_2$ were selected. Their ΔG_{acid}(exptl) values cover the range 408.5–314.3 kcal/mol. Selections for calculation were chosen, first for coplanarity of anions (all but CH_3^- were found by the calculations to be coplanar about the carbanion carbon) and second for the presence of moderate to strong π-electron-pair-acceptor substituents in a variety of structures.

Table 8. Values of ΔE_{el}, $\Delta E_{1/2h\nu o}$, $T\delta S$, and ΔG_{theor} Obtained Using HF/3-21G//3-21G[a]

acids	ΔE_{el}	$\Delta E_{1/2h\nu o}$	$T\delta S$	ΔG_{theor}	ΔG_{exptl}	ΔG_{theor} – ΔG_{exptl}
CH_4	462.8	11.6	8.1	443.6	408.5	35.1
$C_6H_5CH_3$	415.0	10.4	8.1	397.4	373.7	23.7
CH_3CN	405.0	10.4	7.9	387.5	364.1	23.4
CH_3COCH_3	401.7	8.9	8.6	385.9	361.9	24.0
CH_3CHO	397.4	8.9	8.6	380.1	359.0	21.1
$C_6H_5CH_2CN$	376.7	9.8	6.5	360.6	341.1	19.5
fluorene	381.7	9.9	7.1	365.2	344.0	21.2
HCN	379.1	7.4	7.6	363.8	343.8	20.0
$CF_3SO_2CH_3$	378.1[b]	10.2[b]	7.2[b]	361.0[b]	339.8	21.2
CH_3COCN	371.2	8.9	7.8	355.4	337.7	15.7
$CH_2(CN)_2$	357.2	9.3	7.6	340.8	328.3	12.5
p-$CNC_6H_5CH_2CN$	357.8	9.4	6.5	342.3	327.9	14.4
9-cyanofluorene	353.1	9.2	7.4	336.9	321.4	15.5
$C_6H_5CH(CN)_2$	342.5	8.8	6.5	327.6	314.3	13.3

[a] Basis compared with their corresponding ΔG_{exptl} values, in kcal/mol at 298 K. [b] HF/3-21G*//3-21G* calculations.

The above calculated ΔG_{acid} values (except that for CH_3NO_2, cf. Table 8) give a remarkably good linear correlation with the corresponding experimental ΔG_{acid} values (n = 14, R = 0.9981, SD = 1.6 kcal/mol (i.e., ca. 1 pK_a unit)):

$$\Delta G_{acid}(\text{exptl}) = (0.811 \pm 0.014)\Delta G_{acid}(\text{theor}) + (49.7 \pm 5.3) \quad (9)$$

The ΔE_{el}, $\Delta E_{1/2h\nu o}$ and $T\Delta S$ values obtained by these calculations are recorded in Table 8. Values of calculated ΔG_{acid} are not equal to corresponding ΔE_{el} values, but are less by 19.2 (CH_4) to 14.9 ($PhCH(CN)_2$) kcal/mol over the above indicated range of experimental values of 93.8 kcal/mol. There is over this range an approximate 5% monotonic decrease in the difference between the corresponding calculated ΔE_{el} and ΔG_{acid} values, which is due to the effects of $\Delta E_{1/2h\nu o}$ (predominant) and of $T\Delta S$. Finally, of particular importance, the values of the difference, ΔG_{acid}(theor) – ΔG_{acid}(exptl), also decrease approximately monotonically from 35.1 kcal/mol for CH_4 to 12.9 kcal/mol for $C_6H_5CH(CN)_2$ (cf. Table 8). This strongly suggests that at this level of theory the internal anionic repulsion energies are calculated to be too large (therefore, ΔG_{acid} is too large). With increasing electron delocalization in the carbanion, presumably the anionic repulsion energy calculation (and thus the calculation of ΔG_{acid}) improves.

Similar results also have been obtained for the series of XNH_2 acids NH_3, $C_6H_5NH_2$, CH_3CONH_2,[26c] $HCONH_2$,[26c] H_2NCN, CF_3CONH_2,[26c] and $CF_3SO_2NH_2$ (n = 7; R = 0.998; SD = 1.5 kcal/mol):

$$\Delta G_{acid}(\text{exptl}) = (0.705 \pm 0.018)\Delta G_{acid}(\text{theor}) + (83.7 \pm 7.0) \quad (10)$$

These results give ΔG_{acid}(theor) – ΔG_{acid}(exptl) = 47.7 kcal/mol for NH_3. Values of this difference then decrease approximately monotonically to 12.1 kcal/mol for $CF_3SO_2NH_2$. Both the larger intercept and the smaller slope for NH compared with CH acids (eq 9) are in the direction expected from poorer calculation of the internal anionic repulsion energies for charged localized XNH^- anions. All of the above differences, as well as the significant deviation of CH_3NO_2 from eq 9, point to the drawbacks of conclusions and estimated ΔG_{acid} values that are based upon empirical correlations between relative values of ΔE_{el} and corresponding $\delta\Delta G_{acid}$(exptl) values.

We turned next to the MP2/6-311++G(d,p) basis and learned that calculations of absolute gas-phase ΔG_{acid} values can be obtained for very strong acids that are in agreement with experimental ΔG_{acid} values to within ±2 pK_a units (<3 kcal/mol). Our results also give evidence that at this basis the inclusion of MP2 makes little or no improvement over HF calculations for acids of equal or of greater strength than that for acetyl cyanide. The results are given in Table 9 for fully optimized MP2 or HF/6-311++G(d,p) calculations and for single point calculations at this level obtained using the optimized structures, the $\Delta E_{1/2h\nu o}$, and the $T\Delta S$ values of the corresponding HF/3-21G//3-21G (or

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Table 9. Comparison of Experimental and Theoretically Calculated ΔG_{acid} Values (kcal/mol)

acid	MP2/6-311++G(d,p) 3-21G//3-21G	FOPT[a]	SP[b]	exptl	eq 9
CH_4	443.6	410.6	409.2	408.5	409.3
CH_3CN	387.5	367.2	366.8	364.1	363.8
CH_3NO_2	355.6	352.3[c]	358.8	349.7	338.1
HCN	363.8	343.7	342.0	343.8	344.6
CH_3COCN	355.4		336.2	337.7	337.8
$CH_2(CN)_2$	340.8	328.5	327.8	328.3	326.0
$CH(CN)_3$	303.0	294.2[c]	293.5	293[d]	295.4
$CF_3SO_2CH(CN)_2$	282.3[e]			282[d]	278.6

[a] Calculations fully optimized at this high-level basis. [b] Single point calculations using fully optimized geometries at the 3-21G basis. [c] Calculations fully optimized at the Hartree–Fock level only. [d] Estimate based on fractional additivity of 0.86 for $CH(CN)_3$ and 0.80 for $CF_3SO_2CH(CN)_2$. [e] 3-21G*//3-21G*.

Table 10. Comparison of Values of $\Delta E_{1/2h\nu o}$ and $T\delta S$ Calculated at the Two Levels of HF Theory Based upon Corresponding Optimized Structures

acid	$\Delta E_{1/2h\nu o}$ (kcal/mol) 3-21G(G*)	$\Delta E_{1/2h\nu o}$ (kcal/mol) 6-311++G(d,p)	$T\delta S_{298}$ (kcal/mol) 3-21G	$T\delta S_{298}$ (kcal/mol) 6-311++G(d,p)
CH_4	11.6	10.8	8.1	7.5
CH_3CN	10.4	10.5	7.9	6.7
CH_3NO_2	9.0	9.3	7.9	7.4
HCN	7.4	7.8	7.6	7.5
CH_3COCN	8.7		7.8	
$CH_2(CN)_2$	9.0	9.3	7.6	7.7
$CH(CN)_3$	8.4	8.3	7.6	7.0
$CF_3SO_2CH(CN)_2$	8.1[a]		7.2[a]	

[a] HF/3-21G*//3-21G*.

Table 11. Additional Predicted Gas-Phase Acidity ΔG_{acid} Values (kcal/mol) Calculated from Eq 9

acid	ΔG_{acid} eq 9	ΔG_{acid} theor
CH_3CF_3	371	395.8[a]
$CH_3N{=}N{-}CN$	322	336.2[a]
$CH_3CH{=}NSO_2CF_3$	313	324.7[b]
p-$CNC_6H_4CH(CN)_2$	304	313.5[a]
$CH_3N{=}NSO_2CF_3$	299	307.1[b]
$CH(N{=}NCH_3)_3$	275	277.4[a]

[a] HF/3-21G//3-21G calculated ΔG_{acid} value. [b] HF/3-21G*//3-21G* calculated ΔG_{acid} value.

HF/3-21G*//3-21G*) calculations. Table 10 shows that these $\Delta E_{1/2h\nu o}$ and $T\Delta S$ values are in satisfactory agreement, for present purposes, with the corresponding values obtained at high-level basis.

Table 9 shows that the use of the single point calculation of ΔG_{acid} at the HF/6-311++G(d,p) level and the use of calculations from eq 9 or 10 at the HF/3-21G//3-21G basis (or, if appropriate, HF/3-21G*//3-21G* provide very useful guidelines for indicating interesting and potentially very useful superacid synthetic targets. Work is in progress to attemp to find lower level basis single point calculations of ΔG_{acid} that will be of comparable usefulness for predicting ΔG_{acid} values for superacids with appropriate structures. This possibility appears likely in view of the results given in Table 9 for $CF_3SO_2CH(CN)_2$. Table 11 gives some additional predicted values of ΔG_{acid} obtained by the second method (eq 9) above.

Experimental Section

The gas-phase acidity measurements reported in this paper were performed at the Chemistry Department of the University of California, Irvine, with a pulsed FT ion cyclotron resonance mass spectrometer manufactured by the IonSpec Corp. (Irvine, CA). The major details of the experimental techniques used for the measurements of the equilibrium constants, *K*, of the reversible proton-transfer reaction 2 and experimental $\Delta G = -RT \ln K$ values (given in Table 1) are mostly the same as those previously described.[9c,28] Only significant changes and/or additional procedures will be given here.

All equilibrium measurements were performed at a 1-T uniform magnetic field strength using a one region square (2 × 2 × 2 in.) trapped analyzer cell with the trapping voltage around −1.0 V. The typical operating pressures were in the range of 10^{-6}–10^{-8} Torr. The gas-phase proton-transfer reactions were initiated by a 5–20-ms pulse of a low-energy electron beam (0.5–2.5 eV) through the ICR cell. For the acids whose acidities are lower than that of the hydrogen atom ($\Delta G_{acid} = 312.5$ kcal/mol), the addition of *iso*-amyl nitrite ca. 10^{-7} Torr was used for the initiation of the chemical ionization of the acids studied. For the compounds which are stronger Brφnsted acids than the hydrogen atom, the pulsed beam of electrons acts essentially as the conjugate anion of the hydrogen atom and is a sufficiently strong base to initiate the deprotonation. Reaction times from several to 10 s were usually necessary to reach the equilibrium. All experiments reported here were carried out at cell temperature of 100 °C. The mass spectra and the timeplots for proton- transfer equilibria were acquired and processed in a FT mode. The IonSpec Omega program (version 3.1) was used for these purposes. The equilibrium constants for any proton-transfer reaction 2 were calculated by using the expression:

$$K = A_1^- P_{A_0H} / A_0^- P_{A_1H} \tag{11}$$

where A_1^-or $A_0^-$are the equilibrium abundances (mass spectrometric integrated intensities) of the anions A_1^- (sample) and A_0^- (reference) as measured by the FT-ICR technique, whereas P_{A_0H} and P_{A_1H} are the partial pressures of the neutral acids A_0H and A_1H with appropriate correction factors applied to the direct ion gauge readings for the different ionization cross sections of the various compounds.[9c,28,29]

Each experiment was performed at several ratios of partial pressures and at different overall pressures of the reagents. Arithmetic mean values of K were obtained and used to calculate ΔG_{acid} values at 373 K (see Tables 1 and 2). The latter are in most cases characterized by an average uncertainty (standard deviation) which does not exceed ± 0.2 kcal/mol. Due to the extremely low volatility of the acids involved in the acidity range below ca. 290 kcal/mol, the internal consistency of the ΔG values is ±0.3 to ±0.5 kcal/mol. With a few exceptions, multiple overlaps were performed to insure internal consistency of the data, see Table 1.

The samples of some of the acids studied contained small impurities of more volatile compounds (e.g., moisture, air, solvents, and other unidentified compounds). The "adequate representation" of the major components in these cases was achieved after many repeated freeze–pump–thaw cycles of the sample under vacuum from 10^{-3} to 10^{-8} Torr (depending on the nature of the sample). Positive and negative ion mass scans were used to check the purity of each compound after such degassing and/or sublimation cycles.

Unfortunately, we were not able to generate in our spectrometer the anions needed to determine ΔG_{acid} values for $HClO_4$, $ClSO_3H$, HPO_3, and H_2SO_4. The volatility of FSO_3H is sufficiently high to get a stable signal for the FSO_3^- anion. A direct experiment for the comparison of the acidities of FSO_3H and $MeSO_3H$ indicated that the former was by 1 kcal/mol more acidic than the latter. However, we feel that this apparent value of ΔG_{acid} may be significantly in error because the experimentally measured gross partial pressure for fluorosulfonic acid probably includes some unknown contributions from its highly volatile decomposition products, HF and SO_3. Several unsuccessful attempts were made to liberate cyanoform,[30–32] pentacyanopropene,[33] pentacyanocyclopentadiene,[33] $CF_3SO_2CH(CN)_2$,[34] and $(CF_3SO_2)_2CHCN$[34] from their corresponding salts in order to study their gas-phase acidities. Samples of a number of compounds were found to give no M-1 but only fragment ions in their ICR mass spectra. These compounds include $(FSO_2)_3CH$, $C_4F_9SO_2NHCOC_7F_{15}$, $[2,4,6\text{-}(CF_3SO_2)_3C_6H_2]_2CH_2$, $C_6H_5S(O)({=}NSO_2CF_3)NH_2$, *p*-$CH_3C_6H_4S({=}NSO_2CF_3)_2NH_2$, *p*-$CH_3C_6H_4S(O)({=}NSO_2CF_3)NH_2$, *p*-$NO_2C_6H_4S({=}NSO_2CF_3)NHSO_2CF_3$, $(C_6F_5)_2CH_2$, 1,3,5-$(CF_3SO_2)_3C_6H_3$, $(CF_3)_3CC_6H_5$, and $(CF_3)_3CCH_3$.

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Table 12. Additional New ΔG_{acid} Values (kcal/mol) Obtained for Comparison Purposes Derived from $\delta\Delta G$ Values (kcal/mol) for the Indicated Proton-Transfer Equilibria

acid	ΔG_{acid}	exptl $\delta\Delta G$
F_2NH	36.3	1.4 stronger for $(CH_3)_2CO$ (361.9); 0.7 weaker than for CH_3CN (364.0)
$C_6F_5CH_3$	354.7	0.8 stronger than for m-$FC_6H_4NH_2$ (353.9); 0.6 weaker than for CF_3CH_2OH (354.1)
$(CF_3)_3CNH_2$	350.1	1.5 stronger than for m-$ClC_6H_4NH_2$ (351.6); 0.6 weaker than for m-$CF_3C_6H_4NH_2$ (349.6)
p-$(CF_3)_3CC_6H_4NH_2$	345.9	0.2 weaker than for p-$CF_3C_6H_4NH_2$ (346.0); 0.8 weaker than for p-$CH_3C_6H_4CH_2CN$ (354.0); 1.4 stronger than for 3,5-dimethylpyrazole (347.1)
H_2NCN	344.1	2.0 weaker than for $HC\equiv CCN$ (342.1)
$(CF_3)_2CH_2$	343.9	0.2 weaker than for fluorene (344.0); 0.3 weaker than for o-$CH_3C_6H_4OH$ (343.4); 0.5 weaker than for 9-methoxyfluorene (343.3)
$C_6F_5NH_2$	341.3	2.1 stronger than for p-$CH_3C_6H_4OH$ (343.4); 0.7 weaker than for 3,5-$(CF_3)_2C_6H_3NH_2$ (340.6)
$CH_3SO_2NH_2$	338.8	0.1 stronger than for 1,2,3-triazole (338.9); 0.6 weaker than for $(CH_3)_3CCH_2COOH$ (338.1); 1.0 weaker than for succinimide (338.0)
$C_6H_5SO_2NH_2$	333.2	0.8 stronger than for C_6H_5SH (333.8); 0.7 stronger than for $NCCH_2CO_2Et$ (333.6)
4-$NH_2C_5F_4N$	332.7	equal with that for o-OH-C_6H_4OH
$(CH_3CO)_3CH$	328.9	0.6 weaker than for $CH_2(CN)_2$ (328.3); 2.0 weaker than for CF_3SH (327.5)
$(C_6F_5)_2CHC_6H_5$	328.4	1.8 weaker than for $(CF_3)_3CH$ (326.6)
$C_6F_5CH_2CN$	327.6	0.1 weaker than for CF_3SH (327.1); 1.2 weaker than for $(CF_3)_3CH$ (326.6); 0.7 stronger than for $CH_2(CN)_2$ (328.3)
$(CF_3)_3CH$[a]	326.6	2.1 stronger than for $CH_2(CN)_2$ (328.3); 1.2 stronger than for $C_6H_5SO_2NH_2$; 0.7 stronger than for p-$CNC_6H_4CH_2CN$ (326.3)
p-$CNC_6F_4NH_2$	326.2	2.3 stronger than for $CH_2(CN)_2$ (328.3); 0.2 weaker than for p-$CHOC_6H_4OH$ (326.1)

[a] Koppel, I. A.; Pihl, V.; Koppel, J.; Anvia, F.; Taft, R. W. *J. Am. Chem. Soc.*, submitted.

Since $T\Delta S_{acid}$(298 K) values for many of the acids studied center at 7 ● 0.8 kcal/mol (cf. Tables 8 and 10), it can be assumed for the present purposes that $\delta\Delta G_{373}$ and $\delta\Delta G_{298}$ are nearly the same. With this assumption, the values of ΔG_{acid} at 298 K given in Tables 1 and 2 have been obtained. The di- and tri-substituted methanes and di-substituted ammonias with significant concentrations of chelated enolic forms are likely to involve the largest error in this approximation. In a later report, further evaluations of ΔS_{acid} and of keto–enol equilibria for the above compounds will be made to obtain improved values of ΔG_{298}.

Table 12 gives additional new ΔG_{acid} values that have been obtained for structural effect comparison with literature and Table 1 values for the very strong Brφnsted acids.

Chemicals. When available, the commercial samples of the compounds were used. Samples of the nine substituted phenylmalononitriles of Table 7 were provided by E. M. Arnett. Their preparation and properties have been described.[35] The following compounds were prepared at the Institute of Organic Chemistry in Kiev as previously described: p-$CF_3(O)(=NSO_2CF_3)SC_6H_4NH_2$,[17] p-$CH_3C_6H_4S(O)(=NSO_2CF_3)NH_2$,[34] p-$CH_3C_6H_4S(=NSO_2CF_3)_2NH_2$,[34] $C_6H_5S(O)(=NSO_2CF_3)NH_2$,[34] p-$NO_2C_6H_4S(=NSO_2CF_3)NHSO_2CF_3$,[34] $(CF_3SO_2)_2(CN)CCs$,[34] $(CF_3SO_2)(CN)_2CNa$,[34] $C_4F_9SO_2NH_2$,[36] $(FSO_2)_2CH_2$,[37] $C_6H_5CH(SO_2F)_2$,[38] $C_6H_5CH(SO_2CF_3)_2$,[39] $CF_3SO_2NHC_6H_5$,[40] 2,4,6-$(FSO_2)_3C_6H_2NH_2$,[41] 2,4,6-$(CF_3SO_2)_3C_6H_2CH_3$,[42] 2,4,6-$(CF_3SO_2)_3$- $C_6H_2CH_2NO_2$,[42] 2,4,6-$(CF_3SO_2)_3C_6H_2CH_2COCH_3$,[42] 2,4,6-$(CF_3SO_2)_3C_6H_2CH_2CHO$,[42] [2,4,6-(CF3$SO_2)_3C_6H_2]_2CH_2$,[42] 1,3,5-$(CF_3SO_2)_3C_6H_3$,[42] 2,4,6-$(CF_3SO_2)_3C_6H_2NH_2$,[43] 2,4,6-$(CF_3SO_2)_3$ C_6H_2OH,[43] $(FSO_2)_3CH$,[44,45] p-$(CF_3)_3CC_6H_4NH_2$,[46] and p-$(CF_3)_3CC_6H_5$.[46] The following compounds were prepared at the Institute of Organoelement Compounds in Moscow as previously described: $(CF_3CO)_2CHCO_2CH_3$,[47] $(CF_3CO)_2CHCF_3$,[47] $(C_3F_7CO)_2CHCF_3$,[47] $(CF_3CO)_3CH$,[47] $(C_3F_7CO)_3CH$,[47] and $(CF_3)_3CCH_3$.[48] The samples of the following compounds were prepared as previously described at the Institute of Organic Chemistry in Novosibirsk: p-$CH_3C_6F_4CH(CN)_2$,[49] p-$HC_6F_4CH(CN)_2$,[49] $C_6F_5CH(CN)_2$,[49] $C_6F_5CH(CN)CO_2C_2H_5$,[49] 4-$[CH(CN)CO_2C_2H_5]C_5F_4N$,[49] p-$CF_3C_6F_4CH(CN)_2$,[49] β-$C_{10}F_7CH(CN)_2$,[50] $C_6F_5NH_2$,[51] (4-$C_5F_4N)_2NH$,[52] p-$NO_2C_6H_4NHC_6F_5$,[52] p-$CNC_6F_4NHC_6F_5$,[53] 4-$C_5F_4N(NHC_6F_5)$,[53] p-$CNC_6F_4NH_2$,[53] 4-$NH_2C_5F_4N$,[53] p-$HC_6F_4NHC_6F_5$,[54] $C_6F_5NH_2$,[54] 9-C_6F_5-octafluorofluorene,[55] p-$CF_3C_6F_4CH(CN)C_6F_5$,[56] (4-$C_5F_4N)_2CHCN$,[57] (4-$C_5F_4N)CH(CN)C_6F_5$,[57] 4-OH-C_5F_4N,[58] β-$OHC_{10}F_7$,[59] α-$OHC_{10}F_7$,[60] $(C_6F_5)_3CH$,[61] [a] C_6F_5OH,[61a] $C_6F_5CH_3$,[61a] $(C_6F_5)CHC_6H_5$,[61b] $(C_6F_5)_2CH_2$,[62] $(C_6F_5)_2CHCN$,[62] and p-$(CF_3C_6F_4)_2CHCN$.[63] The following compounds were prepared at Clemson University as previously described: $(C_4F_9SO_2)_2NH$,[36] $(C_4F_9SO_2)_2CH_2$,[39] $(CF_3SO_2)_2CH_2$,[39] $(CF_3)_2CH_2$,[64] $(CF_3)_2NH$,[65] $(CF_3SO_2)_2NH$,[7,66] $(CF_3SO_2)_3CH$,[67] $CF_3CONHSO_2CF_3$,[68] $C_3F_7CONHSO_2CF_3$,[68] $C_7F_{15}CONHSO_2CF_3$,[68] $CF_3CONHSO_2C_4F_9$,[68] $C_3F_7CONHSO_2C_2F_5$,[68] $C_3F_7CONHSO_2C_4F_9$,[68] $CF_3SO_2NHSO_2C_6F_{13}$,[69] $CF_3SO_2NHSO_2C_4F_9$,[70] $CF_2(CF_2SO_2)_2NH$,[70,71] $(C_2F_5SO_2)_2$-

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NH,[72] $CF_3SO_2NHSO_2C_2F_5$,[72] and $CF_3SO_2NHSO_2C_3F_7$.[72] The late Dr. M. J. Kamlet supplied the sample of TNT, whereas Prof. D. Aue supplied the sample of $(CF_3)_3CNH_2$. $(CF_3)_3CH$ was prepared from $(CF_3)_2C{=}CF_2$ and HF as previously described.[73] Similarly, $C_6F_5CH_2CN$ was prepared at UCI according to the procedure previously described.[74] F_2NH was liberated with concentrated H_2SO_4 from $(C_6H_5)_3CNF_2$ (PCR) before each experiment.

Conclusions

This study has demonstrated that inherent acidities of neutral molecules that are stronger than Conant's H_2SO_4 standard (ΔG_{acid} = 302 ± 2 kcal/mol[8b]) are readily achievable. By following the historical precedents of Conant[1] and Gillespie,[2] we therefore take $\Delta G_{acid} < 300$ kcal/mol as the basis for a useful gas-phase superacidity classification. More importantly, this study has shown that very strong inherent acidities are not (as conventional lore has it) the private property of OH acids. We report in Table 1 many acids stronger than superacid CF_3SO_3H ($\Delta G_{acid} = 299.5$ kcal/mol). Although our structural effect studies have already achieved landmark inherent acidities, they also provide well-founded predictions based upon substituent structures and fractional additivities that are likely to lead to acids that greatly exceed the present levels. Theoretical calculations provide further confirmation of the predicted gas-phase superacid molecular structures. In subsequent publications, we will report comparative acidities of strong acids in the gas phase and condensed phases and discuss the nature of structural effects on solvation energies. Also in progress are bracketing studies to determine approximate ΔG values for acids (e.g., $HC(CN)_3$) where a laser desorption method yields the gaseous conjugate anion. Meanwhile, the preparation of new superacid molecules with new superstrong anion stabilizing substituents is in progress.

The chemistry involved in our continuing studies provides exciting prospects for new practical applications in many areas. For example, the substructures of very strong inherent acidity can be introduced in molecules (including polymers) to achieve unusual catalytic and other properties.[3,75–77] Due to the low bond energies and high electron affinities involved, metal hydrides have been found[78] by bracketing methods of measurements to have very strong gas-phase acidities. The introduction of ligands bearing superstrong acceptor substituents offers the promise of whole families of metal hydride superacids. However, any acid (like the metal hydrides) for which reversible equilibrium protonation to give the original acid structure does not occur cannot be regarded as a Brønsted acid. Nevertheless, this qualifier in no way diminishes the interest in such compounds as a disposable superacidic *proton source*.

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