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Generalized Principle of Designing Neutral Superstrong Brønsted Acids

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Abstract: A generalized principle of designing superstrong Brønsted acids is suggested according to the following scheme: $M{=}O \rightarrow M{=}Z(X)_n$. It consists of the formal replacement of $=$O fragment in carbonyl, sulfonyl, etc. groups in various acidic systems (e.g., CH_3CHO, FSO_3H, where M is the $CH_3CH{=}$ or $FSO_2H{=}$ fragment, respectively) by $=NSO_2F$, $=NCN$, $=C(CN)_2$, $=P(SO_2F)_3$, $=S(CN)_4$, or any other formally bivalent group $=Z(X)_n$ (where the formal valency of the central atom Z is $n + 2$), leading to highly acidic systems (e.g., $HC({=}P(CN)_3)NH_2$, $FS({=}C(CN)_2)_2OH$, etc.). It is demonstrated that in several cases the introduction of the double-bonded substituent at the central atom (e.g., N, C, P, S, Cl) that carries the potentially acidic proton or the acidity site (e.g., OH, NH_2, CH_3, etc. groups) will lead to the enormous (up to ca. 120 kcal/mol or 88 pK_a units!) increase of the intrinsic acidity of the respective parent acid. The acidity of the resulting acids and the scope and limitations of the principle are explored using density functional theory calculations at B3LYP 6-311+G** level. Some of the resulting acids (or their anions) were found to undergo fragmentation in the course of the geometry optimization. The general trend that follows from the results of the calculations is that the stability of the resulting compounds is influenced by both the M and the Z. If M is a first row element (carbon or nitrogen), then stable species are produced with almost any Z. If M is a second row element (sulfur or phosphorus), then the species with first row Z are mostly predicted to be stable, but most of the species with second row Z are expected to undergo fragmentation during the geometry optimization. The $Z = N$ and $Z = C$ derivatives (e.g., $=NSO_2CF_3$, $=C(CN)_2$, $=C(SO_2CF_3)_2$, etc.) are predicted to be the most stable. However, they have relatively modest electron-accepting power as compared to their penta-, hexa-, and heptavalent counterparts. The acidifying effects of the $=Z(X)_n$ groups with the same X increase with increasing n: $=NCN < =C(CN)_2 < =P(CN)_3 < =S(CN)_4$ and $=NSO_2F < =C(SO_2F)_2 < =P(SO_2F)_3$. Also, the acidifying effect of a fluorosulfonyl-substituted substituent is higher than that of the corresponding cyano-substituted substituent.

Introduction

General principles of designing progressively stronger neutral superacids seem to be rather well established.[1−4] It has been shown that the introduction into the acidic molecule X−Y−H of (several) highly dipolar superacceptor and strongly polarizable substituents which simultaneously form a very extensive conjugated system with the anionic protonation center of the conjugated anion $X{-}Y^-$ is the simplest strategy to develop progressively more acidic neutral superacidic systems (e.g., $(CF_3SO_2)_3CH$,[5a] $HC(CN)_3$, $(CF_3SO_2)_2NH$,[5b] etc.). As indicated by recent ab initio and DFT calculations,[6,7] the intrinsic acidity of several conjugate Brønsted−Lewis superacids ($HSbF_6$, $HAlCl_4$, $HAlBr_4$, HBF_4, etc.) can reach at least the same, and in some cases even significantly higher, acidity values. Still much stronger acidities are expected[6] to be characteristic for conjugate acids of polyhalogenated or polytrifluoromethyl-substituted derivatives of carboranes.[8]

About a decade ago,[9] a principle of building superstrong electron-acceptor substituents with extensive conjugated chains was introduced by L. M. Yagupolskii and co-workers. The principle assumes the creation of superstrong electron-attractive substituents by replacement of a double-bonded sp^2 oxygen atom in XYH systems by $=NSO_2CF_3$, $=NSO_2F$, or similar groups, according to, for example, the following scheme:

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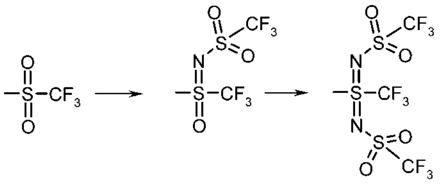


(1)

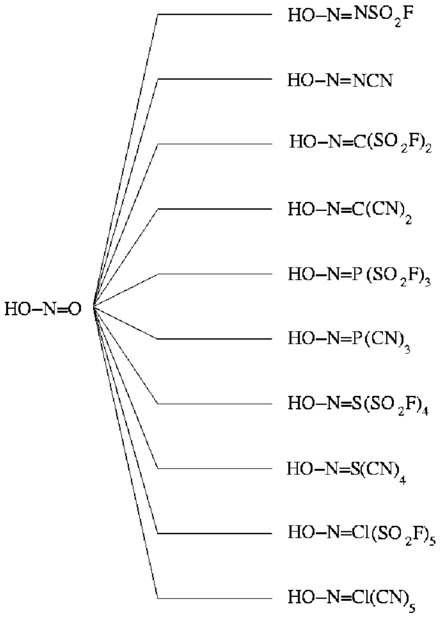
The resulting substituents, for example, $-S(=NSO_2CF_3)_2$-CF_3, were shown to surpass by far the electron-accepting properties of such traditional strong electron-acceptor groups as $-NO_2$, $-SO_2CF_3$, $-CN$, etc. For example, as evidenced by the Hammett σ_p constants[10] for para $-S(=NSO_2F)_2F$ and para $-NO_2$ groups (1.7 and 0.70, respectively), the former has 10 times stronger electron-accepting powers. Many new compounds which include substituents of Yagupolskii type have been synthesized.[9-11] In several cases, the enormously strong acidifying effect of Yagupolskii-type substituents has been demonstrated for the gas phase as well as for the DMSO and acetonitrile solutions.[1,11,12]

The Yagupolskii principle of designing new strongly electronegative substituents by using $=NSO_2CF_3$ or similar substituents can be generalized for any arbitrarily chosen substituent X ($-NO_2$, $-CN$, $-CF_3$, $-SO_2CH_3$, $-SO_2CN$, etc.) in $=NX$. Naturally, one can hardly expect to generate stronger electron-acceptor substituents than those which include $-SO_2CF_3$ or similar groups. Therefore, this is not a new way for generating potentially even stronger Brønsted acids.

Similar principles have been used by other authors.[13-16] The formal replacement of sp^2 bonded oxygen atom by another superstrong double-bonded substituent, $=C(CN)_2$, in derivatives of formic, cyanoformic, or similar carboxylic acids leads to various cyano-substituted vinyl alcohols. For example, the pK_a of tricyanovinyl alcohol, $(NC)_2C=C(CN)OH$, in aqueous solution has been estimated by Boyd[14] to be around -5, thus definitely exceeding the acidity of H_2SO_4, HNO_3, etc. in water. Several other derivatives which include $=C(CN)_2$ groups have also been reported.[13,14]

Also, the recent findings[16] of drastically increased CH acidity of the BF_3 complexes of acetaldehyde, acetone, and trifluoroacetone refer to the strongly acidifying effect of highly electronegative groups $=O^+-B^-F_3$ similar to the structures of the above-mentioned acidifying bivalent groups $=NSO_2F$, $=NCN$, $=C(CN)_2$.

Scheme 1. Illustration of the Generalized Principle $M=O \rightarrow M=Z(X)_n$ in the Case of Nitrous Acid HO−N=O: M Is HO−N, Z Is N, C, P, S, or Cl, and X Is Either SO_2F or CN



The above-mentioned enormous acidifying effects are due to the replacement of already relatively strong electron-acceptor substituent, double-bonded oxygen atoms, by another double-bonded, even stronger electron-acceptor substituent $=NCN$, $=NSO_2CF_3$, $=C(CN)_2$, etc., which combine much superior electron-withdrawing power of the resulting complex substituent (roughly at the same or even at somewhat lower levels of the electronegativities of the multivalent "central" atom) with the significantly enhanced charge delocalization ability and much higher polarizability (as compared with the sp^2 oxygen atom).

In this paper, we report a generalization of this principle. It is based on the following scheme:

$$M=O \rightarrow M=Z(X)_n \qquad (2)$$

It consists of the formal replacement of a double-bonded $=O$ atom in carbonyl, sulfonyl, etc. groups in various acidic systems (e.g., CH_3CHO, H_2SO_4, $HCONH_2$, HCOOH, FSO_3H, HNO, HONO, $HOPO_2$, CF_3SO_2OH, CF_3COOH, etc.) by $=NSO_2F$, $=NCN$, $=C(CN)_2$, $=P(SO_2F)_3$, $=S(CN)_4$, or any other formally bivalent group $=Z(X)_n$, where the formal valency of the central atom Z is $n + 2$. M is the residue of the molecule, for example, $CH_3CH=$, $H_2SO_3=$, etc. Depending on the central atom (e.g., N(III), C(IV), P(V), S(VI), Cl(VII)), it can carry from one to five strong electronegative electron-acceptor groups. The generalized principle is visualized in Scheme 1.

In the case of trivalent Z − nitrogen atom − and X as SO_2F or SO_2CF_3, we obtain the Yagupolskii substituents. For $X = NO_2$ and $X = CN$, one obtains the substituents described in ref 15 and references therein. For $n = 2$, $Z = C$, and $X = CN$, one obtains the above-mentioned $=C(CN)_2$ substituent.[13,14]

In a similar way, the above-mentioned replacement of the double-bonded sp^2 oxygen atom by a $=C(CN)_2$ group can be generalized into replacement by any $=CX_1X_2$ (where X_1 and X_2 are arbitrarily chosen strong electron-acceptor substituents) group. As a matter of fact, compounds $C_6H_5O(F)S(O)=C(SO_2F)_2$ and $C_6H_5O(F)S(O)=C(SO_2CF_3)_2$, involving substituents such as $(FSO_2)_2C=$ and $(CF_3SO_2)_2C=$, were synthesized and described by two groups of authors.[17-20]

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The existence of another group of even stronger electron-acceptor substituents could be anticipated on the basis of replacement of the sp^2 bonded atom, for example, by pentavalent phosphorus-containing double-bonded fragment $=PX_1X_2X_3$. In principle, due to the possibility of simultaneous inclusion of three superstrong substituents ($-SO_2CF_3$, $-SO_2F$, $-CN$, $-NO_2$, etc.) at the central atom, the design of very strong electron-acceptor substituents (e.g., $=P(SO_2CF_3)_3$, $=P(CN)_3$, etc.) seems probable.

In a similar way, one can expect to design double-bonded highly electron-acceptor substituents using hexa- (e.g., sulfur) or hepta- (e.g., chlorine or iodine) valent "central" atoms Z which would carry, correspondingly, four or five strongly electronegative electron-acceptor substituents X_i, for example, $=S(X_i)_4$ and $=Cl(X_i)_5$, where X = CN, NO_2, SO_2F, SO_2CF_3, etc.

The acidity of the acids designed according to the proposed principle and the scope and limitations of the principle are explored using density functional theory calculations at B3LYP 6-311+G** level.

Methods

Density functional theory (DFT) calculations at B3LYP 6-311+G** level were used throughout this work. This computational level has been tested and found suitable for prediction of acidity of strong acids (see ref 21 and references therein). All the computations reported in this work were carried out on IRIX based SGI Origin 200 workstations of the Institute of Chemical Physics of University of Tartu using Gaussian 98 system of programs.[22]

The effect of modification of various parent acids according to the proposed principle (eq 2) was explored in this work for three groups of parent acids: a series of carbonyl compounds (acetaldehyde, formamide, and formic acid), a series of sulfonyl compounds – derivatives of fluorosulfonic acid (FSO_2CH_3, FSO_2NH_2, and FSO_2OH), and some other acids of interest (sulfuric acid, HPO_3, nitrous acid, HNO, and cyanoformic acid).

Full geometry optimizations were carried out for all acids and anions. Several different starting geometries were used in doubtful cases. To confirm that calculated structures correspond to true minima, frequency calculations were run in all cases, and the absence of imaginary frequencies (NImag = 0) was taken as the criterion of the stability of the species. This stability, of course, refers to the stability of a single molecule (or ion) in the gas phase, not in the condensed phase. Also, this is not a confirmation that the molecule or ion cannot rearrange to a more stable geometry (or split into fragments), but it indicates that an activation barrier exists to these rearrangements.

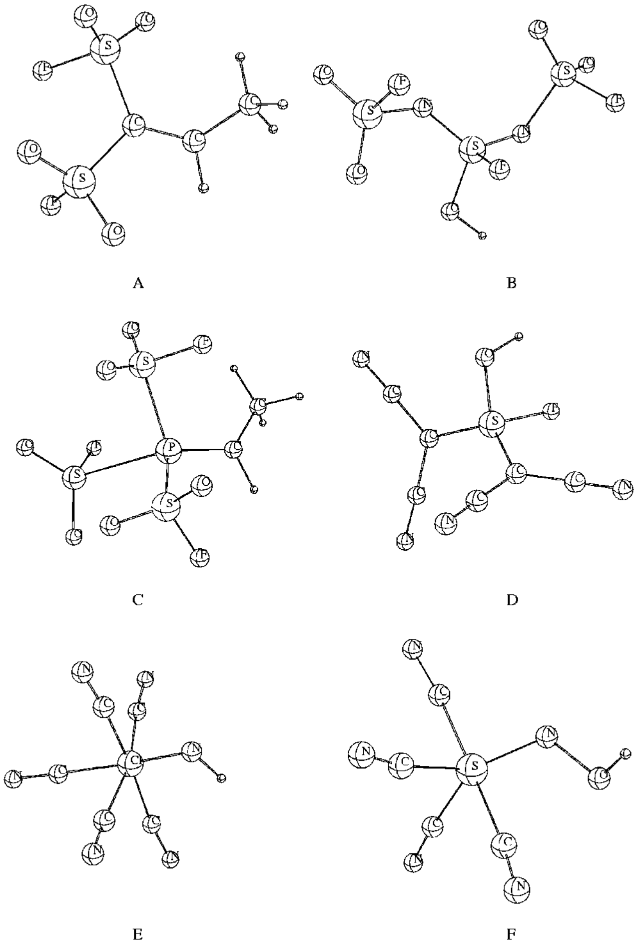

Figure 1. Some optimized structures of the acids investigated in this work: $FS(=NSO_2F)_2OH$ (A), $CH_3CH=C(SO_2F)_2$ (B), $CH_3CH=P(SO_2F)_3$ (C), $FS[=C(CN)_2]_2OH$ (D), $HON=Cl(CN)_5$ (E), and $HON=S(CN)_4$ (F).

The resulting gas-phase acidities (GA) of the acids HA and proton affinities (PA) of the anions A^- were calculated in the usual way[6] taking into account zero-point energies, finite temperature (298 K) correction, and the pressure–volume work term.

$$\mathrm{HA} \underset{\Delta H_{\mathrm{acid}}}{\overset{\Delta G_{\mathrm{acid}}}{\rightleftharpoons}} \mathrm{H}^+ + \mathrm{A}^- \qquad (3)$$

$$\Delta G_{\mathrm{acid}} = \mathrm{GA}$$

$$\Delta H_{\mathrm{acid}} = \mathrm{PA}$$

Results

The results of these calculations are reported in Table 1. The acidifying effects of different substitutions in different acids are presented in Table 2. Some optimized structures of studied acidic molecules and the respective anions are given in Figure 1 and Figure 2. The detailed results of the calculations (geometries, energetics, etc.) are available in Supporting Information and from the authors upon request.

Discussion

Neutral Molecules. Structure of the Substitution Products. It follows from Table 1 that most substitutions of doubly bonded oxygen atoms for $=C(CN)_2$, $=NCN$, $=C(SO_2CF_3)_2$, $=C(SO_2F)_2$, $=NSO_2F$, $=NSO_2CF_3$ have led to stable species. The only exceptions belong to substitution products of HN=O by =NCN and $=NSO_2F$ groups which are unstable toward the ejection of the N_2 molecule (structure A in Figure 3). Introduction of the

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Table 1. Calculated Deprotonation Enthalpies (ΔH, kcal/mol) and Acidities (ΔG, kcal/mol) of the Acids

X	ΔH	ΔG	X	ΔH	ΔG	X	ΔH	ΔG	X	ΔH	ΔG
$\mathrm{CH_3C(=X)H}$											
$=\mathrm{O}$[a]	364.6	357.2	$=\mathrm{SH_4}$	354.3	346.6	$=\mathrm{CHCN}$	356.5	349.2	$=\mathrm{P(SO_2F)_3}$	241.5	233.5
$=\mathrm{NH}$	375.2	367.9	$=\mathrm{ClH_5}$	307.8	298.4	$=\mathrm{C(CN)_2}$	328.4	321.1	$=\mathrm{S(CN)_4}$	244.1	234.9
$=\mathrm{CH_2}$	387.2	379.4	$=\mathrm{NCN}$	338.2	331.1	$=\mathrm{C(SO_2F)_2}$	307.1	299.9			
$=\mathrm{PH_3}$	366.7	357.7	$=\mathrm{NSO_2F}$	323.6	316.4	$=\mathrm{P(CN)_3}$	289.1	281.0			
$\mathrm{HC(=X)NH_2}$											
$=\mathrm{O}$[a]	364.6	352.6	$=\mathrm{CH_2}$	373.6	366.1	$=\mathrm{ClH_5}$	343.6	335.9	$=\mathrm{C(CN)_2}$	329.8	322.5
$=\mathrm{S}$	344.6	337.3	$=\mathrm{PH_3}$	350.4	343.0	$=\mathrm{NCN}$	340.6	333.3	$=\mathrm{C(SO_2F)_2}$	313.5	305.6
$=\mathrm{NH}$	367.5	360.2	$=\mathrm{SH_4}$	342.0	332.7	$=\mathrm{NSO_2F}$	328.3	320.6	$=\mathrm{P(CN)_3}$	290.6	283.1
$\mathrm{HC(=X)OH}$											
$=\mathrm{O}$	341.0	333.5	$=\mathrm{CH_2}$	353.6	346.1	$=\mathrm{ClH_5}$	316.8	308.9	$=\mathrm{C(CN)_2}$	302.7	295.3
$=\mathrm{S}$	331.5	324.2	$=\mathrm{PH_3}$	335.7	328.4	$=\mathrm{NCN}$	311.2	303.8	$=\mathrm{C(SO_2F)_2}$	288.0	280.6
$=\mathrm{NH}$	346.8	339.4	$=\mathrm{SH_4}$	349.2	341.2	$=\mathrm{NSO_2F}$	305.3	297.4	$=\mathrm{P(CN)_3}$	271.0	262.5
$\mathrm{FSX_2CH_3}$											
$=\mathrm{O}, =\mathrm{O}$	346.9	339.3	$=\mathrm{NH}, =\mathrm{O}$	351.5	343.5	$=\mathrm{NCN}, =\mathrm{O}$	328.5	321.0	$=\mathrm{NSO_2F}, =\mathrm{O}$	323.0	315.5
$=\mathrm{CH_2}, =\mathrm{O}$	356.5	349.0	$=\mathrm{C(CN)_2}, =\mathrm{O}$	317.5	310.2	$=\mathrm{C(SO_2F)_2}, =\mathrm{O}$	309.5	301.8			
$\mathrm{FSX_2NH_2}$											
$=\mathrm{O}, =\mathrm{O}$	324.9	317.9	$=\mathrm{NH}, =\mathrm{O}$	328.8	321.4	$=\mathrm{NCN}, =\mathrm{O}$	307.2	300.1	$=\mathrm{NSO_2F}, =\mathrm{O}$	303.6	295.9
$=\mathrm{CH_2}, =\mathrm{O}$	332.5	324.6	$=\mathrm{C(CN)_2}, =\mathrm{O}$	295.9	288.4	$=\mathrm{C(SO_2F)_2}, =\mathrm{O}$	289.7	282.2			
$\mathrm{FSX_2OH}$											
$=\mathrm{O}, =\mathrm{O}$	297.4	290.6	$=\mathrm{CHCN}, =\mathrm{O}$	282.1	274.7	$=\mathrm{NSO_2F}$[b]$, =\mathrm{O}$	270.8	263.9	$(=\mathrm{NSO_2F})_2$	256.7	249.9
$=\mathrm{CH_2}, =\mathrm{O}$	303.7	296.3	$=\mathrm{C(CN)_2}, =\mathrm{O}$	265.1	257.8	$=\mathrm{C(SO_2F)_2}, =\mathrm{O}$	265.1	257.0	$[=\mathrm{C(CN)_2}]_2$	254.6	247.1
$=\mathrm{NH}, =\mathrm{O}$	302.5	295.3	$=\mathrm{NCN}, =\mathrm{O}$	277.0	269.9	$(=\mathrm{NCN})_2$	262.7	255.8	$=\mathrm{P(SO_2F)_3}, =\mathrm{O}$[c]		
$\mathrm{X_2S(OH)_2}$											
$=\mathrm{O}, =\mathrm{O}$	309.0	301.2	$=\mathrm{NH}, =\mathrm{O}$	312.7	305.3	$=\mathrm{NSO_2F}, =\mathrm{O}$	286.1	277.7	$=\mathrm{NCN}, =\mathrm{NCN}$	272.5	265.0
$=\mathrm{CH_2}, =\mathrm{O}$	314.8	307.6	$=\mathrm{NCN}, =\mathrm{O}$	287.3	280.0	$=\mathrm{C(CN)_2}, =\mathrm{O}$	273.8	266.9			
$\mathrm{PX_2OH}$											
$=\mathrm{O}, =\mathrm{O}$	309.5	303.2	$=\mathrm{NH}, =\mathrm{O}$	314.7	307.6	$=\mathrm{NCN}, =\mathrm{O}$	288.8	281.8	$=\mathrm{NSO_2F}, =\mathrm{O}$	280.8	274.3
$=\mathrm{CH_2}, =\mathrm{O}$	319.7	312.7	$=\mathrm{C(CN)_2}, =\mathrm{O}$	279.2	272.4	$=\mathrm{C(SO_2F)_2}, =\mathrm{O}$	273.3	264.7	$=\mathrm{P(CN)_3}, =\mathrm{O}$		
HONX											
$=\mathrm{O}$	337.0	328.8	$=\mathrm{SH_4}$	326.0	315.0	$=\mathrm{NSO_2CF_3}$[c]			$=\mathrm{CHSO_2F}$	317.9	310.7
$=\mathrm{NH}$	346.0	338.4	$=\mathrm{ClH_5}$[c]			$=\mathrm{CHCN}$	332.0	324.6	$=\mathrm{P(CN)_3}$	294.0	286.6
$=\mathrm{CH_2}$	355.2	347.7	$=\mathrm{NCN}$	313.6	306.1	$=\mathrm{C(CN)_2}$	310.5	303.0	$=\mathrm{P(SO_2F)_3}$	283.7	277.8
$=\mathrm{PH_3}$	355.1	347.4	$=\mathrm{NSO_2F}$	304.3	296.9	$=\mathrm{C(SO_2F)_2}$	296.5	289.0	$=\mathrm{S(CN)_4}$[c]		
HNX											
$=\mathrm{O}$	382.2	375.8	$=\mathrm{PH_3}$	382.3	375.6	$=\mathrm{C(CN)_2}$	338.3	330.4	$=\mathrm{S(CN)_4}$	305.0	296.2
$=\mathrm{S}$	368.7	362.4	$=\mathrm{SH_4}$	386.5	378.8	$=\mathrm{C(SO_2F)_2}$[c]			$=\mathrm{Cl(CN)_5}$[c]		
$=\mathrm{CH_2}$	387.1	379.9	$=\mathrm{ClH_5}$[c]			$=\mathrm{NSO_2F}$[c]					
$=\mathrm{NH}$	364.3	355.2	$=\mathrm{NCN}$[c]			$=\mathrm{P(CN)_3}$	326.5	318.7			
$\mathrm{NC{-}C(=X)OH}$											
$=\mathrm{O}$	315.3	307.6	$=\mathrm{NSO_2F}$	285.8	278.4	$=\mathrm{C(CN)_2}$[d]	290.8	283.2			

[a] Values from ref 21. [b] The respective sulfo form $\mathrm{(FSO_2)_2NH}$ has $E = -1352.3744$ au, $H^{298} = -1352.3233$ au, $G^{298} = -1352.3688$ au, $\Delta H = 289.1$ kcal/mol, $\Delta G = 281.9$ kcal/mol, see also ref 5. For the $=\mathrm{NSO_2CF_3}$ derivative of triflic acid $\mathrm{CF_3SO_2OH}$(at DFT B3LYP/6-31+G* level), the neutral enol form $\mathrm{CF_3S(=O)(=NSO_2CF_3)OH}$ has $E = -1827.6746$ au, $H^{298} = -1827.6589$ au, $G^{298} = -1827.7189$ au; the respective sulfo form $\mathrm{(CF_3SO_2)_2NH}$ has $E = -1827.6924$ au, $H^{298} = -1827.6764$ au, $G^{298} = -1827.7370$ au; the common anion $\mathrm{(CF_3SO_2)_2N^-}$ has $E = -1827.2821$ au, $H^{298} = -1827.2145$ au, $G^{298} = -1827.2755$ au. The calculated $\Delta H = 291.3$ kcal/mol, $\Delta G = 283.3$ kcal/mol for the sulfo form and $\Delta H = 280.4$ kcal/mol, $\Delta G = 271.9$ kcal/mol for the enol form, which is by 17.3 kcal/mol stronger acid than that predicted at the same level of theory for $\mathrm{CF_3SO_2OH}$.[30] [c] One of the forms fragments during the geometry optimization. [d] Tautomeric keto form $\mathrm{HC(CN)_2C(=O)CN}$ of tricyanovinyl alcohol: $E = -430.6280$ au, $H^{298} = -430.5666$ au, $G^{298} = -430.6107$ au.

Table 2. Acidifying Effects ($\Delta\Delta G$, kcal/mol, Relative to the $=\mathrm{O}$ Substituent) of Different Substitutions in Different Acids[a]

	$=\mathrm{Z(X)}_n$								
acid	$=\mathrm{CH_2}$	$=\mathrm{C(CN)_2}$	$=\mathrm{C(SO_2F)_2}$	$=\mathrm{NH}$	$=\mathrm{NCN}$	$=\mathrm{NSO_2F}$	$=\mathrm{PH_3}$	$=\mathrm{P(CN)_3}$	$=\mathrm{P(SO_2F)_3}$
$\mathrm{CH_3C(=X)H}$	−22.2	36.1	57.3	−10.7	26.1	40.8	−0.5	76.2	123.7
$\mathrm{HC(=X)NH_2}$	−13.5	30.1	47.0	−6.8	19.3	32.0	9.6	69.5	
$\mathrm{HC(=X)OH}$	−12.6	38.2	52.9	−5.9	29.7	36.1	5.1	71.0	
$\mathrm{FSX_2CH_3}$	−9.6		37.5	−4.2	18.4	23.8			
$\mathrm{FSX_2NH_2}$	−6.7		35.7	−3.6	17.8	22.0			
$\mathrm{FSX_2OH}$	−5.7	32.8	33.6	−4.7	20.7	26.7			
$\mathrm{PX_2OH}$			38.5	−4.4	21.4	28.9			
$\mathrm{X_2S(OH)_2}$	−6.4	34.3		−4.1	21.2	23.5			
HONX	−18.9	25.8	39.8	−9.6	22.7	31.9	−18.6	42.2	51.0
HNX	−4.1	45.4		20.6			0.2	57.1	
$\mathrm{NC{-}C(=X)OH}$		24.4				29.2			

[a] The $\Delta\Delta G$ values given are the changes of acidity (defined as in eq 3) of the species $\mathrm{M{=}O}$ undergoing the transformation to $\mathrm{M{=}Z(X)}_n$: $\Delta\Delta G = \Delta G_{\mathrm{acid}}(\mathrm{M{=}O}) - \Delta G_{\mathrm{acid}}(\mathrm{M{=}Z(X)}_n)$. Negative values correspond to the decrease of acidity.

$=\mathrm{P(CN)_3}$ group into $\mathrm{CH_3CHO}$, nitrous acid, $\mathrm{HN{=}O}$, and $\mathrm{HCONH_2}$ also leads in the course of optimization to a stable molecule. Also, the substitution of the $=\mathrm{P(SO_2F)_3}$ group into $\mathrm{CH_3CHO}$ and HONO leads to the stable substitution products

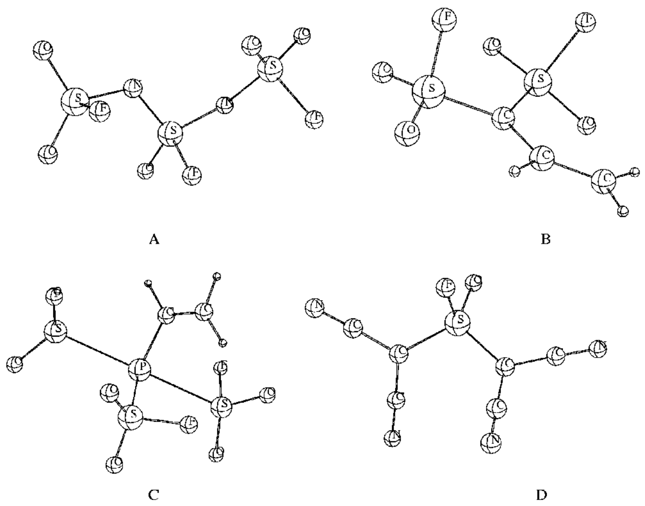

Figure 2. Some optimized structures of the deprotonated forms of the acids investigated in this work: $FS({=}NSO_2F)_2O^-$ (A), $CH_2CH{=}C(SO_2F)_2^-$ (B), $CH_2CH{=}P(SO_2F)_3^-$ (C), and $FS[{=}C(CN)_2]_2O^-$ (D).

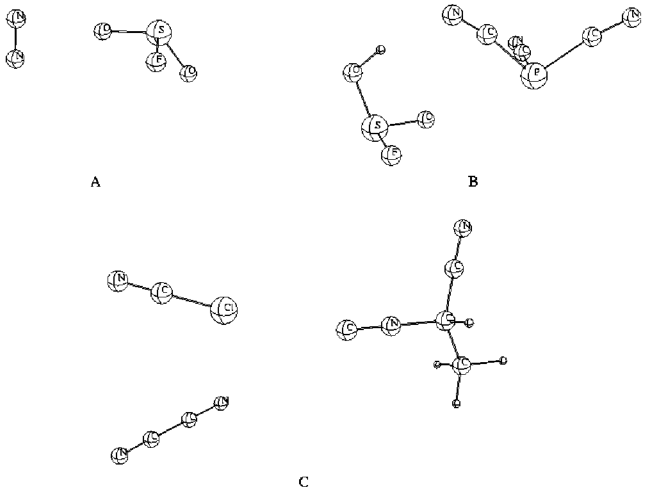

Figure 3. Some representatives of molecules that underwent fragmentation in the course of the geometry optimization: $N{=}NSO_2F^-$ (A), $FSO({=}P(CN)_3)OH$ (B), $CH_3CH{=}Cl(CN)_5$ (C).

$CH_3CH{=}P(SO_2F)_3$ and $HON{=}P(SO_2F)_3$, respectively, which are characterized by two P−S bond lengths around 2.27 Å and a third one (2.55 Å) which evidences a somewhat looser (but not yet broken!) P−S bond.

On the contrary, the attempts to introduce $=P(CN)_3$, $=P(SO_2F)_3$, or $=P(SO_2CF_3)_3$ into sulfuric acid and fluorosulfonic acid failed − a rather significant fragmentation of the generated species (see, e.g., structure B in Figure 3) occurred in the course of the geometry optimization. The major fragmentation products appear to be $P(SO_2F)_3$ or the corresponding CF_3SO_2 derivative − $P(SO_2CF_3)_3$. According to our calculations, they are predicted to be thermodynamically stable molecules.[23] The same seems to be true for the $(CF_3SO_2)_2C{=}O$ and its FSO_2 analogue. To the best of our knowledge, none of these compounds have been characterized in the literature. In the case of $CF_3S[P(CN)_3]_2OH$, the fragmentation product is predicted to be $P(CN)_3$ which is known as a stable molecule since the 19th century.

In the case of replacement of =O in HONO, CH_3CHO, and HN=O with hexavalent ($=SH_4$ and $=S(CN)_4$) groups, the substitution products are predicted to be stable. Similar behavior is also characteristic for the substitution products of double-bonded oxygen in CH_3CHO, HONO, and HNO for heptavalent groups ($=ClH_5$ group). The substitution of double-bonded oxygen atom for $=Cl(CN)_5$ is also predicted to lead to a stable product in the case of HONO and HNO. However, the attempts to introduce the same group into CH_3CHO are predicted to lead to the fragmentation products including $(CN)_2$ (structure C in Figure 3).

The general trend that follows from Table 1 is that the stability of the resulting compounds is influenced by both the M and the Z (see eq 2). If M is a first row element (carbon or nitrogen), then stable species are produced with almost any Z. If M is a second row element (sulfur or phosphorus), then the species with first row Z are mostly stable, but most of the species with second row Z fragment during the geometry optimization.

The structures such as $CH_3CHC(CN)_2$, $CH_3CHC(SO_2F)_2$ are characterized by the equal distances between the central C atom of the supersubstituent and carbon atoms of the CN groups or S atoms of the SO_2F groups, respectively.

However, in the case of substituents which include a pentavalent central atom, for example, $=P(CN)_3$, $=P(SO_2F)_3$, a hexavalent central atom, for example, $=SH_4$, $=S(CN)_4$, or a heptavalent central atom, for example, $=ClH_5$ or $=Cl(CN)_5$, the respective bond distances in these substituents (e.g., P−C, P−S, S−H, S−C, Cl−H, or Cl−C) are calculated not to be equal to each other. So, the P−C bond distances between P atom and CN groups in $CH_3CH{=}P(CN)_3$ are, respectively, 1.78, 1.77, and 1.85 Å, in $CH_3CH{=}S(CN)_4$ ca. 1.92, 1.92, 2.22, and 2.22 Å, in $HON{=}P(CN)_3$ 1.80, 1.80, and 1.76 Å, in $HON{=}S(CN)_4$ 1.78, 1.91, 1.84, and 1.83 Å, in $HON{=}Cl(CN)_5$ 1.77, 2.05, 2.04, 2.07, and 2.03 Å, in $HN{=}P(CN)_3$ 1.80, 1.80, and 1.77 Å, in $HN{=}S(CN)_4$ 1.79, 1.79, 1.90, and 1.83 Å, in $HN{=}Cl(CN)_5$ 1.87, 1.85, 1.95, 1.95, and 1.95 Å, etc.

The situation is similar in the case of $CH_3CH{=}P(SO_2F)_3$ where the two P−S bonds are predicted to have bond lengths 2.26−2.27 Å, whereas the third P−S bond is somewhat longer (2.55 Å) and looser.

Similar asymmetry in bond lengths is also expected to be characteristic for derivatives including $=SH_4$ and $=ClH_5$ groups where the calculated S−H or Cl−H bond lengths sometimes differ from each other by up to 0.05 Å.

Attempts to introduce $=S(SO_2F)_4$ and $=Cl(SO_2F)_5$ substituents or their respective tetra- or pentatrifyl derivatives into any of the parent acids (e.g., CH_3CHO, HONO, H_2SO_4, etc.) used in this work failed due to a fragmentation of the substitution products, for example, $CH_3C(H)[S(SO_2F)_4]$, $CH_3C(H)[Cl(SO_2F)_5]$, etc., and their respective deprotonated forms.

It has been suggested that the extremely high acidity of tris-fluorosulfuryl methane[17] and tris-trifyl methane[20] could be complicated by the presence of tautomeric equilibria involving the respective tautomeric forms of those two CH acids:

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(23) DFT B3LYP/6-311+G** calculations lead to the stable pyramidal structures, $P(SO_2F)_3$: $E = -2286.8837$ au, $H^{298} = -2286.8302$ au, $G^{298} = -2286.8908$ au. Calculated dipole moment 2.34 D. P−S bond lengths (Å): 2.274, 2.263, 2.272. F−S bond lengths (Å): 1.634, 1.628, 1.635. S−O bond lengths (Å): 1.438...1.441 (Å). Angles SPS (deg): 94.8, 100.2, 96.7. $P(SO_2CF_3)_3$: $E = -3000.4435$ au, $H^{298} = -3000.3454$ au, $G^{298} = -3000.4287$ au. Calculated dipole moment 2.32 D. P−S bond lengths (Å): 2.314, 2.305, 2.300. S−C bond lengths (Å): 1.945, 1.932, 1.945. S−O bond lengths (Å): 1.453...1.461 (Å). Angles SPS (deg): 102.1, 104.3, 97.2.

$$(FSO_2)_3CH \rightleftarrows (FSO_2)_2C{=}S({=}O)(F)OH \qquad (4)$$

$$(CF_3SO_2)_3CH \rightleftarrows (CF_3SO_2)_2C{=}S({=}O)(CF_3)OH \qquad (5)$$

However, the acidifying effects of these two groups have never been quantitatively evaluated. At least in the latter case, the ^{19}F NMR experiments at lower temperatures seem to confirm the simultaneous presence of both tautomers.[20] The possibility and significance of a similar tautomeric equilibrium of formation of dicyanoketeneimine from cyanoform have been an object of

$$HC(CN)_3 \rightleftarrows (NC)_2C{=}C{=}NH \qquad (6)$$

a long-time discussion.[14,24−27]

The relative stability of some tautomers participating in the equilibria 4−6 was studied at DFT B3LYP/6-311+G** level. It was found that in most cases (see Table 1), the enol forms are less stable (higher in energy) than their keto (sulfo, etc.) counterparts. So, $(FSO_2)_2NH$ is calculated to be by 18.0 kcal/mol more stable than the corresponding enol, $FS(O)({=}NSO_2F)$-OH, tris-fluorosulfurylmethane by 16.7 kcal/mol more stable than $FS(O){=}C(SO_2F)_2OH$, cyanoform by 0.8 kcal/mol more stable than dicyanoketimine,[28] and bis-trifylimide by 11.4 kcal/mol more stable (DFT B3LYP/6-31+G* level) than $CF_3S({=}O)$-$(NSO_2CF_3)OH$. However, tricyanovinyl alcohol as an enol form is calculated to be (B3LYP/6-311+G**) by 8.7 kcal/mol more stable than the corresponding keto form, $HC(CN)_2C({=}O)CN$ (see Table 1).

Deprotonation process of tautomers leads to the common anion. That means that the acidities of most of the corresponding enol forms are calculated to be by 7−18 kcal/mol more acidic than their keto, sulfonic, etc. counterparts, whereas in the case of tricyanovinyl alcohol the opposite situation holds.

Anions of the Newly Designed Brønsted Acids. Almost all substitutions of $=O$ for $=NCN$, $=NSO_2F$, $=C(CN)_2$, $=NSO_2F$, $=C(SO_2CF_3)_2$, and $=C(SO_2F)_2$ are predicted to lead to stable anionic species at the DFT B3LYP 6-311+G** level of theory. The only exceptions are the substitution products of HNO by $=NCN$, $=NSO_2F$ (ejection of N_2), and $=C(SO_2F)_2$ (disruption of one C−S bond), and the substitution products of HONO by $=NSO_2F$ and $=NSO_2CF_3$.

Contrary to that, all anionic structures, generated by replacement of $=O$ with $=P(SO_2CF_3)_3$ or $=P(SO_2F)_3$ or $=P(CN)_3$ groups in HSO_4^- or FSO_3^-, are predicted to be unstable regarding the ejection of $P(SO_2F)_3$, $P(SO_2CF_3)_3$, or $P(CN)_3$ molecules, again paralleling the behavior of the neutrals (vide supra). Negatively charged species derived from CH_3CHO, HONO, HNO, HCOOH, $HCONH_2$ by substitution of $=O$ with $=P(SO_2F)_3$ and $=P(CN)_3$ are also predicted to be stable.

In some cases, those substitution products have asymmetric structures in which one CF_3SO_2−P bond has variable length of ca. 2.6−2.7 Å (i.e., one CF_3SO_2 fragment is relatively loose from the rest of the anion, whereas the other two S−P bond lengths are at the normal 2.15−2.25 Å level). With the exception of the substituted formiate ion, the substitution product with $=P(CN)_3$ has structures with somewhat longer C−P bond lengths than in the corresponding neutral species.

So, the bond lengths between P atom and C atoms of the cyano groups in $^-CH_2CH{=}P(CN)_3$ are 2.1, 2.0, and 1.8 Å, in $^-CH_2CH{=}S(CN)_4$ − between S atom and C atoms of the cyano groups − 1.92, 1.92, 2.23, and 2.23 Å. Similar P−C bonds between P atom and C atoms of CN groups are also found in the anionic form of $HC(OH)({=}P(CN)_3)$ or in the deprotonated form of $HC(NH_2)({=}P(CN)_3)$. The S−P bonding in $^-CH_2CHP$-$(SO_2F)_3$ is characterized by one shorter (normal) S−P bond (2.30 Å) and two relatively longer (ca 2.57 Å) and looser highly polar S−P bonds. One Cl−CN bond in $N{=}Cl(CN)_5^-$ is clearly broken.

The deprotonated forms of the substitution products of CH_3-CHO with $=S(CN)_4$, $=SH_4$, $=ClH_5$, and $=Cl(CN)_5$ are not fragmented.

Some typical calculated structures of these molecules and anions are indicated in Figures 1 and 2, respectively.

Acidifying Effects of the New Superstrong Substituents. Some decrease of the Pauling electronegativities[29] of the central atom Z ($=N-$, $=C=$, $=P$, etc.) takes place while going from double-bonded oxygen substituent to the double-bonded nitrogen-, phosphorus-, sulfur-, or chlorine-based substituents. In fact, electronegativity of atoms decreases when going from O ($\chi = 3.44$) to N ($\chi = 3.04$), C ($\chi = 2.55$), S ($\chi = 2.58$), and P ($\chi = 2.19$), and remains almost on the same level in the case of Cl ($\chi = 3.16$). Therefore, depending on the nature of the substituents attached to the central atom of the complex double-bonded substituents, their acidifying effect (as compared with the parent $=O$ compound) might be either absent or even negative, leading to the decrease of the acidity of the resulting neutral Brønsted acid.

However, one can expect that in case of the strong electron-acceptor substituents X_i (e.g., −CN, $-SO_2F$, $-SO_2CN$, $-SO_2$-CF_3, etc.), maximum occupation of available substitution sites at the central atom, rough additivity of substituent effects, and favorable steric conditions for the resonance stabilization, the electron-accepting power, and, consequently, also the acidifying effect of the novel supersubstituents, will increase in the following order: $=NX_i < =CX_{i2} < =PX_{i3} < =SX_{i4} < =ClX_{i5}$.

The acidifying effects of the substitutions are presented in Table 2. From Table 2 it is clearly seen that substitution of $=O$ for $=NH$ or $=CH_2$ leads to a decrease of acidity in all the parent compounds (with the exception of $=NH$ substitution in HNO) and that the $=CH_2$-substituted derivative is less acidic than the corresponding $=NH$ derivative in all cases. However, the acidity decrease of the same substitution differs widely in different parent compounds. The general trend is that the stronger decrease takes place in the case when the central atom of M is a first row element. The substitution by $=PH_3$ leads to a very complicated picture ranging from strongly acidifying (9.6 kcal/mol in formamide) to strongly acidity decreasing effect (−18.6 kcal/mol in nitrous acid), while substitution by $=SH_4$ or $=ClH_5$ leads to an increase in acidity.

Contrary to the situation with the simple fragments ($=NH$, $=CH_2$, $=PH_3$), the introduction of the supersubstituents (e.g., $=NCN$, $=NSO_2F$, $=C(SO_2F)_2$, $=C(CN)_2$, $=P(CN)_3$, $=P(SO_2F)_3$, $=S(CN)_4$, $=Cl(CN)_5$) into these parent acids instead of the

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(27) Bock, H.; Dammel, R. *Z. Naturforsch.* **1987**, *42b*, 315−322.

(28) DFT B3LYP/6-311+G** calculations give the following results for cyanoform, its tautomer, and their common deprotonated form: $HC(CN)_3$, $E = -317.2778$ au, $H^{298} = -317.2274$ au, $G^{298} = -317.2647$ au; $HN{=}C{=}C(CN)_2$, $E = -317.2750$ au, $H^{298} = -317.2252$ au, $G^{298} = -317.2632$ au; $C(CN)_3^-$, $E = -316.7986$ au, $H^{298} = -316.7605$ au, $G^{298} = -316.7963$ au.

(29) Atkins, P. W. *Quanta*; Oxford University: Oxford, 1994.

doubly bonded oxygen atom is calculated to increase significantly the acidity of all parent acids (see Tables 1 and 2). In some cases, this acidifying effect is expected to exceed 120 kcal/mol, that is, 88 powers of 10 as compared with the corresponding parent compound! As a result, the acidities of some of the derivatives (e.g., substituted by $=C(CN)_2$, $=C(SO_2F)_2$, $=S(CN)_4$, $=P(SO_2F)_3$, etc.) of rather modest acids can reach acidities of 233−250 kcal/mol level which is at least comparable to the most acidic complex Brønsted−Lewis superacids ($HSbF_6$, $HAlCl_4$, $HAlBr_4$, magic acid, etc.) or other superstrong Brønsted acids (e.g., pentacyanocyclopentadiene).[6]

On the basis of the data in Table 2 it is seen that the acidifying effects of the $-Z(X)_n$ groups with the same X increase with increasing n:

$$=NCN < =C(CN)_2 < =P(CN)_3 < =S(CN)_4$$

$$=NSO_2F < =C(SO_2F)_2 < =P(SO_2F)_3$$

Also, the acidifying effect of a fluorosulfonyl-substituted substituent is higher than that of the corresponding cyano-substituted substituent.

Comparing the effects of the same substitution on different parent acids does not lead to a clear picture. There is no dependence of the acidifying effect on the acidity of the parent acid. The only trend that can be pointed out is that the family of carbonyl compounds is more sensitive to the substitution than the family of sulfonyl compounds.

There is no straightforward dependence between the acidifying effect of a given substitution and the acidity center ($-CH_3$, $-NH_2$, or $-OH$). The only observation that can be pointed out is that in the group of carbonyl compounds formamide is clearly less sensitive to the substitution than either acetaldehyde or formic acid.

For the practical realization of the suggested principle, there evidently exists a tradeoff between the extent of the potentially achievable acidifying effect of the above-discussed bivalent supersubstituents which carry the strong electron-acceptor substituents and the stability of the resulting neutral and anionic species toward fragmentation.

As already mentioned in the present work, the compounds which include supersubstituents with the trivalent (e.g., nitrogen) and tetravalent (e.g., carbon) central atoms which carry the strongest electron-acceptor substituents (CN, SO_2F, SO_2CF_3, etc.) were experimentally synthesized and proved to be stable. However, no Brønsted acids carrying $=C(SO_2CF_3)_2$ or $=C(SO_2F)_2$ supersubstituents have been synthesized to date.

Conclusions

A generalized principle of designing superstrong Brønsted acids is suggested according to the following scheme:

$$M{=}O \rightarrow M{=}Z(X)_n$$

It consists of the formal replacement of =O fragment in carbonyl, sulfonyl, etc. in various acidic systems (e.g., CH_3CHO, FSO_3H, where M is the $CH_3CH=$ or $FSO_2H=$ fragment, respectively) by $=NSO_2F$, $=NCN$, $=C(CN)_2$, $=P(SO_2F)_3$, $=S(CN)_4$, or any other formally bivalent group $=Z(X)_n$ (where the formal valency of the central atom Z is $n + 2$), leading to highly acidic systems (e.g., $HC(=P(CN)_3)NH_2$, $FS(=C(CN)_2)_2OH$, etc.).

It is demonstrated that in several cases the introduction of the double-bonded substituent at the central atom (e.g., N, C, P, S, Cl) that carries potentially acidic proton or the acidity site (e.g., OH, NH_2, CH_3, etc. groups) will lead to the enormous (up to ca. 120 kcal/mol or 88 pK_a units!) increase of the intrinsic acidity of the respective parent acid.

Some of the resulting acids (or their anions) were found to undergo fragmentation and decomposition reactions in the course of the geometry optimization. The general trend that follows from the results of the calculations is that the stability of the resulting compounds is influenced by both the M and the Z. If M is a first row element (carbon or nitrogen), then stable species are produced with almost any Z. If M is a second row element (sulfur or phosphorus), then the species with first row Z are mostly stable, but most of the species with second row Z fragment during the geometry optimization. The Z = N and Z = C derivatives (e.g., $=NSO_2CF_3$, $=C(CN)_2$, $=C(SO_2CF_3)_2$, etc.) are predicted to be the most stable. However, they have relatively modest electron-accepting power as compared to their penta-, hexa-, and heptavalent counterparts. The acidifying effects of the $=Z(X)_n$ groups with the same X increase with increasing n:

$$=NCN < =C(CN)_2 < =P(CN)_3 < =S(CN)_4$$

$$=NSO_2F < =C(SO_2F)_2 < =P(SO_2F)_3$$

Also, the acidifying effect of a fluorosulfonyl-substituted substituent is higher than that of the corresponding cyano-substituted substituent.

The N and C derivatives (e.g., $=NSO_2CF_3$, $=C(CN)_2$, $=C(SO_2CF_3)_2$, etc.) are predicted to be the most stable. However, they have relatively modest electron-accepting power as compared to their penta-, hexa-, and heptavalent (i.e., Z is P, S, or Cl) counterparts.

The neutral and protonated forms of the $=P(CN)_3$ and $=P(SO_2F)_3$ (or $=P(SO_2CF_3)_3$) derivatives of some relatively weak parent Brønsted acids (CH_3CHO, HONO, HCOOH, $HCONH_2$) were calculated to be stable toward the fragmentation pathways. At the same time, significantly stronger acidities than in the case of derivatives of supersubstituents with the trivalent nitrogen or tetravalent carbon central atoms were predicted. However, derivatives of $=P(CN)_3$ or $=P(SO_2F)_3$ supersubstituents of much stronger parent acids, for example, fluorosulfonic acid and sulfuric acid, are not expected to be stable. Even more so, the $=S(SO_2F)_4$ and $=Cl(SO_2F)_5$ derivatives of even weaker Brønsted acids (CH_3CHO, HONO) are found to be unstable. At the same time, some derivatives of somewhat weaker supersubstituents, $=S(CN)_4$ and $=Cl(CN)_5$, are in some cases ($CH_3CHS(CN)_4$, $HONCl(CN)_5$, $HNS(CN)_4$, $HNCl(CN)_5$, etc.) predicted to be stable.

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Supporting Information Available: Calculated total energies (E, au), enthalpies (H, at 298 K, au), and free energies (G, at 298 K, au) of the neutrals and anions (Table S1) and additional structures of the most important acids and their deprotonated forms (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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