DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS

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THEORETICAL STUDY OF GAS-PHASE ACID-BASE EQUILIBRIA

by

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Secretary of the Council: A. Tuulmets

The permanent address of the author is Institute of Chemical Physics, University of Tartu, Jakobi 2, EE2400 Tartu, Estonia.

Gaasifaasiliste happelis-aluseliste tasakaalude teoreetiline uurimine.

Peeter Burk

Kokkuvõte

Gaasifaasilised happelis-aluselised tasakaalud on viimasel paarikümnel aastal tõusnud füüsikalise orgaanilise keemia tähelepanu keskpunkti, kuna nad võimaldavad uurida asendaja ja rektsioonitsentri vahelist vastasmõju tingimustes, kus keskkonna (solvendi) mõju on välistatud. See võimaldab ülalnimetatud vastasmõju olemuse ja mehhanismi uurimist, samuti avaneb uudne võimalus selgitamaks solvendi mõju lahuses toimuvatele protsessidele.

Viimastel aastatel on kiiresti kasvanud ka kvantkeemiliste arvutuste kasutamine mitmesuguste keemiliste probleemide uurimiseks, kuna sellised arvutused annavad sageli kasulikku lisainformatsiooni uuritavate molekulide ja ioonide struktuuri ja laengujaotuse kohta, võimaldades nii paremini mõista uuritavate süsteemide käitumise fundamentaalseid seaduspärasusi ning võimaldavad uurida ka süsteeme, mis on eksperimentaalselt raskesti käsitletavad.

Käesolevas töös on kvantkeemilisi arvutusi rakendatud gaasifaasiliste happelis-aluseliste tasakaalude uurimiseks. On teostatud poolempiirilise PM3 meetodi testimine gaasifaasiliste prootonafiinsuste ja deprotoneerimisentalpiate arvutamiseks.

Kasutades poolempiirilisi ja *ab initio* arvutusmeetodeid on uuritud mitmesuguste tugevate hapete ja aluste omadusi (energiad, geomeetriad, laengujaotused) ning nende võimalikku prototroopset tautomerismi. Põhinedes nendel arvutustel on välja pakutud uute rekordilist aluselisust või happelisust omavate ühendite loomise võimalused.

Contents

List of Publications

The thesis consists of the review and the six articles listed below. They are referred in the text by Roman numerals I-VI. The review summarizes and supplements the articles.

I. Peeter Burk and Ilmar A.Koppel
An AM1 and PM3 study of hexafluoroacetylacetone.
J.Mol.Struct.(Theochem), 1993, **282**, 277.
II. Peeter Burk and Ilmar A.Koppel
Critical test of PM3 calculated gas-phase acidities.
Theor.Chim.Acta, 1993, **86**, 417.
III. Peeter Burk, Koit Herodes, Ivar Koppel and Ilmar Koppel
Critical test of PM3 calculated proton affinities.
Int.J.Quant.Chem.: Quant.Chem.Symposium, 1993, **27**, 633.
IV. Peeter Burk, Ilmar A. Koppel and Jüri Tapfer
Theoretical study of structure and basicity of some alkali metal oxides, hydroxides and amides.
Int.J.Quant.Chem., submitted.
V. Peeter Burk, Ilmar A. Koppel, Jüri Tapfer, Frederick Anvia and Robert W. Taft
Theoretical Study of Prototropic Tautomerism and Acidity of Tris(fluorosulfonyl)methane.
J.Mol.Struct.(Theochem), submitted.
VI.Peeter Burk, Ilmar A. Koppel, Ivar Koppel, Lev M. Yagupolskii and Robert W. Taft
Superacidity of neutral brönsted acids in gas phase. PM3 study.
J.Comp.Chem., submitted.

1. Introduction

Proton transfer reactions are among the most extensively studied of simple chemical reactions. Over many decades, the careful scrutinity of such processes in solutions has provided much insight into the nature of substituent-reaction center interactions and into the role of the solvent in directing molecular stability and reactivity. The interpretation of results from these studies (in solution), however, has not always been straightforward, since the acidity or basicity of the compound could be modified by the solvent so that experimentally observed thermochemical quantities may differ from those that can be attributed strictly to intrinsic molecular properties.

In the past two decades, several experimental techniques such as high-pressure mass spectrometry [1,2], flowing afterglow [3] and Fourier transform ion cyclotron resonance spectrometry [4] has provided an accurate set of thermochemical data for acidities and basicities of organic and also inorganic compounds in gas phase. Since then, there have been a increasing interest in using such information to distinguish intrinsic molecular acidities and basicities from the chemical effect of solvation, and to interpret the thermochemistry of proton transfer and bonding [5].

At the same time, in recent years quantum chemical calculations have become a widely used tool for investigation of wide range of problems [6]. Both *ab initio* and semiempirical self-consistent field molecular orbital calculations are often used. If these methods can be used to calculate gas phase (intrinsic) acidities and basicities with sufficient accuracy, it would be of great value, while such calculations can be carried out much faster and supposedly at much less cost than experiments. Such calculations are also not limited by the physical properties of the samples (stability, vapor pressure, etc.) or the availability of sufficient number of reference compounds. Although PA calculations, at present, have been carried out mostly on neutrals and anions, it should be possible to calculate the proton affinities of radicals, a quantity that is quite difficult to obtain experimentally.

Besides of serving as another "experimental" method for determining the thermochemical parameters, theoretical calculations provide also structural information on ions and can be used quantitatively to determine the difference in energy for protonation or deprotonation of two different sites in the same molecule. A more detailed understanding can be gained by examining various electronic energy components, for example, using the Bader´s "atoms in molecule" method [7]. Finally, more detailed information about the intrinsic nature of the proton affinity can be determined from theory, for example, the separation of chemical and physical effects (e.g., zero-point energy differences), thus enabling us to get better understanding of chemical and physical processes lying behind the acid-base equilibria.

2. Literature overview

As it was already mentioned above, quantum chemical molecular orbital calculations have become very widely used tool for investigating gas-phase proton transfer equilibria. Publications on this field can be divided roughly into two classes: 1. works, which investigate the usability of certain methods for calculating gas-phase deprotonation enthalpies and proton affinities, and 2. works, where such calculations are used to study some aspects of acid-base equilibria. However, it must be mentioned, that practically in all publications of latter class also the verification of usability of applied calculation methods is given. Short overview of recent publications of both classes is given below.

2.1. Evaluation of different methods for calculating gas phase proton affinities and deprotonation enthalpies

Chandrasekhar, Andrade and Schleyer showed, that MNDO is quite good for estimating acidities with average error near 10 kcal/mol [8]. However, they noticed also that the ordering of acidities of some compounds (e.g. methanol and ethanol) is not given correctly and MNDO geometries have also deficiencies.

Dewar and Dieter have carried out a systematic study of reliability of PM3 calculated proton affinities and deprotonation enthalpies [9]. They have shown, that with a few exceptions the errors in calculated proton affinities of bases and deprotonation enthalpies of acids are comparable with those in the calculated heats of formation of corresponding neutral molecules. The average errors in calculated proton affinities and deprotonation enthalpies were 6.0 and 8.2 kcal/mol respectively. The main reported problem involves anions in which the charge is largely concentrated on one atom.

Very similar results for AM1 predicted deprotonation enthalpies of large collection of C-H acids were reported by Kass

[10]. The use of empirical correction, which reduces the average unsigned error to 4.2 kcal/mol was proposed.

Catalan et al. have found [11], that the AM1 method doesn't handle correctly the effect of adjacent lone pairs on the relative basicity of pyridazine and pyrimidine, and on the relative gas-phase acidity of pyrazole and imidazole. At the same article it was also found that INDO method handles these effects correctly.

Good starting point for choosing adequate ab initio method for studies of gas-phase acid-base equilibria is given by Hehre, Radom, Schleyer and Pople [6] and by Dixon and Lias [5]. Authors stress, that for comparison of calculated and experimental numbers corrections for differential zero-point energies and to uniform temperature are needed, as uncorrected values often differ from the corrected ones by 5 kcal/mol or more, primarily as a consequence of differing number of reactant and product molecules in (de)protonation reactions. It was shown, that for successful reproduction of experimental absolute proton affinities at least 6-31G* basis set must be employed. It is concluded, that for calculation of absolute acidities (more precisely, deprotonation enthalpies) basis sets which incorporate diffuse functions are required, and the use of 3-21+G* and 6-31+G* basis sets for such calculations is encouraged. This conclusion agrees with earlier works of Chandrasekhar et al. [8] and Kollmar [12], where it was established, that inclusion of diffuse AOs in basis sets of modest size (3-21G, 4-31G) improves the description of acidity more than use of correlation corrected calculations with very extended basis sets. However, Hehre et al. also state [6], that for calculations of relative proton affinities, deprotonation enthalpies and effects of remote substitutions on acid and base strength even the minimal STO-3G basis set reproduces the majority of experimental data accurately.

Koppel, Mõlder and Palm have carried out ab initio calculations of proton affinities and deprotonation enthalpies using various basis sets (STO-3G, 3-21G, 4-31G, 6-31G*, 3-21+G, 4-31+G) and with the 6-31G** basis set using fourth order

Moller-Plesset perturbation theory [13]. They showed, that the fit with experiment can be substantially improved by using empirical corrections based on linear regression between calculated and experimental values.

Extensive study of the basis set dependencies of proton affinities of carbonyl bases calculated both at Hartree-Fock level and using MP2 and MP3 levels of correlation have been carried out by Del Bene [14-16]. At the STO-3G level differences in both absolute and relative proton affinities from their experimental values were too large. Quantitatively correct results were found for relative proton affinities at the 4-31G level. Remarkably good agreement in the relative and absolute proton affinities was found 6-31G*, 6-31G** and 6-311G** basis sets, especially when the MP2 and MP3 were used.

In a later work [17] Del Bene and Shavitt have used 6-31+G(2d,2p) basis set to study the influence of different basis sets and electron correlation methods like many-body (Moller-Plesset) perturbation theory at second, third and fourth order; the linearized coupled-cluster method; the averaged coupled-pair functional; configurational interaction with all single and double excitations; and configurational interaction with all single and double excitations with the Davidson and Pople corrections on proton affinities and deprotonating energies. All calculations were carried out at MP2/6-31+G** geometries. The basis set superposition error was evaluated using counterpoise correction. It was shown, that MP2 values for the protonation and deprotonation energies are always the lowest, while the CISD values are often highest. The results of various correlation methods agree with each other within 2 kcal/mol for almost all protonation energies and within 2-7 kcal/mol for deprotonation. The protonation and deprotonation energies computed with various methods generally agree with experimental values to about 1%. It was shown, that the counterpoise correction is quite big for even such large basis sets as 6-31+G** and 6-311+G(2d,2p) - ranging from 4.1 to 4.6 and from 2.0 to 2.8 respectively. The inclusion of counterpoise correction generally improves the agreement between different basis sets and correlation methods.

Eades et al. have carried out two studies on proton affinities of N-bases [18,19]. It was shown that at the DZ+d level qualitatively accurate relative proton affinities can be obtained at Hartree-Fock level.

Nicholas et al. have recently carried out the study of the effects of basis set size on the calculated structure and acidity of some compounds which mimic the zeolites [20]. They have come to conclusion, that TZ+d level of theory is required for prediction of geometry, while the trends in proton affinities and deprotonation enthalpies can be predicted at DZ level.

DeFrees and McLean have demonstrated [21], that ab initio molecular orbital theory at the MP4/6-311++G(3df,3pd) level yields proton affinities for small neutral and anionic bases to within 2 kcal/mol of accuracy. The usefulness of MP4/6-311++G(2d,2p) and MP2/6-311G** theoretical models for bigger systems is pointed out.

Pople and coworkers represented recently two methods for accurate calculation of energetic properties of molecules - G1 [22] and G2 [23]. They have found [23], that these methods yield the proton affinities consistently within 2.5 kcal/mol of experimental values. This statement was later confirmed by Smith and Radom [24].

2.2.Applications of molecular orbital calculations to study of the acid-base equilibria

Berthelot and coworkers have studied the gas-phase basicity of biologically interesting molecules such as nicotines, nicotinic acid derivatives, etc. [25]. They used AM1 method to predict the site of protonation and found, that nornicotine and nicotine protonate preferentially on the five membered ring amino nitrogen, while for methyl nicotinate and nicotineamide the pyridine nitrogen appears clearly as the favored site of protonation.

Benedetti and coworkers calculated AM1 proton affinities for prazosin analogues (2-substituted 4-amino-6,7-dimethoxy derivatives of quinazoline, quinoline and isoquinoline) [26]. these values were correlated with corresponding experimental basicity constants and α^1-adenoceptor binding affinities. The results confirm the crucial role of the N1 protonated form of these derivatives for a selective and productive binding with the α^1 adrenergic receptor.

Ogretir and Kaninskan showed using ab initio calculations with minimal basis set, that the protonation of imidazo[4,5-f]quinolines take place at the pyridine nitrogen atom rather than at the imidazole nitrogen atom [27]. The preferred form of imidazo[4,5-f]quinolines was found to be the 3H form. A satisfactory correlation between experimentally obtained pKa values and computed electron densities at the protonation site was found.

Abboud and coworkers investigated the gas phase basicities of β-lactams and azetidines [28] at the 6-31G* level of theory. They showed, that in gas phase β-lactams are weaker bases than acyclic amides. It was found, that both β-lactams and acyclic amides are oxygen bases, but the gap between the nitrogen and oxygen intrinsic basicities is much smaller in the former. This is the result of the charge redistribution due to the hybridization changes at the carbonyl carbon, which are well described by the topological analysis of the corresponding charge densities. The cyclization effects of proton affinities of amines were found to be almost negligible.

Sabio and Topiol calculated at 4-31G* and MP2/4-31G* level of theory the basicities of several N-methyleformamidine analogues to find out whether these compounds can serve as H^2-receptor agonists [29], where the simultaneous domination of N3-H tautomeric form and lower basicity than that of N-(3-aminopropyl)formamidine is required.

Tang et al. [30] calculated within the charge density topological approach the $-\nabla^2\rho$ values of nonbonded charge concentrations of methylamines and some other nitrogen bases. Very good linear relationship between those values and gas phase basicities of studied molecules was found.

Shambayati et al. have used ab initio calculations of basicity of silyl ethers as inquiry into the nature of silicon-oxygen interactions [31].

Tunon, Silla and Tomasi [32] calculated the basicities of various methylamines both in vacuo and solution using the 6-31G* basis set. Polarizable continuum model of solvent was used for calculations in solution. It was shown, that correlation effects are very important in order to have a good estimation of the inductive effect produced by methyl substitution.

Gordon, Damrauer and Kremp have studied gas-phase acidities of silanols and their sulfur analogues [33] using ab initio calculations with up to 6-31++G(2df,2p) basis sets to asses β-methyl and β-ethyl substitution effects and demonstrated, that such effects are very small both in silanols and thioles.

Siggel and Thomas [34] have investigated the anomalous gas phase acidity of formic acid using ab initio calculations at 6-31+G* level. They showed, that the anomalously high acidity of formic acid in gas phase when compared with to that of acetic, propionic and butyric acids, arises because replacement of hydrogen by alkyl group in carboxylic acid gives a rise to an unusually high change in the potential at the acidic proton in the neutral acid and a smaller change in the relaxation that occurs when the proton is removed. Analysis of the charge distribution in these molecules shows that there is a significant charge transfer from the alkyl group to the carboxyl group - especially to the carboxyl carbon.

Fleicher et al. [35] performed ab initio molecular orbital calculations of both the ^{1}H NMR chemical shifts and deprotonation energies of wide variety of small hydroxyl containing inorganic and organic molecules, some of which is are the models of surface oxygen groups in zeolites, to check whether the postulated property-reactivity relationship between the chemical shift of the hydroxyl proton and its acidity exists. It was found, that this is not the case for the general set of studied systems. That was attributed to the non-constant and non-negligible contributions to the chemical shift by the X-O bond and the lone pairs of oxygen.

Abboud et al. have carried out a comparison of intrinsic

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reactivities of thiocarbonyl and carbonyl compounds using ab initio calculations at HF and MP2 levels with different basis sets and also AM1 calculations [36]. It was shown, that all investigated thiocarbonyl compounds are sulfur bases. Experimental data on both thiocarbonyl and carbonyl compounds were correlated and the features found were rationalized in terms of the interactions between the MOs of the parent compound and substituent using topological analysis of charge densities.

Ventura et al. performed high-level ab initio calculations using basis sets with several diffuse and polarization functions and including correlation energy through MP2 theory on the different possible structures of formo- and acetohydroxamate anions to determine their preferred conformations in gas-phase [37]. It was found, that in gas phase both acids behave as NH acids rather that OH acids.

Komornicki and Dixon [38] have performed a set of large scale ab initio molecular orbital calculations on proton affinities of N_2, CO, CO_2 and CH_4 to establish very accurate proton affinities for each of those molecules. The influence of basis set superposition error was also studied. Authors claim, that they have obtained final proton affinities at the chemical accuracy (the errors are supposed to be less than 1 kcal/mol). Good agreement with recently revised absolute proton affinity scale is reported.

Smith and Radom [24] used G2 level of theory to calculate proton affinities for 31 small molecules to evaluate different competing proton affinity scales. Calculated proton affinities were in good agreement with those of Lias et al. [39]. It was found, that various experimental proton affinity scales can be substantially reconciled, if the currently accepted value of the proton affinity of isobutene, used as an absolute standard in several of the experimental determinations, is adjusted downwards by 2-5 kcal/mol. Recent experimental results [40].

3. Results and discussion

3.1. Critical test of the PM3 method for calculating gas-phase (intrinsic) proton affinities

In order to test the usefulness of the PM3 method for calculating proton affinities the calculations for a wide range of acids and bases (175 acids and 119 bases) for whom the corresponding experimental quantities are known were carried out. The species to be calculated were chosen so that they covered wide ranges on the acidity (314.3 - 421.0 kcal/mol) and basicity (63.6 - 240.6 kcal/mol) scales and represented also a wide variety of different classes of acids and bases: hydrocarbons, amines, anilines, aldehydes, ketones, nitriles, alcohols, phenols, etc.; nitro-, fluoro-, cyano-, etc. substituted acids and bases, etc. Numerical results of these calculations as well as results of statistical analysis of calculated and experimental acidities and basicities are presented in articles [II] and [III].

From those results one can conclude that PM3 method can in many cases provide an useful and rather satisfactory quantitative estimate of gas-phase acidities and basicities. However, one has to keep in mind that the average errors are rather big (more than 8 kcal/mol) and in many cases even bigger. Besides to random errors there seem to be also the systematic ones for some classes of compounds, as characterized by the non-zero intercept, non-unity slope and good correlation for these series (see Table 3 in [II], Table 2 in [III] and Table 2 in [VI]. It should be mentioned that for bases and acids the deviations from the unity slope are to the different sides - acids have slope 1.1 while for the bases the corresponding value is 0.8. Similar behavior is earlier noted also for *ab initio* calculated proton affinities [13]. It should also be noted that using the empirical correction, especially for certain classes of compounds, the acidities and basicities can be estimated much more accurately.

The comparison of results from PM3 calculations and *ab initio* calculations shows, that the better fit with experiment can be achieved only using 6-31G* (6-31+G* for deprotonation enthalpies) or higher basis sets (frequently using corrections for electron correlation effects at the post Hartree-Fock level), which makes the use of PM3 method for investigating of larger systems (with 50-100 atoms) quite feasible. When one compares the reliability of PM3 calculated basicities and acidities with the results of AM1 calculations, it could be concluded, that for the prediction of the acidities both methods are roughly of the same quality and also share the same deficiencies: big errors for small anions and also for relatively big and bulky anions. For the calculation of basicities the AM1 method seems somewhat superior. At the same time, the PM3 method can be an useful tool for investigation of proton transfer equilibria of hypervalent compounds of second row elements, for whom the AM1 method is not very reliable [41,42].

3.2 Theoretical Study of Structure and Basicity of Some Alkali Metal Oxides, Hydroxides and Amides

Gas-phase proton affinities and geometries of Li_2O, LiOH, $LiNH_2$, Na_2O, NaOH, $NaNH_2$, K_2O, KOH and KNH_2 were found [IV] using *ab initio* (TZV*, SBK* and 3-21G* or 6-31G* basis sets) calculations. The proton affinities, geometries and charge distributions, obtained using these basis sets were considerably consistent. So one can conclude, that all used basis sets are equally good for that sort of calculations and SBK* basis set as computationally most efficient should be suggested for investigation of similar systems.

Our calculations confirm the experimentally established superiority of intrinsic proton affinities of alkali metal oxides over their hydroxylic counterparts. Also the extremely high basicity of alkali metal amides, often used in organic synthesis as highly effective deprotonating agents, was confirmed. The calculated (SBK* basis set) and experimental proton affinities are collected in Table 1.

Table 1.

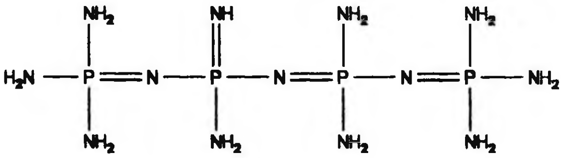
Me	PA(calculated)			PA(experimental)[a]	
	Me_2O	MeOH	MeNH2	Me_2O	MeOH
Li	299.9	250.5	276.8	285.9	239.8
Na	340.8	246.7	297.0	306.7	272.6
K	370.3	287.1	314.0	318.2	262.9

[a] Ref.1 in [IV]

The difference between calculated and experimental proton affinities is considerable (mean average error is more than 25 kcal/mol), but there is good correlation between the above mentioned proton affinities. The latter fact enables us to predict the proton affinities of $LiNH_2$, $NaNH_2$ and KHN_2 to be 257.0, 271.9 and 284.5 kcal/mol respectively.

The oxides and hydroxides of alkali metals were found to be linear. Corresponding cations were planar, as well as were the neutral amides. The cations of latter species were tetrahedral. This is obviously caused by the strong coulombic repulsion forces between hydrogen and metal atoms, which both bear rather big positive charges both in neutrals and cations as evidenced by Mulliken population analysis. The latter also shows big negative charges on oxygen and nitrogen atoms. These facts evidence that the Me-O or Me-N bonds are fairly ionic and the high basicity of title compounds is mainly caused by coulombic stabilization due to the interaction of proton with the highly negatively charged protonation center (oxygen or nitrogen atom).

Our later PM3 calculations on phosphazenes indicate, that such high basicity values are accessible also for organic neutral Brönsted bases. So, for the below presented simple P4 phosphazene



the predicted proton affinity is 281 kcal/mol. That is by ca 30 kcal/mole more than that of 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, which has the highest proton affinity (250.8 kcal/mol) reported [43] so far in the literature.

3.3. Theoretical Study of Prototropic Tautomerism and Acidity of Tris(fluorosulfonyl)methane and hexafluoroacetylacetone

Recently it was suggested [44], that the high acidity of perfluorosulfonyl compounds may be affected by the prototropic tautomerism. Tris-fluorosulfonylmethane was chosen as a model for such systems, and the ability of different molecular orbital calculation methods (PM3, *ab initio* at STO-3G* and 3-21G* levels) to describe prototropic tautomerism was studied in article [V].

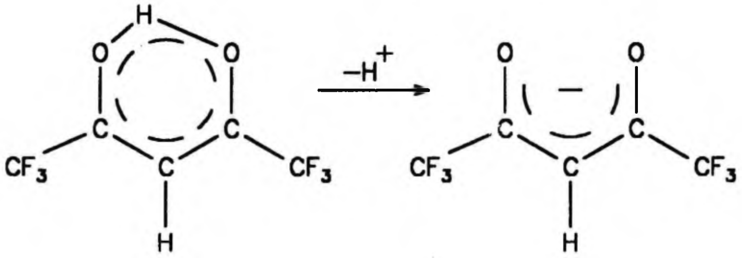
It was shown, that PM3 method totally fails to describe energetics of prototropic tautomerism of $(FSO_2)_3CH$. At the same time it predicts the geometries of both the neutral sulfo form and its anion in good agreement with experiment. Both *ab initio* methods used predicted in accordance with experiment that the sulfone form is more stable than enol form. The conformity between calculated and experimental geometries was also satisfactory.

The gas-phase deprotonation enthalpy of $(FSO_2)_3CH$ was calculated. The analysis of changes in charge distribution upon deprotonation indicate, that the high acidity of this compound is caused by strong charge delocalization in its anionic form.

Keto-enol tautomerism, acidity and intramolecular hydrogen bonding of hexafluoroacetylacetone was studied in article [I] using semiempirical AM1 and PM3 methods without and with the inclusion of limited configuration interaction. It was shown, that both used semiempirical models were able to reproduce the experimental data at least qualitatively (with the preference of enol form) only when CI was taken in account. Using this approach it was shown in accordance with experiment that the most stable conformation of hexafluoroacetylacetone is cyclic hydrogen-bonded enol form. The geometry found for that conformation, however, differs remarkably from that found experimentally [45]: the hydrogen bond O··H-O was found to be nonlinear and also nonsymmetric. On the basis of recent experimentally reestablished geometry of hexafluoroacetylacetone analogue acetylacetone we consider that our geometry may be more proper and the experimental re-examination of hexafluoroacetylacetone geometry is needed.

The hydrogen bond energy was found to be 4.5 kcal/mol and the O···H and O···O distances were 2.09 and 2.86 Å respectively using AM1 method. The proton transfer potential curve was found to have two minima separated by the barrier, which height was predicted to be 24.1 kcal/mol.

Based on the above facts it was suggested that the hexafluoroacetylacetone is rather O-H than C-H acid, which dissociates according formula



The gas-phase deprotonation enthalpy of hexafluoroacetylacetone was found to be 318.8 kcal/mol, what is in satisfactory agreement with experimentally found value 311.2 kcal/mol.

3.4. Superacidity of Neutral Brőnsted Acids in Gas Phase

Previous results and the analysis given in Refs.4-7 in [VI] evidence that three major kinds of substituent effects i.e.,

1. field/inductive effect (F),
2. π-electron acceptor (resonance) effects (R), and
3. substituent polarizability (P) effect,

determine the gas-phase acidity of neutral Brőnsted superacids. For all of those three influencing factors the acidity increases for AH acids are due to much stronger substituent stabilizing interactions with the deprotonated protonization center of A^- (e.g., O^-, N^-, C^-, etc..) than with the protonated reaction center in AH (e.g., OH, NH, CH, etc..).

Therefore, the simplest strategy to develop progressively more acidic superacid systems would be the synthesis of molecules which, along with the acidity site (C-H, O-H, N-H, S-H, etc..), include (several) highly dipolar superacceptor and strongly polarizable substituents which form very extensive, strongly conjugated system with the anionic protonization center of A^-.

Very strong increase in acidities is expected for compounds where sp^2 oxygen is replaced by NSO2CF3 group (Yakupolsii's principle). In the present work PM3 calculations of many potentially superacidic neutral Brőnsted acids designed according this principle were carried out.

The geometries of known superacidic systems were reproduced quite good, so the PM3 method can be recommended for the studies of that kind. Charge distribution, predicted by PM3 for hypervalent compounds is however unreliable, because due to the lack of *d*-orbitals "hypervalent" atoms of these molecules must bear big formal charge to give needed number of formal bonds.

From the geometries of analyzed superacids it can be concluded that the most stable conformations are determined by the resonance interaction which requires the coplanarity of certain molecular fragments. This resonance stabilization seems to be rather strong and sometimes dominates over the electrostatic repulsion between closely located trifluoromethyl groups.

The possibility of creating new, more acidic superacids by continuous replacement of sp^2 oxygens with NSO_2CF_3 groups was proposed.

Acknowledgements

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An AM1 and PM3 study of hexafluoroacetylacetone

Peeter Burk, Ilmar A. Koppel*

Department of Analytical Chemistry, Tartu University, EE2400, Jakobi 2, Tartu, Estonia

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Abstract

The AM1 and PM3 methods with the inclusion of a limited configuration interaction (CI) approach were used to study the stabilities of the tautomers of hexafluoroacetylacetone (HFAA). It was found that the most stable tautomer is the hydrogen bonded cyclic asymmetric enol form, the energy of which is lower than that of any keto tautomer by at least 2.5 kcal mol^{-1} with the AM1 model and 0.9 kcal mol^{-1} with the PM3 model. It was shown that HFAA should be an O–H acid. The intramolecular hydrogen bond energy is 4.5 kcal mol^{-1} with the AM1 model and 4.8 kcal mol^{-1} with the PM3 model. It was shown that proton transfer from one oxygen atom to the other is controlled by the double minimum potential curve and the correspondig energy barrier height is 24.1 kcal mol^{-1} with the AM1 model and 27.4 kcal mol^{-1} with the PM3 model.

Introduction

Hexafluroracetylacetone (HFAA) is a simple, a highly acidic [1] β-diketone, which is most widely known for its ability to form rather stable and specific chelate-type complexes with many cations [2]. Members of the β-diketone family are characterized by keto–enol tautomerism in both the gas and liquid phases. It has been suggested [3,4], that in both phases the enol tautomer generally predominates due to the extra stabilization of a strong intramolecular hydrogen bond and resonance interaction.

Despite numerous theoretical and experimental studies neither the details of the electronic structure nor the geometry of HFAA itself or its chelates seem to have been established with reasonable accuracy. Thus whether there is a centred or noncentred hydrogen bond and whether a single or double minimum potential curve controls the proton transfer from one oxygen atom to the other are hotly debated issues [5]. The earlier gas-phase electron-diffraction measurements [6] indicate that the HFAA molecule forms a planar symmetric ring, from which it can be deduced that proton transfer is controlled by a single minimum potential curve. However, the most recent gas-phase electron-diffraction measurements of the HFAA analogue acetylacetone [7] support the conclusion that the molecular skeleton is planar but asymmetric and the hydrogen atom involved in the hydrogen bond may be located out of the molecular plane (in the case of acetylacetone the angle of rotation of OH around the C–O bond is ca. 26°).

Another question is the evaluation of the hydrogen bond strength. The hydrogen bond in β-diketone enol tautomers is strong and was deduced from the very short O$\cdots$O distance (2.38–2.55 Å) [6,8–10] found in these compounds, in contrast with the usual value of ca. 2.7–3.0 Å in other hydrogen-bonded systems such as acid and water dimers [11–13].

While sophisticated high level ab initio calculations are too expensive, especially when geometry optimization is carried out, the most recent

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* Corresponding author.

semiempirical methods AM1 [14] and PM3 [15] have been shown to evaluate molecular geometries and hydrogen-bond strengths well [16,17] and within an acceptable computation time, thus making calculations on large compounds feasible.

In the present study we used the AM1 and PM3 approaches to investigate HFAA in both its keto and enol tautomeric form, with special emphasis on the determination of the minimum-energy molecular geometries of all possible conformations of neutral HFAA and its cation. The hydrogen bond strength and barrier, the potential energy curve governing the proton transfer process, and the gas-phase acidity were calculated. At the same time a comparison between theoretical and experimental results could give useful indications as to the reliability of the method used.

Methods

The MOPAC 6.0 package from the Quantum Chemistry Program Exchange [18] was used. Calculations were performed on a MicroVAX II computer. All the geometries of the various conformations of HFAA were fully optimized at the limited configuration interaction (CI) level using standard procedure: no restrictions were imposed. For this purpose 36 configurations, arising from the two highest occupied and the two lowest virtual orbitals, were included in each calculation. Although it has been pointed out [19] that adoption of such a method (semiempirical method with CI) leads to calculation of twice the correlation energy (because the electron correlation effects are partially included in the parameterization of the method) we included CI because it improves the calculated enthalpies of formation (using the AM1 model without CI the most stable keto and enol tautomers had practically the same heat of formation, while with CI the most stable enol tautomer was approximately 2.5 kcal mol^{-1} lower in energy than any keto tautomer, which agrees with the experimental results).

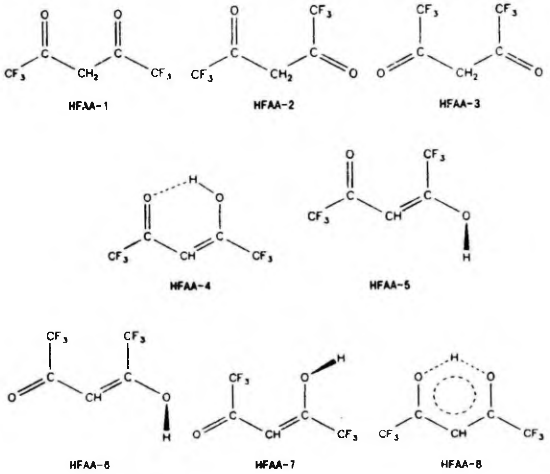
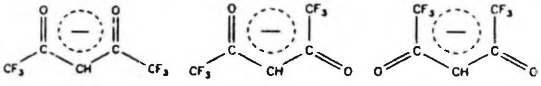


Fig. 1. Calculated conformations of neutral hexafluoroacetylacetone.



HFAN-1 HFAN-2 HFAN-3

Fig. 2. Calculated conformations of the hexafluoroacetylacetone anion.

Results and discussion

Three keto and five enol tautomers and the proton transfer transition state of neutral HFAA were taken into account (see Fig. 1). In the estimation of the gas-phase acidity of HFAA the geometries and heats of formation of all the conformations of the deprotonated form were also calculated. Three calculated conformations of deprotonated HFAA (HFAN) are shown in Fig. 2. For all enol tautomers calculations were also done for conformations where the O–H bond is rotated by 180° in order to avoid premature completion of calculations of the local minimum. In the tables and figures only the most stable conformations are presented.

The diketo structures differ from the enol structures mainly in the position of the two double bonds: in the former the two C=O groups are isolated, being separated by a CH_2 group; in the latter the C=C and C=O double bonds are conjugated so that the enol tautomer is resonance stabilized and forced to planarity by both conjugation and the presence of a hydrogen bond.

The planarity of the cis-diketo isomers might be perturbed by the repulsion between the two oxygen atoms (HFAA-1) or by the steric hindrance between the two trifluoromethyl groups (HFAA-3). An analogous situation may occur in the case of cis-enol conformations without a hydrogen bond.

In fact HFAA-1 was found to be almost planar when using PM3 parameterization. It should be mentioned that AM1 could not locate an energy minimum corresponding to HFAA-2 when geometry optimization was started from this structure; the result was the geometry of the most stable keto tautomer (HFAA-1). The results of

Table 1
Results of the calculation on the HFAA keto structures

	HFAA-1		HFAA-2 PM3	HFAA-3 AM1	HFAA-3 PM3
	AM1	PM3			
Bond length (Å)					
R(C=O)	1.221	1.202	1.207	1.232	1.212
R(C–F)	1.370	1.349	1.348	1.371	1.348
R(C–H)	1.129	1.113	1.113	1.138	1.116
R(C1–C2)	1.569	1.590	1.586	1.569	1.565
R(C2–C3)	1.494	1.504	1.513	1.498	1.516
∠C2–C3–C4=O[a] (deg)	39.9	0.5	166.8	176.4	178.0
ΔH (kcal mol^{-1})	−370.9	−377.5	−374.9	−354.6	−363.8
μ[b] (D)	2.012	1.727	2.311	2.281	2.279

[a] The carbon atoms in Fig. 1 are numbered from left to right.

[b] Calculated using AM1 or PM3 without CI at the geometries calculated with AM1 or PM3 with CI.

Table 2
Results of the AM1 calculation on the HFAA enol tautomers

	HFAA-4	HFAA-5	HFAA-6	HFAA-7	HFAA-8
Bond length (Å)					
R(C=O)	1.236	1.229	1.223	1.231	1.291
R(C–O)	1.350	1.357	1.361	1.350	1.291
R(O–H)	0.978	0.972	0.972	0.972	1.248
R(C4–C5)	1.566	1.572	1.577	1.566	1.551
R(C3–C4)	1.445	1.450	1.459	1.352	1.403
R(C2–C3)	1.356	1.357	1.356	1.446	1.404
R(C1–C2)	1.550	1.544	1.543	1.569	1.550
R(C–F)	1.370	1.370	1.369	1.369	1.370
R(C–H)	1.105	1.106	1.108	1.113	1.097
∠C2–C3–C4–O[a] (deg)	0.1	176.0	129.2	0.8	1.2
ΔH (kcal mol^{-1})	−373.4	−368.2	−368.6	−369.1	−349.2
μ[b] (D)	0.828	4.310	3.949	0.679	0.295

[a] The carbon atoms in Fig. 1 are numbered from left to right.
[b] Calculated using AM1 or PM3 without CI at the geometries calculated with AM1 or PM3 with CI.

the calculations on the keto tautomers are presented in Table 1.

The structures of the HFAA-4 and HFAA-5 enol tautomers are planar, while HFAA-6 is non-planar. The transition state HFAA-8 is planar and symmetrical. The results of the calculations on the enol tautomers are presented in Tables 2 and 3.

The heats of formation for all the calculated tautomers are presented in Tables 1 to 3. It can be seen that in the case of both AM1 and PM3

Table 3
Results of the PM3 calculation on the HFAA enol tautomers

	HFAA-4	HFAA-5	HFAA-6	HFAA-7	HFAA-8
Bond length (Å)					
R(C=O)	1.222	1.210	1.205	1.210	1.279
R(C–O)	1.338	1.349	1.351	1.341	1.280
R(O–H)	0.967	0.951	0.950	0.956	1.183
R(C4–C5)	1.575	1.589	1.585	1.560	1.556
R(C3–C4)	1.453	1.461	1.474	1.354	1.405
R(C2–C3)	1.362	1.358	1.356	1.463	1.404
R(C1–C2)	1.552	1.554	1.549	1.590	1.556
R(C–F)	1.349	1.349	1.349	1.349	1.350
R(C–H)	1.097	1.102	1.101	1.104	1.095
∠C2–C3–C4–O[a] (deg)	1.1	176.5	121.2	2.8	2.0
ΔH (kcal mol^{-1})	−378.5	−373.2	−376.9	−374.4	−351.1
μ[b] (D)	0.359	4.312	4.339	0.716	0.480

[a] The carbon atoms in Fig. 1 are numbered from left to right.
[b] Calculated using AM1 or PM3 without CI at the geometries calculated with AM1 or PM3 with CI.

Table 4
Results of the calculation on the HFAA anions

	HFAN-1		HFAN-2		HFAN-3	
	AM1	PM3	AM1	PM3	AM1	PM3
Bond length (Å)						
R(C=O)	1.241	1.225	1.246	1.229	1.253	1.235
R(C–F)	1.374	1.354	1.372	1.354	1.374	1.353
R(C–H)	1.098	1.093	1.099	1.095	1.113	1.102
R(C1–C2)	1.591	1.612	1.572	1.588	1.582	1.596
R(C2–C3)	1.399	1.404	1.401	1.408	1.398	1.405
∠C2–C3–C4=O[a] (deg)	0.1	0.5	175.9	174.8	176.7	173.8
ΔH(kcal mol^{-1})	−433.5	−439.0	−431.5	−438.0	−422.4	−434.2
μ[b] (D)	3.907	4.212	1.807	1.900	3.688	2.798

[a] The carbon atoms in Fig. 2 are numbered from left to right.
[b] Calculated using AM1 or PM3 without CI at the geometries calculated with AM1 or PM3 with CI.

the most stable tautomer is the enol having an intramolecular hydrogen bond (HFAA-4). The energy of HFAA-4 is lower than that of any keto tautomer by at least 2.5 kcal mol^{-1} with the AM1 model and by 0.9 kcal mol^{-1} with the PM3 model.

The enol tautomer with a hydrogen bond was found to be antisymmetrical. This does not agree with the experimentally determined geometry, but on the basis of calculations [20] and experiments [7] on the HFAA analogue, acetylacetone, we consider that further experimental investigation of the HFAA structure will agree with the results of our calculations. The distance between oxygen atoms was 2.86 Å with AM1 and 2.65 Å with PM3. The hydrogen bond length was 2.09 Å with AM1 and 1.83 Å with PM3. This also agrees with both calculated [20] and measured [7] values for acetylacetone.

On the basis of the total energy, and in agreement with experimentally determined keto–enol equilibrium [3,4], enol forms prevail over the corresponding diketo conformers.

In the case of anions, the most stable one is the symmetrical conformation HFAN-1, which would be expected because this conformer corresponds to the most stable enol conformer (HFAA-4) and also to the keto conformation (HFAA-1). The energies and geometries of the most stable anions are presented in Table 4. The conformation HFAN-4 is much more unstable than the others (its heat of formation is −403.7 kcal mol^{-1} with AM1 and −405.2 kcal mol^{-1} with PM3. Thus, because the most stable conformation of neutral HFAA is the hydrogen bonded cyclic enol (HFAA-4) and the most stable HFAA anion is HFAN-1, it can be concluded that HFAA is an O–H acid. The deprotonation energy (acidity) (DPE) of HFAA was calculated as

$$\mathrm{DPE} = \Delta H(\mathrm{H}^+) + \Delta H(\mathrm{An}^-) - \Delta H(\mathrm{AnH})$$

where $\Delta H(\mathrm{An}^-)$ is the calculated heat of formation of the HFAA anion, ΔH(AnH) is that for neutral HFAA, and $\Delta H(\mathrm{H}^+)$ is the heat of formation of a proton (in the case of PM3 the calculated value (353.6 kcal mol^{-1}) was used, while in the case of AM1 the experimental value (367.2 kcal mol^{-1}) was used, because AM1 gives a very poor estimate of the heat of formation of a proton). The DPE was found to be 318.8 kcal mol^{-1} with AM1 and 293.1 kcal mol^{-1} with PM3, which is in reasonable agreement with the experimentally determined value of 311.2 kcal mol^{-1} [1].

The hydrogen bond energy, which was found as the difference between the energy of HFAA-4 and the energy of the HFAA-4 analogue with the O–H bond rotated by 180°, was 4.5 kcal mol^{-1} with the AM1 model and 4.8 kcal mol^{-1} with the PM3 model.

On the basis of the results obtained here, and in agreement with suggestions in the literature [5,20], the hydrogen atom implied in the hydrogen bridge can transfer from an oxygen atom of the asymmetrical cis-enol tautomer to the other position via a transition state (HFAA-8). The proton transfer potential curve was calculated assuming that this process is slow enough for geometry relaxation [20]. The curve shows two minima separated by an energy barrier, the height of which (calculated as the difference between the energies of the transition state (HFAA-8) and the asymmetrical hydrogen bonded enol form (HFAA-4)) is 24.1 kcal mol^{-1} in the AM1 model and 27.4 kcal mol^{-1} in the PM3 model.

Conclusions

It was found that the most stable tautomer of HFAA is the hydrogen bonded cyclic asymmetrical enol form. The energy of this tautomer is lower than that of any keto tautomer, by at least 2.5 kcal mol^{-1} (AM1) or 0.9 kcal mol^{-1} (PM3). It was shown that HFAA preferentially dissociates as a rather strong O–H acid. The intramolecular hydrogen bond energy is 4.5 kcal mol^{-1} (AM1 model) or 4.8 kcal mol^{-1} (PM3 model). Our calculations show that the proton transfer from one oxygen atom to another is controlled by the double well potential curve and the corresponding energy barrier height is 24.1 kcal mol^{-1} (AM1) or 27.4 kcal mol^{-1} (PM3).

Both the AM1 and PM3 methods were able to reproduce the experimental data at least qualitatively only when CI was taken into account.

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Critical test of PM3 calculated gas-phase acidities

Peeter Burk and Ilmar A. Koppel
Department of Analytical Chemistry, Tartu University EE2400, Jakobi 2, Tartu, Estonia

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Summary. Gas-phase acidities have been calculated for 175 compounds using the PM3 semiempirical molecular orbital model. With some exceptions, PM3 seems to be a useful tool for the investigation of gas-phase acidities. The main problems encountered involve two rather different classes of acids: one which generates small anions (e.g., halide ions, hydride ion, etc.), in which the charge is localized on one atom, and, a second, represented by anions that contain bulky electron acceptor substituents characterized by an extensive negative charge delocalization. In some cases (anilines, amides, alcohols, and phenols) the average error in predicted gas-phase acidity can be significantly reduced by employing an empirically derived correction.

Comparison with AM1 results shows that both methods are of roughly equal quality with the exception of hypervalent molecules where PM3 is better (averaged unsigned errors are 11.8 and 17.0 kcal/mol for PM3 and AM1, respectively).

Key words: Gas-phase acidities - PM3 - AM1

1 Introduction

In recent years quantum chemical calculations have become a widely used tool for the investigation of a wide range of problems [1]. Both *ab initio* and semiempirical self-consistent field molecular orbital calculations are often used. The widespread application of the semiempirical MINDO/3 [2], MNDO [3], AM1 [4], and PM3 [5] methods is due to the fact that they often give reliable answers, are easy to use, require relatively little computer time, and can handle large molecules.

Proton transfer reactions play a basic role in chemistry and in biochemistry. As a result, besides the gas phase basicities or proton affinities of neutral bases, also numerous calculations of gas phase acidities of neutral Bronsted acids have appeared [1, 6, 7 and references therein]. These computations require the heats of formation of the acid and the conjugated base, the latter being an anion for uncharged acids. It is known [1, 8], that *ab initio* methods require the addition of diffuse orbitals in order to obtain reliable energies for anions. This requirement further limits the size of a molecule that can be calculated in a reasonable time. Semiempirical methods, at the same time, are reported to reproduce the energies of anions almost as well as for neutral molecules [4, 6, 9–13]. Known exceptions are small anions with charge predominantly localized on a single atom, such as CH_3^- and OH^- where the calculated energies are consistently too positive. This error is probably [14] due to failure to allow for orbital expansion accompanying large localized negative charge.

However, there have been only a few systematic investigations [1, 6, 7, 11, 15–17] testing the reliability of different methods for prediction of gas-phase acidities and none dealing with the PM3 method. Therefore the current investigation was undertaken to evaluate the reliability of the PM3 method for predicting gas-phase acidities.

A useful way to consider agreement between experiment and theory is to calculate the linear regression between the theoretical and experimental quantities and to calculate the mean difference (unsigned average error) between the experimental and theoretical quantities. The degree of agreement between the two is then reflected by the slope and intercept of the correlation line, the unsigned average error, the standard deviation from the correlation line and the correlation coefficient. The last two depend on the scatter of the points about the correlation line. A *slope different from unity* and a *non-zero intercept* imply systematic deviation between experiment and theory and means that the theoretical values of relative acidities will be systematically either too high or too low. A non-zero mean difference between theory and experiment reflects an overall bias in the absolute values of the calculated acidity.

2 Method

The acidity (ΔH_{acid}) of compound HA was found as the heat of reaction for the proton abstraction equilibrium to form the conjugate base A^-:

$$HA \rightleftharpoons H^+ + A^- \quad \Delta H_{acid}(HA) = \Delta H_f(H^+) + \Delta H_f(A^-) - \Delta H_f(HA) \qquad (1)$$

where $\Delta H_f(H^+)$, $\Delta H_f(HA)$, and $\Delta H_f(A^-)$ are the heats of formation for proton, acid, and its conjugated anion. In case of proton the experimental heat of formation (367.2 kcal/mol [19]) was used instead of the calculated value (353.6), because it improves the calculated acidities considerably. We acknowledge that this is not quite a correct procedure, despite the fact that such a way was also used in earlier works on semiempirical calculations of acidities and basicities [6, 11].

The calculations were carried out on a MicroVAX II computer using the standard PM3 procedure, as implemented in the MOPAC 6.0 program package [20]. All geometries were fully optimized by minimizing the energy with respect to all geometrical variables without using the aid of symmetry. In order to avoid premature completion of calculations in local minimum, the calculations were carried out starting off from several different initial geometries.

3 Results and discussion

Acidities for 175 compounds, calculated using the PM3 method, are given in Table 1, along with corresponding experimentally measured values when avail-

Table 1. Comparison with experiment of PM3 heats of formation and acidities (kcal/mol)

	calc ΔH_f		ΔH_{acid}			exp ΔH_f (HA)	error in calc ΔH_f (HA)
	HA	A^-	calc	exp[a]	error		
			C–H acids				
Methane	−13.0	51.5	430.2	416.6	13.6	−17.8	4.8
Ethane	−18.1	31.7	415.5	421.0	−5.5	−20.1	2.0
Propane	−23.6	14.8	404.1	419.0	−14.9	−25.0	1.4
Cyclopropane	16.3	60.2	409.7	412.0	−2.3	12.7	3.6
t-Butane	−24.4	0.0	390.1	414.0	−23.9	−32.1	7.7
Ethene	16.6	61.7	410.8	406.0	4.8	12.5	4.1
Propene	6.4	25.2	384.5	387.5	−3.0	4.8	1.6
2-Methylpropene	−2.8	16.1	384.6	390.3	−5.7	−4.0	1.2
2-Methyl-1,3-butadiene	22.8	39.0	381.9	385.7	−3.8	17.9	4.9
Cyclopentadiene	31.8	15.9	349.8	353.9	−4.1	31.0	0.8
Ethyne	50.7	76.4	391.4	376.7	14.7	54.5	−3.8
Propyne	40.2	64.2	389.7	381.1	8.6	44.6	−4.4
1-Pentyne	40.2	54.5	380.0	379.8	0.2	34.4	5.8
t-Bu-acetylene	31.8	47.4	381.3	378.0	3.3	25.0	6.8
Phenylacetylene	74.7	86.8	377.8	370.7	7.1	73.1	1.5
Benzene	23.5	51.7	393.9	400.7	−6.8	19.8	3.7
Toluene	14.1	18.5	370.1	380.8	−10.7	12.0	2.1
1,4-Dimethylbenzene	4.8	8.7	369.6	381.9	−12.3	4.3	0.5
Ethylbenzene	9.5	8.5	364.7	379.8	−15.1	6.9	2.5
i-Propylbenzene	4.9	−1.2	359.6	379.0	−19.4	1.0	3.9
Cycloheptatriene	46.4	43.1	362.3	375.2	−12.9	43.7	2.7
Fluorene	49.0	27.7	344.4	353.3	−8.9	44.9	4.1
9-Ph-fluorene	79.6	43.6	329.7	343.3	−13.6	76.0[b]	3.6
Fluoradene	10.0	72.9	328.7	332.5	−3.8		
Diphenylmethane	43.0	26.8	349.5	363.6	−14.1	33.5	9.6
1,4-DiPh-cyclo-pentadiene	78.4	42.5	329.8	337.7	−7.9	77.0[b]	1.4
CH_3Br	−5.0	27.2	397.9	392.7	5.2	−9.1	4.1
CH_3Cl	−14.7	20.7	401.1	396.0	5.1	−19.6	4.9
CH_2Cl_2	−17.1	−7.9	374.9	374.6	0.3	−22.9	5.8
$CHCl_3$	−20.9	−35.2	351.4	357.1	−5.7	−25.0	4.1
$ClCH_2$-acetylene	38.2	50.1	377.6	368.1	9.5	39.0[b]	−0.8
Cl-benzene	16.7	35.8	384.8	387.2	−2.4	13.0	3.7
Nitromethane	−15.9	−43.3	338.3	356.4	−18.1	−17.9	2.0
Nitroethane	−19.7	−53.3	332.1	356.0	−23.9	−24.4	4.7
2-Nitropropane	−27.1	−61.8	331.0	356.1	−25.1	−33.2	6.1
Nitromethyl-*t*-butane	−51.1	−68.2	348.6	355.2	−6.6	−45.2[h]	−6.0
m NO_2-toluene	5.1	−7.7	352.9	362.9	−10.0	7.0	−1.9
HCN	33.0	27.7	360.5	351.2	9.3	32.3	0.7
Cyanomethane	23.3	28.5	370.9	372.9	−2.0	18.0	5.3
Cyanoethane	18.5	17.1	364.2	375.0	−10.8	12.3	6.3
2-Cyanopropane	13.4	6.1	358.4	375.2	−16.8	5.8	7.6
Cyanocyclopropane	52.2	53.7	367.2	375.4	−8.2	44.0	8.2
2-Cyanopropene	41.0	42.6	367.4	370.7	−3.3	31.0	10.0
*p*CN-toluene	49.0	34.7	351.4	360.8	−9.4		
Cyanotoluene	43.2	28.6	351.1	351.9	−0.8		
$PhCH(CN)_2$	94.7	47.5	318.5	322.1	−3.6		
FCH_2CN	−13.1	−20.5	358.3	369.2	−10.9		
Metoxycyanomethane	−10.2	−13.7	362.1	371.8	−9.7	−8.0[h]	−2.2
m CF_3-$C_6H_4CH_2CN$	−105.3	−138.2	332.8	341.9	−9.1	−115.9[h]	10.6

Table 1. (continued)

	calc ΔH_f		ΔH_{acid}			exp ΔH_f (HA)	error in calc ΔH_f (HA)
	HA	A^-	calc	exp[a]	error		
*p*COCN-toluene	19.7	−2.6	343.4	345.7	−2.3	3.6[b]	16.2
Methyl ether	−46.9	−5.0	407.7	407.0	0.7	−44.0	−2.9
Ethanal	−44.2	−39.9	370.0	365.8	4.2	−39.6	−4.6
Propanal	−47.1	−51.4	361.5	365.3	−3.8	−44.8	−2.3
Propanone	−53.0	−48.6	370.0	369.1	0.9	−51.9	−1.1
Phenylmethylketone	−17.7	−20.2	363.2	361.3	1.9	−20.8	3.1
Benzylmethylketone	−23.0	−43.7	345.0	351.8	−6.8	−23.4	0.4
Ethylphenylketone	−22.8	−20.6	358.9	360.5	−1.6	−26.1	3.3
MeCO-acetylene	9.4	15.9	372.2	360.1	12.1	15.6	−6.2
MeOCO-acetylene	−29.6	−26.9	368.4	358.8	9.6	−24.0[b]	−5.6
4-Methoxyphenylmethylketone	−54.8	−58.5	362.0	362.8	−0.8	−58.3	3.5
Methyl acetate	−92.8	−92.8	365.7	371.9	−6.2	−98.0	5.2
Dimethyl ethane-amide	−52.2	−49.0	368.9	374.9	−6.0	−55.9	3.7
Me_2S	−10.4	2.3	378.4	393.2	−14.8	−9.0	−1.4
$PhSCH_3$	23.9	25.0	366.8	381.6	−14.8	23.4	0.5
$MeSOM_e$	−10.4	2.3	378.4	373.5	4.9	−36.2	25.8
$MeSO_2Me$	−76.2	−90.6	351.3	365.8	−14.5	−89.0	12.8
pSO_2Me-toluene	−51.0	−71.7	345.0	358.8	−13.8	−65.2	14.2
CF_3SO_2Me	−207.7	−250.5	322.9	347.0	−24.1		
$CF_3SO_2CH = CHMe$	−192.8	−239.0	319.5	343.3	−23.8	−222.0[b]	29.2
pSO_2CF_3-toluene	−182.8	−217.7	330.8	347.4	−16.6		
Pyridine	30.4	48.2	383.5	391.9	−8.4	33.0	−2.6
Pyrimidine	38.0	43.6	371.4	383.3	−12.4	47.0	−9.0
Me_3P	−29.8	−4.3	391.2	391.3	−0.1	−24.1	−5.7
$CH_2 = Se(Me)CH_3$	3.5	29.8	392.0	385.6	6.4	5.0	−1.5
$SiMe_4$	−53.5	−18.7	400.5	397.0	3.5	−55.7	2.2
N–H acids							
Ammonia	−3.1	38.3	407.1	403.6	3.5	−11.0	7.9
Methylamine	−5.2	38.3	407.1	403.6	3.5	−11.0	7.9
Methylamine	−5.2	21.7	392.6	403.3	−10.7	−5.5	0.3
Ethylamine	−11.1	17.0	393.8	399.3	−5.5	−11.3	0.2
Dimethylamine	−8.0	7.8	381.5	396.2	−14.7	−4.4	−3.6
Me_3SiNH_2	−57.9	−41.6	382.0	378.8	3.2		
Aniline	21.3	14.3	358.7	366.4	−7.7	20.8	0.5
pCH_3-aniline	12.1	4.7	358.3	367.3	−9.0	14.1[b]	−2.1
*m*Cl-aniline	14.4	1.5	352.8	358.9	−6.1	13.0[b]	1.4
*p*Cl-aniline	14.4	1.2	352.5	360.4	−7.9	13.0[b]	1.4
mOCH_3-aniline	15.2	5.2	355.7	366.8	−11.1	12.9[b]	2.3
pOCH_3-aniline	−15.4	−25.8	355.3	367.1	−11.8	−14.1[b]	−1.3
*p*CHO-aniline	−13.6	−34.8	344.5	349.6	−5.1	−8.1[b]	−5.4
mNO_2-aniline	12.5	−10.4	342.7	352.3	−9.6	15.0	−2.4
pNO_2-aniline	10.7	−24.1	330.9	343.5	−12.6	13.0	−2.3
mSO_2CF_3-aniline	−174.9	−202.7	337.9	346.9	−9.0		
pSO_2CF_3-aniline	−178.4	−209.5	336.1	338.6	−2.5		
Pyrrole	27.1	11.5	350.0	358.7	−8.7	25.9	1.2
$HCONH_2$	−41.8	−50.5	357.0	359.9	−2.9	−44.0	2.1
$PhCONH_2$	−16.1	−28.7	353.2	354.1	−0.9	−24.0	7.9
H_2NCONH_2	−45.8	−53.8	357.7	362.6	−4.9	−58.8	13.0
CF_3CONH_2	−196.2	−223.8	338.1	343.8	−5.7	−200.0[b]	3.8
Cl_3CCONH_2	−55.7	−81.1	340.3	343.2	−2.9	−56.2[b]	0.4

Table 1. (continued)

	calc ΔH_f		ΔH_{acid}			exp ΔH_f (HA)	error in calc ΔH_f (HA)
	HA	A^-	calc	exp[a]	error		
HCONHMe	−43.7	−53.0	356.3	360.4	−4.1	−45.0[b]	1.3
Acetaminobenzene	−22.0	−47.2	340.4	347.5	−7.2	−30.8	8.9
$CF_3CONHPh$	−165.2	−209.4	321.4	333.4	−12.0	−168.7[b]	3.6
		O–H acids					
Water	−43.4	−17.5	401.6	390.7	10.9	−57.8	4.4
Methanol	−51.1	−37.9	378.8	380.6	−1.8	−48.2	−2.9
Ethanol	−58.7	−44.8	379.7	378.0	1.7	−56.1	−2.6
Propanol	−64.1	−51.4	378.3	376.0	2.3	−60.9	−3.2
Isopropanol	−65.8	−54.9	376.6	375.4	1.2	−65.1	−0.7
Isobutanol	−67.7	−56.9	376.5	374.7	1.8	−67.8	0.1
t-Butanol	−65.7	−54.9	376.6	374.6	2.0	−74.7	9.0
t-Bu-methanol	−75.5	−58.8	382.3	372.6	9.7	−76.0[b]	0.5
1-*t*-Bu-ethanol	−79.2	−64.2	380.7	371.1	9.6	−83.9[b]	4.7
1-*t*-Bu-propanol	−81.2	−74.0	372.8	370.0	2.8	−88.7[b]	7.5
1-*t*-Bu-isobutanol	−89.6	−76.2	379.0	368.5	10.5	−93.7[b]	4.1
1-*t*-Bu-methanol	−88.2	−78.9	375.0	366.4	8.6	−99.2[b]	11.0
Phenylmethanol	−22.4	−18.6	369-5	370.0	−0.5	−23.9	1.5
2-Methoxyethanol	−92.7	−83.6	374.7	373.8	0.9	−87.0[b]	−5.7
F_2CHCH_2OH	−151.8	−155.6	361.9	366.4	−4.5	−148.2[b]	−3.6
$CF_3CH(Me)OH$	−214.4	−231.5	348.5	360.3	−11.8	−216.3[b]	1.9
$(CF_3)_2CHOH$	−360.6	−398.4	328.2	344.9	−16.7	−367.0[b]	6.4
$CF_3CH_2CH_2OH$	−305.6	−325.7	345.5	355.4	−9.9	−313.9	7.4
$(CF_3)_3COH$	−516.6	−572.6	309.7	331.6	−21.9	−549.0[b]	32.4
Et_3SiOH	−133.2	−125.8	373.1	360.5	12.6	−133.6[b]	0.4
Phenol	−21.7	−44.1	343.3	349.2	−5.9	−23.0	1.3
*p*Me-phenol	−30.9	−53.9	342.8	351.6	−8.8	−29.9	−1.0
*m*Et-phenol	−35.6	−56.5	344.8	349.3	−4.5	−34.9	−0.7
*m*F-phenol	−65.4	−94.5	336.5	344.5	−8.0	−71.0[b]	5.6
pCF_3-phenol	−180.6	−219.1	327.2	337.2	−10.0	−182.8[b]	2.2
*p*CN-phenol	13.1	−25.8	326.9	332.2	−5.3	10.3[b]	2.8
mNO_2-phenol	−29.9	−68.7	326.8	334.6	−7.8	−27.0[b]	−2.9
pNO_2-phenol	−31.7	−81.5	315.8	327.8	−12.0	−28.0[b]	−3.7
*m*COMe-phenol	−63.0	−91.5	337.2	342.5	−5.3	−78.5	15.7
mSO_2Me-phenol	−85.6	−121.5	329.9	336.1	−6.2	−105.9[b]	20.3
pSO_2CF_3-phenol	−219.6	−275.7	309.6	322.6	−13.0		
$CH_3CH{=}NOH$	−2.9	−14.9	353.7	365.6	−11.9	−4.8	1.9
$C_6H_5CH{=}NOH$	30.6	3.4	338.5	352.9	−14.4	25.8[b]	4.8
$(CH_3)_3CCH{=}NOH$	−17.5	−31.1	352.1	364.6	−12.5	−32.3[b]	14.8
$(CH_3)_2C{=}NOH$	−11.6	−24.9	352.5	366.1	−13.6	−15.0[b]	3.4
Et_2NOH	−27.7	−14.8	378.6	370.6	8.0	−8.6[b]	−19.1
Formic acid	−90.1	−110.9	344.9	345.2	−0.3	−90.5	0.4
Acetic acid	−99.3	−119.6	345.3	348.5	−3.2	−103.3	4.0
Propanoic acid	−104.3	−124.9	345.1	347.3	−2.2	−107.0	2.7
t-BuCOOH	−113.8	−129.6	349.9	344.6	5.3	−122.0[b]	8.2
$MeOCH_2COOH$	−133.3	−154.3	344.7	341.6	3.1	−132.9[b]	−0.4
FCH_2COOH	−139.7	−165.8	339.6	338.8	0.8	−140.1[b]	0.4
CHF_2COOH	−186.6	−222.8	329.5	330.0	−0.5	−196.9[b]	10.3
CF_3COOH	−244.0	−290.4	319.3	322.7	−3.4	−246.3	2.3
CF_3CH_2COOH	−254.9	−287.2	333.4	334.8	−1.4	−259.3[b]	4.4
$ClCH_2COOH$	−101.3	−127.4	339.6	336.3	3.3	−104.0	2.7

Table 1. (continued)

	calc ΔH_f		ΔH_{acid}			exp	error
	HA	A^-	calc	exp^a	error	ΔH_f (HA)	in calc ΔH_f (HA)
$CHCl_2COOH$	−102.4	−135.1	333.0	327.3	5.7	−102.1^b	−0.4
$Cl(CH_2)_3COOH$	−109.0	−135.0	339.7	345.4	−5.7	−119.7^b	10.8
$BrCH_2COOH$	−89.6	−116.4	338.9	334.0	4.9	−94.4^b	4.8
MeCHBrCOOH	−99.0	−125.2	339.5	336.2	3.3	−103.3^b	4.2
EtCHBrCOOH	−103.9	−130.4	339.2	336.4	2.8	−114.0^b	10.1
Benzoic acid	−66.2	−89.7	342.2	338.3	3.9	−70.3	4.1
pCH_3-benzoic acid	−223.1	−254.9	333.9	332.4	1.5	−233.3^b	10.2
3,5-DiCF_3-benzoic acid	−378.7	−416.8	327.7	324.4	3.3	−391.3^b	12.5
*p*CN-benzoic acid	−30.0	−61.4	334.3	328.5	5.8	−37.8^b	7.8
mNO_2-benzoic acid	−66.4	−97.1	335.0	329.5	5.5	−94.3	27.9
pNH_2-benzoic acid	−69.2	−91.5	343.4	341.1	2.3	−70.0	0.8
*m*OH-benzoic acid	−110.9	−136.3	340.3	337.9	2.4	−112.3^b	1.4
			S–H acids				
H_2S	−0.9	−15.9	350.8	351.2	−0.4	−4.9	4.0
MeSH	−5.5	−22.1	349.1	356.9	−7.8	−5.5	0.0
EtSH	−8.4	−25.2	348.9	355.2	−6.3	−11.1	2.7
n-PrSH	−13.7	−31.1	348.3	354.2	−5.9	−16.2	2.5
i-PrSH	−14.4	−28.1	352.0	353.4	−1.4	−18.2	3.8
n-BuSH	−24.5	−42.3	347.9	353.7	−5.8	−21.1	−3.4
i-BuSH	−16.0	−33.5	348.2	353.1	−4.9	−23.3	7.3
t-BuSH	−17.8	−35.7	347.8	353.0	−5.2	−26.2	8.4
t-BuCH_2SH	−24.7	−43.1	347.3	351.7	−4.4	−30.8	6.2
			Other acids				
H_2	−13.2	91.8	470.9	400.4	70.5	0.0^c	−13.4
Me_3SiH	−37.2	−50.7	352.2	381.2	−29.0	−39.0	1.8
SiH_4	13.1	−2.8	349.8	372.3	−22.5	8.0	5.1
PH_3	0.2	−14.5	351.0	370.9	−19.9	1.3	−1.1
HF	−59.7	−17.1	409.8	371.4	38.4	−65.1	5.4
HCl	−20.5	−51.2	336.5	333.7	2.8	−22.1	1.6
HBr	5.3	−56.2	305.7	322.4	−16.7	−8.7	14.0
HI	28.8	−64.6	273.8	314.3	−40.5	6.3	22.5

^{a} – from Ref. [19]
^{b} – estimated in Ref. [19]
^{c} – by definition

able. These particular compounds were chosen because they cover a wide range of acidities for different classes of compounds (C–H, O–H, N–H, S–H acids; alcohols, amines, anilines, phenols, hydrocarbons, etc., fluoro-, nitro-, cyano-, etc. substituted acids, etc.). In Table 2 the analogous results, calculated with AM1 method, for 11 hypervalent compounds are presented.

The results of statistical (regression) analysis according to the formula:

$$\Delta H_{acid}(\text{calc}) = a + b \cdot \Delta H_{acid}(\text{exp}) \tag{2}$$

are presented in Table 3, where N is the number of points, ΔH_{acid}^{min} is minimal and ΔH_{acid}^{max} maximal experimental gas-phase acidity in considered group; $\delta\Delta H_{acid}$ is the average unsigned error in acidities, R is the correlation coefficient, σ is the

Table 2. Comparison with experiment of AM1 heats of formation and acidities (kcal/mol) for hypervalent compounds

	calc ΔH_f		ΔH_{acid}			exp ΔH_f (HA)	error in calc ΔH_f(HA)
	HA	A^-	calc	exp[a]	error		
mSO$_2$Me-phenol	−82.9	−115.9	334.2	336.1	−1.9	−105.9	23.0
pSO$_2$Me-toluene	−46.6	−72.8	341.0	358.8	−17.8	−65.2	18.7
MeSO$_2$Me	−70.0	−94.0	343.2	365.8	−22.6	−89.0	19.0
MeSOMe	−8.7	8.6	384.5	373.5	11.0	−36.2	27.5
pSO$_2$CF$_3$-phenol	−222.4	−282.7	307.0	322.6	−15.6		
CF$_3$SO$_2$CH=CHMe	−193.8	−251.8	309.2	343.3	−34.1	−222.0	28.2
mSO$_2$CF$_3$-aniline	−177.1	−202.1	342.2	346.9	−4.7		
CF$_3$SO$_2$Me	−204.3	−262.2	309.3	347.0	−37.7		
pSO$_2$CF$_3$-toluene	−184.7	−277.5	324.3	347.4	−23.1		
pSO$_2$CF$_3$-aniline	−186.5	−213.6	340.1	338.6	1.5		

[a] – from Ref. [19]

Table 3. Results of statistical analysis of gas-phase acidities, calculated with PM3 method

	N	ΔH^{min}_{acid}	ΔH^{max}_{acid}	$\delta\Delta H_{acid}$	a	b	R	σ	γ
All	175	314.3	421.0	8.2	−30.4	1.1	0.903	11.2	7.3
All[a]	165	314.3	421.0	7.5	−4.8	1.0	0.937	7.9	6.3
All[b]	80	338.3	421.0	7.6	−8.6	1.0	0.900	9.2	7.2
C–H acids	75	322.1	421.0	8.8	−33.8	1.0	0.923	9.4	7.0
C–H acids[b]	46	351.2	421.0	8.2	−8.4	1.0	0.891	10.2	7.6
N–H acids	25	333.4	403.6	7.2	−14.3	1.0	0.975	4.7	3.6
N–H acids[b]	10	347.6	403.6	7.8	−28.9	1.0	0.977	5.0	3.1
Amines	5	378.8	403.6	7.5	110.6	0.7	0.691	8.7	7.7
Amides	8	333.4	362.6	5.1	−80.6	1.2	0.979	2.8	1.7
Anilines	11	338.6	367.3	8.4	30.0	0.8	0.959	2.9	2.5
O–H acids	58	322.6	390.7	6.2	−36.2	1.0	0.934	7.5	5.6
Alcohols	29	322.6	380.6	6.8	−113.9	1.3	0.970	5.7	3.1
Carboxylic acids	22	322.7	348.5	3.2	53.3	0.8	0.897	3.2	2.9
Nitro-compounds	9	327.8	362.9	13.2	123.5	0.6	0.717	8.4	11.1
Diatomic hydrides	5	314.3	400.4	34.1	−410.3	2.2	0.995	8.5	2.4
Hypervalent comp.	10	322.6	373.5	11.8	−65.8	1.1	0.895	9.1	6.3
Trifluoromethyl-sulfonyl compounds	6	322.6	347.4	14.8	71.0	0.7	0.662	9.1	8.5

[a] – without Si–H and P–H acids, H_2, C_2H_2, CH_4, H_2O, HF, and HCN

[b] – compounds, calculated by Dewar [6] with AM1 and used by us to compare AM1 and PM3

standard deviation, and γ is the average unsigned error, when ΔH_{acid} is corrected using formula:

$$\Delta H^{cor.}_{calc.} = \frac{\Delta H_{calc.} - a}{b} \tag{3}$$

Table 4 gives the analogous results for AM1 calculated acidities from Ref. [6], [11], and from this work.

Table 4. Results of statistical analysis of gas-phase acidities, calculated with AM1 method

	N	$\Delta H^{\text{min}}_{\text{acid}}$	$\Delta H^{\text{max}}_{\text{acid}}$	$\delta\Delta H_{\text{acid}}$	a	b	R	σ	γ
All	97	338.3	421.0	7.9	−28.7	1.1	0.894	9.6	7.2
All^1	80	338.3	421.0	8.2	−31.6	1.1	0.892	10.1	7.4
C–H acids	63	350.3	421.0	7.7	−25.1	1.1	0.894	9.5	6.8
C–H acids[a]	46	351.2	421.0	8.1	−19.0	1.0	0.890	10.4	7.4
N–H acids	10	352.7	403.2	6.7	−136.5	1.4	0.975	6.4	2.9
O–H acids	24	338.3	390.8	9.0	−87.3	1.2	0.860	9.6	5.5
Hypervalent compounds	10	322.6	373.5	17.0	−68.9	1.1	0.740	16.5	11.5

[a] – compounds, calculated by Dewar [6] with AM1 and used by us to compare AM1 and PM3

The average unsigned error in the heats of formation for all 175 neutrals is 5.1 kcal/mol. This error is fairly typical for the PM3 method and is in keeping with what has previously been found [18]. Knowing that the heats of formation of the anions are reproduced more poorly, it is not surprising, that the calculated absolute acidities are not very reliable. At the same time, the average unsigned error in acidities of the same collection of acids is 8.1 kcal/mol, compared with 7.9 kcal/mol for AM1 method obtained by us (Table 4) from analysis of results of calculations for 97 compounds presented in Ref. [6] and [11]. But when we compare the results only for compounds calculated by both methods, the errors are 8.2 kcal/mol and 7.6 kcal/mol for AM1 and PM3 respectively. *It should be mentioned that in case of* PM3 *nearly one third of calculated acidities have errors greater than 10* kcal/mol *and more than half deviate more than 5* kcal/mol *(see also Fig. 1).*

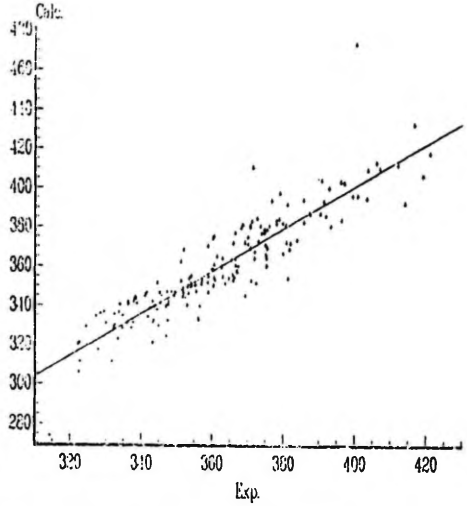

Fig. 1. Calculated and experimental gas-phase acidities (kcal/mol) for all acids surveyed

From Tables 1 and 2 it can be seen, that the behavior of the five calculated diatomic hydrides (H_2, HF, HCl, HBr, HI) is quite different from that for the rest of the compounds. For these molecules the average error is as big as 34.1 kcal/mol, but when we use empirical correction according Eq. (3), the error reduces to 2.4 kcal/mol. It should also be mentioned, that in case of these compounds the slope of the correlation line is 2.21 and intercept is −410.4 which both display the largest deviations of these quantities from their ideal values, i.e. the unity slope and zero intercept.

For a few calculated Si–H and P–H acids and for acetylene, methane, water and HCN, the calculated values are also far from their experimental values. When these compounds are excluded from the statistical analysis, the average unsigned error reduces to 7.3 kcal/mol. The poor results for these acids can be attributed to the failure of methods from the MNDO family to allow for orbital expansion on atoms bearing large negative charge. The calculated heats of formation are expected to be, and are, too positive whereas the formal charge in an anion is largely concentrated on a single atom.

On the other hand, it should be mentioned that the PM3 tends to overestimate the charge delocalization in a relatively bulky anions, such as $(CH_3)_3C^-$, $CF_3SO_2CH_2^-$, $(CF_3)_3CO^-$, etc., which results in too negative heats of formation. In turn this leads to too high acidities for these acids. This can be also the reason for which the PM3 method and also AM1, as mentioned by Dewar [6], mostly overestimate the stabilizing effect of methyl and phenyl substitution at the anionic center.

On the basis of the results of the overall correlation analysis, one can conclude that the errors in calculated acidities are not systematic, while the slope b of the correlation line is practically unity and the intercept a is also reasonably small. But such an inference turns out to be false, while examining the results of correlation analyses obtained for different classes of compounds (compare with Ref. [7], where the theoretical values for the slope b and intercept a were obtained for the simultaneous comparison of the calculated and experimental acidities of neutral and cationic Bronsted acids). It becomes evident that in many cases (amides, alcohols, and phenols) there are excellent correlations between calculated and experimental acidities with the intercept and slope considerably differing from theoretical (see Table 3). So, it can be concluded that overall good agreement with theoretical regression with zero intercept and unity slope is due to using in the same correlation several classes of compounds. However, in different classes, correlated one by one, the differences from the theoretical correlation are large enough to decide that there are still remaining systematic errors.

The average unsigned error in calculated acidities for the *carbon* acids is 8.8 kcal/mol, which is comparble with that found by us for the AM1 method (7.7 kcal/mol). But when we compare the results only for compounds calculated by both methods, the errors are 8.1 kcal/mol and 8.2 kcal/mol for AM1 and PM3, respectively.

The average unsigned error for acidities of 26 *nitrogen acids* is 7.2 kcal/mol. That is slightly better than the overall average unsigned error and average unsigned error for C–H acids and worse than that found by us for the AM1 method (6.7 kcal/mol). When one compares the results only for compounds calculated by both methods, the errors are 6.7 kcal/mol and 7.8 kcal/mol for AM1 and PM3, respectively.

The reasonable closeness of the slope of correlation line and the intercept to the theoretical values is due to fact that in the same regression are amines.

anilines, and amides. If we consider these classes of compounds separately, a different view appears. Amines have an average unsigned error of 7.5 kcal/mol and a rather scattered correlation. At the same time, amides have an excellent fit with a slope and intercept different from expected ideal values. In case of anilines, p-CF_3SO_2-aniline deviates considerably. After the exclusion of this point a very good correlation with slope and intercept close to their theoretical values appears (see Table 3).

For the *oxygen acids* listed in Table 1 the average unsigned error in acidities is 6.2 kcal/mol, compared with 9.0 kcal/mol found by us using AM1. When we compare the results only for compounds calculated by both methods, the errors didn't change. The reasons for big errors in calculated acidities of water and $(CF_3)_3COH$ have already been discussed. The errors for oximes are also significantly larger than those for the other compounds. Excluding water, $(CF_3)_3COH$ and oximes from the statistical analysis, the average unsigned error for the remaining 51 O–H acid falls to 5.2 kcal/mol. This value compares favorably with the corresponding error (4.4 kcal/mol) in the heats of formation of the corresponding neutrals and is only slightly larger than that of N–H acids and smaller than C–H acids. This is a bit surprising, as Dewar has reported that for the AM1 method the acidities of the oxygen acids are reproduced worse than C–H and N–H acids.

As in the case of N–H acids, the different classes of O–H acids show different correlations between calculated and experimentally measured acidities. The correlation for the carboxylic acids is rather poor, while in case of phenols and alcohols the fit is significantly better (see Table 2).

The average unsigned error of nine calculated S–H *acids* is 4.7 kcal/mol. However, no conclusions about effectiveness of PM3 to estimate the acidities of S–H acids can be made since a very narrow (351.2–356.9 kcal/mol) range of experimentally measured acidities was available.

For the nitrosubstituted acids given in Table 1, the average unsigned error is 13.2 kcal/mol, which is too big compared with the overall average unsigned error. For the AM1 model Dewar has attributed this mainly to the failure of method to predict the heats of formation rather neutrals than anions, which is supported by his calculation results. For the PM3 method, however, for nitrocompounds, Stewart had reported a great improvement of calculated heats of formation, which was also confirmed by us in this work (average unsigned error is 6.4 kcal/mol). However, the errors in the calculated acidities of nitrosubstituted acids remain too big. It must be pointed out that all the calculated acidities for nitrocompounds are too high and the bigger errors are associated mostly with the small compounds.

For the calculated acidities of six trifluoromethylsulfonylsubstituted acids the average unsigned error is 14.8 kcal/mol, which is too large when compared with the overall error. At the same time we should not forget that we deal here with hypervalent compounds for which the reported [18] error of calculated heats of formation of neutrals is 13.6 kcal/mol.

4 Conclusions

With a few exceptions, PM3 seems to be a useful tool for the investigation of gas-phase acidities. The errors in calculated acidities (8.1 kcal/mol) are comparable with those reported [18] in calcualted heats of formation of the neutrals

(7.8 kcal/mol). However, it should be mentioned that in case of PM3 nearly one third of calculated acidities have errors greater than 10 kcal/mol and more than half deviate more than 5 kcal/mol.

The main problems encountered involve relatively small, often diatomic, neutral hydrides whose anions are usually characterized by the charge localization on one atom, as well as acids whose conjugated anions contain bulky electron acceptor substituents, capable to the extensive delocalization of the negative charge from the protonization center to the other regions of the anions. Probably for the same reason the large errors accompany also the introduction of methyl and phenyl substituents at anionic centers.

In some cases (anilines, amides, alcohols, and phenols) the average error in acidity can be significantly reduced by employing an empirically derived correction.

Comparison with AM1 results show that both methods are of roughly equal quality with the exception of hypervalent molecules, where PM3 is clearly better (average unsigned errors are 17.0 and 11.8 kcal/mol for AM1 and PM3, respectively). Shortcomings of both MNDO family-based methods for the correct description of hypervalent compounds are rather evident and another approach with proper inclusion of *d*-orbitals [21] is needed.

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Critical Test of PM3-Calculated Proton Affinities

PEETER BURK, KOIT HERODES, IVAR KOPPEL,
and ILMAR KOPPEL
Institute of Chemical Physics, Tartu University EE2400, Jakobi 2, Tartu, Estonia

Abstract

Proton affinities have been calculated for 119 compounds using the PM3 semiempirical molecular orbital model. PM3 seems to be not as good as AM1 for the calculation of proton affinities. At the same time, it can be a valuable tool for investigation of proton affinities, when AM1 is not usable (for hypervalent compounds of second-row elements). © 1993 John Wiley & Sons, Inc.

Introduction

Molecular orbital calculations are carried out by an increasing number of chemists on a widest range of problems. Both *ab initio* and semiempirical self-consistent field molecular orbital calculations are often used. The widespread use of the semiempirical MINDO/3 [1], MNDO [2], AM1 [3], and PM3 [4] methods is due to the fact that they often give reliable answers, are easy to use, require relatively little computer time, and can handle large molecules.

Proton transfer reactions are widespread and of fundamental importance in chemistry and in biochemistry. Therefore, the knowledge of the proton affinities of neutral bases is essential. If these quantities could be calculated theoretically by some quantum chemical procedure with sufficient accuracy, this would be a great value, while such calculations can be carried out much faster and supposedly at much less cost than experiments. Such calculations are also not limited by the physical properties of the samples (stability, vapor pressure, etc.). As a result, numerous calculations of gas-phase (intrinsic) basicities (or proton affinities) of neutral bases have appeared [5–7 and references therein].

However, there have been only a few systematic investigations [5–10] testing the reliability of different methods for prediction of proton affinities of neutral bases and none dealing with the reliability of the PM3 method on the large scale of compounds. Therefore the current investigation was undertaken to evaluate the reliability of PM3 method for predicting gas-phase proton affinities.

A useful way to compare the experiment and theory is to calculate the linear regression between the theoretical and experimental quantities and to calculate the mean difference (unsigned average error) between the experimental and theoretical quantities. The degree of agreement between the two is then reflected by the slope and intercept of the correlation line, the unsigned average error, the standard deviation from correlation line, and the correlation coefficient. The last two depend

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on the scatter of the points about the correlation line. A *slope different from unity* and a *nonzero intercept* imply systematic deviation between experiment and theory and means that the theoretical values of relative proton affinities will be systematically either too high or too low. A nonzero mean difference between theory and experiment reflects an overall bias in the absolute values of the calculated proton affinity.

Method

The proton affinity (PA) of compound B was found as the heat of reaction for the proton addition equilibrium to form the conjugate acid BH$^+$:

$$B + H^+ \rightleftarrows BH^+ \qquad PA(B) = \Delta H_f(H^+) + \Delta H_f(B) - \Delta H_f(BH^+) \quad (1)$$

where $\Delta H_f(H^+)$, $\Delta H_f(B)$, and $\Delta H_f(BH^+)$ are the standard heats of formation for proton, neutral base and its conjugated acid, BH$^+$. In the case of proton the experimental heat of formation (367.2 kcal/mol [11]) was used instead of the calculated value (353.6), because it improves the calculated proton affinities considerably. We acknowledge that this is not quite a correct procedure, despite the fact that such a way was also used in earlier works on semiempirical calculations of acidities and basicities [7,12].

The calculations were carried out on MicroVAX II and VAX 8650 computers using the standard PM3 procedure, as implemented in the MOPAC 6.0 program package [13]. All geometries were fully optimized by minimizing the energy with respect to all geometrical variables without using the aid of symmetry. In order to avoid premature completion of calculations by reaching some local minimum, the calculations were carried out starting off from several different initial geometries.

Results and Discussion

Proton affinities for 119 compounds, calculated using PM3 method, are given in Table I, along with the corresponding "experimental" values. These particular compounds were chosen because they cover a wide range of basicities for different classes of neutral Bronsted bases (C-, O-, N-, S-, P-bases; alcohols, amines, hydrocarbons, etc.).

The results of statistical (regression) analysis of the relationship between the calculated, PA(calc), and experimental proton affinities, PA(exp) according to formula

$$PA(\text{calc}) = a + b \cdot PA(\text{exp}) \quad (2)$$

are presented in Table II (see also Fig. 1), where N is the number of points, PA$^{\min}$ is minimal, and PA$^{\max}$ maximal experimental gas-phase proton affinity in a considered group; ΔPA is the average unsigned error in proton affinities, R is the correlation coefficient, σ is the standard deviation, and γ is the average unsigned error, when PA$_{\text{calc}}$ is corrected using formula

TABLE I. Comparison with experiment of PM3 heats of formation and proton affinities (kcal/mol, experimental values from Refs. [11], [15], and [16]).

	Calc ΔH_f		PA				Error in calc
	B	BH^+	Calc	Exp	Error	Exp $\Delta H_f(B)$	$\Delta H_f(B)$
			Carbon bases				
Methane	−13.0	228.9	125.2	132.0	−6.8	−17.8	4.8
Ethane	−18.1	221.5	127.6	143.6	−16.0	−20.1	2.0
Ethene	16.6	222.5	161.4	162.6	−1.2	12.5	4.1
Propene	6.4	197.3	176.3	179.5	−3.2	4.8	1.6
1-methylcylcohexene	−14.4	168.6	184.2	197.5	−13.3	−10.3	−4.1
Benzene	23.5	212.5	178.2	181.3	−3.1	19.8	3.7
Naphthalene	40.7	218.1	189.8	194.7	−4.9	35.9	4.8
Toluene	14.1	197.5	183.8	189.8	−6.0	12.0	2.1
Styrene	39.2	210.6	195.8	200.9	−5.1	35.3	3.9
Hexamethylbenzene	−20.9	151.0	195.3	207.0	−11.7	−21.0	0.1
pMe-C_8H_4-C(Me)=CH_2	21.8	183.9	205.1	211.2	−6.1		
1,3,5-trimethoxybenzene	−90.8	73.6	202.8	220.0	−17.2	−86.7	−4.1
Acetylene	50.7	263.9	154.0	153.3	0.7	54.5	−3.8
Propyne	40.2	238.2	169.2	182.0	−12.8	44.6	−4.4
CO	−19.7	176.9	170.6	168.4	2.2	−26.4	6.7
			Nitrogen bases				
N_2	17.6	237.2	147.6	118.2	29.4	0.0	17.6
Ammonia	−3.1	153.4	210.7	204.0	6.7	−11.0	7.9
HNF_2	−11.4	193.4	162.4	160.0	2.4	−16.0	4.6
NF_3	−24.4	201.7	141.1	136.9	4.2	−31.0	6.6
Methylamine	−4.0	153.3	209.9	214.1	−4.2	−5.5	1.5
Ethylamine	−12.5	144.3	210.4	217.0	−6.6	−11.3	−1.2
Propylamine	−17.7	138.5	211.0	217.9	−6.9	−17.3	−0.4
Iso-propylamine	−17.3	135.1	214.8	218.6	−3.8	−20.0	2.7
Butylamine	−21.7	132.9	212.6	218.4	−5.8	−22.0	0.3
Iso-butylamine	−23.0	131.8	212.4	218.8	−6.4	−23.6	0.6
tert-butylamine	−18.7	125.7	222.8	220.8	2.0	−28.9	10.2
Neopentylamine	−26.9	125.4	215.0	219.3	−4.3	−31.0	4.1
Cyclohexylamine	−26.0	125.8	215.4	221.2	−5.8	−25.0	−1.0
2-aminonorbornane	−9.5	142.3	215.4	221.7	−6.3	−8.0	−1.5
Etylideneamine	9.5	168.5	208.2	213.9	−5.7	2.0	7.5
Dimethylamine	−5.4	152.6	209.3	220.6	−11.3	−4.4	−1.0
N-ethylmethylamine	−13.0	143.7	210.4	222.8	−12.4	−11.0	−2.0
Diethylamine	−20.3	135.0	211.9	225.9	−14.0	−17.4	−2.9
Hydrazine	20.7	191.8	196.0	204.7	−8.7	22.8	−2.1
1,2-diaminoethane	−3.9	146.4	216.8	225.9	−9.1	−4.3	0.4
1,3-diaminopropane	−9.3	138.9	218.9	234.1	−15.2	−4.2	−5.1
3-aminopropan-1-ol	−56.4	92.5	218.3	228.6	−10.3	−52.0	−4.4
1,4-diaminobutane	−17.4	129.7	220.1	237.6	−17.5	−13.0	−4.4
$(CH_3)_2N(CH_2)_4N(CH_3)_2$	−26.0	134.4	206.8	240.6	−33.8		
1,8-diaminonaphtalene	43.3	184.2	226.3	223.8	2.5	46.0	−2.7
Trimethylamine	−10.9	155.6	200.7	225.1	−24.4	−5.7	−5.2
N,N-dimethylethylamine	−15.9	143.2	208.1	227.5	−19.4	−11.0	−4.9
N,N-dimethylmethylamine	−20.5	141.9	204.8	230.0	−25.2	−17.0	−3.5

(*Continued*)

TABLE I. (*Continued*)

	Calc ΔH_f		PA				Error
	B	BH^+	Calc	Exp	Error	Exp $\Delta H_f(B)$	in calc $\Delta H_f(B)$
			Nitrogen bases				
Tributylamine	−58.8	92.3	216.1	236.0	−19.9	−53.0	−5.8
N-methylformamide	−43.7	133.5	190.1	204.6	−14.5	−45.0	1.3
Aniline	21.3	175.1	213.4	209.5	3.9	20.8	0.5
Pyrrolidine	−12.0	144.8	210.5	225.2	−14.7	−0.8	−11.2
Piperidine	−16.5	137.2	213.5	226.4	−12.9	−11.7	−4.8
2,2,6,6-tetramethyl-piperidine	−39.7	105.4	222.1	231.7	−9.6	−38.0	−1.7
1-methylpyrrolidine	−14.6	143.7	208.9	228.7	−19.8	−0.5	−14.1
1-methylpiperidine	−19.3	136.2	211.7	229.7	−18.0	−12.0	−7.3
Quinuclidine	−13.1	142.9	211.2	232.1	−20.9	−1.0	−12.1
1-asabicyclo[2,2,2]-oct-2-ene	16.8	171.1	212.9	228.5	−15.6	37.0	−20.2
Pyridine	30.4	187.3	210.3	220.8	−10.5	58.0	−27.6
2-methylpyridine	21.1	174.7	213.6	225.0	−11.4	23.7	−2.6
3-methylpyridine	20.8	175.7	212.3	224.1	−11.8	25.4	−4.6
4-methylpyridine	20.8	175.1	212.9	225.2	−12.3	24.8	−4.0
Tetrazole	86.3	261.1	192.4	197.8	−5.4	80.0	6.3
HCN	33.0	213.6	186.6	171.4	15.2	32.3	0.7
Acetonitrile	23.3	197.9	192.6	188.4	4.2	18.0	5.3
Butyronitrile	14.7	188.0	193.9	192.4	1.5	7.0	7.7
$(CH)_2C{=}C(CN)_2$	169.2	353.1	183.3	166.6	16.7	169.0	0.2
Trichloroacetonitrile	18.5	201.5	184.2	175.7	8.5	20.0	−1.5
FCN	6.5	196.0	177.7	163.0	14.7		
Trifluoroacetonitrile	−115.0	78.6	173.5	164.1	9.4	−119.4	4.4
$(CN)_2$	77.5	266.6	178.1	163.5	14.6	73.8	3.7
			Oxygen bases				
O_2	−4.2	257.8	105.2	105.5	−0.3	0.0	−4.2
Water	−53.4	159.1	154.7	166.5	−11.8	−57.8	4.4
Methanol	−51.9	156.6	158.8	181.9	−23.1	−48.2	−3.7
Ethanol	−56.9	143.9	166.5	188.3	−21.8	−56.1	−0.8
2-methyl-2-propanol	−71.3	120.0	175.9	193.7	−17.8	−74.7	3.4
2,2-difluoroethanol	−151.8	64.7	150.8	175.2	−24.4		
$(CF_3)_3COH$	−501.0	−266.6	132.7	163.0	−30.3	−54.90	48.0
$(CF_3)_2CHOH$	−360.7	−132.8	139.4	163.4	−24.1	−367.0	6.4
Methyl ether	−46.9	157.0	163.2	192.1	−28.9	−44.0	−2.9
Ethyl ether	−59.6	135.9	171.7	200.2	−28.5	−60.1	0.5
tert-butylmethyl ether	−64.4	116.5	186.3	202.2	−15.9	−67.8	3.4
tert-butyl ether	−75.0	102.3	189.8	212.0	−22.2	−87.0	12.0
$(CF_3)_2O$	−381.4	−134.9	120.7	158.0	−37.3		
Carbondioxide	−85.0	139.5	142.7	130.9	11.8	−94.5	9.5
Formaldehyde	−34.1	166.3	166.8	171.7	−4.9	−26.0	−8.1
Acetaldehyde	−44.2	144.7	178.3	186.6	−8.3	−39.6	−4.6
F_2CO	−138.5	75.4	153.3	158.2	−4.9	−153.0	14.5
Hexafluoroacetone	−338.4	−105.6	134.5	159.3	−24.8	−334.0	−4.4

TABLE I. (*Continued*)

	Calc ΔH_f		PA			Exp	Error in calc
	B	BH$^+$	Calc	Exp	Error	$\Delta H_f(B)$	$\Delta H_f(B)$
			Oxygen bases				
CF_3COCl	−194.3	12.7	160.3	163.1	−2.8		
CF_3COOH	−244.0	−39.8	163.0	171.1	−8.2	−246.3	2.3
Methylacetate	−92.7	89.3	185.3	197.8	−12.5	−98.0	5.3
Acetylacetone	−86.9	91.5	188.8	206.9	−18.1	−92.0	5.1
Formamide	−41.8	128.3	197.1	198.4	−1.3	−44.0	2.2
Sulphurdioxide	−50.8	135.3	181.2	160.2	21.0	−70.9	20.1
Dimethylsulfoxide	−38.6	117.2	211.4	210.9	0.5	−36.2	−2.4
Methylsulfonylbenzene	−40.6	111.8	214.8	194.8	20.0	−60.6	20.0
$CF_3SO_2NH_2$	−207.8	−11.0	170.4	176.0	−5.6		
F_2SO_2	−184.3	9.3	173.6	157.3	16.3		
Trimethylphosphineoxide	−81.9	51.3	234.0	216.5	17.5		
$(C_3H_9)_3PO$	−101.4	32.2	233.6	225.3	8.3		
bis(dimethylamino)-methylphophineoxide	−85.1	51.2	230.9	226.3	4.6		
Diethylchloromethylphosphonate	−191.9	−46.6	222.0	211.2	10.8		
Trimethylphosphate	−239.1	−89.1	217.2	212.5	4.7		
Triethylphosphate	−250.1	−84.6	201.6	216.5	−14.9	−284.0	33.9
Hexamethylphosphoric Amide	−85.0	53.7	228.5	227.4	1.1		
			Phosphor bases				
Phosphine	0.2	117.2	250.3	188.0	62.3	1.3	−1.1
Methylphosphine	−9.5	114.8	243.0	203.5	39.5	−4.0	−5.5
Dimethylphosphine	−18.5	112.8	235.9	216.5	19.4	−14.0	−4.5
Trimethylphosphine	−28.6	109.7	228.8	226.5	2.3		
Triethylphosphine	−35.2	109.3	222.6	232.0	−9.4	−54.0	18.8
Phosphorustrifluoride	−252.2	−70.4	185.5	164.4	21.1	−229.0	−23.2
			Sulphur bases				
H_2S	−0.9	175.6	190.7	171.1	19.6	−4.9	4.0
Ethanethiol	−8.7	161.4	197.1	189.8	7.3	−11.1	2.4
tert-butanethiol	−13.2	153.7	200.3	195.9	4.4	−26.2	13.0
Methylsulfide	−10.4	159.4	197.4	199.1	−1.7	−9.0	−1.4
Ethylmethylsulfide	−14.5	155.7	197.0	202.3	−5.3	−14.2	−0.3
Propylsulfide	−30.1	135.3	201.9	206.3	−4.4	−29.9	−0.2
			Other bases				
H	52.1	344.7	74.6	63.6	11.0	52.1	0.0
H_2	−13.4	215.2	138.6	101.2	37.4	0.0	−13.4
HCl	−20.5	184.2	162.5	128.0	34.5	−22.1	1.6
HI	28.8	256.0	140.0	150.0	−10.0	6.3	22.5
CF_3Br	−157.9	93.6	115.7	137.5	−21.8	−155.0	−2.9
CF_3Cl	−169.2	51.6	146.4	136.0	10.4	−169.7	0.5

TABLE II. Results of statistical anlaysis of calculated (PM3) and experimental proton affinities in terms of Eq. (2).

	N	PA^{min}	PA^{max}	ΔPA	*a*	*b*	*R*	*σ*	*γ*
All	119	63.6	240.6	12.9	28.3	0.8	0.884	14.9	12.8
All[1]	118	63.6	240.6	12.5	27.2	0.8	0.901	13.6	12.2
All[2]	60	130.9	237.6	11.2	14.4	0.9	0.937	8.7	7.4
Carbon bases	15	132.0	220.0	7.8	9.4	1.0	0.962	6.8	5.8
Nitrogen bases	51	118.2	240.6	11.7	73.5	0.6	0.931	6.6	7.8
Oxygen bases	35	105.5	227.4	14.5	−12.7	1.0	0.875	16.0	12.8
Phosphor bases	6	164.4	232.0	22.6	149.9	0.3	0.408	21.3	42.1
Phosphor bases[1]	5	164.4	232.0	16.0	97.9	0.6	0.711	15.9	18.9
Sulphur bases	6	171.1	206.3	7.0	144.1	0.3	0.889	2.0	5.2

[1] Without PH_3.

[2] Compounds, calculated by Dewar [7] with AM1.

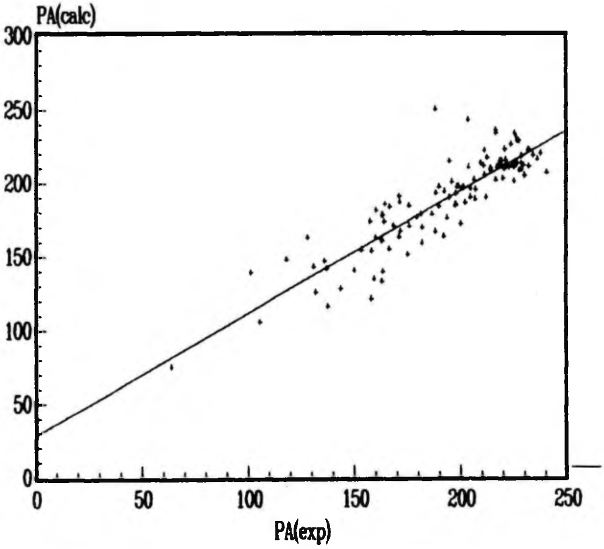

Figure 1. Calculated and experimental proton affinities (kcal/mol) for all bases surveyed.

$$PA_{\text{calc.}}^{\text{cor.}} = \frac{PA_{\text{calc.}} - a}{b} \quad (3)$$

Table III gives analogous results for the statistical analysis of AM1-calculated proton affinities (from Ref. [7]).

The average unsigned error in the heats of formation for all neutrals is 7.9 kcal/mol. This error is fairly typical for the PM3 method and is in keeping with what has previously been found [14]. At the same time, the average unsigned error in proton affinities of the same collection of bases is 12.9 kcal/mol, compared with 6.0 kcal/mol for the AM1 method obtained by us from analysis of results of calculations for 60 compounds presented in Ref. [7]. But when we compare the results only for compounds calculated by both methods, the average unsigned error for the PM3 method reduces to 11.2 kcal/mol, which is, however, still larger than the same quantity for the AM1 method. It should be mentioned that in the case of PM3, nearly one fifth of calculated proton affinities have errors greater than 20 kcal/mol and more than half deviate more than 10 kcal/mol (see also Fig. 1).

From Table I it can be seen that extremely large error (62.3 kcal/mol) corresponds to PH_3. When the phosphine is excluded from the statistical analysis, the average unsigned error reduces to 12.5 kcal/mol. It should be mentioned that alongside with a big error in the calculated heat of formation the PM3 method also gives an unrealistic charge distribution for phosphonium cation—the calculated Mulliken charge on phosphor atom is 2.42.

On the basis of the results of the overall correlation analysis one can conclude that in the calculated proton affinities there is also present a systematic error, as indicated by the nonunity slope of the correlation line b and by the nonzero intercept a.

Carbon Bases

The average unsigned error in calculated proton affinities for the carbon bases is 7.8 kcal/mol, which is considerably higher than that found by us for AM1 method (2.9 kcal/mol). The correlation between experimentally found and calculated proton affinities seems to be reasonably good as evidenced by the lack of the systematic

TABLE III. Results of statistical analysis of proton affinities, calculated with AM1 method in terms of Eq. (2).

	N	PA^{min}	PA^{max}	ΔPA	a	b	R	σ	γ
All	60	130.9	237.6	6.0	23.8	0.9	0.979	4.8	4.5
Carbon bases	9	132.0	194.7	2.9	9.5	1.0	0.987	3.7	2.7
Nitrogen bases	33	171.4	232.1	5.8	76.4	0.6	0.934	3.0	3.8
Oxygen bases	12	130.9	202.2	6.9	38.9	0.8	0.948	5.4	5.4

error (see results of correlation analysis in Table II), but the existence of big random errors makes one prefer the AM1 method for calculation of proton affinities of carbon bases.

Nitrogen Bases

The average unsigned error in calculated proton affinities for the nitrogen bases is 11.7 kcal/mol, which is again considerably higher than that found by us for AM1 method (5.8 kcal/mol). However, it seems that these errors are systematic for both methods while the slopes of correlation lines are 0.62 ± 0.04 and 0.63 ± 0.04 for PM3 and AM1 methods, respectively, and the application of empirical correction reduces the errors in calculated proton affinities considerably (to 7.8 and 3.8 kcal/mol for PM3 and AM1 methods, respectively). Once again, the AM1 method seems to be superior for the calculation of proton affinities of nitrogen bases.

Oxygen Bases

The average unsigned error in calculated proton affinities for the oxygen bases is 14.5 kcal/mol, which similarly to that of the carbon and nitrogen bases is still significantly larger than the average unsigned error that is found in the present work for AM1 method (6.9 kcal/mol). As a rule, in case of alcohols, ethers, and carbonyl compounds the predicted proton affinities are lower than the experimental values.

Phosphor Bases

The average unsigned error in calculated proton affinities for the phosphor bases is 22.6 kcal/mol. However, if we exclude from the comparison the extremely strongly deviating value for the phosphine (vide supra), the unsigned average error reduces to 16.0 kcal/mol. Still, the statistical analysis (see Table II) shows that there is practically no correlation between calculated and experimental proton affinities, so one must exercise extreme caution, when using PM3 for investigation of phosphor bases.

Sulphur Bases

The average unsigned error in calculated proton affinities for the sulphur bases is 7.0 kcal/mol, which when compared with the previous groups of bases is a surprisingly good result.

Conclusions

On the basis of the above results one can conclude that the PM3 method is not as good as AM1 for the calculation of proton affinities of neutral Bronsted bases (see Table II). At the same time, it can be a useful tool for investigation of proton affinities, when the AM1 method is not usable, e.g., for hypervalent compounds of second-row elements.

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THEORETICAL STUDY OF STRUCTURE AND BASICITY OF SOME ALKALI METAL OXIDES, HYDROXIDES AND AMIDES

Peeter Burk[a], Ilmar A.Koppel[a] and Jüri Tapfer[b]
[a]Institute of Chemical Physics, Tartu University, EE2400 Tartu, Estonia
[b] Computational Center, Tartu University, Liivi 2, EE2400 Tartu, Estonia

Abstract. *Ab initio* (TZV*, SBK* and 3-21G* or 6-31G* basis sets) calculations were performed to predict the geometries and gas-phase proton affinities of Li_2O, LiOH, $LiNH_2$, Na_2O, NaOH, $NaNH_2$, K_2O, KOH and KNH_2.

Key words: alkali metal oxides, hydroxides and amides; proton affinities.

1. Introduction.

The oxides of alkaline metals are known to be the strongest bases in gas-phase [1,2]. Their reported proton affinities exceed by a very wide margin (by 45-60 kcal/mol) the similar quantity for the alkali metal hydroxides [2,3], usually considered the strongest existing bases, at least in the aqueous solution. However, till now very little is known about their geometry and electron structure. Surprisingly, the same refers also to the study of the geometry and electronic structure of the alkali metal hydroxides and amides. So the current investigation of these compounds was undertaken to gain some knowledge about above mentioned problems.

2. Method.

All calculations were performed on IBM 4381 computer using '13 nov 1992' version of Gamess-US [4] program package. All calculations were executed with full optimization of geometry in respect of energy without aid of symmetry. The calculations were performed at RHF level using 6-31G* [5,6,7], TZV* [8,9,10]

and SBK* [11,12] basis sets, when available for elements considered, as implemented in Gamess program package. For the K_2O, KOH and KNH_2, where the 6-31G* set is not available, similar calculations were performed at 3-21G* [13,14] level. The results of calculations are presented in Tables I-IX where bond lengths (r) are given in Å, angles ($\angle$) in deg, dipole moments (μ) in D, charges (q) in a.u., total electronic energies (E) in hartrees and proton affinities (PA) in kcal/mol.

3.Discussion.

As a rule, all used basis sets give identical conformations of both neutrals and cations. Both oxides and hydroxides are found to be linear, while corresponding cations and the neutrals of amides are planar. This is obviously caused by strong coulombic impact forces between hydrogen and metal atoms, which bear considerably big positive charges (see Mulliken charges in Tables I-IX). As expected the cations of amides are tetrahedrical. The bond lengths and angles obtained with employed basis sets are also in good agreement with some minor exceptions.

Proton affinities, calculated at three different levels of theory are also considerably consistent. All calculations using different basis sets confirm the experimentally established superiority of the intrinsic (gas-phase) proton affinities of alkali metal oxides over their hydroxilic counterparts, as found by mass-spectrometric techniques [1]. Also, the calculations confirm the extremely high basicity of the alkali metal amides, often used in chemical synthesis as highly effective deprotonating agents. So one can conclude, that all three methods are equal in description of small molecules containing alkali metal atoms. That's not surprising while all used basis sets are very similar.

Nevertheless, the deviations from experimentally established proton affinities are considerable (average unsigned errors are 26.5, 30.1 and 27.4 kcal/mol for 6-31G*,

TZV^* and SBK^* basis sets respectively). As it is mentioned in earlier works [15], the errors in *ab initio* calculated proton affinities have rather systematic than random nature. So there is quite good correlation between calculated and experimentally determined proton affinities for all compounds calculated. For example for SBK^* basis set the slope of correlation line, intercept, correlation coefficient and the absolute mean difference between experimentally measured and empirically corrected calculated values are 1.35, -70.1, 0.9749 and 5.6. For other two basis sets these parameters are very similar. So using this correlation we predict the proton affinities of $LiNH_2$, $NaNH_2$ and KHN_2 to be 257.0, 271.9 and 284.5 kcal/mol respectively.

The Mulliken charges at the metal and oxygen (nitrogen) atom in neutral species evidence (as expected) that the Me-O or Me-N bonds are fairly ionic. It means that the resulting Coulombic stabilization due to the interactions between the highly negatively charged protonation center (oxygen or nitrogen atom) and proton could be considered as a main contribution into the extremely high basicity of the title compounds. It is also interesting to mention that there are several truly good correlations between calculated proton affinities and Mulliken charges on different atoms in both neutrals and cations.

4.Conclusions.

It was shown that the alkali metal oxides and hydroxides are linear, while corresponding cations and also amides have a planar structure. The employed basis sets ($6\text{-}31G^*$ or $3\text{-}21G^*$, TZV^* and SBK^*) were shown to be of the same quality for investigating of small alkali metal containing molecules (and corresponding cations) in both geometric and energetic aspect and the SBK^* basis set can be recommended as the fastest.

The calculations confirm the much higher basicity of the alkali metal oxides relative to the alkali metal hydroxides.

However, for predicting proton affinities from results of calculations empirical corrections are needed. Using these corrections the most probable "experimental" proton affinities of $LiNH_2$, $NaNH_2$ and KHN_2 were estimated to be 257.0, 271.9 and 284.5 kcal/mol respectively. We hope that these theoretical predictions will be helpful in future experimental determinations of proton affinities of very strong **bases**.

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Table I. Molecular Geometries, Dipole Moments, Mulliken Charges and Energetics of Li_2O and Li_2OH^+.

	TZV*		SBK*		6-31G*	
	Li_2O	Li_2OH^+	Li_2O	Li_2OH^+	Li_2O	Li_2OH^+
r(OLi)	1.598	1.742	1.619	1.791	1.614	1.758
r(OH)	-	0.943	-	0.963	-	0.951
∠LiOLi	180.0	137.7	180.0	144.5	180.0	140.1
∠LiOH	-	111.1	-	107.8	-	110.0
∠HOLiLi	-	179.9	-	180.0	-	180.0
μ	0.001	2.312	0.001	2.079	0.001	2.228
q(Li)	0.455	0.818	0.412	0.700	0.484	0.799
q(O)	-0.911	-1.073	-0.624	-0.777	-0.967	-1.058
q(H)	-	0.438	-	0.378	-	0.460
E	-89.7985	-90.2817	-16.1294	-16.6074	-89.7698	-90.2564
PA	-	303.2	-	299.9	-	305.3
PA_{exp} [1]	-	285.9	-	285.9	-	285.9

Table II. Molecular Geometries, Dipole Moments, Mulliken Charges and Energetics of LiOH and $LiOH_2^+$.

	TZV*		SBK*		6-31G*	
	LiOH	$LiOH_2^+$	LiOH	$LiOH_2^+$	LiOH	$LiOH_2^+$
r(OLi)	1.571	1.833	1.640	1.986	1.592	1.858
r(OH)	0.931	0.944	0.949	0.965	0.938	0.954
∠LiOH	180.0	126.2	179.9	127.6	180.0	126.8
∠HOLiH	-	180.0	-	180.0	-	179.9
μ	4.154	3.326	4.977	4.027	4.314	3.479
q(Li)	0.618	0.928	0.535	0.861	0.612	0.898
q(O)	-0.999	-0.970	-0.826	-0.718	-1.016	-0.943
q(H)	0.381	0.521	0.291	0.428	0.405	0.522
E	-82.931490	-83.334951	-16.4959	-16.8950	-82.9032	-83.3093
PA	-	253.2	-	250.5	-	254.8
PA_{exp} [1]	-	239.8	-	239.8	-	239.8

Table III. Molecular Geometries, Dipole Moments, Mulliken Charges and Energetics of $LiNH_2$ and $LiNH_3^+$.

	TZV*		SBK*		6-31G*	
	$LiNH_2$	$LiNH_3^+$	$LiNH_2$	$LiNH_3^+$	$LiNH_2$	$LiNH_3^+$
r(NLi)	1.728	1.975	1.786	2.118	1.750	2.002
r(NH)	1.002	1.004	1.019	1.020	1.005	1.008
∠LiNH	127.4	113.3	128.1	113.9	127.4	113.2
∠HNLiH	180.0	120.0	180.0	120.0	179.9	120.0
μ	4.530	3.850	5.074	4.323	4.617	3.968
q(Li)	0.563	0.875	0.361	0.761	0.535	0.851
q(N)	-1.141	-1.132	0.730	-0.689	-1.130	-1.133
q(H)	0.289	0.419	0.184	0.309	0.297	0.427
E	-63.0618	-63.5081	-11.0291	-11.4703	-63.0419	-63.4506
PA	-	283.1	-	276.8	-	281.6

Table IV. Molecular Geometries, Dipole Moments, Mulliken Charges and Energetics of Na_2O and Na_2OH^+.

	TZV*		SBK*		6-31G*	
	Na_2O	Na_2OH^+	Na_2O	Na_2OH^+	Na_2O	Na_2OH^+
r(ONa)	1.974	2.108	1.976	2.148	1.951	2.093
r(OH)	-	0.945	-	0.962	-	0.950
∠NaONa	180.0	140.9	180.0	144.8	180.0	144.4
∠NaOH	-	109.5	-	107.6	-	107.8
∠HONaNa	-	180.0	-	180.0	-	180.0
μ	0.005	2.229	0.001	2.080	0.003	1.869
q(Na)	0.642	0.928	0.546	0.838	0.505	0.816
q(O)	-1.284	-1.231	-1.093	-1.010	-1.009	-1.042
q(H)	-	0.374	-	0.334	-	0.410
E	-398.5302	-399.0756	-16.0011	-16.5449	-398.4858	-399.0358
PA	-	342.3	-	340.8	-	345.2
PA_{exp}[1]	-	306.7	-	306.7	-	306.7

Table V. Molecular Geometries, Dipole Moments, Mulliken Charges and Energetics of NaOH and $NaOH_2$.

	TZV*		SBK*		6-31G*	
	NaOH	$NaOH_2^+$	NaOH	$NaOH_2^+$	NaOH	$NaOH_2^+$
r(ONa)	1.941	2.218	1.973	2.335	1.921	2.214
r(OH)	0.937	0.947	0.952	0.964	0.941	0.952
∠NaOH	180.0	126.6	180.0	127.9	179.8	127.2
∠HONaH	-	180.0	-	179.9	-	179.9
μ	6.636	1.860	6.937	2.214	6.208	1.838
q(Na)	0.821	0.982	0.720	0.949	0.696	0.925
q(O)	-1.168	-0.935	-0.986	-0.775	-1.068	-0.930
q(H)	0.347	0.476	0.266	0.413	0.373	0.502
E	-237.3174	-237.7518	-16.4477	-16.88214	-237.2725	-237.7155
PA	-	272.6	-	272.6	-	278.0
PA_{exp}[1]	-	246.7	-	246.7	-	246.7

Table VI. Molecular Geometries, Dipole Moments, Mulliken Charges and Energetics of $NaNH_2$ and $NaNH_3^+$

	TZV*		SBK*		6-31G*	
	$NaNH_2$	$NaNH_3^+$	$NaNH_2$	$NaNH_3^+$	$NaNH_2$	$NaNH_3^+$
r(NNa)	2.096	2.365	2.150	2.508	2.080	2.357
r(NH)	1.005	1.004	1.022	1.019	1.007	1.007
∠NaOH	127.7	113.1	128.5	114.2	127.8	113.3
∠HNNaH	180.0	120.0	179.9	120.0	179.9	120.0
μ	6.824	2.141	7.026	2.418	6.320	2.052
q(Na)	0.788	0.959	0.610	0.913	0.636	0.900
q(N)	-1.313	-1.093	-0.935	-0.776	-1.180	-1.116
q(H)	0.263	0.378	0.162	0.288	0.272	0.405
E	-217.4452	-217.9181	-10.9803	-11.4536	-217.4148	-217.8945
PA	-	296.7	-	297.0	-	301.0

Table VII. Molecular Geometries, Dipole Moments, Mulliken Charges and Energetics of K_2O and K_2O^+.

	TZV*		SBK*		3-21G*	
	K_2O	K_2OH^+	K_2O	K_2OH^+	K_2O	K_2OH^+
r(OK)	2.329	2.501	2.257	2.476	2.268	2.440
r(OH)	-	0.946	-	0.963	-	0.977
∠KOK	180.0	142.1	180.0	147.4	180.0	144.8
∠KOH	-	109.0	-	106.4	-	107.6
∠HOKK	-	180.0	-	180.0	-	180.0
μ	0.000	2.515	0.002	2.252	0.004	2.524
q(K)	0.747	0.954	0.564	0.877	0.801	0.930
q(O)	-1.494	-1.253	-1.128	-1.060	-1.602	-1.255
q(H)	-	0.346	-	0.307	-	0.396
E	-1273.0763	-1273.6816	-15.9031	-16.4932	-1266.6998	-1267.2777
PA	-	379.8	-	370.3	-	362.7
PA_{exp} [1]	-	318.2	-	318.2	-	318.2

Table VIII. Molecular Geometries, Dipole Moments, Mulliken Charges and Energetics of KOH and KOH_2^+.

	TZV*		SBK*		3-21G*	
	KOH	KOH_2^+	KOH	KOH^2_+	KOH	KOH^2_+
r(OK)	2.294	2.675	2.223	2.709	2.170	2.550
r(OH)	0.940	0.946	0.955	0.963	0.969	0.968
∠KOH	180.0	126.7	180.0	128.1	180.0	125.9
∠HOKH	-	180.0	-	179.7	-	179.6
μ	8.339	1.256	8.432	1.514	6.802	1.154
q(K)	0.910	0.992	0.773	0.968	0.843	0.967
q(O)	-1.240	-0.909	-1.026	-0.76	-1.294	-1.020
q(H)	0.330	0.459	0.253	0.399	0.452	0.526
E	-674.6085	-675.0704	-16.4142	-16.8	-671.1768	-671.6441
PA	-	289.9	-	287.1	-	293.3
PA_{exp} [1]	-	262.9	-	262.9	-	262.9

Table IX. Molecular Geometries, Dipole Moments, Mulliken Charges and Energetics of KNH_2 and KNH_3^+.

	TZV*		SBK*		3-21G*	
	KNH_2	KNH_3^+	KNH_2	KNH_3^+	KNH_2	KNH_3^+
r(KN)	2.486	2.858	2.501	2.919	2.395	2.802
r(NH)	1.008	1.003	1.026	1.019	1.023	1.019
∠KNH	128.3	113.0	129.3	114.3	128.1	110.3
∠HNKH	180.0	120.0	180.0	120.0	180.0	120.0
μ	8.943	1.602	9.126	1.749	7.41	1.87
q(K)	0.913	0.987	0.720	0.956	0.839	0.933
q(N)	-1.380	-1.074	-0.994	-0.767	-1.628	-1.193
q(H)	0.234	0.362	0.137	0.270	0.394	0.420
E	-654.7325	-655.2343	-10.9404	-11.4407	-651.4155	-651.9260
PA	-	314.9	-	314.0	-	320.4

Theoretical Study of Prototropic Tautomerism and Acidity of Tris(fluorosulfonyl)methane

Peeter Burk[a], **Ilmar A.Koppel**[a], **Jüri Tapfer**[b], **Frederick Anvia**[c] and **Robert W.Taft**[c]

[a] Institute of Chemical Physics, Tartu University, Jakobi 2, EE2400 Tartu, Estonia

[b] Computational Center, Tartu University, Liivi 2, EE2400 Tartu, Estonia

[c] Department of Chemistry, University of California at Irvine, Irvine, California 92717, USA

The prototropic tautomerism and acidity of $(FSO_2)_3CH$ was studied at both the semiempirical (PM3) and ab initio (HF/STO-3G* and 3-21G*) level. It was shown, that PM3 fails to describe the energetics of prototropic tautomerism, while giving the geometry of the sulfo form in good agreement with the experimental data. The ab initio calculations predict in accordance with the experiment, that the sulfone form is more stable than enol form. The conformity between calculated and experimental geometry was also satisfactory.

The gas phase acidity of $(FSO_2)_3CH$ was calculated and the factors which contribute to the extremely high gas phase acidity of the title compound were discussed.

1. Introduction

Fluorosulfonyl and trifluoromethylsulfonyl substituted compounds such as $(FSO_2)_3CH$ [1], $(FSO_2)_2NH$ [2], $(CF_3SO_2)_3CH$ [3] and $(CF_3SO_2)_2NH$ [4] are known as very strong acids in liquid phase. Recent gas-phase measurements [5] indicate, that at least some of them are relatively even stronger in the gas-phase exceeding the strength of such a commonly known strong acid as HI by many powers of ten.

However, there is very little known about these compounds. Only for a very few of them the geometries are established and even less is known about their electronic structure and relations between geometry, electronic structure and chemical properties.

Recently it was suggested[6] that the superacidic behavior of $(CF_3SO_2)_2NH$ and $(C_4F_9SO_2)_2NH$ could be ascribed to the presence of the prototropic tautomerism according to the scheme presented on Fig.1. For $(FSO_2)_2NH$ such a tautomerism was indirectly suggested already in 1965 by J.K.Ruff[2]. However, such a prototropic tautomerism is very hard to investigate experimentally, while due to extremely strong acidity of the above mentioned molecules they exist in solutions in completely dissociated form.

In recent years the semiempirical calculations (MNDO[7], AM1 [8] and PM3 methods[9]) have been widely used to investigate the prototropic tautomerism[10,11], geometries and energetics[12,13,14,15] of medium-sized and large systems. The only one of them with declared[16] ability to reproduce and predict the properties of hypervalent molecules correctly is PM3, while the others are known to fail to describe such systems[16].

The current investigation of $(FSO_2)_3CH$ was undertaken as one of the first steps in the investigation of the sulfonylsubstituted superacids to find out their geometry, electronic structure, prototropic equilibria and relationships between the abovementioned properties and extremely high intrinsic acidity of such compounds. Another aim of this study was to establish the usefulness of the PM3 method and *ab initio* calculations at STO-3G* and 3-21G* levels

The energies and geometries for most stabile sulfone and enol forms as well as that of anion are presented in Tables 1-3. The corresponding conformations are presented on the Fig. 2 alongside with used numbering scheme for atoms.

The PM3 method predicts the hydrogen bonded enol form to be the most stabile one (27.8 kcal/mol more stable than the most stabile sulfone form), while the experimental data[1,17] clearly indicates, that the sulfone form is at least predominant. The results of *ab initio* calculations at both STO-3G* and 3-21G* level agree with experiment giving the sulfone form respectively 15.2 and 3.5 kcal/mol more stabile.

The gas phase acidity of the title compound predicted by the PM3 method was found to be 261.3 kcal/mol when using the sulfone forms heat of formation for the calculation of acidity what doesn't agree with its predicted value 295 kcal/mol [5]. Gas phase acidities found from results of *ab initio* calculations are 385.7 and 279.8 kcal/mol respectively for STO-3G* and 3-21G* levels of theory. However, it should be mentioned, that such failure of predicting the absolute gas-phase acidities is common for the PM3 method in case of hypervalent molecules[22] and peculiar also to *ab initio* calculations[23].

The geometries of anion and sulfone form found both by PM3 and *ab initio* calculations at STO-3G* and 3-21G* level are in excellent agreement with experiment. The bond lengths differ from the experimentally determined ones less than 0.05 angstroms (the only exception is S-C bond length in sulfone form found by PM3 method differing from experimental value by 0.08 angstroms) and angles less than 5°.

The reasons for very high acidity of $(FSO_2)_3CH$ were investigated by means of Mulliken population analysis. In Tables 4 and 5 are given total atomic charges and selected bond populations obtained by all three methods.

The interesting fact is that the PM3 method predicts the Mulliken charge on the sulphonyl sulphur to be nearly +2.5 in both neutral molecule and anion, what seems improbable. Also *ab initio* for above mentioned tasks, while the title compound is the one of a few sulfonyl-containing superacids, for whom alongside with the geometry of anion in the crystal phase[1] also the gas-phase geometry of neutral acid is properly established[17].

2.Method

The first step of the calculations was carried out on MicroVAX II computer using the standard PM3 procedure, as implemented in the MOPAC 6.0 program package[18]. All geometries were fully optimized by minimizing the energy with respect to all geometrical variables without using the aid of symmetry. All possible rotational conformations of sulfo and enol forms alongside with these of anion were studied. Then the most stabile conformations were calculated on the Convex 240 computer using Gaussian 92 [19] program package at HF/STO-3G* and HF/3-21G* levels with full optimization of geometry.

The acidity (ΔH_{acid}) of compound HA was found as the heat of reaction for the proton abstraction equilibrium to form the conjugate base A^-:

$$HA \rightleftharpoons H^+ + A^- \qquad \Delta H_{acid}(HA) = \Delta H_f(H^+) + \Delta H_f(A^-) - \Delta H_f(HA) \qquad (1)$$

where $\Delta H_f(H^+)$, $\Delta H_f(HA)$ and $\Delta H_f(A^-)$ are the heats of formation for proton, acid and its conjugated anion. In case of the PM3 method the experimental heat of formation for proton (365.7 kcal/mol [20]) was used instead of the calculated value (353.6), because it improves the calculated acidities considerably. We acknowledge that this is not quite a correct procedure, despite the fact that such a way was also used in earlier works on semiempirical calculations of acidities and basicities[21].

3.Results and discussion

The energies and geometries for most stabile sulfone and enol forms as well as that of anion are presented in Tables 1-3. The corresponding conformations are presented on the Fig. 2 alongside with used numbering scheme for atoms.

The PM3 method predicts the hydrogen bonded enol form to be the most stabile one (27.8 kcal/mol more stable than the most stabile sulfone form), while the experimental data[1,17] clearly indicates, that the sulfone form is at least predominant. The results of *ab initio* calculations at both STO-3G* and 3-21G* level agree with experiment giving the sulfone form respectively 15.2 and 3.5 kcal/mol more stabile.

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The reasons for very high acidity of $(FSO_2)_3CH$ were investigated by means of Mulliken population analysis. In Tables 4 and 5 are given total atomic charges and selected bond populations obtained by all three methods.

The interesting fact is that the PM3 method predicts the Mulliken charge on the sulphonyl sulphur to be nearly +2.5 in both neutral molecule and anion, what seems improbable. Also *ab initio* calculations at 3-21G* level give very big charges. So, as it is noted already earlier[24], most reliable charges were obtained at STO-3G* level. Hence, the further discussion bases on the charge distribution obtained at this level of theory. Also it should be mentioned, that the changes in Mulliken charges upon deprotonation are very similar for all three methods. The only considerable difference is the fact that the PM3 method estimates the change of Mulliken charge on carbon athom to be much higher (0.41)than both *ab initio* methods (0.09 and 0.08).

The most notable feature in the changes of total atomic charges upon deprotonation is its uniformity. These changes vary from -0.09 at carbon atom to -0.05 on the sulphur atom which indicates very strong and uniform charge delocalization in tris(fluorosulfonyl)methane's anion. This delocalization is undoubtly the main reason for extremely high acidity of title compound.

The changes in bond populations calculated from Mulliken population analysis exhibit somewhat bigger changes upon deprotonation. So the C-S bond populations rises notably (0.2 units) while S-F and S-O bond populations lover slightly (0.03 and 0.02 units respectively). This, alongside with the fact, that the biggest changes in total atomic charges (excluding carbon atom as deprotonation center) take place on oxygen atoms, suggests that alongside with induction also resonance stabilization takes place.

This is of course disputable while all six S-O bonds are by no means coplanar. However, recent investigations by Mezey[25] of N-sulfonylsylfilimines indicates, that whereas in carbon compounds the prerequisite for optimum conjugation is a rather strict geometrical condition of exact or near coplanarity of the participating carbon atoms, the geometrical conditions are much more relaxed for third-row atoms if valence-shell *d* orbitals are involved in bonding. Further investigations in this direction were undertaken by the present authors and will be discussed elsewhere.

4. Conclusions

The above presented facts show clearly that PM3 should not be used to investigate the keto-enol tautomerism at least when the sulfonyl group is involved.

From the other hand it must be stated, that PM3 gives good prediction of bond lengths and angles, when the conformation of investigated molecule is known or predictable.

The analysis of changes in charge distribution upon deprotonation of trisfluorosulfonylmethane indicate, that its high acidity is caused by strong charge delocalization in anion form both by field inductive and resonance interaction mechanisms.

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Table 1. Geometry of the most stabile conformation of tris(fluorosulfonyl)methanes sulfonyl form.

	PM3	STO-3G*	3-21G*	Exp.
C-S	1.874Å	1.844Å	1.791Å	1.831Å
C-H	1.120Å	1.097Å	1.083Å	-
F-S	1.551Å	1.558Å	1.542Å	1.558Å
S-O^1	1.405Å	1.444Å	1.406Å	1.416Å
S-O^2	1.413Å	1.445Å	1.407Å	1.416Å
H-C-S	103.2°	109.5°	107.1°	-
C-S-F	100.8°	96.0°	96.4°	97.4°
C-S-O^1	110.9°	108.3°	109.8°	109.6°
C-S-O^2	106.3°	107.4°	107.6°	-
H-C-S-S	120.0°	120.0°	120.0°	-
H-C-S-F	39.4°	42.8°	38.6°	41.0°
H-C-S-O^1	112.8°	11.3°	111.8°	-
H-C-S-O^2	-108.3°	-110.7°	-110.3°	-
E	-332.200 kcal/mol	-1954.912643 a.u.	-1968.460818 a.u.	-
Dipole moment	3.751D	3.658D	4.064D	-

Table 2. Geometry of the most stabile conformation of tris(fluorosulfonyl)methanes enol form.

	PM3	STO-3G*	3-21G*
C-S^1	1.739Å	1.696Å	1.687Å
C-S^2	1.771Å	1.750Å	1.708Å
C-S^3	1.642Å	1.699Å	1.668Å
S^1-F	1.547Å	1.558Å	1.542Å
S^2-F	1.554Å	1.565Å	1.547Å
S^3-F	1.517Å	1.559Å	1.533Å
S^1-O^1	1.416Å	1.447Å	1.406Å
S^1-O^2	1.468Å	1.517Å	1.445Å
S^2-O^3	1.418Å	1.448Å	1.410Å
S^2-O^4	1.432Å	1.447Å	1.416Å
S^3-O^5	1.397Å	1.445Å	1.402Å
S^3-O^6	1.638Å	1.516Å	1.503Å
O^6-H	0.972Å	1.170Å	1.037Å
S^1-C-S^2	116.1°	133.9°	118.0°
S^1-C-S^3	125.2°	110.7°	120.1°
C-S^1-F	105.6°	105.1°	104.6°
C-S^2-F	103.6°	100.1°	101.8°
C-S^3-F	110.9°	104.3°	105.0°
C-S^1-O^1	113.6°	115.0°	111.7°
C-S^1-O^2	105.5°	106.9°	107.4°
C-S^2-O^3	111.6°	108.3°	110.9°
C-S^2-O^4	106.5°	108.0°	106.2°
C-S^3-O^5	120.3°	116.5°	120.0°
C-S^3-C^6	110.2°	106.3°	106.7°
S^3-O^6-H	118.4°	108.0°	119.1°
O^5-S^3-O^6-H	33.0°	11.4°	2.2°
E	-360.9 kcal/mol	-1954.8884 a.u.	-1968.4553 a.u.
Dipole moment	3.121D	3.204D	4.159D

Table 3. The most stabile conformation of tris(fluorosulfonyl)methyl anion.

	PM3	STO-$3G^*$	3-$21G^*$	Exp.
C-S	1.716Å	1.716Å	1.683Å	1.7Å
F-S	1.579Å	1.578Å	1.563Å	-
S-O^1	1.442Å	1.453Å	1.419Å	-
S-O^2	1.449Å	1.454Å	1.423Å	-
S-C-S	120.0°	120.0°	120.0°	-
C-S-F	104.9°	102.0°	102.5°	-
C-S-O^1	114.5°	113.0°	114.7°	-
C-S-O^2	112.2°	108.3°	108.1°	-
S-C-S-S	179.7°	180.0°	180.0°	180.0°
S-C-S-F	302.0°	21.7°	12.5°	-
C-S-F-O^1	113.2°	111.5°	112.5°	-
C-S-F-O^2	-108.3°	108.3°	-110.6°	-
E	-436.6 kcal/mol	-1954.297888 a.u.	-1968.015820 a.u.	-
Dipole moment	2.892D	2.904D	1.722D	-

Table 4. Net atomic charges, calculated from Mulliken population analysis.

	Neutral (sulfone form)			Anion		
	PM3	STO-3G*	3-21G*	PM3	STO-3G*	3-21G*
H	0.197	0.119	0.391			
C	-1.538	-0.062	-1.324	-1.952	-0.152	-1.404
S	2.444	0.449	1.651	2.442	0.397	1.673
F	-0.327	-0.059	-0.337	-0.361	-0.119	-0.379
O^1	-0.818	-0.199	-0.492	-0.871	-0.278	-0.567
O^2	-0.852	-0.209	-0.512	-0.890	-0.283	-0.593

Table 5. Bond populations, calculated from Mulliken population analysis.

	Neutral (sulfone form)			Anion		
	PM3	STO-3G*	3-21G*	PM3	STO-3G*	3-21G*
C-H	0.489	0.735	0.593			
C-S	0.165	0.624	0.054	0.201	0.822	0.178
S-F	0.420	0.593	0.466	0.419	0.565	0.476
S-O^1	0.739	1.029	1.049	0.708	1.014	1.094
S-O^2	0.727	1.026	1.044	0.698	1.010	1.039

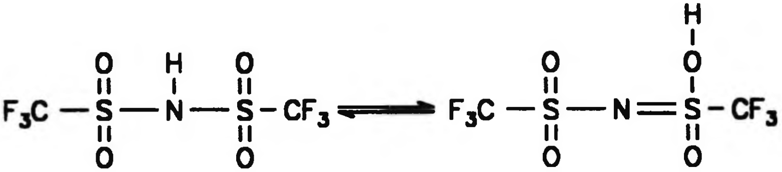
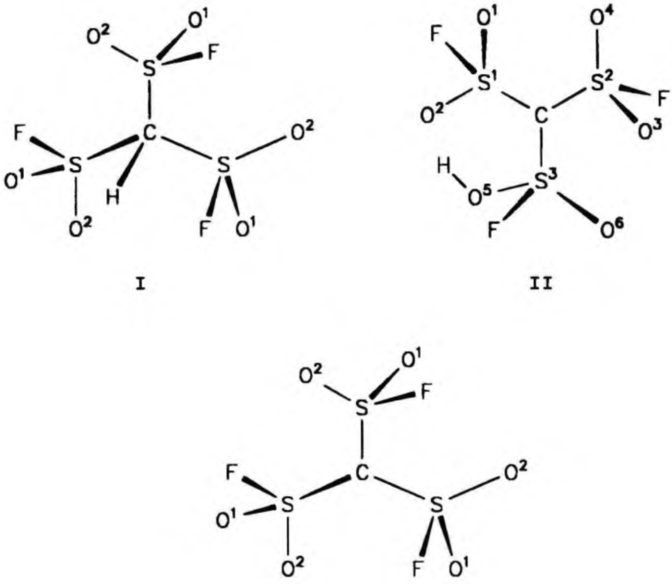


Figure 1. Suggested prototropic tautomerism of $(CF_3SO_2)_2NH$.



I

II

III

Figure 2. The most stabile conformations of tris(fluorosulfonyl)methanes sulfonyl form (I), enol form (II) and anion (III).

SUPERACIDITY OF NEUTRAL BRÕNSTED ACIDS IN GAS PHASE. PM3 STUDY.

Peeter Burk[a], Ilmar Koppel[a], Ivar Koppel[a],
Lev M. Yagupolskii[b] and Robert W. Taft[c]

[a] Institute of Chemical Physics, Tartu University,
EE2400 Tartu, Estonia
[b] Institute of Organic Chemistry, Academy of Sciences of
Ukrainian Republic, Kiev, Ukraine
[c] Department of Chemistry, University of California at Irvine,
Irvine, California 92717, USA

Abstract.

PM3 calculations of potentially superacidic neutral Brõnsted acids were carried out. It was shown, that PM3 method can be used to predict the gas-phase acidities of very acidic compounds only if the empirical corrections are made. Very strong acidifying effect is predicted for substitution of sp^2 oxygen by $=NSO_2CF_3$ group. The possibility of further increase of acidities of such compounds by further stepwise substitutions of $=O$ by $=NSO_2CF_3$ has been predicted. The geometries of known superacidic systems are reproduced quite well, so the PM3 method can be recommended for studies of that kind. The geometries of several superacidic systems were analyzed.

1. Introduction.

The name "superacid" was first used by J.B.Conant in 1927 [1] for the acid systems more acidic than the traditional mineral acids. Superacid media, much more acidic (H_0 > -30) than anhydrous sulfuric acid (H_0 = -12) were created by O.A.Olah and coworkers [2], which was important progress in developing new superacid systems.

Unfortunately, due to the substantial experimental and theoretical difficulties, besides the knowledge of some acidity function of the neat Brõnsted acid (AH) or related conjugated superacid system, far less quantitative and practically not self-consistent information is available on the pK_a values of strong or superstrong mineral or organic Brönsted acids, referred to their dilute solutions in water, nonaqueous solvent, or gas phase as standard state.

The intrinsic gas-phase equilibrium acidity (ΔG) scale (see [3]), where ΔG refers to the following proton transfer equilibrium

$$AH \rightleftharpoons A^- + H^+$$

for various neutral Brönsted acids includes more than 700 weak, moderately strong, or relatively strong acids whose ΔG varies from 415 kcal/mol to 315 kcal/mol, i.e. more than 70 pK_a units. Recently, this scale was further extended [4] from ΔG=318 kcal/mol to ΔG=284 kcal/mol to involve many very strong Brönsted acids off different structure.

Previous results and the analysis given in Refs.4-7 evidence that three major kinds of substituent effects i.e.,

1. field/inductive effect (F),
2. π-electron acceptor (resonance) effects (R), and
3. substituent polarizability (P) effect,

determine the gas-phase acidity of neutral Brönsted superacids (see also Ref.9). For all of those three influencing factors the acidity increases for AH acids are due to much stronger substituent stabilizing interactions with the deprotonated protonization center of A^- (e.g., O^-, N^-, C^-, etc..) than with the protonated reaction center in AH (e.g., OH, NH, CH, etc..).

Therefore, the simplest strategy to develop progressively more acidic superacid systems would be the synthesis of molecules which, along with the acidity site (C-H, O-H, N-H, S-H, etc..), include (several) highly dipolar superacceptor and strongly polarizable substituents which form very extensive, strongly conjugated system with the anionic protonization center of A .

It should be kept in mind [4,6-9] that no simple pattern for the influence of the above mentioned three major kinds of substituent effects on the acid strength of neutral Brönsted acids is expected because of the interdependence of the contributions for the F, P, and R-effects for the strongly electron-withdrawing, acceptor substituents, at least for some reaction series. So, increasing π-electron acceptor effects can decrease the P- and F-effects of the given substituent due to the increasing reduction of the negative charge of the anionic center. In its turn, the R effects could be significantly decreased by steric repulsion and non-coplanarity effects. All these phenomena lead to some, sometimes rather significant, reduction of the acidities expected on the grounds of the substituent effect additivity principle.

Proceeding from the above described principles several new families of superstrong Brönsted acids could be anticipated.

A particular attention should be called on the derivatives with a new family of superstrong electron-withdrawing substituents [10,11], generated according to Yagupolskii's principle by the replacement by the $=NSO_2CF_3$ group of an sp^2 oxygen atom(s) bonded to S,P or I-systems.

Only a few physical and chemical properties of these novel compounds have been studied so far, whereas the theoretical study of their electronic structure, reactivity and applications is practically absent. Due to the involvement of hypervalent fragments (CF_3SO_2, FSO_2, Cl^{VII}, etc.) the theoretical investigation of the structure and reactivity of more conventional superacids ($(CF_3SO_2)_3CH$, $(FSO_2)_3CH$, $HClO_4$, FSO_3H, etc.) is also on its initial phase.

2.Methods.

In recent years the semiempirical calculations (MNDO [12], AM1 [13] and PM3 [14] methods) have been widely used to investigate the properties of medium-sized and large systems. The only one of them with declared [15] ability to reproduce and predict correctly the properties of hypervalent molecules is PM3, while the others are known to fail to describe such systems.

In the present work an attempt to study the electronic structure and acidity of a wide range of potentially superacidic molecules - neutral Brönsted acids - was undertaken using the semiempirical PM3 method. Calculations were carried on MicroVAX II and VAX 8650 computers using the MOPAC 6.0 [16] program package. A full optimization of the structures of neutral molecules as well as their conjugated anions was used throughout this work.

The deprotonation enthalpy (DPE) of compound HA was found as the heat of reaction for loss of a proton to form the conjugate base:

$$HA \rightarrow H^{+}+A^{-} \qquad DPE(HA)=\Delta H_f(H^{+})+\Delta H_f(A^{-})-\Delta H_f(HA)$$

where $\Delta H_f(H^+)$, $\Delta H_f(A^-)$ and $\Delta H_f(HA)$ are the heats of formation for proton, acid and acids anion. In case of proton the experimental heat of formation (365.7 kcal/mol [3]) was used instead of calculated value (353.6), while it improves the calculated deprotonation enthalpy considerably. We understand, that this is not a quite correct procedure, but such a way was also used in earlier works on semiempirical calculations of acidities and basicities [17,18,19] of wide variety of molecules.

3.Results and discussion.

Calculated deprotonation enthalpies (DPE) for several potentially superacidic substances alongside with several reference acids (CH_4, NH_3, H_2O, etc.) are presented in Table 1. When available, also the experimentally measured acidities (ΔG^0) are given.

The results of statistical (regression) analysis of the relationship between the calculated deprotonation enthalpies and experimental gas-phase acidities according to formula

$$DPE(calc)=a+b\cdot DPE(\exp) \qquad (2)$$

are presented in Table 2, where N is the number of points, STDV is the average unsigned error in proton affinities, R is the correlation coefficient, σ is the standard deviation and δ is the average unsigned error, when DPE_{calc} is corrected using formula

$$DPE^{cor.}_{calc.} = \frac{DPE_{calc.} - a}{b} \tag{3}$$

It is not the most correct way to compare deprotonation enthalpies with gas-phase acidities as they must differ by $T\Delta S^0$, but this approach was selected as it saves a lot of computer time and the $T\Delta S^0$ values for many of the acids studied center at 7.0 kcal/mol [4].

As it can be seen, the correlation between calculated and experimentally measured acidities should be considered as fair (R^2=0.9194 and STDV=12.7), which is comparable to the similar results for the wide range of acids 0.903 and 11.2 [18]. However, at closer look one can see that at the acidity scale region below 340 kcal/mol, which is most important for current work, the correlation is rather bad (R^2=0.7613 and STDV=12.9) and continues to become even worse when we are omitting regions of lower acidity (see Table 2). It is not surprising, as these highly acidic compounds contain highly electronacceptor substituents, their anions are usually relatively bulky, whereas the PM3 method is reported to overestimate the stabilization energies of such anions [18] and, hence, also the acidity of their conjugated neutral acids. This statement is confirmed by constantly growing slope when going down in Table 2.

At the same time it can be said that the errors are some ways systematic, as for a series of substitutions in methane or ammonia with common substituent the correlation is very good (see trifluoromethyl-, trifluoroacetyl- and trifluoromethylsulfonyl-substituted acids in Table 2). In all these correlations also the corresponding parent acids (methane or ammonia) are included. So if the acidities of some members of the series are known, the acidities for the others can be predicted.

In a qualitative accordance and by analogy with the earlier experimental results, Table 1 shows that the introduction of the "conventional" strong polarizable electron-acceptor groups (CN, NO_2, CF_3SO_2, FSO_2) immediately at the deprotonation center of the studied CH-, NH-, OH- and SH acids, or in the aromatic ring attached to the protonation center, increases by many powers of ten the acidity of their unsubstituted parents. The calculated $\Delta H_f(AH)$ values obey roughly the same non-additivity and partial additivity trends as found for the experimentally measured values in Ref. 4.

In case of OH, NH and SH aliphatic Brönsted acids PM3 reproduces the experimental acidity of these compounds with a satisfactory precision. However, especially in case of sulfonyl-containing substituents, this method greatly overestimates the stability of the corresponding anions and therefore leads to very significantly overestimates acidities of those compounds. The largest deviation (49 kcal/mol) is noticed for $(CF_3SO_2)_3CH$ whereas, as a rule, differences in the calculated and measured acidities for different acids range from 10-40 kcal/mol.

From the compounds listed in Table 1 probably the most acidic is 4,7,10-CF_3SO_2 substituted fluoradene, for which on grounds of the additivity rule, an ΔG value ca 229 could be predicted assuming that all three CF_3SO_2 substituents in the fluoradene ring display the same acidifying substituent effect as para-CF_3SO_2 group in p-$CF_3SO_2C_6H_4CH_3$ (ΔG=340.7 kcal/mol) as compared with toluene itself (ΔG=373.7 kcal/mol), i.e. 33 kcal/mol per one CF_3SO_2 group or $3\cdot 33=99$ kcal/mol assuming 100% additive effect (ΔG for unsubstituted fluoradene is 324.9 kcal/mol). Assuming ca 60% fractional additivity correction this value becomes ca 260-265 kcal/mol. However, much higher acidity could be expected for 4,7,10-fluoradene derivative with supersubstituents $CF_3S(O)(NSO_2CF_3)$ or $CF_3S(NSO_2CF_3)_2$.

Enormous acidifying effect of supersubstituents $CF_3SO(N_8O_2CF_3)$ or $CF_3S(N_8O_2CF_3)_2$, as compared with the trifyl group, on the acidity of H2O, NH3 and methane could be seen from the Table 3.

The effects of replacement of sp^2 oxygen in various SO_2, SO, NO, =CO, etc. containing acids by NSO_2CF_3 group could be seen from Table 4. One can see that the present calculations predict in most cases extremely significant increases (up to 47 kcal/mol) of the acidity of compounds in which =O is replaced by $=NSO_2CF_3$ or $=NSO_2F$ group. Tables 1 and 4 show that similar very substantial increases (up to 50 kcal/mol) of the acidity are also predicted for such organic and inorganic superacids as CF_3SO_3H, FSO_3H, $HONO_2$, H_2SO_4, $(CF_3SO_2)_2NH$. On can see (Table 1), that in the case of the latter molecule, the replacement of all four oxygen atoms by $=NSO_2CF_3$ group is predicted by the PM3 approach to lead to the acidity in the range of 240 kcal/mol.

As each such replacement includes also two new sp^2 oxygens into molecule, further replacements of =O by $=NSO_2CF_3$ are possible with subsequent increase of acidity. One must of course consider, that with each such replacement the increase in acidity will diminish so that at some point the plateau will be achieved, where further substitutions will not increase the acidity.

Somewhat confused is the situation in case of the replacement of =O atoms in the perchloric acid by NSO_2CF_3 groups. The first NSO_2CF_3 leads to some modest (by 3.4 kcal/mol) increase of the acidity of the parent acid. The PM3 calculations of $HOCl(O)(NSO_2CF_3)_2$ and $HOCl(NSO_2CF_3)_3$ as neutral Brõnsted acids show that to those hypothetical compounds correspond two different potential minima. The first ones evidently correspond to the structures given above. One can see from Tables 1 and 4 that in both cases also the modest increases of the acidity upon consecutive introduction of $=NSO_2CF_3$ groups into the molecule of perchloric acid is expected. The second minimum on potential curve, however, corresponds to much lower energy (by 160-170 kcal/mol) and to the structures where intramolecular spontaneous proton transfer to $=NSO_2CF_3$ group occurs. The formation of "internal" ion pair seems to stabilize the AH form of the neutral acid even to a such extent that it´s formation enthalpy is lower than that of the anion, A^-.

The disappointing fact is that for the compounds containing the hypervalent sulphur PM3 predicts the Mulliken charge on the sulphur to be nearly +2.5 in both neutral molecules and anions, what is improbable and also contradictory with our *ab initio* calculations results at STO-3G* and 3-21G* level, where the charges on sulphonyl sulphur vary near the 0.8-0.9 and 1.6-1.65, respectively [20]. However, this is predictable, as PM3 model uses currently only s and p orbitals [18], so the sulphur atom must bear charge +2 to give "four" bonds. Thus no proper analysis of electron structure of above mentioned acids and conjugated anions can be made based on the PM3 charge distribution.

In many cases also the possibility of prototropic tautomerism, which lowers the acidity of corresponding compound should be considered. So it is established both experimentally [21] and computationaly [22] that hexafluoroacetylacetone exists predominantly in enol form. Also direct and indirect [4,23,24] suggestions about possible prototropic tautomerism in fluorosulfonyl- and trifluorosulfonyl compounds are made.

However, this rather intriguing question remains unanswered for further studies, as PM3 method is shown to be unusable for investigation of tautomeric equilibria in sulfonyl compounds [20] and even for trifluoroacetyl compounds at least limited CI is needed in framework of AM1 or PM3 methods for qualitative description of keto-enol tautomerism [22]. Further study of these phenomena using more sophisticated computational methods is in progress in our laboratory.

In Table 5 geometries of several calculated acids and their conjugated anions are given alongside with corresponding experimental data. As it can be seen, the PM3 method reproduces the geometries of presented compounds quite well, which generally seems to be the strongest point of PM3 method. Based on this we believe that the geometries of other investigated compounds are also correctly predicted. Calculated geometries of several interesting compounds are presented in Tables 4-5.

The geometries of trifluoromethylsulfonyl substituted methanes are presented in Table 6. Some interesting geometrical properties of these compounds are discussed below on the example of $(CF_3SO_2)_3CH$. The central carbon atom and three sulphur atoms in anion are located on the same plane as found experimentally by crystallographic study of hydrate of its K-salt [25]. Also the trend of oxygen atoms in both anionic and neutral form to be as close as possible to the plane, defined by the central carbon atom and sulphur atoms, can be expected (resonance stabilization). Somewhat surprising is the prevalation of this trend over the repulsion between CF_3 groups, as in both anion and neutral molecule of $(CF_3SO_2)_3CH$ the CF_3SO_2 groups are oriented so that the perfluoromethyl groups are cis to each other (in the same side of the above-mentioned S,C,S,S plane), while the oxygen atoms are on the other side of the plane. It is also somewhat surprising that the hydrogen atom in neutral tris-trifluoromethylsulfonylmethane is on the same side with perfluoromethyl groups. The differences in energies between different conformers are, however, not too big - the heats of formation of conformations, where one or more trifluoromethylsulfonyl groups are rotated 180° around S-C bonds is only ca 5-10 kcal/mol higher for both neutral and anion. Also, in comparison with the experiment [25], the rather long calculated C-S bond length (more than 2.00Å) between the sulphur and carbon atom of trifluoromethyl group should be noted (the experiment gives 0.1-0.15 nm shorter values). Similar trends can be found also in other trifluoromethylsulfonyl substituted compounds.

In Table 5 the geometries of sulphuric acid and its derivatives obtained by stepwise substitution of double-bonded oxygen atoms with $=NSO_2CF_3$ groups according to Yagupolskii's principle as well as corresponding anions are given. In case of $(HO)_2S(=NSO_2CF_3)_2$ we once more see the strong influence of resonance to the molecular structure. In both neutral and anionic forms the C-S-N=S=N=S-C skeleton is close to planar. In case of neutral the S=O bonds of substituent are also coplanar with parent's S-O bonds. As in above-mentioned case of $(CF_3SO_2)_3CH$ the C-S bonds are found to be rather long and trifluoromethylsulfonyl groups tend to be rather cis than trans. However, in $(HO)_2S(O)=NSO_2CF_3$ molecule the above-mentioned trend to position S=O bonds in the same plane don't hold. But despite this the hydrogen atoms and trifluoromethyl groups are in cis position.

Conclusions.

It was shown, that PM3 method can be used to predict the gas-phase acidities of many new very acidic compounds. However, quantitative predictions could be made only on assumption that the empirical corrections are made.

Very strong acidifying effect is predicted for substitution of sp^2 oxygen by $=NSO_2CF_3$ group in a wide variety of acids (sulfonic acids, ketones, aldehydes, nitric and nitrous acids, imides, etc.). The possibility of further increase of acidities of such compounds by further stepwise substitutions of $=O$ by $=NSO_2CF_3$ was predicted.

The geometries of the known superacidic systems were reproduced quite well, so the PM3 method can be recommended for studies of that kind. Charge distribution, predicted by PM3 method for hypervalent compounds is, however, not reflecting the real picture due to the lack of the inclusion of *d*-orbitals, so that "hypervalent" atoms of these molecules must bear big formal charge to give needed number of formal bonds.

From the geometries of analyzed superacids it can be concluded, that the most stable conformations are predominantly determined by the resonance interactions which require the coplanarity of certain molecular fragments. This resonance stabilization seems to be rather strong as it often overpowers even the electrostatic repulsion between closely located trifluoromethyl groups.

For the further quantitative study of the electronic structure, geometry and reactivity of hypervalent superacids internal shortcomings of PM3 approach are rather evident and another approach with the inclusion of d-orbitals is needed [26].

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Table 1. Calculated heats of formation, deprotonation entalpies and exprimental gas-phase acidities of investigaed compounds.

Acid	DPE	$\Delta H_f(AH)$	$\Delta H_f(A^-)$	ΔG^0
	C-H acids			
CH_4	430.2	-13.0	51.5	408.5[a]
CH_3NO	355.1	7.0	-3.6	
CH_3CN	370.9	23.3	28.5	364.0[b]
$CH_2(NC)_2$	334.6	64.4	33.3	328.3[a]
$CH(NC)_3$	308.4	109.2	51.9	294[c]
CF_3CH_3	376.3	-172.3	-161.7	370.4[c]
$(CF_3)_2CH_2$	339.0	-326.7	-353.4	343.9[b]
$(CF_3)_3CH$	310.1	-478.4	-533.9	326.6[b]
$(CF_3)_3CCH_3$	352.4	-483.0	-496.3	
CF_3COCH_3	346.1	-199.2	-218.8	342.1[a]
$(CF_3CO)_2CH_2$	306.9	-379.7	-438.5	310.3[b]
$(CF_3CO)_3CH$	287.0	-554.3	-633.0	300.6[b]
$(CH_3CO)_3CH$	329.2	-129.1	-165.6	328.9[b]
$(CF_3CO)_2CHCF_3$	289.5	-528.9	-605.1	305.0[b]
FSO_2CH_3	339.8	-128.9	-154.9	
$(FSO_2)_2CH_2$	287.4	-236.6	-314.9	307.3[b]
$(FSO_2)_3CH$	261.3	-332.2	-436.7	
$FS(O)(=NSO_2CF_3)CH3$	318.1	-28.5	-76.1	
$CF_3SO_2CH_3$	323.4	-207.8	-250.1	339.8[a]
$(CF_3SO_2)_2CH_2$	268.5	-390.4	-487.6	301.5[b]
$(CF_3SO_2)_3CH$	240.4	-552.4	-677.7	289.0[b]
$CF_3SO_2NNCH_3$	307.6	-171.2	-229.3	299[c]
CH_3COCN	349.3	-5.9	-22.3	338[c]
$CF_3SO_2N{=}C(CN)CH_3$	306.8	-156.5	-215.4	
$(CF_3SO_2)_2CHCN$	275.2	208.0	128.1	
$CF_3SO_2CH(CN)_2$	278.1	-112.4	-199.9	280[c]

Table 1. (Continued).

Acid	DPE	$\Delta H_f(AH)$	$\Delta H_f(A^-)$	ΔG^0
$CF_3SO(NSO_2CF_3)CH_3$	301.2	-361.1	-425.6	
$CF_3S(NSO_2CF_3)_2CH_3$	284.7	-517.0	-598.0	
$C_6H_5CH(CN)_2$	318.3	94.6	47.2	314.3[b]
$C_6F_5CH(CN)_2$	298.5	-105.6	-172.8	303.6[b]
$C_6H_5CH(SO_2F)_2$	287.1	-199.1	-277.7	307.0[b]
$C_6H_5CH(SO_2CF_3)_2$	269.6	-350.8	-448.0	298.2[b]
2,4,6-$(CF_3SO_2)_3C_6H_2CH(CN)_2$	266.0	-458.7	-558.4	
fluoradene	328.6	109.9	72.8	324.9[c]
4,7,10-$(CF_3SO_2)_3$fluoradene	278.6	-473.1	-560.2	
$(CN)_2C=C(CH_3)CH(CN)_2$	285.4	208.0	128.1	
pentafluorocyclopentadiene	308.0	-174.5	-232.3	
pentacyanocyclopentadiene	264.4	-737.9	-839.3	
	N-H acids			
NH_3	407.1	-3.1	38.3	396.1[a]
CF_3NH_2	353.0	-166.6	-179.3	
$(CF_3)_2NH$	317.4	-325.0	-373.3	324.3[b]
$(CF_3)_3CNH_2$	333.0	-472.6	-505.2	350.1[b]
CF_3CONH_2	335.9	-196.2	-226.0	336.7[b]
$(CF_3CO)_2NH$	301.5	-378.6	-442.8	307.5[b]
2,4,6-NO_2 aniline	300.5	0.0	-65.2	
2,4,6-CF_3SO_2 aniline	291.5	-559.2	-633.4	304.8[b]
2,4,6-FSO_2 aniline	303.2	-328.0	-390.5	307.2[b]
FSO_2NH_2	331.3	-130.9	-165.3	
$(FSO_2)_2NH$	296.4	-261.8	-331.2	301.2[b]
$CF_3SO_2NH_2$	317.0	-207.8	-256.5	321.3[a]
$(CF_3SO_2)_2NH$	278.4	-412.9	-500.1	291.8[b]
$CF_3SO(NSO_2CF_3)NH_2$	293.5	-364.3	-436.5	

Table 1. (Continued).

Acid	DPE	$\Delta H_f(AH)$	$\Delta H_f(A^-)$	ΔG^0
$CF_3S(NSO_2CF_3)_2NH_2$	280.8	-521.0	-605.9	
$[CF_3S(N_8O_2CF_3)_2]_2NH$	240.5	-1026.0	-1151.2	
ON-NH_2	342.1	20.4	-3.1	
$CF_3SO_2NNNH_2$	302.1	-156.0	-219.5	
$CF_3SO_2NHCOCF_3$	287.7	-392.1	-470.1	298.2[b]
$PhSO_2NH_2$	340.6	-43.4	-68.5	333.2[b]
$PhSO(NSO_2CF_3)NH_2$	312.2	-203.7	-257.2	
$PhS(NSO_2CF_3)_2NH_2$	307.4	-233.2	-291.5	
2,3,4,5-tetratrifylpyrrole	262.6	-717.9	-821.0	
	O-H	acids		
H_2O	401.6	-53.4	-17.5	384.1[a]
FOH	364.9	-29.2	-30.0	
CF_3OH	332.2	-222.7	-256.3	340.7[d]
$(CF_3)_3COH$	309.7	-516.6	-572.6	324.0[b]
CF_3CSOH	296.0	-159.2	-228.9	
CF_3COOH	319.3	-244.0	-290.4	316.3[b]
$(CN)_3CCOOH$	297.3	32.0	-36.3	
C_6F_5COOH	326.8	-272.3	-311.1	316.6[b]
C_6F_5OH	312.9	-231.3	-284.0	320.8[b]
2,4,6-$(CF_3SO_2)_3C_6H_2SO_3OH$	292.3	-637.5	710.0	
2,4,6-$(CF_3SO_2)_3C_6H_2COOH$	307.8	-624.8	-682.7	
2,4,6-$(NO_2)_3C_6H_2OH$	284.7	-41.2	-122.2	302.8[b]
FSO_2OH	318.4	-186.4	-233.7	299.8[e]
$FSO(NSO_2CF_3)OH$	289.5	-339.3	-415.5	
$FS(NSO_2CF_3)_2OH$	269.2	-488.7	-585.2	
$(CF_3)_3CSO_2OH$	292.8	-566.3	-639.2	
CF_3SO_2OH	302.4	-260.3	-323.5	299.5[b]
$CF_3SO(NSO_2CF_3)OH$	279.7	-412.5	-498.5	

Table 1. (Continued).

Acid	DPE	$\Delta H_f(AH)$	$\Delta H_f(A^-)$	ΔG^0
$CF_3S(NSO_2CF_3)_2OH$	266.3	-566.1	-665.5	
ONOH	336.1	-13.3	-42.9	330.5
CF_3SO_2NNOH	294.3	-182.2	-253.6	
H_2SO_4	324.0	-188.1	-229.8	302.2[e]
$NCSO_3H$	314.1	-90.9	-142.6	
$CLSO_3H$	303.6	-135.5	-197.6	
H_2SO_4	324.0	-188.1	-229.8	302.2[e]
$H_2SO_3{=}NSO_2CF_3$	292.3	-342.2	-415.7	
$H_2SO_2(=NSO_2CF_3)_2$	273.2	-495.5	-588.0	
$HOClO_3$	264.0	-26.4	-128.0	
$HOClO_2{=}NSO_2CF_3$	260.6	-216.9	-322.0	
$HOClO(=NSO_2CF_3)_2$	414.2	-565.4	-517.0	
$HOClO(=NSO_2CF_3)_2$[f]	253.5	-405.2	-517.0	
$HOCl(=NSO_2CF_3)_3$	430.2	-777.3	-712.9	
$HOCl(=NSO_2CF_3)_3$[f]	252.4	-599.8	-712.9	
$HONO_2$	310.0	-38.0	-93.3	317.8[a]
$HONO(=NSO_2CF_3)$	282.3	-197.2	-280.6	
$HON(=NSO_2CF_3)_2$	261.9	-353.7	-457.5	
$(CN)_3COH$	317.0	73.6	24.9	
$(CN)_2C{=}C(CN)OH$	294.1	84.7	13.1	
FSH	335.3	-40.4	-70.7	
CF_3SH	320.0	-137.5	-183.2	
$(CF3)_3CSH$	306.7	-446.0	-505.0	
CF_3COSH	314.8	-178.0	-228.9	312.5[b]
HCl	348.7[g]	-20.5	-51.2	328.0[a]
HI	272.1[g]	28.8	-64.6	309.3[a]
HBr	304.0[g]	5.3	-56.2	318.2[a]
HF	408.3[g]	-59.7	-17.1	371.4[a]

[a] from Ref.3; [b] from Ref.4; [c] predicted in Ref.4; [d] from Ref.5; [e] from Ref.24; [f] energies, corresponding to second minima on potential surface, discussed in text; [g] from Ref. 18

Table 2. Results of statistical analysis of calculated deprotonation enthalpies and experimental gas-phase acidities in terms of Eq. (2).

	n	STDV	a	b	R^2	σ	δ
All acids	54	12.7	-85.5	1.23	0.919	14.6	8.7
Acids with $\Delta G<340$	44	12.5	-91.4	1.24	0.761	15.2	9.3
Acids with $\Delta G<330$	39	13.0	-97.2	1.24	0.691	15.8	9.6
Acids with $\Delta G<320$	30	14.2	-102.4	1.26	0.531	17.1	10.7
Acids with $\Delta G<310$	23	16.6	-109.5	1.27	0.301	18.9	16.4
Acids with $\Delta G<300$	9	16.8	-266.4	1.88	0.514	22.3	8.9
CF3 subst. acids	12	11.9	-110.0	1.31	0.948	11.3	5.9
CF3CO subst. acids	8	9.3	-104.1	1.31	0.997	3.6	2.0
CN subst. acids	9	9.7	-69.3	1.21	0.977	6.2	3.6
CF3SO2 subst. methanes	5	29.6	-193.0	1.52	0.997	6.3	2.4
CF3SO2 subst. ammonias	4	9.7	-78.2	1.22	0.999	1.2	0.6

Table 3. Comparision of acidifying effect of CF_3SO_2, $CF_3SO(=NSO_2CF_3)$ and $CF_3S(=N_SO_2CF_3)_2$ substituents on H_2O, NH_3 and CH_4.

Substituent	XOH	XNH_2	XCH_3
H	401.6	407.1	430.2
CF_3SO_2	302.4	317.0	323.4
$CF_3SO(NSO_2CF_3)$	279.7	293.5	301.2
$CF_3S(NSO_2CF_3)_2$	266.3	280.8	284.7

Table 4. The effect of replacement of sp^2 oxygen by $=NSO_2CF_3$ group in various oxygen containing acids.

	DPE (X=O)	DPE ($X=NSO_2CF_3$)	ΔDPE
$FSO(X)CH_3$	339.8	318.1	21.7
$CF_3SO(X)CH_3$	323.4	301.2	22.2
$CF3_sX(NSO_2CF_3)CH_3$	301.2	284.7	16.5
CH_3NX	355.1	307.6	47.5
CH_3CXCN	349.3	306.8	42.5
$ONNH_2$	342.1	302.1	40.0
$CF_3SO(X)NH_2$	317.0	293.5	23.5
$CF_3SX(NSO_2CF_3)$	293.5	280.8	12.7
$PhSO(X)NH_2$	340.6	312.2	28.4
$PhSX(NSO_2CF_3)NH_2$	312.2	307.4	4.8
CF_3CXOH	319.3	283.8	35.5
$FSO(X)OH$	318.4	289.5	28.9
$FSX(NSO_2CF_3)OH$	289.5	269.2	20.3
$CF3SO(X)OH$	302.4	279.7	22.7
$CF_3SX(NSO_2CF_3)OH$	279.7	266.3	13.4
$XNOH$	336.1	294.3	41.8
$(HO)_2SO(X)$	324.0	292.3	31.7
$(HO)_2SX(NSO_2CF_3)$	292.3	273.2	19.1
$HOClO_2(X)$	264.0	260.6	3.4
$HOClO(X)(NSO_2CF_3)$	260.6	414.2	-153.6
$HOClO(X)(NSO_2CF_3)$	260.6	253.5	7.1
$HOClX(NSO_2CF_3)_2$[a]	414.2	430.2	-16.0
$HOClX(NSO_2CF_3)_2$[a]	253.5	252.4	1.1
$HONO(X)$	310.0	282.3	27.7
$HONX(NSO_2CF_3)$	282.3	261.9	20.4

[a] using energies, corresponding to second minima on potential surface, discussed in text

Table 5. Calculated and experimental geometries of some investigated acids (bond lenghts (R) in Å, angles (A) in degrees).

	Calc.	Exp.		Calc.	Exp.
	$(CF_3)_3CH^a$			$(CF_3)_3COH^b$	
R(C-H)	1.117	1.110	R(C-C)	1.589	1.566
R(C-C)	1.566	1.537	R(C-F)	1.345	1.335
R(F-C)	1.347	1.334	R(C-O)	1.391	1.414
A(C-C-C)	109.2	112.9	A(C-C-F)	113.0	110.6
A(C-C-F)	112.3	110.9	A(C-C-C)	108.4	110.4
A(H-C-C)	109.8	105.8	A(C-C-O)	112.3	108.5
	$H_2SO_4^c$			$HCLO_4^d$	
R(O-H)	0.947	0.970	R(CL-O)	1.645	1.635
R(S-O)	1.668	1.574	R(CL=O)	1.455	1.408
R(S=O)	1.407	1.422	A(O=CL=O)	101.6	112.8
A(H-O-S)	117.6	108.5	A(O=CL-O)	104.8	105.8
A(O-S-O)	97.9	101.3		$FSO_2NH_2^e$	
A(O=S=O)	107.4	123.3	R(N-S)	1.742	1.610
A(O-S=O)	107.3	108.6	R(S-F)	1.560	1.560
A(H-O-S=O)	20.9	20.8	R(S=O)	1.425	1.412
A(H-O-S-O)	-89.9	-90.9	R(N-H)	1.000	1.020
	$(CF_3CO)_2CH_2^f$		A(N-S-F)	100.0	99.0
R(HC-C)	1.362	1.407	A(O=S=O)	108.8	123.4
R(C-C)	1.552	1.546		$(FSO_2)_3CH^e$	
R(C-O)	1.280	1.259	R(C-S)	1.874	1.831
R(C-F)	1.349	1.337	R(S-F)	1.551	1.558
A(OC-C-C)	111.7	115.2	R(S-O)	1.409	1.416
A(HC-C-O)	124.2	126.4	A(C-S-F)	100.8	97.4
A(HC-C-C)	117.6	119.7	A(C-S-O)	111.0	109.6
A(C-C-F)	112.5	110.6	A(S-C-S)	115.0	111.1

Table 5. (Continued).

	Calc.	Exp.		Calc.	Exp.
	CF_3SO_2OH[g]			CF_3COOH[h]	
R(S-C)	2.002	1.833	R(C-F)	1.348	1.325
R(F-C)	1.351	1.332	R(C-C)	1.568	1.546
R(S=O)	1.401	1.418	R(C=O)	1.208	1.192
R(S-O)	1.662	1.558	R(C-O)	1.344	1.353
R(O-H)	0.949	0.960	R(O-H)	0.952	0.960
A(S-C-F)	113.7	110.3	A(C-C=O)	127.1	126.8
A(C-S-O)	96.8	102.3	A(C-C-O)	112.0	111.1
A(O-S=O)	107.5	109.9	A(C-O-H)	148.0	107.0
A(S-O-H)	118.1	115.0	A(C-C-F)	113.1	109.5
			A(F-C-C=O)	1.5	17.3

[a] Experimental geometry from Ref. 25

[b] Experimental geometry from Ref. 26

[c] Experimental geometry from Ref. 27

[d] Experimental geometry from Ref. 28

[e] Experimental geometry from Ref. 29

[f] Experimental geometry from Ref. 20

[g] Experimental geometry from Ref. 30

[h] Experimental geometry from Ref. 31

Table 6. Selected geometrical parameters of neutrals and anions of the trifluorosulfonyl substituted methanes.

	$CF_3SO_2CH_3$		$(CF_3SO_2)_2CH_2$		$(CF_3SO_2)_3CH$		
Parameter	Neutral	Anion	Neutral	Anion	Neutral	Anion	Exp. anion[a]
R(C-S)	1.769	1.538	1.812	1.620	1.872	1.722	1.69 1.73
R(S-CF)	2.012	2.123	2.010	2.053	2.020	2.040	1.84 1.90
R(C-F)	1.351	1.357	1.351	1.354	1.351	1.352	1.30 1.34
R(S=O)	1.428	1.483	1.414	1.452	1.411	1.436	1.43 1.44
R(C-H)	1.101	1.084	1.117	1.100	1.148		
A(O=S-C)	112.0	116.9	111.3	118.2	112.6	116.5	109 110
A(O'=S-C)	112.0	116.9	110.8	113.6	110.8	113.4	107 108
A(F-C-S)	114.3	115.7	114.3	115.2	114.3	115.2	107 108

[a] from Ref. 25

Table 7. Selected geometrical parameters of neutrals and anions of the CF3SO2N= substituted sulphuric acids.

	H_2SO_4		$H_2SO_3(=NSO_2CF_3)$		$H_2SO_2(=NSO_2CF_3)_2$	
Par	Neutral	Anion	Neutral	Anion	Neutral	Anion
R(O-H)	0.947	0.945	0.950	0.948	0.952	0.949
R(S-O)	1.668	1.718	1.660	1.691	1.661	1.682
R(S=O)	1.407	1.478	1.401	1.443		1.436
R(S=N)			1.585	1.675	1.567	1.630
R(S=N')					1.567	1.646
R(N-S)			1.681	1.627	1.694	1.657
R(N'-S')					1.694	1.649
R(S'=O)			1.415	1.417	1.410	1.440
R(S'=O')			1.415	1.417	1.414	1.434
R(S-C)			2.007	2.050	2.007	2.031
R(C-F)			1.351	1.354	1.351	1.354
A(H-O-S)	117.6	113.7	117.2	114.6	116.2	115.2
A(O-S-O)	97.9		99.3		98.9	
A(O=S=O)	107.4	115.6				
A(O-S=O)	107.3	103.7	109.7	118.2		105.0
A(H-O-S=O)	20.9	60.5	31.9	65.2		
A(N=S-O)			105.0	113.0	111.6	107.1
A(N'=S'-O)					105.6	100.5
A(N=S=O)			111.5	116.3	109.5	110.8
A(N=S=O')				113.8	110.3	115.3
A(N'=S'=O)					109.5	114.1
A(N'=S'=O')					110.3	114.5
A(N=S-C)			93.8	100.0	97.6	101.8
A(N'=S-C)					97.4	97.0

TÜ 94. 56. 150. 6,52. 6,0.