The enormous acidifying effect of the supersubstituent $=NSO_2CF_3$ on the acidity of derivatives of benzenesulfonamide and toluene-*p*-sulfonamide in the gas phase and in dimethyl sulfoxide

Ilmar A. Koppel,[*a] **Juta Koppel,**[a] **Ivo Leito,**[a] **Ivar Koppel,**[a] **Masaaki Mishima**[b] **and Lev M. Yagupolskii**[c]

[a] *Institute of Chemical Physics, University of Tartu, Jakobi 2, Tartu 51014, Estonia. E-mail: ilmar@chem.ut.ee; Fax: +372 7 375 264; Tel: +372 7 375 263*
[b] *Institute for Fundamental Research of Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan*
[c] *Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya 5, 253660 Kiev-94, Ukraine*

Received (in Cambridge, UK) 18th July 2000, Accepted 15th November 2000
First published as an Advance Article on the web 18th December 2000

The effect of stepwise replacement of =O oxygen atoms by $=NSO_2CF_3$ fragments in the sulfonyl group of toluene-*p*-sulfonamide and benzenesulfonamide on their acidity has been studied in the gas phase and dimethyl sulfoxide (DMSO). Incorporation of the first $=NSO_2CF_3$ group into $4\text{-}MeC_6H_4SO_2NH_2$ increases its gas-phase acidity by 23.6 kcal mol^{-1}. Substituting the second =O by the $=NSO_2CF_3$ group leads to an additional acidity increase of 10.7 kcal mol^{-1}; the total acidity increase is thus 34.3 kcal mol^{-1} (25 powers of ten!). In DMSO solution the total acidity increase is 13 pK_a units (17.7 kcal mol^{-1}). These findings are also supported by computational studies using DFT B3LYP at the 6-31+G* level and the semiempirical PM3 method. The results of this work have potentially important implications for the design of new strongly acidic catalytic materials.

A principle for the building of novel, very strong electron-acceptor substituents with an extensive conjugated chain was suggested by one of us[1–3] some time ago. It uses the creation of superstrong electron-acceptor substituents by replacement of a double bonded sp^2 oxygen or sulfur atom in different (*e.g.* acidic) systems by $=NSO_2CF_3$, $=NSO_2F$, or similar groups.

It was shown[3] that the resulting new substituents, *e.g.*, $-S(=NSO_2CF_3)_2CF_3$, $-S(=NSO_2CF_3)_2F$, *etc.* significantly surpass in their electron-acceptor properties all traditionally strong acceptor substituents like –CN, $-NO_2$, $-SO_2CF_3$, *etc.* In particular, it was demonstrated *via* ^{19}F NMR spectroscopy that the Hammett σ_p constant (1.7) for the $4\text{-}S(=NSO_2F)_2F$ group exceeds by far the similar constant for the $4\text{-}NO_2$ group (0.7).[2,3]

Since then, a large variety of compounds, including those with new superstrong electron-acceptor substituents, have been synthesized.[4–6]

The introduction of electron-acceptor supersubstituents into acidic systems is predicted to lead to very significant increases in their acidity[7] but the number of experimental studies of the acidity of these novel, potentially highly acidic compounds is very limited.

Indeed, introducing the $-S(O)(=NSO_2CF_3)CF_3$ substituent into the *para* position of aniline results in a 17.9 kcal mol^{-1} increase in its acidity compared with $4\text{-}CF_3SO_2$-aniline.[8] However, this measurement is the only successful gas-phase acidity measurement of a system containing the $=NSO_2CF_3$ fragment accomplished to date. Several attempts have been made to measure the acidities of other acids modified using the $=NSO_2CF_3$ substituent, but none of them were successful.[9] In particular, no gas-phase acidity data are available for compounds bearing the $=NSO_2CF_3$ fragment in the immediate vicinity of the acidity center.

The situation is only slightly better in the condensed phase. In acetonitrile solution it was demonstrated that in the case of the introduction of one $=NSO_2CF_3$ group into the sulfonyl group of $4\text{-}ClC_6H_4SO_2NHSO_2C_6H_4\text{-}4\text{-}Me$, $(4\text{-}ClC_6H_4SO_2)_2NH$ or $4\text{-}NO_2C_6H_4SO_2NHSO_2C_6H_4\text{-}4\text{-}Cl$ the acidity of these compounds increases significantly—more than 5 pK_a units.[10]

In this paper we report the results of studies (experimental and theoretical) of the intrinsic (gas phase) and solution (DMSO) acidity of some derivatives of toluene-*p*-sulfonamide (see Scheme 1) and benzenesulfonamide which are synthesized by replacement of one or two oxygen atoms of the sulfonyl group in the immediate vicinity of the acidity center by the $=NSO_2CF_3$ supersubstituent.[11]

Experimental

Acidity measurements in the gas phase

The gas-phase acidity of an acid HA, $\Delta G_{acid}(HA)$, refers to eqn. (1), and is defined as the Gibbs free energy change of the reaction (1).

$$HA \rightleftharpoons A^- + H^+ \tag{1}$$

The gas-phase acidity measurements were carried out according to eqn. (2), where HA_{ref} denotes a reference acid

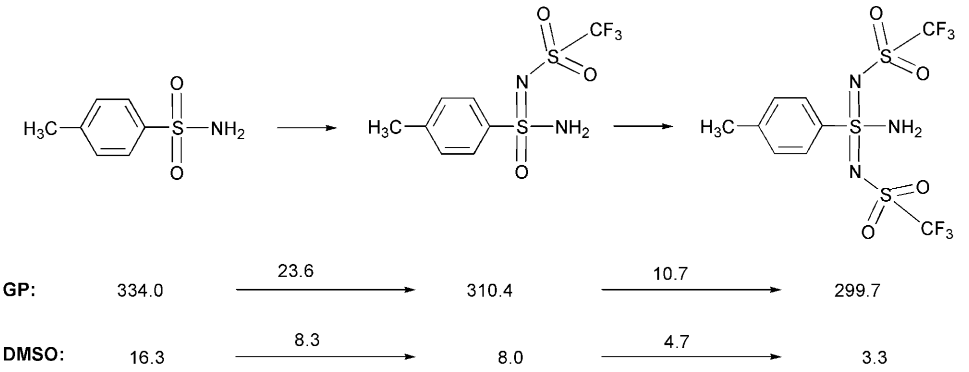
$$HA + A_{ref}^- \rightleftharpoons A^- + HA_{ref} \tag{2}$$

with a known gas-phase acidity value $\Delta G_{acid}(HA_{ref})$. The directly measured quantity is the equilibrium constant K of eqn. (2), from which the Gibbs free energy change $\Delta\Delta G_{acid}$ and the $\Delta G_{acid}(HA)$ can be found [eqn. (3)].

$$\Delta\Delta G_{acid} = -RT \ln K = \Delta G_{acid}(HA) - \Delta G_{acid}(HA_{ref}) \tag{3}$$

The FT ICR technique was used for the gas-phase acidity measurements. The Extrel FT MS 2001 instrument of Kyushu University was used. The measurements were performed at the cell temperature of 373 K. The direct inlet of the sample into the ICR cell was used with $4\text{-}MeC_6H_4S(O)(=NSO_2CF_3)NH_2$

DOI: 10.1039/b005765g



Scheme 1 The acidifying effects of stepwise introduction of $=NSO_2CF_3$ into toluene-*p*-sulfonamide in the gas phase (ΔG_{acid}, kcal mol^{-1}) and DMSO (pK_a).

Table 1 The solution phase (pK_a in DMSO) and experimental gas-phase acidities (ΔG_{acid}) and the computational results (ΔG_{acid}(DFT) for DFT B3LYP 6-31+G* and ΔG_{acid}(PM3) for PM3) of some derivatives of benzenesulfonamide and toluene-*p*-sulfonamide[a]

Compound	pK_a	ΔG_{acid}	ΔG_{acid} (DFT)	ΔG_{acid} (PM3)
$C_6H_5SO_2NH_2$	16.0[b]	333.2[c]	333.5	332.5
$4\text{-}MeC_6H_4SO_2NH_2$	16.3	334.0	334.7	332.9
$C_6H_5S(O)(=NSO_2CF_3)NH_2$	7.8	—	—	305.9
$4\text{-}MeC_6H_4S(O)(=NSO_2CF_3)NH_2$	8.0	310.4	310.0	308.2
$4\text{-}NH_2C_6H_4S(O)(=NSO_2CF_3)NH_2$	8.6	—	—	309.4
$4\text{-}MeC_6H_4S(=NSO_2CF_3)_2NH_2$	3.3	299.7	292.4	292.6

[a] This work, unless indicated otherwise. The experimental ΔG_{acid} values (at 373 K) and the calculated ΔG_{acid} values are in kcal mol^{-1} (1 cal = 4.184 J). [b] Ref. 13, see also ref. 12. [c] Ref. 9.

and $4\text{-}MeC_6H_4S(=NSO_2CF_3)_2NH_2$. This method proved to work nicely, giving stable signals from M − 1 anions of these compounds. Earlier attempts to introduce these compounds into the ICR spectrometer using the conventional system failed.[9] Other details of the measurements were the same as in ref. 9.

It has been shown that when using the direct inlet of a compound into the ICR cell the actual partial pressure of the compound can sometimes (depending on the particular system) be rather different from the one calculated using the readings of the pressure gauge. The situation for our particular system was checked with the measurement of the couple $C_6H_5SO_2NH_2$ *vs.* $4\text{-}MeC_6H_4SO_2NH_2$. This measurement was performed in two ways: in one run $C_6H_5SO_2NH_2$ was introduced using the direct inlet and $4\text{-}MeC_6H_4SO_2NH_2$ was introduced from the oven. In the other run the situation was *vice versa*. Both ways gave identical results, from which it can be concluded that the readings of the pressure gauge can be used to calculate also the partial pressures of the compounds introduced using the direct inlet.

Acidity measurements in DMSO

In DMSO the pK_a values were measured at 25 °C by means of potentiometric titration with a glass electrode as the indicator electrode. The solutions of the acids (the concentrations were in the range 2×10^{-3} to 8×10^{-3} M) were titrated with a standard *ca.* 0.01 M solution of Bu_4NOH. Titration of solutions of benzoic acid (pK_a(DMSO) = 11.0[12]) and 2,6-dinitrophenol (pK_a(DMSO) = 4.9[12]) was used to calibrate the glass electrode. In order to avoid the influence of water vapor and oxygen from the ambient air, all the titration experiments were performed under an atmosphere of dry argon. See refs. 13 and 14 for further details.

Chemicals

The $C_6H_5SO_2NH_2$, $(CF_3CO)_2CH_2$, $(CF_3CO)_2NH$ and $4\text{-}MeC_6H_4SO_2NH_2$ were commercial reagents. $(CF_3SO_2)_2CH_2$ was the same sample as in ref. 9. $C_6H_5S(O)(=NSO_2CF_3)NH_2$, $4\text{-}MeC_6H_4S(=NSO_2CF_3)_2NH_2$ and $4\text{-}MeC_6H_4S(O)(=NSO_2CF_3)NH_2$ were synthesized according to the procedures described in refs. 6 and 11 and had the same characteristics as indicated therein.

Computational methods

The quantum-chemical calculations at PM3 and DFT B3LYP 6-31+G* levels were carried out using the Gaussian 98 software package[15] on Silicon Graphics Origin 200 workstations running the IRIX 6.2 operating system. Full geometry optimizations and vibrational analyses were carried out in all cases. The DFT B3LYP ΔG_{acid} values (at 298 K) were calculated taking into account zero-point energies, finite temperature (0 to 298 K) correction and the pressure–volume work term pV. The calculated PM3 deprotonation enthalpies (at 298 K) were calculated using standard procedures (see ref. 7 and references therein). They were corrected for the $T\Delta S$ term to get the respective gas-phase acidity values ΔG_{acid}(PM3).

Results

The experimental ΔG_{acid} and pK_a values together with the computational results are listed in Table 1.

The experimental ΔG_{acid} values given in Table 1 have been extracted from the following direct equilibrium measurements: $4\text{-}MeC_6H_4SO_2NH_2$ was by 0.7 kcal mol^{-1} a weaker acid than $C_6H_5SO_2NH_2$ (ΔG_{acid} = 333.2[9]) and by 0.8 kcal mol^{-1} a stronger acid than $3\text{-}ClC_6H_4OH$ (ΔG_{acid} = 335.0[16]). $4\text{-}MeC_6H_4S(O)(=NSO_2CF_3)NH_2$ was by 3.1 kcal mol^{-1} a weaker acid than $(CF_3CO)_2NH$ (ΔG_{acid} = 307.5[9]) and equal to $(CF_3CO)_2CH_2$ (ΔG_{acid} = 310.4[9]). $4\text{-}MeC_6H_4S(=NSO_2CF_3)_2NH_2$ was by 1.7 kcal mol^{-1} a stronger acid than $(CF_3SO_2)_2CH_2$ (ΔG_{acid} = 301.5[9]).

Discussion

Acidity in DMSO solution

In DMSO the effect of the first substitution of a double-bonded oxygen =O of the sulfonyl group of toluene-*p*-sulfonamide by the $=NSO_2CF_3$ supersubstituent results in a very sharp increase of the acidity which amounts to 8.3 pK_a

units (see Scheme 1). The lower acidifying effect of the same substitution found in arenesulfonimides in acetonitrile[10] can be connected to the decreased sensitivity of the acidic dissociation of the reaction series of substituted arenesulfonimides to the substituent effects. A similar acidifying effect was also noticed in DMSO solution in a study of the introduction of the $=NSO_2CF_3$ supersubstituent into the remote $4\text{-}SO_2CF_3$ group in $4\text{-}CF_3SO_2C_6H_4NH_2$.[8] The resulting species, $4\text{-}CF_3S(O)(=NSO_2CF_3)C_6H_4NH_2$, was by 4.7 p$K_a$ units a stronger acid than $4\text{-}CF_3SO_2C_6H_4NH_2$.[17] In this case the substituent effect of the $-S(O)(=NSO_2CF_3)CF_3$ supersubstituent on the acidic dissociation of the NH_2 group is attenuated by transfer *via* the benzene ring which leads to *ca.* 40% reduction of the acidifying effect noticed in the present work for the introduction of the $=NSO_2CF_3$ group into the SO_2 fragment adjacent to the acidity center.

At the same time, the acidity of 4-substituted arenesulfonamides $4\text{-}XC_6H_4S(O)(=NSO_2CF_3)NH_2$ has a rather low sensitivity towards the replacement of the *para* H atom by a 4-methyl (pK_a increase by 0.2 pK_a units) or by a 4-amino (pK_a increase by 0.8 pK_a units) group.

The consecutive introduction of the second $=NSO_2CF_3$ fragment into the sulfonyl group of toluene-*p*-sulfonamide leads to an additional acidity increase by 4.7 pK_a units. The total acidifying effect is thus enormous: 13 powers of ten. The acidity increase is not additive: the effect of the second substitution is by 3.6 pK_a units lower than the first one. This corresponds to an $8.3:4.7 = 1.77$ ratio for the effects of the first and the second substitution in the SO_2 group or 78% additivity. Similar non-additivity effects were found[9] to be operational and rather typical for the gas-phase acidic dissociation of the derivatives of multiply substituted ammonia and methane. The heavily nonadditive behavior in the case of introduction of $=NSO_2CF_3$ groups into the sulfonyl group can be attributed to the significant saturation of the donor anionic charge distribution at the deprotonation site with successive introduction of the strong π-acceptor $=NSO_2CF_3$ substituents and to the strengthening of the repulsive steric interactions between the nonbonded charge-enriched substituents of the polysubstituted anions.

Acidity in the gas phase

In the gas phase the acidifying effects of consecutive introduction of two $=NSO_2CF_3$ supersubstituents into the sulfonyl group of toluene-*p*-sulfonamide follow roughly the same pattern as is described for DMSO solution. In DMSO the substituent effects are attenuated by solvation phenomena; the respective gas-phase effects of replacement of the oxygen atoms of the sulfonyl group in $4\text{-}MeC_6H_4SO_2NH_2$ are much more pronounced. So, the introduction of the first $=NSO_2CF_3$ group into $4\text{-}MeC_6H_4SO_2NH_2$ increases its gas-phase acidity by about 23.6 kcal mol^{-1}, which exceeds the respective quantity for DMSO more than 2 times. The introduction of the second $=NSO_2CF_3$ supersubstituent still increases the acidity of $4\text{-}MeC_6H_4S(O)(=NSO_2CF_3)NH_2$ by 10.7 kcal mol^{-1} practically up to the intrinsic acidity of triflic acid (299.5[9]) which corresponds to the enormous 34.3 kcal mol^{-1} total acidifying effect (*ca.* 73% of additivity of the effects of replacement of oxygen atoms by $=NSO_2CF_3$ groups in $4\text{-}MeC_6H_4SO_2NH_2$). The total acidifying effect is roughly two times higher than the same quantity for DMSO. A similar attenuation of substituent effects was noticed[14] for several other reaction series of NH acids on transfer from the gas phase into DMSO.

An excellent linear relationship holds between the gas-phase and solution acidities (DMSO) of these acids and some other aliphatic and aromatic sulfonamides and amides (see Fig. 1): $\Delta G_{acid} = (292.9 \pm 2.0) + (2.52 \pm 0.13)$ pK_a (DMSO), $r = 0.992$, $s = 2.3$ kcal mol^{-1}, $n = 8$, the attenuation factor $(1000 \times 2.52/2.30RT) = 1.85 \pm 0.09$.

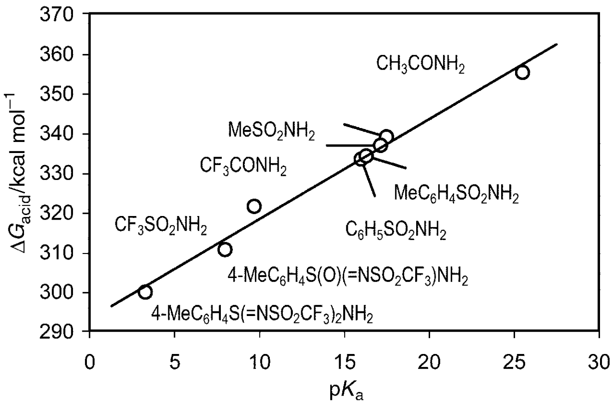


Fig. 1 Plot of ΔG_{acid} values *vs.* pK_a (DMSO) values for a selection of amides. Additional pK_a values have been taken from ref. 17, additional ΔG_{acid} values from refs. 9 and 14.

As in the case of DMSO solution, in the gas phase the acidifying effect of the replacement of an oxygen atom of the $-SO_2CF_3$ group in the more remote *para* position of $4\text{-}CF_3SO_2C_6H_4NH_2$ by the $=NSO_2CF_3$ group leads to a somewhat less noticeable increase in acidity:[8] *ca.* 17 kcal mol^{-1} or 72% of the present effect of replacement of an =O atom by a first $=NSO_2CF_3$ group in the sulfonyl group adjacent to the acidity center of $4\text{-}MeC_6H_4SO_2NH_2$.

Computations

Strongly acidifying non-additive effects of successive replacement of the double bonded oxygen atoms of the sulfonyl group of benzenesulfonamide by two $=NSO_2CF_3$ groups have been predicted by model calculations at the DFT B3LYP 6-31+G* and PM3 levels.

The DFT calculations reproduce the ΔG_{acid} of the weaker members of the series remarkably well: within 1 kcal mol^{-1} of the experimental value. The acidity of the most acidic one—the doubly substituted derivative $4\text{-}MeC_6H_4S(=NSO_2CF_3)_2NH_2$—is, however, overestimated by 7 kcal mol^{-1}.

In a recent study[18] it was noticed that the B3LYP 6-31+G* method tends to overestimate the acidities of strong acids and underestimate the acidities of the weak ones. In another study[19] a similar trend of overestimation of acidity obtained using the B3LYP 6-311+G** method was noticed for a selection of very strong acids (ΔG_{acid} around 300 kcal mol^{-1}). In the same work it was found that for fluorosulfonic and trifluoromethanesulfonic acids (experimental ΔG_{acid} 299.8 and 299.5 kcal mol^{-1} respectively) G2 and G2(MP2) methods also give acidities overestimated by around 5 kcal mol^{-1}. However, the acids with ΔG_{acid} around 300 kcal mol^{-1} for which high-level computational and experimental acidity data are simultaneously available are too scarce for it to be possible to say anything conclusive at this moment.

The accuracy of the PM3 calculated gas-phase acidities is inferior to that of the high-level *ab initio* or DFT methods but their very low cost makes them attractive. There have been several investigations of the applicability of the PM3 method to the prediction of gas-phase basicities[20] and acidities[7] of neutral molecules. The general conclusion from these studies was that PM3 is generally not accurate enough to allow quantitative prediction of gas-phase acidities and basicities, even if empirical corrections (scaling equations) are applied. At the same time, the calculations at the PM3 level can be used to examine trends within families of compounds and to make qualitative predictions.

Calculated at the PM3 level, the gas-phase ΔG_{acid}(PM3) value of toluene-*p*-sulfonamide is predicted to decrease by 24.8 kcal mol^{-1} and by 15.5 kcal mol^{-1} upon the first and the second introduction of $=NSO_2CF_3$ fragments into the SO_2 group, respectively. The overall calculated acidity increase at this level of theory amounts to 40.3 kcal mol^{-1} which corresponds to 81% additivity.

Correlating the experimental gas-phase ΔG_{acid} values *versus* the calculated ΔG_{acid}(PM3) values from Table 1 for the following model compounds: $4\text{-}MeC_6H_4SO_2NH_2$, $C_6H_5SO_2NH_2$, $4\text{-}MeC_6H_4S(=NSO_2CF_3)_2NH_2$ and $4\text{-}MeC_6H_4S(O)(=NSO_2CF_3)\text{-}NH_2$ leads to the approximate linear relationship $\Delta G_{acid} = (46.0 \pm 13.5) + (0.86 \pm 0.04)\ \Delta G_{acid}(\text{PM3})$, $r = 0.998$, $s = 1.5$, $n = 4$. The PM3 method overestimates the total acidity change taking place when going from $4\text{-}MeC_6H_4SO_2NH_2$ to $4\text{-}MeC_6H_4S\text{-}(=NSO_2CF_3)_2NH_2$. At the same time, the r value is high, demonstrating that PM3 can be used to predict trends within a family of compounds.

Conclusions

The experimental results of this investigation demonstrate an unprecedented increase in acidity of aromatic sulfonamides upon stepwise replacement of the =O fragments in the SO_2NH_2 group with $=NSO_2CF_3$ fragments. Incorporation of the first $=NSO_2CF_3$ group into $4\text{-}MeC_6H_4SO_2NH_2$ increases its gas-phase acidity by 23.4 kcal mol^{-1}. Substituting the second =O by $=NSO_2CF_3$ leads to an additional acidity increase by 10.7 kcal mol^{-1}; the total acidity increase is thus 34.3 kcal mol^{-1} (25 powers of ten!). In DMSO solution the total acidity increase is 13 pK_a units (17.7 kcal mol^{-1}). These results are also supported by DFT B3LYP 6-31+G* computational studies. The above-reported findings are expected to have potentially important implications for the design of new strongly acidic catalytic materials.

Acknowledgements

This work was supported by grants no. 3366 and 4376 of the Estonian Science Foundation and by a Grant-in-aid of the Ministry of Education, Culture, Science and Sports (Monbusho), Japan.

References

1 N. V. Kondratenko, V. I. Popov, O. A. Radchenko, N. V. Ignatev and L. M. Yagupolskii, *Zh. Org. Khim.*, 1986, **22**, 1716.

2 L. M. Yagupolskii, V. I. Popov, N. V. Pavlenko, R. Y. Gavrilov and V. V. Orda, *Zh. Org. Khim.*, 1986, **22**, 2169.

3 L. M. Yagupolskii, *Aromatic and Heterocyclic Compounds with Fluorine-Containing Substituents*, Naukova Dumka, Kiev, 1988.

4 V. N. Boiko, N. V. Kirii and L. M. Yagupolskii, *J. Fluorine Chem.*, 1994, **67**, 119.

5 L. M. Yagupolskii, R. Yu. Garlyauskajte and N. V. Kondratenko, *Synthesis*, 1992, 749.

6 L. M. Yagupolskii, N. V. Kondratenko and S. V. Iksanova, *Zh. Org. Khim.*, 1995, **31**, 747.

7 P. Burk, I. A. Koppel, I. Koppel, L. M. Yagupolskii and R. W. Taft, *J. Comput. Chem.*, 1996, **17**, 30.

8 I. A. Koppel, R. W. Taft, F. Anvia, N. V. Kondratenko and L. M. Yagupolskii, *Zh. Org. Khim.*, 1992, **28**, 1764.

9 I. A. Koppel, R. W. Taft, F. Anvia, S.-Z. Zhu, L.-Q. Hu, K.-S. Sung, D.-D. DesMarteau, L. M. Yagupolskii, Y. L. Yagupolskii, N. V. Ignat'ev, N. V. Kondratenko, A. Y. Volkonskii, V. M. Vlasov, R. Notario and P.-C. Maria, *J. Am. Chem. Soc.*, 1994, **116**, 3047.

10 I. Leito, I. Kaljurand, I. A. Koppel, L. M. Yagupolskii and V. M. Vlasov, *J. Org. Chem.*, 1998, **63**, 7868.

11 R. Yu. Garlyauskajte, S. V. Sereda and L. M. Yagupolskii, *Tetrahedron*, 1994, **50**, 6891.

12 F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456.

13 I. Koppel, J. Koppel, F. Degerbeck, L. Grehn and U. Ragnarsson, *J. Org. Chem.*, 1991, **56**, 7172.

14 I. Koppel, J. Koppel, P.-C. Maria, J.-F. Gal, R. Notario, V. M. Vlasov and R. W. Taft, *Int. J. Mass Spectrom. Ion Processes*, 1998, **175**, 61.

15 Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.

16 J. E. Bartmess, *Negative Ion Energetics Data*, eds. W. G. Mallard and P. J. Linstrom, NIST Chemistry WebBook, NIST Standard Reference Database Number 69, August 1997, National Institute of Standards and Technology, Gaithersburg, MD, 20899 (http://webbook. nist. gov).

17 F. G. Bordwell and D. J. Algrim, *J. Am. Chem. Soc.*, 1988, **110**, 2964.

18 P. Burk, I. A. Koppel, I. Koppel, I. Leito and O. Travnikova, *Chem. Phys. Lett.*, 2000, **323**, 482.

19 I. A. Koppel, P. Burk, I. Koppel, I. Leito, T. Sonoda and M. Mishima, *J. Am. Chem. Soc.*, 2000, **122**, 5114.

20 P. Burk, K. Herodes, I. Koppel and I. Koppel, *Int. J. Quantum Chem: Quantum Chem. Symposium*, 1993, **27**, 633.