How Acidic Are the Selenocarboxylic Acids RCSeOH and RCOSeH (R = H, F, Cl, NH_2, CH_3)?

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The structures, gas-phase acidities and vibrational spectra of selenoformic *O*-acid, selenoformic *Se*-acid and several of their derivatives RCSeOH and RCOSeH (R = H, F, Cl, NH_2, CH_3) were investigated by DFT calculations. Geometry optimizations and frequency computations were performed at the Becke3LYP level of theory with the 6-311+G(d,p) basis set. For all 10 acids studied, the syn conformers are predicted to have the lowest energy. The syn−anti enthalpy difference varies between 0.3 and 9.9 kcal mol^{-1}, the syn selenol acids being substantially more stable than their syn selenoxo counterparts. The substitution of oxygen by selenium in the selenocarboxylic acids studied leads to increased acidity. The selenol acids are weaker acids than the selenoxo derivatives.

Introduction

The sulfur derivatives of carboxylic acids—thiocarboxylic acids—are a biologically and pharmacologically important class of compounds with a great variety of uses in chemistry.[1−3] The bioisosteric selenium compounds are highly toxic, and with the exception of ^{75}Se derivatives that serve diagnostic purposes,[4] there is no chemically defined seleno-organic drug on the market. Selenocysteine is present in the catalytic site of mammalian glutathione peroxidase, and this explains the importance of selenium as an essential trace element.[5] Selenocarboxylic acids were prepared recently[6] and some of their physicochemical properties studied experimentally.[7] Experimental gas-phase acidities have not been reported so far for these selenium-containing compounds.

The aim of the present work is to provide a consistent set of gas-phase acidities for 10 simple substituted selenoformic *O*-acids and selenoformic *Se*-acids. These values are used for the determination of an absolute scale of acidity for these compounds, whose experimental acidities are not known.

Computational Details

The geometries of selenoformic *O*-acid, selenoformic *Se*-acid, and their derivatives (Figure 1) have been fully optimized with the Gaussian 94 program,[8] applying the density functional theory[9,10] (DFT) at the Becke3LYP DFT level[11,12] with the polarized triple split valence 6-311+G(d,p) basis set. Vibrational frequency calculations at the same level of theory gave zero-point energies and the number of imaginary frequencies.[13] The results of recent work[14−16] have shown that the DFT performance compares well with the high-level MP2 and G2 ab initio calculations of acidities of organic acids and, therefore, considering its accuracy and speed, is highly attractive.

The gas-phase acidity was defined as the enthalpy of deprotonation (ΔH^{298}) for the reaction 1. The enthalpy of

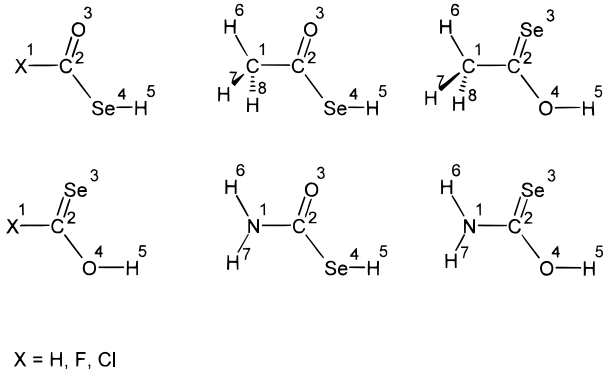

Figure 1. Structures and atom labeling for the acids studied.

$$AH(g) \rightarrow A^-(g) + H^+(g) \quad (1)$$

deprotonation, ΔH,[298] was computed using eqs 2 and 3, where

$$\Delta H^{298} = \Delta E^{298} + \Delta(pV) \quad (2)$$

$$\Delta E^{298} = E^{298}(A^-) + {}^3/_2 RT - E^{298}(AH) \quad (3)$$

E^{298} stands for the total energies of the most stable syn conformations of acids and their anions (including the thermal energy correction at T = 298.15 K). In eq 2, we substituted $\Delta(pV) = RT$ (1 mole of gas is obtained in reaction 1).

Results and Discussion

General Considerations. The enthalpies and Gibbs energies of calculated species are listed in Table 1, and the relative energies, enthalpies, and Gibbs energies of syn and anti conformers of selenocarboxylic acids, in Table 2. An analysis of the harmonic vibrational frequencies at the B3LYP/6-311+G(d,p) level of theory of the optimized syn, anti conformers and anions revealed that these species are minima (zero number of imaginary frequencies). The calculations favor the syn forms over the anti conformers (Table 2). The geometries of the most

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TABLE 1: Enthalpies and Gibbs Energies (hartrees/molecule) of Selenocarboxylic Acid Species

species	form	enthalpy	Gibbs energy
HC(═O)SeH	syn	−2516.077 453	−2516.109 204
HC(═O)SeH	anti	−2516.076 986	−2516.108 767
HC(═O)Se$^-$		−2515.557 691	−2515.588 370
FC(═O)SeH	syn	−2615.370 090	−2615.404 056
FC(═O)SeH	anti	−2615.369 128	−2615.403 184
FC(═O)Se$^-$		−2614.865 772	−2614.898 795
ClC(═O)SeH	syn	−2975.719 427	−2975.754 671
ClC(═O)SeH	anti	−2975.717 856	−2975.753 184
ClC(═O)Se$^-$		−2975.223 761	−2975.259 251
CH_3C(═O)SeH	syn	−2555.384 916	−2555.421 555
CH_3C(═O)SeH	anti	−2555.383 880	−2555.420 147
CH_3C(═O)Se$^-$		−2554.859 193	−2554.892 497
NH_2C(═O)SeH	syn	−2571.459 781	−2571.495 327
NH_2C(═O)SeH	anti	−2571.458 178	−2571.493 609
NH_2C(═O)Se$^-$		−2570.934 217	−2570.967 838
HC(═Se)OH	syn	−2516.068 329	−2516.099 275
HC(═Se)OH	anti	−2516.059 678	−2516.090 738
HC(═Se)O$^-$		−2515.557 694	−2515.588 369
FC(═Se)OH	syn	−2615.348 885	−2615.381 964
FC(═Se)OH	anti	−2615.344 057	−2615.377 340
FC(═Se)O$^-$		−2614.865 775	−2614.898 801
ClC(═Se)OH	syn	−2975.697 829	−2975.732 211
ClC(═Se)OH	anti	−2975.693 005	−2975.727 638
ClC(═Se)O$^-$		−2975.223 761	−2975.259 260
CH_3C(═Se)OH	syn	−2555.374 413	−2555.409 536
CH_3C(═Se)OH	anti	−2555.363 742	−2555.398 936
CH_3C(═Se)O$^-$		−2554.858 188	−2554.894 145
NH_2C(═Se)OH	syn	−2571.452 546	−2571.486 638
NH_2C(═Se)OH	anti	−2571.436 820	−2571.471 286
NH_2C(═Se)O$^-$		−2570.934 218	−2570.967 844
HCOOH	syn	−189.789 000	−189.818 096
HCOOH	anti	−189.782 945	−189.811 222
HCOO$^-$		−189.248 831	−189.276 558
CH_3SeH		−2442.026 996	−2442.057 673
CH_3Se$^-$		−2441.475 496	−2441.503 561
CH_3OH		−115.709 605	−115.736 689
CH_3O^-		−115.107 351	−115.132 413

TABLE 2: Relative Energies (kcal mol^{-1}) of Syn and Anti Conformers of Selenocarboxylic Acids (at 298 K)[a]

		anti−syn difference		
no.	compound	ΔE	ΔH	ΔG
1	HC(═O)SeH	0.29	0.29	0.29
2	FC(═O)SeH	0.61	0.60	0.55
3	ClC(═O)SeH	0.98	0.98	0.93
4	CH_3C(═O)SeH	0.65	0.65	0.88
5	NH_2C(═O)SeH	1.00	1.00	1.07
6	HC(═Se)OH	5.42	5.43	5.36
7	FC(═Se)OH	3.03	3.02	2.90
8	ClC(═Se)OH	3.02	3.02	2.86
9	CH_3C(═Se)OH	6.69	6.69	6.65
10	NH_2C(═Se)OH	9.86	9.87	9.63
11	HCOOH	4.36	3.79	4.31

[a] In all cases the 6-311+G(d,p) basis set was used.

stable syn acids are collected in Table 3. Our calculations indicate that the syn form is always more stable than the anti form. However, the Gibbs energy gap between the anti and syn conformers in selenocarboxylic *Se*-acids is low (Table 2). The lowest Gibbs energy difference (0.29 kcal mol^{-1}) was observed for the unsubstituted acid HC(═O)SeH with the syn:anti populations of 62:38 (at 298.15 K). Substitution of the hydrogen that is attached to the carbon atom by F, Cl, CH_3, and NH_2 stabilizes the syn arrangement of the Se−H group. Comparison of these data with similar values computed for formic acid (4.31 kcal mol^{-1}) shows that the substitution of hydroxyl oxygen by selenium in the −COOH group results in a considerable reduction of syn−anti energy differences and stabilization of anti forms in selenol acids. The syn form of selenoformic acid HC(═Se)OH is, with respect to a high syn−anti Gibbs energy difference of 5.36 kcal mol^{-1}, the prevailing species in the gas phase. This Gibbs energy difference reaches a minimum for fluoro and chloro derivatives and a maximum for amino-substituted selenoxo acids (Table 2). The performance of the DFT method used in the calculations of the absolute syn−anti isomerization energies can be checked by comparison with gas-phase experimental data. For selenocarboxylic acids, the gas-phase values are not known, but the value of $\Delta H = 3.79$ kcal mol^{-1} computed for the HCO_2H syn−anti isomerization is close to the experimentally determined[17] enthalpy of 3.89 ± 0.1 kcal mol^{-1}. On the basis of this comparison, we believe that the DFT syn−anti differences for the selenocarboxylic acids studied represent realistic values for the relative stability of the two isomers of the acids in the gas phase. The syn conformers of formic acid and its silo and thio derivatives were computed recently at the G2 level of theory to be the most stable species.[18] The greater stability of syn conformers in carboxylic acids and their derivatives has been rationalized on the basis of intramolecular effects.[16,18,19] The most important intramolecular effects are an extended syn π electronic delocalization and intramolecular electrostatic attraction (hydrogen bonding) between O and H atoms. Concerning the selenocarboxylic acids studied here, the intramolecular electrostatic stabilization is only important in the case of selenol R−C(═Se)OH acids. The C═Se···H distances in these acids are much less than the sum of the van der Waals radii of selenium and hydrogen (3.2 Å), Table 3. In selenoxo R−C(═O)SeH acids, the O···H equilibrium distances were computed to be larger than the sum of the van der Waals radii (2.6 Å), which practically excludes the stabilization of syn forms via intramolecular H-bond O···H stabilization.

Besides syn−anti isomerism, we also investigated the possible tautomerism between selenol and selenoxo forms (Table 4). The selenol acids are always more stable that the selenoxo forms. Experiments by Kato et al.[6] showed, in agreement with our calculations, that selenoic acids exist in the selenol form in the solid state and in nonpolar solvents. The higher stability of selenol acids in comparison with the selenoxo forms should be explained by the fact that the tendency of selenium to form C═Se double bonds is much lower than the tendency of oxygen to create C═O bonds. The same trend was found recently for the structurally related thiocarboxylic acids.[16,18] Kato et al.[6,7] observed that selenoxo acids may exist as predominant species at low temperature in polar solvents (THF). To model the influence of increasing polarity of solvent on the tautomeric equilibrium between selenol and selenoxo forms of selenoformic acid, we also studied the solvent effect using the SCRF formalism within the isodensity surface polarized continuum model (IPCM) implemented into the Gaussian 94 program by Keith and Frisch.[20] The tautomerization energies for the reaction HC(═O)SeH ⇌ HC(═Se)OH with increase of solvent polarity also increase in the order 3.0, 4.0, 4.1, and 4.2 kcal mol^{-1} for isolated molecules and for molecules immersed in tetrahydrofuran, acetone, and water, respectively. Accordingly, the presence of solvent results in a net stabilization of the selenol form HC(═O)SeH. However, placing such a system with different H-bonding strengths into a cavity within a dielectric medium with an artificially increased dielectric constant does not represent the realistic situation in the H-bonded solvent. For a more quantitative description of the effect of polar solvent on the tautomeric equilibrium, it is necessary explicitly to consider the solvent−solute interaction (within a supermolecule approach) and/or apply one of the simulation techniques.

TABLE 3: B3LYP/6-311+G(d,p) Optimized Geometries of the Syn Selenocarboxylic Acids (Figure 1)

	compound					
parameter[a]	HC(=O)SeH	FC(=O)SeH	ClC(=O)SeH	HC(=Se)OH	FC(=Se)OH	ClC(=Se)OH
d_{1-2}	1.105	1.360	1.809	1.087	1.321	1.739
d_{2-3}	1.194	1.178	1.179	1.775	1.778	1.780
d_{2-4}	1.954	1.925	1.932	1.328	1.320	1.327
d_{4-5}	1.473	1.472	1.475	0.972	0.969	0.971
∠1−2−3	124.0	122.4	122.2	123.1	123.6	124.9
∠1−2−4	110.3	107.7	110.0	110.5	108.0	109.3
∠3−2−4	125.7	129.9	127.7	126.4	128.4	125.8
∠2−4−5	93.2	91.8	92.2	108.6	107.9	107.5
∠3−2−4−5	0	0	0	0	0	0
$d_{3\cdots5}$	2.78	2.79	2.76	2.74	2.76	2.71

	compound			
parameter[a]	$CH_3C(=O)SeH$	$NH_2C(=O)SeH$	$CH_3C(=Se)OH$	$NH_2C(=Se)OH$
d_{1-2}	1.511	1.360	1.495	1.338
d_{2-3}	1.196	1.203	1.793	1.818
d_{2-4}	1.987	1.990	1.337	1.342
d_{4-5}	1.471	1.468	0.971	0.968
d_{1-6}	1.090	1.009	1.086	1.005
d_{1-7}	1.091	1.006	1.095	1.010
d_{1-8}	1.094		1.095	
∠1−2−3	125.0	125.2	126.3	125.7
∠1−2−4	112.9	112.1	111.4	111.3
∠3−2−4	122.0	122.7	122.3	123.0
∠2−4−5	92.5	90.9	108.2	107.1
∠2−1−6	109.2	117.7	111.2	119.3
∠2−1−7	111.4	122.0	109.4	120.6
∠2−1−8	108.6		109.4	
∠3−2−4−5	0	5.5	0	0
∠3−2−1−6	19.2	−5.3	0	0
∠3−2−1−7	141.5	−170.8	121.4	180
∠3−2−1−8	−99.6		−121.6	
$d_{3\cdots5}$	2.72	2.71	2.66	2.68

[a] Bond lengths in angstroms and bond angles in degrees.

TABLE 4: Tautomerization Enthalpies for the Reaction RC(=O)SeH ⇌ RC(=Se)OH

R	ΔH, kcal mol^{-1}	R	ΔH, kcal mol^{-1}
H	5.72	CH_3	6.59
F	13.30	NH_2	4.53
Cl	13.55		

TABLE 5: B3LYP/6-311+G(d,p) Gas-Phase Acidities (Enthalpies ΔH, Entropies ΔS, and Gibbs Energies ΔG) of Acids Studied (at 298 K)

no.	acid	ΔH, kcal mol^{-1}	ΔS, cal K^{-1} mol^{-1}	ΔG, kcal mol^{-1}	ΔH(obs),[a] kcal mol^{-1}
1	HC(=O)SeH	327.6	−2.2	328.3	
2	FC(=O)SeH	317.9	−2.0	318.5	
3	ClC(=O)SeH	312.5	0.0	312.4	
4	$CH_3C(=O)SeH$	331.4	7.0	333.5	
5	$NH_2C(=O)SeH$	331.3	−4.0	332.5	
6	HC(=Se)OH	321.9	−0.5	322.1	
7	FC(=Se)OH	304.6	−0.2	304.7	
8	ClC(=Se)OH	299.0	2.5	298.3	
9	$CH_3C(=Se)OH$	325.4	−1.7	324.9	
10	$NH_2C(=Se)OH$	326.7	−1.0	327.0	
11	HCOOH	340.4	−3.0	341.3	345 ± 3
12	CH_3SeH	347.5	−5.6	349.2	
13	CH_3OH	379.4	−4.2	380.7	380.1 ± 0.2

[a] Reference 21.

Gas-Phase Acidities. The gas-phase acidities (proton affinities of the anions) of the acids are presented in Table 5. For the evaluation of the reaction enthalpies and Gibbs energies, the more stable syn conformers of the acids were used. For reasons of comparison, we also present the B3LYP/6-311+G(d,p) acidities of the parent formic acids and corresponding alcohols in Table 5. Both selenol and selenoxo acids are stronger acids than formic acid. For the selenol acids, the acidity order is ClC(=O)SeH > FC(=O)SeH > HC(=O)SeH > $NH_2C(=O)SeH$ ≥ $CH_3C(=O)SeH$. The electronegative fluorine and chlorine substituents increase the acidity by about 10−15 kcal mol^{-1}. Amino and methyl substitution leads to a slight decrease of the acidity of the unsubstituted HC(=O)SeH acid by about 3 kcal mol^{-1}. In the case of the selenoxo acids, the following acidity order was found: ClC(=Se)OH > FC(=Se)OH > HC(=Se)OH > $CH_3C(=Se)OH$ > $NH_2C(=Se)OH$. The differences in acidities upon substitution are larger in comparison with those of selenol acids, the halogen derivatives being about 15−20 kcal mol^{-1} more acidic than the parent HC(=Se)OH acid. Both methyl and amino substitutions cause a decrease of acidity by about 5 kcal mol^{-1} (Table 5). The chloro derivatives are stronger acids than the fluoro derivatives. This statement is in contradiction to a prediction based on an inductive effect of halogens.[22] The acidity decrease upon fluorination could be explained by a much smaller polarizability, charge capacity, or softness of fluorine.[23,24] The acidity of halogenated acids studied with increasing charge capacity (F < Cl) also increases in the same order.[23,24] The methyl group and, more generally, all alkyl groups are substituents exerting an inductive electron-donating effect. This results in a destabilization of the anion and hence a decrease in the acidity of alkyl-substituted acids (Table 5). The different acidity of selenoacids in comparison with that of the parent formic acid could be explained on the basis of electronegativity and the concept of charge capacity introduced by Politzer et al.[24] The less electronegative selenium has a higher charge capacity than oxygen, which results in a larger stabilization of selenium-containing anions in comparison with formate. The dispersion of charge is largest in the acids containing the

TABLE 6: Calculated B3LYP/6-311+G(d,p) Vibrational Frequencies (cm^{-1}) for Acids[a]

no.	HC(=O)-SeH	FC(=O)-SeH	ClC(=O)-SeH	CH_3C(=O)-SeH	NH_2C(=O)-SeH
1	2942	*2404*	*2382*	3137	3712
2	*2400*	1882	1848	3107	3578
3	1785	1023	851	3039	*2404*
4	1354	817	724	*2401*	1800
5	900	709	532	1809	1622
6	816	599	468	1475	1255
7	541	372	358	1463	1097
8	348	290	326	1384	786
9	329	263	205	1116	656
10				1021	620
11				962	476
12				738	340
13				574	306
14				495	255
15				341	170
16				309	
17				272	
18				49	

no.	HC(=Se)-OH	FC(=Se)-OH	ClC(=Se)-OH	CH_3C(=Se)-OH	NH_2C(=Se)-OH
1	*3684*	*3769*	*3743*	*3706*	*3764*
2	3154	1372	1360	3168	3727
3	1436	1324	1230	3076	3578
4	1282	1087	818	3026	1639
5	1214	721	514	1480	1475
6	929	596	510	1472	1351
7	781	585	436	1403	1186
8	667	422	390	1372	1032
9	384	349	256	1296	666
10				1076	634
11				1018	580
12				1009	497
13				666	397
14				635	338
15				487	323
16				393	
17				326	
18				93	

[a] The O−H and Se−H stretching vibrations are given in italics.

C=Se double bond. The acidity increases in the order HCOOH < HC(=O)SeH < HC(=Se)OH.

The computed acidity for CH_3SeH is larger by 19.9 kcal mol^{-1} than that found for selenoformic HC(=O)SeH acid (Table 5). This difference is, however, smaller than the difference between methanol and formic acid (39 kcal mol^{-1} computed by us and 35.1 kcal mol^{-1} measured experimentally[21]). Thus, the selenoformic HC(=O)SeH acid is, like formic acid, stronger than its parent alcohol. CH_3SeH was computed to be more acidic than methanol by 31.9 kcal mol^{-1} (Table 5), which corresponds well to the substantially lower Se−H bond strength in comparison with the O−H bond.[25] Recent calculations[26] support the traditional view by showing that delocalization is an important factor responsible for the enhanced acidity of carboxylic acids relative to alcohols. However, inductive effects prove to be on the same order of magnitude as delocalization effects in carboxylic acids.[26,27]

The selenocarboxylic acids investigated in this work have not yet been prepared according to our knowledge, so their experimental acidities are not known. Therefore, it is not possible to compare our theoretical results directly with experiments. However, the B3LYP/6-311+G(d,p) acidities computed for formic acid and methanol are in good agreement with the experimentally determined values (Table 5).

Infrared Spectra. The Becke3LYP computed vibrational frequencies of selenocarboxylic acids, summarized in Table 6, give harmonic frequencies whose absolute errors are less than those for MP2 calculations.[28] The frequency shifts of Se−H group valence vibrations upon substitution in R−C(=O)SeH (R = H, F, Cl, CH_3, NH_2) are very small (about 18 cm^{-1} or less), and their absolute values calculated as 2404−2382 cm^{-1} are practically independent of the character of the substituent. Solid-state IR spectra of more complex selenocarboxylic acids were measured by Kato et al.,[6] and the characteristic absorptions of the Se−H stretches were found at slightly lower frequencies (2290−2324 cm^{-1}). A higher shift (about 20−85 cm^{-1}) of the valence O−H vibration was observed in R−C(=Se)OH acids (R = H, F, Cl, CH_3, NH_2) (Table 6).

Summary

The acidities of 10 selenocarboxylic acids were studied at the Becke3LYP level of DFT theory. Both selenol and selenoxo acids prefer syn over anti conformations. The computed acidities increase in the order ClC(=O)SeH > FC(=O)SeH > HC(=O)SeH > NH_2C(=O)SeH ≥ CH_3C(=O)SeH for selenol acids. In the case of the selenoxo acids the following acidity order was found: ClC(=Se)OH > FC(=Se)OH > HC(=Se)OH > CH_3C(=Se)OH > NH_2C(=Se)OH. The selenoformic HC(=O)-SeH acid is, as formic acid itself, stronger than the parent alcohol. Our calculations have shown that selenocarboxylic acids are stronger acids than carboxylic acids.

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References and Notes

(1) Bauer, W.; Khüren, K. In *Methoden der Organischen Chemie*, 5th ed.; Falbe, J., Ed.; Georg Thieme Publishers: Stuttgart, Germany, 1985; pp 832−890.

(2) Voet, D.; Voet, J. G. *Biochemistry*, 2nd ed.; J. Wiley & Sons Inc.: New York, 1995.

(3) *Burger's Medicinal Chemistry and Drug Discovery*; Wolff, M. E., Ed.; J. Wiley & Sons Inc.: New York, 1995, 1996; Vols. 1−5.

(4) *The Practice of Medicinal Chemistry*; Wermuth, C. G., Ed.; Academic Press: London, 1996; pp 231−232.

(5) Reference 2, p 980.

(6) Kageyama, H.; Murai, T.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1994**, *116*, 2195.

(7) Kato, S.; Kawahara, Y.; Kageyama, H.; Yamada, R.; Niyomura, O.; Murai, T.; Kanda, T. *J. Am. Chem. Soc.* **1996**, *118*, 1262.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. A.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Ayala, C. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Barker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(9) Parr, R. G.; Wang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1994.

(10) Neumann, R.; Nobes, R. H.; Handy, N. C. *Mol. Phys.* **1996**, *87*, 1.

(11) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.

(12) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(13) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; J. Wiley & Sons: New York, 1986.

(14) Merrill, G. N.; Kass, S. R. *J. Phys. Chem.* **1996**, *100*, 17465.

(15) Remko, M.; Liedl, K. R.; Rode, B. M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1743.

(16) Remko, M.; Liedl, K. R.; Rode, B. M. *THEOCHEM* **1997**, *418*, 179.

(17) Hocking, W. H. *Z. Naturforsch.* **1976**, *31A*, 1113.

(18) Remko, M.; Liedl, K. R.; Rode, B. M. *Chem. Phys. Lett.* **1996**, *263*, 379.

(19) Fausto, R.; Batista de Carvalho, L. A. E.; Teixeira-Dias, J. J. C.; Ramos, M. N. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 1945.

(20) Keith, T. A.; Frisch, M. J. In preparation.

(21) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Lewin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(22) Pauling, L. *The Nature of Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(23) Damoun, S.; Langenaeker, W.; Van de Woude, G.; Geerlings, P. *J. Phys. Chem.* **1995**, *99*, 12151.

(24) Politzer, P.; Huheey, J. E.; Murray, J. S.; Grodzicki, M. *THEOCHEM* **1992**, *259*, 99.

(25) *CRC Handbook of Chemistry and Physics*, 77th ed.; Lide, D. R., Ed.; CRC Press: New York, 1996; pp 9−54.

(26) Hiberty, P. C.; Byrman, C. P. *J. Am. Chem. Soc.* **1995**, *117*, 9875.

(27) Wiberg, K. B.; Ochterski, J.; Streitwieser, A. *J. Am. Chem. Soc.* **1996**, *118*, 8291.

(28) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.