Gas-Phase Cation Basicities for Sulfuryl Species from Calculation and Experiment[†]

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Gas-phase Brønsted basicity (GB) and lithium cation basicity (LCB) for sulfuryl compounds have been measured using FT-ICR. In addition, GB, LCB, and sodium cation basicity (SCB) have been estimated from MO and DFT calculations for a family of nine sulfuryl compounds including sulfoxides, sulfones, sulfinate, sulfonate, sulfite, and sulfate. The newer DFT-hybrid methods, based upon B3PW91/6-31++G*, provided better correlation with experimental results than MP2 and HF methods. Both the calculated and experimental data provided good linear free energy relationships (LFERs) between the three sets of values, GB, LCB, and SCB, across the series of eight diverse sulfuryl species. Experimental data were in accord with the conclusion from calculations that chelation of lithium provides little if any stabilization over "linear" complexation. The electrostatic interaction of the cation with the sulfuryl bond dipole is indicated to be dominant, based upon (i) previous rationalizations of similar LFERs observed for other families of compounds and (ii) the good linear correlations observed between GB, LCB, SCB, and the calculated S=O bond dipole moment or S=O bond length. Remarkably accurate predictions of basicity are possible simply from S=O bond lengths calculated at the DFT level.

Introduction

A widening range of experimental techniques including Fourier transform ion cyclotron resonance spectroscopy (FT-ICR) allows measurements of basicities and affinities for cations in the gas phase.[1−3] Interest in these measurements lies, in part, in testing the physical methods themselves.[4−7] However, comparison of the gas-phase basicity of molecules toward cations provides fundamental information on intermolecular forces. In addition, gas-phase properties, such as gas-phase Brønsted basicity (GB), lithium cation basicity (LCB), and proton affinity (PA), provide (a) a starting point for theoretical approaches to solution phase properties (e.g., pK_a)[8] and (b) an important means of testing newer molecular orbital (MO) and density functional theory (DFT) computational methods.

Intermolecular interactions, such as hydrogen bonding and metal ion coordination, are of significance in controlling many biological processes. These have been the focus of previous gas-phase basicity studies.[9] Sulfuryl species of biological importance are predominantly esters or amidates of sulfate, including, for example, glycosaminoglycan sulfates, which serve a significant role in biomolecular recognition.[10] Hydrogen-bonding forces appear to be dominant in the recognition of inorganic sulfate and the discrimination of sulfate from phosphate by specific binding proteins.[11] Binding and recognition of sulfate and other sulfuryl species can be better understood by exploring the contributing intermolecular forces involving the sulfuryl moiety. Metal ion interactions are of proven importance in catalysis of biological phosphoryl transfer and by implication in sulfuryl transfer.[12] Moreover, alkali metal ions possess significant biological roles, in particular in Na/K pumps, ion channels, and selective transport and binding mechanisms.

MO calculations, generally at the MP2//HF level (e.g., MP2/6-31+G*//HF/3-21+G(*)), have been used extensively in understanding the reactivity and metal coordination properties of phosphoryl and sulfuryl species.[13] The efficiency of the newer density functional theory

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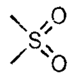
(DFT) methods,[14] including electron correlation contributions, but allowing use of larger basis sets than MP2 methods, holds great promise for such calculations since the importance of electron correlation and diffuse and polarization functions is acknowledged.[13,14]

A preliminary FT-ICR study of GB and LCB for sulfuryl species (limited to sulfoxides, sulfones, and a sulfite) produced a reasonable linear free energy relationship (LFER) between GB and LCB. This LFER was argued to be contraindicative of lithium chelation by the two sulfuryl oxygens of the sulfones,[6] although previous ab initio calculations on Li·triflate complexes had shown the chelate to be dominant.[15] The present work extends this important LFER to a full range of sulfuryl species, including sulfate, sulfonate, and sulfinate, and takes the opportunity to examine chelation and draw comparisons with data from the newer DFT calculations. Thus the DFT method is tested, used to rationalize the experimental observations, and provide predictive values for GB, LCB, and SCB (sodium cation affinity) for sulfuryl species.



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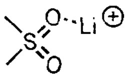

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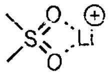

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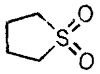

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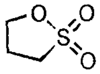

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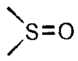

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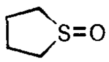

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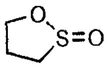

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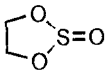

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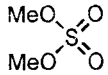

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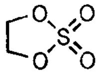

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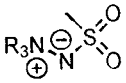

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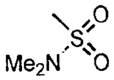

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Methodology

Experimental. All measurements were carried out using the FT-ICR technique.[16] GB values were obtained using the equilibrium method[5] in which relative Gibbs free energy of proton transfer is anchored to absolute gas-phase basicities reported at 289.15 K.[6,17] LCB was obtained using the kinetic method. This method is based upon the collision-induced dissociation of Li^+-bound dimers.[6,16] Dimers were obtained by allowing the laser-generated Li^+ ions to react with the two neutrals at 1−3 10^{-5} Pa partial pressures in the presence of argon for a total pressure of about 1−2 10^{-4} Pa. Reaction delays for heterodimer formation are in the range 1−2 s at these pressures. Ions other than B_1---Li^+---B_2 were ejected using procedures previously described.[6] The fragmentation of B_1---Li^+---B_2 was obtained by collision-induced dissociation (CID) at different center-of-mass kinetic energies in the range 3−30 eV. The natural logarithms of the intensity ratios were extrapolated to zero kinetic energies and calibrated against LCBs independently obtained by the equilibrium method in the Taft laboratory in which FT-ICR experiments were run at 373 K.[7] See footnote b to Table 1. The kinetic data from this work are therefore referred to this temperature.

Table 1. Relative Lithium−Cation Basicities ln[$I(B_1Li+)/I(B_2Li^+)$] Obtained by the Kinetic Method

B_1	B_2	ln[$I(B_1Li^+)/I(B_2Li^+)$][a]	ΔLCB(B_1)[b]
3	*n*-PrCN	1.41 ± 0.13	1.12
	i-PrCN	1.00 ± 0.07	0.80
	n-BuCN	0.95 ± 0.11	0.76
8	*t*-BuOMe	−0.44 ± 0.17	−0.35
	CH_3CN	1.46 ± 0.20	1.16
	HCO_2Et	−0.12 ± 0.11	−0.10
2	c-PrCOMe	2.07 ± 0.15	1.65
	(c-Pr)$_2$CO	0.17 ± 0.14	0.13
6	(*i*-Pr)$_2$CO	1.89 ± 0.10	1.50
	(c-Pr)$_2$CO	0.76 ± 0.14	0.60
	HCONHMe	−0.81 ± 0.20	−0.74
5	Me_2SO	1.14 ± 0.14	0.91
	$HCONMe_2$	2.09 ± 0.13	1.66
	$MeCONMe_2$	0.19 ± 0.08	0.15
9	*n*-PrCHO	−0.64 ± 0.13	−0.51
	EtCHO	0.15 ± 0.11	0.12
	HCO_2Me	0.47 ± 0.08	0.37
	THF	−0.56 ± 0.18	−0.45

[a] Reported uncertainties correspond to the standard deviation on the intercept of the regression ln[$I(B_1Li^+)/I(B_2Li^+)$] vs the center-of-mass kinetic energy. [b] Lithium−cation basicities relative to B_2, in kcal/mol, inferred from the calibration equation ln[$I(B_1Li^+)/I(n\text{-PrCN})$] = (−0.051 ± 0.355) + (1.264 ± 0.071) ΔLCB (ref 6).

Table 2. Gas-Phase Basicities in kcal/mol from Proton-Transfer Measurements (Equilibrium or Kinetic Method) and Lithium Basicities Obtained by Using the Kinetic Method

B_1	B_2	$\Delta_1G°$(338 K)[a]	GB(B_1)[b]	LCB(B_1)[c]
1[d]			186.5 ± 0.4	39.7
4[d]			203.0 ± 0.4	44.4
7[d]			185.5 ± 0.2	38.2
3	MeCN	3.15 ± 0.04		
	EtCHO	1.97 ± 0.05		
	n-PrCHO	0.65 ± 0.03		
	n-BuCHO	−0.49 ± 0.01	184.0 ± 0.4	39.3
2	Me_2CO	0.77 ± 0.03		
	$MeCO_2Me$	−0.16 ± 0.01	189.7 ± 0.1	41.6
6	*n*-Bu_2O	1.49 ± 0.02		
	(*i*-Pr)$_2$CO	1.05 ± 0.02		
	(*i*-Pr)$_2$O	−0.67 ± 0.06	198.1 ± 0.4	41.8
5	$MeNH_2$[e]	1.80 ± 0.06		
	2-chloropyridine	−0.18 ± 0.05		
	c-$PrNH_2$	−0.20 ± 0.04		
	$EtNH_2$	−1.77	206.5 ± 0.1	45.7
8	CH_3CN	0.22 ± 0.07		
	HCO_2Me	−0.56 ± 0.06		
	CH_3CHO	1.10 ± 0.26[f]	180.1 ± 0.5	36.6
9	CH_3CHO	−0.11 ± 0.49[f]		
	C_6H_6	1.22 ± 0.06		
	CF_3CO_2Et	0.81 ± 0.02	177.6 ± 0.9	35.6

[a] Gibbs energy for $B_1H^+ + B_2 = B_1 + B_2H^+$; reported uncertainties correspond to standard deviation on 3−5 determinations of *K*. [b] From GB(B_2) at 298 K (ref 16), no temperature correction, reported uncertainties correspond to the standard deviation estimated from the range of values obtained from different reference bases. [c] Lithium−cation basicities, in kcal/mol, inferred from the calibration equation (as in Table 1); anchor value for the scale; LCB(*n*-PrCN) = 38.1 kcal/mol (ref 7). [d] Ref 6. [e] GB reevaluated (204.6 kcal/mol). [f] Obtained by a CID experiment (kinetic method).

Materials. All compounds employed in this study were obtained from Aldrich Chemical Co. (Millwaukee, WI) or synthesized by literature procedures.[18]

Computational. Calculations were performed using Gaussian 94 running in parallel on IBM SP2 RISC processors at the HF/6-311G*, MP2/6-311G*//HF/6-311G*, B3PW91/6-311G*, B3PW91/6-31++G*, B3PW91/6-311++G**≫B3PW91/6-311G*,

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Table 3. Maximum Energy Differences between Calculated and Experimental LCB, LCA, PA, and GB Values (for 1, 4, 6, 7), at Various Levels of Calculation, kcal/mol. Negative Errors Indicate Overestimation by Calculation. $T_1 = 298$ K; $T_2 = 373$ K

method[a]	LCA_{err}	LCB_{err}	PA_{err}	GB_{err}
B/6-311++G**≫B/6-31++G* T_1	2.6	−4.3	−6.1	−6.9
B/6-311++G**≫B/6-31++G* T_2	7.6	9.8	−7.0	−5.3
B/6-31++G* T_1	4.3	−4.1	4.6	−2.9
B/6-31++G* T_2	4.3	3.6	4.4	5.9
B/6-311++G**≫HF/6-311G* T_1	−4.1	−7.3	−5.5	−6.3
B/6-311++G**≫B/6-311G* T_1	−4.1	−6.4	−6.0	−6.8
HF/6-311G* T_1	−11.6	−13.9	−9.3	−11.7
MP2/6-311G*//HF/6-311G* T_1	−8.7	−11.0	13.0	7.7
B/6-311G* T_1	−6.2	−8.6	−4.0	−4.8

[a] B3PW91 abbreviated B; for explanation of ≫ notation see Methodology.

and B3PW91/6-311++G**≫B3PW91/6-31++G* levels of calculation (where ≫ denotes that energy was obtained from geometry optimization at the higher level and thermochemical data were obtained from normal-mode analysis at the lower level from a geometry optimized at the lower level).[19] Conformational space searches were carried out at the HF/6-311G*, B3PW91/6-31++G*, and B3PW91/6-311G* levels using the NOSYM keyword. Frequency calculations were only performed at the same level at which the geometry was obtained. Calculated MP2 basicities and affinities made use of the HF thermochemical analysis. Basicities and affinities were calculated from ΔG and ΔH, respectively, for comparison with experimental values using the formulas $H = T + V + R + PV$ and $\Delta G = \Delta H + T\Delta S$.[20] Proton enthalpy ($3/2RT + PV$) and entropy (26.04 cal/mol·K at 298 K) were treated classically (1 cal = 4.184 J). Thermochemical analyses were carried out at $T_1 = 298$ K or $T_2 = 373.0$ K and $P = 1$ atm (1 atm = 101.32 kPa). Zero-point energy corrections were scaled by a factor of 0.89.[20a] Errors deriving from various sources in MO calculations have been discussed previously and are estimated as ±1 kcal/mol for molecular energies and ±0.01 Å and ±1° for bond lengths and angles, respectively.[20a]

Results and Discussion

Choice of Computational Method. Experimental GB, LCB, PA, and lithium cation affinity (LCA) values for sulfone **1**, DMSO **4**, and sulfite **7**,[6] together with new measurements for sultine **6** (Tables 1 and 2) were used to benchmark MO calculations at the HF level and calculations including electron correlation at the Moller−Plessett (MP2) and DFT levels. All levels of calculation correctly reproduced the experimental basicity series, DMSO **4** > sultine **6** > sulfone **1** > sulfite **7**, in some cases with good linear correlations. At the 6-311G* level of calculation, B3PW91 yielded the best correlation compared to MP2 and HF. However, as assessed by quantitative comparison with experimental data, the most accurate reproduction was obtained using DFT-hybrid methods,[21] in particular B3PW91/6-31++G* (Table 3). There rests considerable justification in benchmarking calculations on sulfuryl and phosphoryl species using gas-phase experimental data. Gas-phase MO calculations have been used to provide profound and conflicting information on solution-phase experiments.[13,14,22] The B3PW91-based DFT methods appear very promising.[23] These methods were used to calculate LCB and GB for a fifth compound, sulfate **9**, and further extended to calculate SCB and sodium cation affinity (SCA) for **1**, **4**, **6**, and **7**.

Metal Ion Chelates. Compounds capable of chelating lithium are generally observed as outliers in LCB vs GB linear free energy relationships, since chelation can result in approximately 5−10 kcal/mol of stabilization energy over linear complexes.[1,2,7] Surprisingly, in this work, chelation of lithium and sodium by sulfuryl species was found to provide no special stabilization over linear complexation. Structures for lithium chelates were obtained at all levels of calculation for sulfone **1** and sulfate **9**, but no chelates were located for compounds containing the −O−S=O fragment (e.g., **6**). The competitive “linear” complexes were found to contain the Li^+−O=S bonds considerably distorted from collinearity (Table 4). At the preferred DFT levels for sulfone **1**, the “linear” adduct was only marginally less stable (<1.1 kcal/mol) than the chelate.[24] Clearly, the experimental LCB vs GB correlation would not indicate the presence of such marginally stabilized chelates. Indeed, the LCB calculations predicted the linear and chelated complexes to be in equilibrium in the gas phase. Not only does ΔG suggest chelate and linear complex to be in equilibrium, but the energy barrier for conversion of the Li−sulfone (**1**) chelate to the linear complex is low: <1.4 kcal/mol (calculated by varying $d(O-Li^+)$ starting from the chelate at the B3PW91/6-31++G* level). Calculated energies of linear and chelated sodium adducts with sulfone **1** indicated that substitution of Na^+ for Li^+ increased the energy difference between the linear adduct and chelate by approximately 0.5 kcal/mol (Table 5).

DFT calculations on ethylene sulfate, **9**, with lithium located both chelated and linear complexes (Figure 1, Table 6). The affinity for chelate over linear complex formation was calculated as sufficiently weak that basicity values actually marginally favored the linear complex at the DFT levels (Table 7), although small stabilization of the chelate was observed in raw equilibrium energies (Table 7; also δE(chel.) = −1.6 kcal/mol at MP2/6-31+G*//HF/3-21+G(*), but δE(chel.)= +5.7 kcal/mol at HF/3-21+G(*)). It is likely that any electrostatic stabilization of O=S=O chelates is counterbalanced by the enforced proximity of the cation to S (which carries significant positive charge in all calculations) and by bond bending strain at S. The five-membered ring of sulfate **9** has been calculated to have at least 4.6 kcal/mol of ring strain enthalpy, the small endocyclic bond angle at sulfur being symptomatic of this ring strain.[22] Chelation of lithium by sulfate **9** results in contraction of ∠OSOexo by 11.2°

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[23] Recently Amekraz et al. have compared PA obtained by FT-ICR for a single nitrogen base, guanidine, with calculated values from G2, G2(MP2), and DFT methods and comment favorably on the latter [Amekraz, B.; Tortajada, J.; Morizur, J. P.; Gonzalez, A. I.; Mo, O.; Yanez, M.; Leito, I.; Maria, P. C.; Gal, J. F. *New J. Chem.* **1996**, *20*, 1011].

[24] Previous semiempirical PM3 calculations on sulfones indicated the chelated sulfuryl species to be disfavored over the linear complex by approximately 5 kcal/mol [Gal, J. F.; Koppel, I.; Kurg, R.; Maria, P. C. *Int. J. Quantum Chem.* **1996**, *59*, 409].

Table 4. Bond Lengths (Å; 1 Å = 0.1 nm) and Angles for Linear and Chelated Metal Complexes Obtained at the B3PW91/6-311++G Level**

	1-Li linear	**1**-Li chelate	**1**-Na linear	**1**-Na chelate	**4**-Li	**4**-Na	**7**-Li	**7**-Na	**6**-Li	**6**-Na
∠LiOS	146.1	88.5, 88.6	132.3	93.1, 93.2	164.9	163.0	168.0	167.8	157.6	155.6
∠OSZ[a]	116.1	109.0	115.7	112.1			104, 108	104, 109	107.9	108.3
∠CSC	106.3	106.3	105.4	105.5						
∠endo[b]							94.5	93.9	92.5	92.0
d(Li−O)	1.771	2.020	2.169	2.394	1.717	2.094	1.759	2.137	1.742	2.121
d(Li−O)	3.626	2.017	3.598	2.395						
d(S=O)	1.504	1.486	1.457	1.480	1.546	1.540	1.499	1.489	1.527	1.518
d(SO)	1.451	1.486	1.493	1.480			1.63,1.64	1.64, 1.65	1.624	1.635

[a] ∠O=S=O, ∠O=SC, or ∠OSO exocyclic. [b] Endocyclic ∠OSO or ∠CSO.

Table 5. Energy Differences (kcal/mol) in Sulfone (1) Affinities and Basicities for Formation of Linear versus Chelated Complexes with Lithium and Sodium (a Positive Value Indicates a More Stable Chelate)

method[a]	LCA	LCB	SCA	SCB
HF/6-311G*	0.3	−0.4	1.2	0.7
MP2/6-311G*//HF/6-311G*	1.8	1.3	1.5	0.9
B/6-311G*	1.0	0.3	1.6	0.8
B/6-311++G**≫HF/6-311G*	1.3	0.8	1.8	1.0
B/6-311++G**≫B/6-311G*	1.3	0.6	1.8	1.2
B/6-311++G**≫B/6-31++G*	1.2	1.1		
B/6-311++G**〉〉B/6-31++G* T_2	1.2	0.1		
B/6-31++G*	2.0	1.1		
B/6-31++G* T_2	2.0	0.8		

[a] T_2 = 373 K, all others T = 298 K. B3PW91 abbreviated as B.

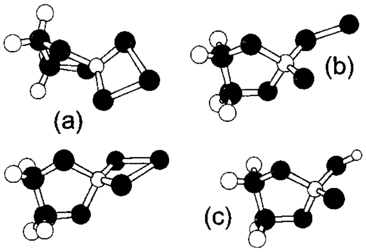

Figure 1. Structures of sulfate **9** obtained at B3PW91/6-31++G*, showing (a) two representations of the Li chelate, (b) Li linear complex, and (c) protonated sulfate **9**.

Table 6. Bond Lengths (Å) and Angles for Sulfate 9, Linear and Chelated Complexes of 9 with Li (Z = Li), and Protonated (Z = H) Complexes at B3PW91/6-31++G*

	9	linear Li	chelate Li	protonated
∠ZOS		137.9	89.1, 89.1	105.0
∠OSOendo	95.5	97.7	98.1	99.3
∠OSOexo	121.2	116.1	110.0	113.6
d(Z−O)		1.811	2.052	0.983
d(Z−O)		3.458	2.052	2.555
d(S=O)	1.445	1.481	1.468	1.570
d(S=O)	1.445	1.438	1.468	1.426
d(S−O)	1.588	1.600	1.588	1.568
d(S−O)	1.588	1.599	1.588	1.572

and expansion of the endocyclic ∠OSO to 98.1°, indicating an increase in ring strain (Tables 6 and 7).

The experimental LCB and GB data shows that the O=S=O compounds (sulfones, sulfates, sulfonate) do not deviate from the LFER observed for all sulfuryl species. This observation is compatible with the DFT calculations which demonstrate feeble stabilization of Li chelates. Recent ab initio studies on the sulfonate monoanion ($CF_3SO_3^-$) have shown the Li chelate to be 4 kcal/mol more stable than the linear complex.[25] This stabilization is at the lower end expected for chelates (*vide supra*) and probably the result of the increased charge on the sulfuryl oxygens and amplified stabilization energies observed. Interestingly, and compatible with our arguments, the bis-sulfone monoanions (e.g., $(CF_3SO_2)_2N^-$) studied at the HF/6-31+G* level were reported to show chelates stabilized by 20 kcal/mol over linear complexes when one sulfuryl oxygen from each sulfone moiety participated in the chelate.[25]

Linear Free Energy Relationships. Calculations on many varied systems, using G1 and G2 theory, have yielded agreement with experiment within ±2−3 kcal/mol.[26] At the DFT levels of calculation, which perform better than HF and MP2, quantitative comparison of calculated with experimental LCB and LCA values yielded errors of ≤4.6 kcal/mol, which can be seen as fair accuracy. However, the slopes of all calculated vs experimental LCB plots were significantly greater than unity (Table 3). The accuracy in GB and PA was fair (≤6 kcal/mol), but again the rise in calculated values was greater than for the experimental data. Nevertheless, LFERs were seen for both calculated and experimental data, for LCB vs GB and LCA vs PA, and for the calculated SCB data when correlated with GB and LCB. GB, PA, LCB, and LCA were calculated for **9** using the DFT methods (Table 7). Values of GB, LCB, PA, and LCA were subsequently measured experimentally for **8**, **9**, **5**, **2**, and **3** to provide a sample of nine varied sulfuryl species.

LFERs were seen across the series of diverse sulfuryl species for both calculated and experimental data, for LCB, GB, and SCB (Figures 2 and 3). Basicity decreases in the order: sulfoxide (**4**, **5**), sulfinate (**6**), sulfone (**1**, **2**), sulfonate (**3**), sulfite (**7**), sulfate (**8**, **9**), corresponding approximately with the degree of oxygen substitution. The observation of an LFER between proton and cation stability constants has been made in a number of systems[1,2,7] but may breakdown for a number of reasons, including chelation of the cation. Taft and co-workers' studies of nitrogen bases identified lithium chelates (e.g. of pyridazine) lying 6−8 kcal/mol above the LCB vs GB LFER.[2] MO calculations on the sulfuryl species are in accord with the good correlation between LCB and GB across the series of sulfuryl species (Figure 3) and are contraindicative of significantly stabilized lithium chelates. For a series of azoles, GB values were observed to be 5-fold greater than LCB.[1] MO calculations supported the rationale that the dominant contribution to LCB was electrostatic stabilization, whereas the larger GB values

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[25] Arnaud, R.; Benrabah, D.; Sanchez, J. Y. *J. Phys. Chem.* **1996**, *100*, 10882.

[26] Gonzalez, A. I.; Mo, O.; Yanez, M.; Leon, E.; Tortajada, J.; Morizur, J. P.; Leito, I.; Maria, P.-C.; Gal, J.-F. *J. Phys. Chem.* **1996**, *100*, 10490. Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885. Yu, D.; Rauk, A.; Armstrong, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 1789. Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991,** *94* (11), 7221.

Table 7. GB, LCB, PA, LCA, and Chelate Stabilization Energies (kcal/mol) for Sulfate 9, at Various Levels of Calculation[a]

	B/6-31++G*(T_1)	B/6-31++G* T_2	B/6-311++G**≫B/6-31++G* T_1	B/6-311++G**≫B/6-31++G* T_2
GB	171.0	168.5	173.3	170.8
LCB linear	32.3	29.4	33.0	30.1
LCB chel.	32.2	29.0	31.9	28.7
δE(chel.)[b]	−0.8	−0.8	+0.3	+0.3
δG(chel.)	+0.1	+0.4	+1.1	+1.3
$\Delta E + E_{zp}$ ($+H^+$)[c]	178.1	178.1	180.3	180.4
$\Delta E + E_{zp}$ ($+Li^+ - l$)	39.1	44.3	40.3	45.0
$\Delta E + E_{zp}$ ($+Li^+ - ch$)	40.2	45.0	39.9	44.7
PA	177.3	177.9	179.6	180.2
LCA linear	38.6	39.1	39.4	39.8
LCA chel.	39.5	39.9	39.2	39.6
δH(chel.)	−0.1	−0.8	+0.2	+0.2

[a] T_1 = 298 K; T_2 = 373 K; B3PW91 abbreviated B. [b] Using SCF energies. [c] $\Delta R + E_{zp}$ for association.

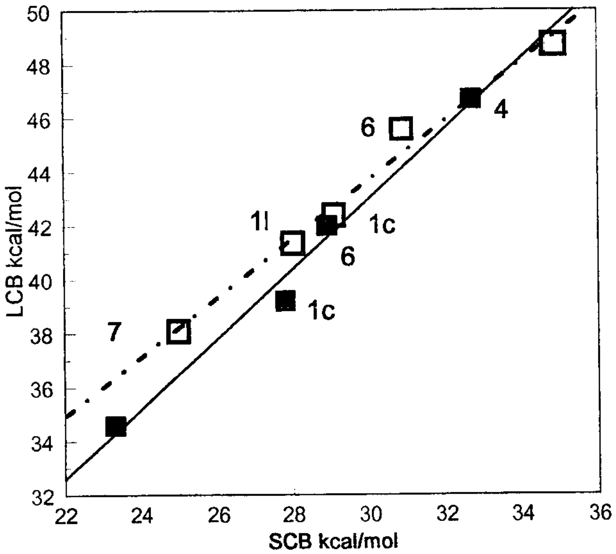

Figure 2. Plots of calculated LCB versus calculated SCB at B3PW91/6-31++G* (solid line, ■) and B/6-311++G**≫B3PW91/6-31++G* (dashed line, □). Lower case l and c denote linear and chelate complexes.

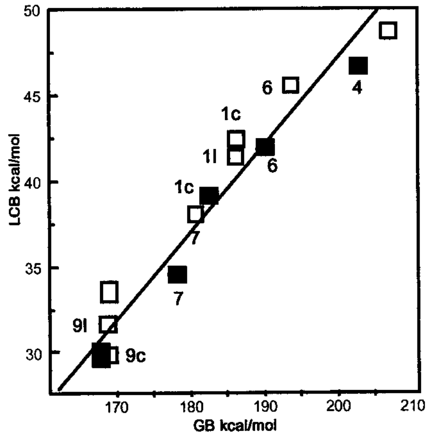

Figure 3. Plots of calculated LCB versus calculated GB at B3PW91/6-31++G* (solid line, ■) and B/6-311++G**≫B3PW91/6-31++G* (dashed line, □). Lower case l and c denote linear and chelate complexes.

reflected the additional influence of covalent bonding.[1] GB values for the sulfuryl series are approximately 4.5× greater than LCB values. Thus, by comparison, sulfuryl bases, comparable in GB with nitrogen bases (i.e. pyrazole), are significantly stronger bases toward lithium (LCB).[1] The recent ab initio calculations on Li complexes with monoanionic sulfuryl species determined an 85% electrostatic contribution to stabilization using NBO analysis.[25]

Electrostatic Stabilization and S=O Bond Dipole. For a diverse selection of azoles, Taft and co-workers formulated a relationship between experimental LCB and contributions from both the calculated dipole moment and polarizability.[1,2] Calculations on the lithium complexes themselves were required to provide the input parameters to calculate LCB. For azoles there is no simple bond dipole that would be expected to provide a dominant contribution to the electrostatic stabilization. However, for the sulfuryl compounds, the S=O bond dipole moment might be anticipated to provide such a strong, dominant contribution through cation−dipole electrostatic stabilization. If lithium chelates are indeed insignificant, even O=S=O containing species may be treated by calculating the single S=O bond dipole moment. Molecular dipole moments, molecular polarizability (α′), atomic charges from electrostatic potential (CHELP),[27] Mulliken atomic charges, natural bond orbital (NBO) charges,[28] and S=O bond length were calculated for all compounds. A good correlation was obtained between both the experimental GB and LCB data and S=O bond length (d(S=O); Table 8, Figure 4)). A reasonable correlation was obtained for the bond dipole using Mulliken atomic charges, but considerable differences were seen between charges obtained by the different methods.

The linear correlations observed allow accurate estimation of GB, LCB, and predictions of SCB simply from calculation of the S=O bond length of the parent compound (Table 8, Figures 4 and 5). For example, GB, LCB, and SCB were estimated for **8** from the calculated S=O bond length (see Table 8 for formulas). The experimental values of GB and LCB subsequently measured were found to be in excellent agreement (error <3 kcal/mol; Table 8).

As a further example of the application of the d(S=O) correlation, the structures of the "superbasic" sulfonamidate, **10**, and its parent sulfonamidate, **11**, were located at the B3PW91/6-31++G* level to obtain the calculated S=O bond lengths. Chardin et al. report that *N*-(trimethylammonio)octanesulfonamidate (AMS), for which **9** is a model, is the strongest sulfonyl base known and, further exceeds DMSO on the pK_{HB} hydrogen-

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[27] Chirlian, L. E.; Francl, M. M. *J. Comput. Chem.* **1987**, *8*, 894.

[28] Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. Reed, A. E.; Weinhold, F. *J. Chem Phys.* **1983**, *78*, 4066. Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41.

Table 8. GB, LCB, SCB, Bond Length (*s*(S=O)), Bond Dipole (*μ*(S=O)), and Molecular Polarizability (α′) from Calculation and Experiment

	d(S=O),[a] Å	μ(S=O),[b] Cm × 10^{32}	α′,[a] cm^3 × 10^{24}	LCB exp[c]	kcal/mol DFT low (373 K)[d]	$f(d$(SO))[e]	GB exp[i]	kcal/mol DFT low (373 K)[d]	DFT low (298 K)[d]	DFT high (298 K)[f]	$f(d$(SO))[e]	SCB DFT low (373 K)[d]	kcal/mol DFT high (298 K)[f]	$f(d$(SO))[g]
5	1.517	1.658	10.05	45.7		45.5	206.4				206.0			33.5
4	1.512	1.595	7.35	44.4	46.7	44.9	203.0	204.3	205.9	209.9	204.2	32.7	35.0	32.7
6	1.490	1.421	8.73	41.7	42.0	42.2	198.0	191.7	193.4	196.8	196.3	28.9	30.8	29.1
10 (H)	1.483	1.416	8.52			41.4					193.8			28.1
10 (Me)	1.484	1.336	13.54			41.4					193.9			28.1
2	1.471	1.252	10.15	41.6		40.1	189.7				189.6			26.1
1	1.468	1.162	7.51	39.7	39.2[h]	39.6	186.5	184.1	185.8	189.1	188.4	27.8[h]	29.0[h]	25.6
7	1.466	1.308	7.54	38.2	34.6	39.4	185.5	179.6	181.2	183.7	187.8	23.3	25.0	25.3
11	1.466	1.330	7.3			39.3					187.6			25.3
3	1.453	1.202	8.94	39.3		38.0	183.9				183.8			23.5
8	1.445	1.340	8.43	36.6		36.9	180.0				180.4			22.0
9	1.445	1.210	7.79	35.6	29.4[h]	36.8	177.5	168.5	171.0	173.3	180.3			21.9

[a] B3PW91/6-31++G*, average is used for O=S=O species. [b] Calculated using $\mu = d$(S=O)(qO), where qO is the averaged Mulliken charge on sulfuryl oxygen. [c] From FT-ICR corrected to 373 K (see Tables 1 and 2) estimated uncertainty ±2 kcal/mol. [d] B3PW91/6-31++G* (at 298 K or 373 K). [e] From correlation of d(S=O), calculated at B3PW91/6-31++G*, with exp values, using the formulas GB = (357.0)d(S=O) − 335.6; LCB = (120.2)d(S=O) − 136.9. GB correlation $r^2 = 0.92$, for bond dipoles calculated using Mulliken charge on O and remainder of molecular charge located on S, $r^2 = 0.80$. [f] B3PW91/6-311++G**//B3PW91/6-31++G*. [g] From correlation of SCB(DFT low) with d(S=O): SCB = (160.6)d(S=O) − 210.1. [h] Chelate. [i] From FT-ICR (see Tables 1 and 2).

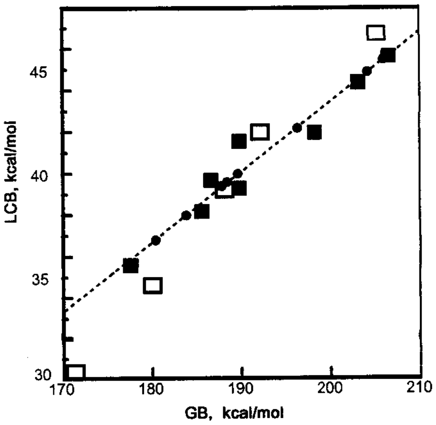

Figure 4. Plots of (i) experimental LCB vs experimental GB data (■); (ii) LCB vs GB values obtained from correlation of experimental data with d(S=O) (- - ● - -); (iii) calculated LCB vs calculated GB from B3PW91/6-31++G* calculations (- - □ - -). See Table 8 for full data and correlation formulas.

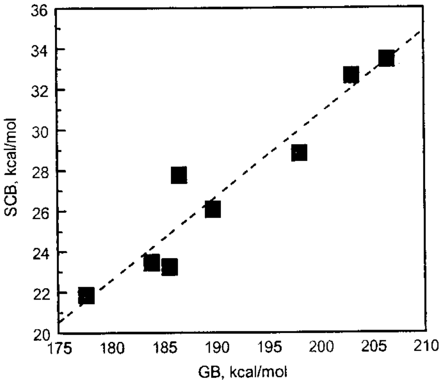

Figure 5. Plot of calculated SCB vs experimental GB. Calculated SCB data are either derived directly from the DFT-calculated energies (**1**, **3**, **4**, **5** only) or calculated from the correlation relationship of the DFT-calculated SCB values with d(S=O)). Full data are in Table 8.

bonding scale.[29] Calculations on the model compound, **10** (R = H), gave a value of d(S=O) yielding calculated GB, LCB, and SCB values that do indeed rank **10** as the strongest sulfonyl base in this present study (i.e. GB = 4 kcal/mol above sulfone **2**).[30] But, with respect to GB, **10** is predicted to be considerably weaker than DMSO (by approximately 10 kcal/mol) (Table 8). For the limited pK_{HB} data, published, there appears to be a reasonable correlation between d(S=O) and pK_{HB} for simple sulfuryl species, including the sulfonamidate **11**. Interestingly, however, the pK_{HB} for **10** would be predicted to be a full unit lower than that actually observed experimentally for AMS. The breakdown in correlation of GB and pK_{HB} scales has been remarked upon previously in comparison of amines with nitrile "super bases".[31] The latter are observed as super bases only with respect to hydrogen bonding with phenols in organic solvents (pK_{HB}). This anomaly prompted calculations on the extended model, **10** (R = Me), which yielded a similar d(S=O) but revealed, not unexpectedly, a markedly increased molecular polarizability (Table 8).[32] These observations further indicate the utility of the d(S=O) correlation in indicating anomalous behavior, such as cation chelation and superbasicity.

Summary. GB, PA, LCB, and LCA were measured using FT-ICR for five sulfuryl species and DFT calculations at the B3PW91/6-31++G* and B3PW91/6-311++G** levels found to give the best reproduction of the experimental data. Linear free energy relationships were observed between both experimental and calculated proton and cation stability constants. The linear correlation between LCB and GB was in accord with the marginal stabilization of lithium chelates over linear complexes with sulfuryl compounds observed in the DFT calculations. Structures for sodium chelates and linear

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(29) Chardin, A.; Laurence, C.; Berthelot, M.; Morris, D. G. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1047.

(30) The minimum energy structure for AMS(R = H) was initially located, showing stabilization by an internal hydrogen bond (−NH···O=S−) which significantly distorts the SO_2 moiety. The NN−SO dihedral was constrained to eschew this hydrogen bond in obtaining the optimized structure from which d(S=O) was obtained. The relatively low basicity predicted for AMS required location of a minimum energy structure for AMS(R = Me). This calculation confirmed that the low basicity was not the result of the truncated model, AMS(R = H).

(31) Berthelot, M.; Helbert, M.; Laurence, C.; Le Questel, J. V.; Anvia, F.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1993**, 625.

(32) The importance of dispersion forces in interactions involving phenols and other arenes, coupled with the significant contribution of polarizability to dispersion forces, provides one possible rationale for the observed superbasicity in CCl_4 solution. The polarizability of CCl_4 calculated at the B3PW91/6-31++G* level is 8.802 × 10^{-24} cm^3. The contribution of other aggregation forces such as direct dipole−arene interactions must also be considered.

complexes were calculated along with SCB, which showed LFERs with both GB and LCB. The experimental LCB/GB LFER, from FT-ICR, was extended for a complete family of nine diverse, sulfuryl compounds (Figure 4). The observed good linear correlation between S═O bond length (or S═O bond dipole moment), calculated from DFT, and both experimental GB and LCB data is most simply explained by the dominance of the S═O bond dipole in cation−dipole electrostatic stabilization. This LFER allows accurate estimation of GB, LCB, and SCB for sulfuryl species from calculation of the S═O bond length alone and can be used to predict anomalous behavior in sulfuryl species.

Acknowledgment. Caroline S. Walkinshaw is thanked for technical assistance. NSERC Canada and NATO (CRG931176) are thanked for financial support.

Supporting Information Available: Structures of sodium complexes (top row) and lithium complexes (bottom row) for (a) sulfite **7**, (b) sulfoxide **4**, (c) sultine **6**, (d) sulfone **1** chelate, and (e) sulfone **1** linear. All structures were obtained at B3PW91/6-311++G** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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