account for the existence of TlI_3 as $Tl^+I_3^-$ in the solid state.

In summary, we have calculated a number of molecular properties, such as bond lengths, dipole moments, and dissociation energies, for a range of inorganic molecules, and where experimental data are available, the agreement is satisfactory. The most informative quantities for comparative purposes are the internal energies (ΔU_0) for eq 1. For the 6th period elements, we have identified the relativistic and nonrelativistic contributions to ΔU_0 and find that, although the former contribute as much as 25% to the reduction of ΔU_0, they are not decisive in determining the trend along the period and are not associated with a particular corelike character of the 6s electrons. It is true that, in many of the compounds we have considered, the s electrons play only a small part in bonding and in that sense can be regarded as corelike, even for the lighter elements. Thus, σ-bonding involves mainly the valence p electrons, and the familiar concept of s–p hybridization is not relevant to the calculated electronic structures. The term inert pair effect has also been used in overlap and density arguments (see, for example, ref 73). As Drago[4] suggested, however, there is no special inert pair effect on valency for the 6th period elements; moreover, there is no particular relativistic contribution that determines preferred oxidation states. Finally, although the ab initio calculations satisfactorily reproduce the trends in ΔU_0, there remains the challenge of relating the resulting numerical data to an intuitively comprehensible bonding model within the framework of descriptive inorganic chemistry.

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Registry No. BH, 13766-26-2; BH_3, 13283-31-3; AlH, 13967-22-1; AlH_3, 7784-21-6; GaH, 13572-92-4; GaH_3, 13572-93-5; InH, 13939-13-4; InH_3, 15060-45-4; TlH, 13763-69-4; TlH_3, 82391-14-8; BF, 13768-60-0; BF_3, 7637-07-2; AlF, 13595-82-9; AlF_3, 7784-18-1; GaF, 13966-78-4; GaF_3, 7783-51-9; InF, 13966-95-5; InF_3, 7783-52-0; TlF, 7789-27-7; TlF_3, 7783-57-5; TlCl, 7791-12-0; $TlCl_3$, 13453-32-2; TlBr, 7789-40-4; $TlBr_3$, 13701-90-1; TlI, 7790-30-9; TlI_3, 13453-37-7; AuH, 13464-75-0; HgH_2, 72172-67-9; PbH_2, 101764-35-6; PbH_4, 15875-18-0; PbF_2, 7783-46-2; PbF_4, 7783-59-7; BiH, 17000-07-6; BiH_3, 18288-22-7; BiH_5, 124652-39-7; BiF, 13827-23-1; BiF_3, 7787-61-3; BiF_5, 7787-62-4.

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Structures, Bonding, and Absorption Spectra of Amine–Sulfur Dioxide Charge-Transfer Complexes

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Abstract: The 1:1 and 2:1 charge-transfer (CT) molecular complexes between ammonia and the methyl-substituted amines, CH_3NH_2 (MA), $(CH_3)_2NH$ (DMA), and $(CH_3)_3NH$ (TMA), and SO_2 have been examined using ab initio molecular orbital theory. Equilibrium structures have been obtained at a variety of levels of theory including MP2/6-31G(d), and binding energies were determined at the MP3/6-31+G(2d,p) level. Correction for electron correlation is found to be necessary for an accurate description of the structures and stabilities of these amine·SO_2 complexes. For TMA·SO_2, the calculated N–S equilibrium distance is reduced dramatically, by 0.18 Å, in going from the Hartree–Fock level to the MP2 level of theory. The calculated enthalpies of complex formation (ΔH, 298 K) for NH_3·SO_2, MA·SO_2, DMA·SO_2, and TMA·SO_2 are 4.5, 6.7, 7.9, and 10.7 kcal mol^{-1}, respectively, and the corresponding N–S bond lengths are 2.79, 2.62, 2.46, and 2.36 Å, respectively. The computed formation enthalpy and geometry for TMA·SO_2 are in good accord with experimental data. The trends of geometry and stability of these amine·SO_2 complexes can be rationalized in terms of the donor strength of the amines (TMA > DMA > MA > NH_3). The 2:1 adducts, $(NH_3)_2$·SO_2, MA_2·SO_2, DMA_2·SO_2, and TMA_2·SO_2, are all predicted to be thermodynamically stable, with binding energies slightly less than the corresponding 1:1 complexes, and are predicted to be experimentally accessible species in the gas phase. The bonding characteristics of the amine·SO_2 CT complexes have been investigated by charge density analysis. The N–S bond is characterized by a strong ionic interaction. The charge-transfer component plays an important role in determining the stabilities of these donor–acceptor complexes. The calculated amount of charge transfer from the amine to SO_2 are 0.04, 0.08, 0.13, and 0.18 eV for NH_3·SO_2, MA·SO_2, DMA·SO_2, and TMA·SO_2, respectively. The infrared and ultraviolet spectra of the 1:1 and 2:1 CT complexes were calculated for the first time. The computed vibrational frequencies and transition energies are consistent with experimental data.

Introduction

Charge-transfer (or donor–acceptor) complexes are of importance in several phenomena of chemistry and biology.[1] The trimethylamine–sulfur dioxide (TMA·SO_2) complex represents one of the best characterized charge-transfer complexes. The gas-phase and crystal structures have been determined by Fourier transform microwave spectroscopy[2] and X-ray crystallography,[2,3] respectively. The reaction thermodynamics have been studied in the gas phase as well as in solution by ultraviolet spectroscopy.[4]

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Furthermore, matrix infrared[5] and gas-phase photoelectron[6] spectra have been recently investigated. Other 1:1 molecular complexes between ammonia and the methyl-substituted amines, CH_3NH_2 (MA) and $(CH_3)_2NH$ (DMA), and sulfur dioxide have also been examined by matrix IR spectroscopy.[5] The existence of a 2:1 complex, $(NH_3)_2\cdot SO_2$, has been demonstrated by spectroscopic experiments, but no stable 2:1 adducts between the larger methyl-substituted amine and SO_2 have yet been reported.[7] The 1:1 molecular complexes between amines (NH_3, MA, DMA, and TMA) and sulfur dioxide have been the subject of several theoretical studies.[8] The structures and interaction energies of these complexes have been examined with small and moderate-size Gaussian basis sets at the Hartree–Fock (HF) level.

The goal of this paper is to systematically study the theoretically determined properties, at a level of theory substantially higher than those previously reported, of both the 1:1 and 2:1 molecular complexes between methyl-substituted amines and SO_2 and to compare the results to experiments where possible. The properties considered in this study are the equilibrium geometries, dipole moments, binding energies relative to amine and SO_2, harmonic vibrational frequencies, and vertical transition energies. In particular, the calculated structures and stabilities of the 2:1 complexes as well as the IR and UV spectra of the 1:1 complexes are reported for the first time. Special emphasis is placed on the effect of successive methyl substitution of ammonia on the structure and charge distribution on the SO_2 acceptor. To provide further insight into the nature and origin of bonding in the amine$\cdot SO_2$ donor–acceptor complexes, we have also carried out a charge density analysis, based on Bader's theory of atoms in molecules,[9] for these compounds. This technique has proved to be a useful tool in the understanding of the structure and bonding characteristics of molecules.[10] Hence, this study may shed light on the nature of intermolecular interactions in charge-transfer complexes.

Theoretical Methods and Results

Standard ab initio molecular orbital calculations[11] were performed using a development version of the Gaussian 91 series of programs.[12] Three types of basis sets were employed for the geometry optimizations: minimum STO-3G, split-valence 3-21G, and polarized split-valence 6-31G(d) basis sets.[11] Geometry optimizations for all species were carried out with the three basis sets at the Hartree–Fock (HF) level. In addition, all the 1:1 complexes and the two smaller 2:1 complexes, $(NH_3)_2\cdot SO_2$ and $MA_2\cdot SO_2$, were also optimized with the larger 6-31G(d) basis set at the second-order Møller–Plesset (MP2) level.[13] Unless otherwise noted, geometric parameters in the text refer to the MP2/6-31G(d) values. The 1:1 and 2:1 molecular complexes considered here were assumed to have C_s and C_{2v} symmetries, respectively. Harmonic vibrational frequencies were calculated analytically at the HF/6-31G(d) level. The directly calculated zero-point energies (ZPE) were scaled by a factor of 0.9 to allow for the overestimation of vibrational frequencies at the HF level.[14] To examine the effect of basis set on the calculated binding energies of amine$\cdot SO_2$ complexes, we have calculated the stabilization energies of $NH_3\cdot SO_2$ and $TMA\cdot SO_2$ with a sequence of standard basis sets,[11] including 6-31G(d), 6-31G(d,p), 6-31+G(d), 6-31G(2d), and 6-311G(d), at the HF level. Finally, improved relative energies were obtained through third-order Møller–Plesset calculations[13] with the larger 6-31+G(2d,p) basis set at the MP2/6-31G(d) optimized geometries. Our best relative energies correspond to MP3/6-31+G(2d,p)//MP2/6-31+G(2d) values with zero-point energy and thermal corrections. Calculations of bonding energies are complicated by the basis set superposition error, but with reasonably large basis sets such as 6-31+G(2d,p) they should be relatively small. Further, our main interest is in the relative binding energies of the amine complexes, and the relative superposition errors should be small. In the case of the $NH_3\cdot SO_2$ complex, the superposition error was estimated via the counterpoise method.[15] The vertical transition energies of the CT complexes were calculated via the configuration interaction with singles (CIS) method[16] using the 6-311+G(d,p) basis set. The frozen-core approximation was employed for the MP3 and CIS calculations.

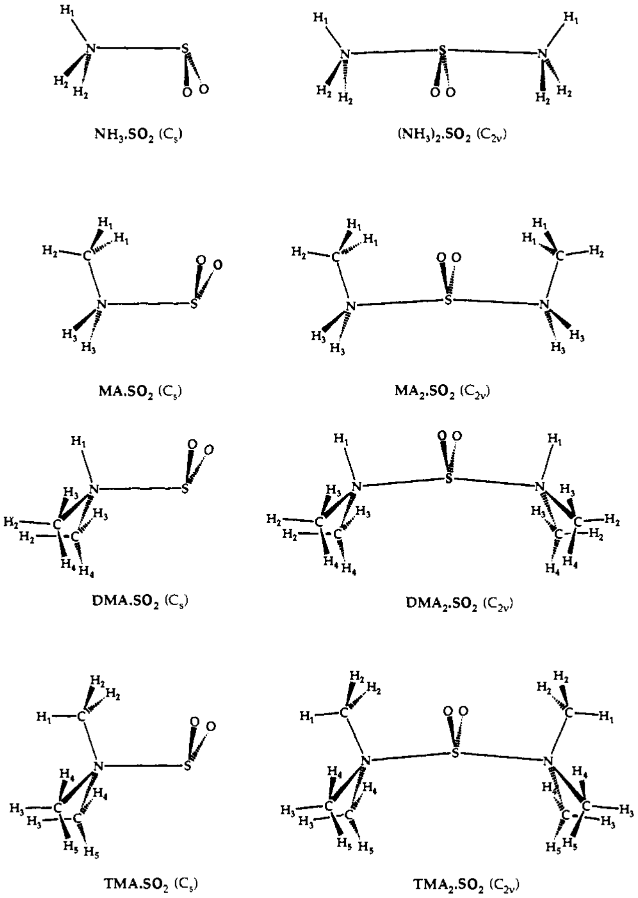

Figure 1. Structures of 1:1 and 2:1 amine$\cdot SO_2$ molecular complexes.

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Table I. Calculated Geometries, Dipole Moments, and Binding Energies of 1:1 Amine·SO_2 Complexes

level	$NH_3{\cdot}SO_2$	MA·SO_2	DMA·SO_2	TMA·SO_2
	N–S Bond Length/Å			
HF/STO-3G	2.875	2.869	2.870	2.868
HF/3-21G	2.414	2.240	2.112	2.051
HF/6-31G*	2.764	2.654	2.589	2.525
MP2/6-31G*	2.797	2.617	2.459	2.359
	α^a/Degree			
HF/STO-3G	89.6	89.8	90.3	89.8
HF/3-21G	84.8	82.9	82.4	80.5
HF/6-31G*	83.4	82.7	82.2	80.5
MP2/6-31G*	85.8	84.9	82.9	81.3
	Dipole Moment/D			
HF/STO-3G	2.87	2.82	2.61	2.58
HF/3-21G	5.24	5.77	6.78	6.96
HF/6-31G*	3.76	3.86	3.78	3.89
MP2/6-31G*	3.38	3.66	4.10	4.48
	Binding Energy $(\Delta E)^b$/kcal mol^{-1}			
HF/STO-3G	4.49	4.35	4.15	4.01
HF/3-21G	15.62	19.13	20.63	25.61
HF/6-31G*	7.34	7.94	7.99	8.08
MP2/6-31G*	7.03	9.36	10.27	13.43

[a] Tilt angle of the SO_2 plane off the N–S axis. [b] Based on calculated total energies from Table VI.

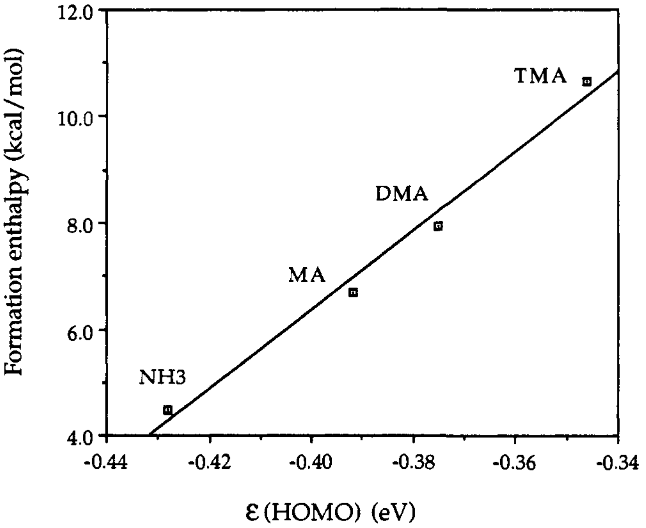

Figure 2. Correlation of the eigenvalues of the frontier orbitals ϵ_{HOMO} of the amine donor molecules (eV) with the formation enthalpies of the 1:1 amine·SO_2 complexes (kcal mol^{-1}, Table V).

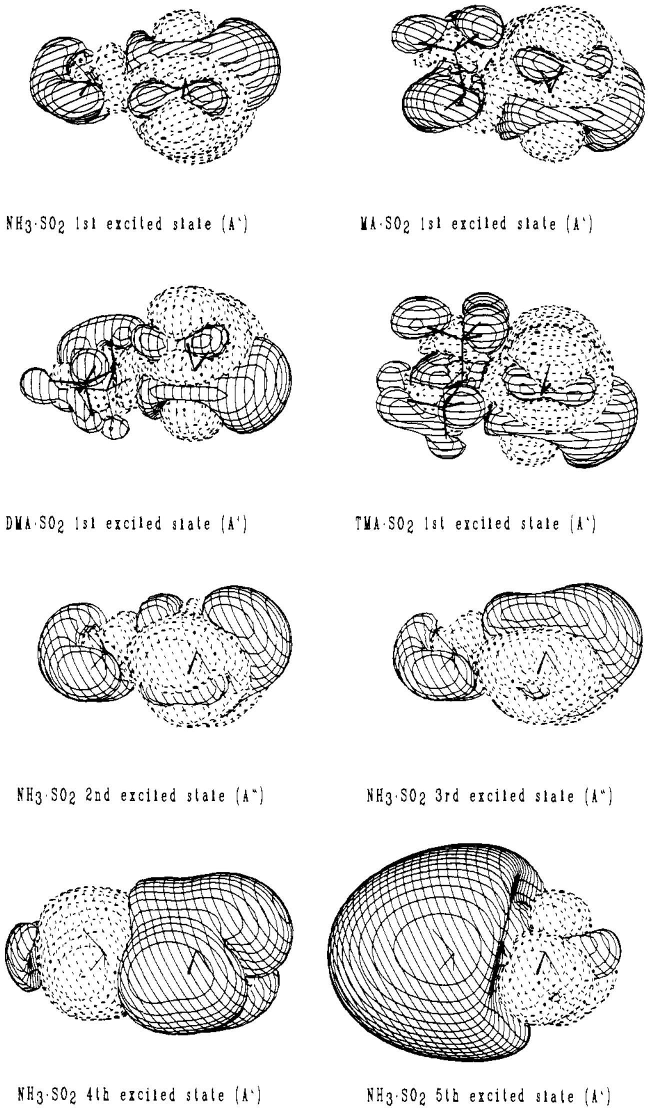
$NH_3{\cdot}SO_2$ 1st excited state (A')
MA·SO_2 1st excited state (A')
DMA·SO_2 1st excited state (A')
TMA·SO_2 1st excited state (A')
$NH_3{\cdot}SO_2$ 2nd excited state (A")
$NH_3{\cdot}SO_2$ 3rd excited state (A")
$NH_3{\cdot}SO_2$ 4th excited state (A')
$NH_3{\cdot}SO_2$ 5th excited state (A')

Figure 3. Charge density difference plots of the 1:1 amine·SO_2 charge-transfer complex for going from the ground state to the vertical excited states. Solid contours indicate regions where the charge density is increased in the excited state. The amine moiety is shown to the left and the SO_3 group to the right. The contour level is 1×10^{-4} e/B^3.

In order to gain further information on the electronic structure and the strength of the donor–acceptor complexes, we have carried out topological analyses defined within the framework of Bader's theory of atoms in molecules.[9] Here, the bond critical points (the point having the minimum charge density along a bond) are first located. Starting at a critical point, rays are developed normal to the bond for which the charge density decreases most rapidly. A set of such rays will define a zero-flux surface across which the rate of change of the charge density is 0. The set of these surfaces (one per bond) will separate a molecule into a set of unique atomic domains. The electron populations were derived by numerical integration of the charge densities, using the above boundary conditions. The charge densities were obtained from the HF/6-31+G(2d,p) calculations based on the MP2/6-31G(d) optimized geometries. At the bond critical points we calculated ρ_b, the electronic density; $\nabla^2\rho_b$, the Laplacian of the density which is a measure of the concentration or depletion of electronic charge; H_b, the local energy density ($H_b = G_b + V_b$, i.e., sum of kinetic and potential energy densities); and $\epsilon = (\lambda_1/\lambda_2) - 1$, the bond ellipticity (where λ_1 and λ_2 are the major and minor curvatures perpendicular to the bond line). In addition, covalent bond orders were evaluated by a partition scheme proposed by Cioslowski and Mixon.[17] The analysis of the wave functions was carried out with the PROAIM program.[18] The bond orders were calculated using BONDER.[17]

The calculated interaction energies, dipole moments, and some optimized structural parameters for the 1:1 amine·SO_2 complexes are given in Table I. The geometries of all molecules are illustrated in Figure 1, and the optimized parameters (except for methyl hydrogens) are collected in Table II. The effect of basis set on the calculated binding energies of $NH_3{\cdot}SO_2$ and TMA·SO_2 are summarized in Table III. The calculated energies and dipole moments of all complexes and related systems are given in Table IV, and the computed formation enthalpies (ΔH, 298 K) are presented in Table V. The correlation between the eigenvalues of the frontier orbitals ϵ_{HOMO} of amines with the calculated formation enthalpies of the 1:1 amine·SO_2 complexes are presented in Figure 2. The atomic charges are given in Table VI, and the topological quantities calculated at N–S and S–O bond critical points are listed in Table VII. The calculated transition energies for the first five excited states are summarized in Table VIII. Figure 3 presents the charge density difference plots for the first

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Table II. Optimized Structural Parameters[a]

parameter[b]	SO_2	$NH_3{\cdot}SO_2$	$MA{\cdot}SO_2$	$DMA{\cdot}SO_2$	$TMA{\cdot}SO_2$	$(NH_3)_2{\cdot}SO_2$	$MA_2{\cdot}SO_2$	$DMA_2{\cdot}SO_2$	$TMA_2{\cdot}SO_2$
r(N–S)		2.764 (2.797)	2.654 (2.617)	2.589 (2.459)	2.525 (2.359)	2.852 (2.859)	2.780 (2.719)	2.732	2.707
r(S–O)	1.414 (1.477)	1.418 (1.475)	1.419 (1.477)	1.421 (1.479)	1.422 (1.482)	1.421 (1.476)	1.422 (1.478)	1.423	1.424
$r(X_s–N)$		1.003 (1.018)	1.460 (1.467)	1.003 (1.021)	1.454 (1.458)	1.003 (1.018)	1.458 (1.466)	1.002	1.451
$r(X_e–N)$		1.003 (1.018)	1.002 (1.018)	1.453 (1.458)	1.452 (1.457)	1.003 (1.018)	1.002 (1.018)	1.451	1.449
∠OSO	118.6 (119.8)	117.7 (118.6)	117.5 (118.2)	117.4 (118.2)	117.1 (117.7)	116.8 (117.5)	116.6 (117.0)	116.4	116.5
$\angle X_6NS$		123.0 (127.8)	105.1 (99.7)	97.5 (97.3)	104.2 (101.9)	129.9 (139.9)	103.1 (97.8)	92.7	102.6
$\angle X_eNS$		105.2 (103.3)	111.6 (114.2)	112.4 (111.6)	108.1 (107.9)	101.2 (96.7)	112.6 (115.5)	114.3	108.9
α[c]		83.4 (85.8)	82.7 (84.9)	82.1 (82.9)	80.5 (81.3)	87.7 (91.1)	86.2 (88.4)	87.2	85.0

[a] HF/6-31G(d) values, with MP2/6-31G(d) values in parentheses. [b] X refers to C or H atom staggered (s) or eclipsed (e) with respect to the SO_2 plane. [c] Tilt angle of the SO_2 plane off the N–S axis.

Table III. Effect of Basis Set and Electron Correlation on Calculated Binding Energies (ΔE) of $NH_3{\cdot}SO_2$ and $TMA{\cdot}SO_2$

	total energy[a,b]	
level	$NH_3{\cdot}SO_2$	$TMA{\cdot}SO_2$
HF/6-31G(d)	−603.365 06 (7.34)	−720.451 34 (8.18)
HF/6-31G(d,p)	−693.375 88 (7.11)	−720.465 14 (8.25)
HF/6-311G(d)	−603.438 04 (7.66)	−720.541 80 (8.55)
HF/6-31+G(d)	−603.375 67 (6.61)	−720.461 02 (7.80)
HF/6-31+G(2d)	−603.387 39 (5.53)	−720.472 63 (6.44)
MP2/6-31(d)	−604.038 59 (7.54)	−721.521 51 (13.22)
MP3/6-31+G(2d,p)	−604.174 91 (6.46)	
QCISD/6-31+G(2d,p)	−604.195 44 (5.96)	
QCISD(T)/6-31+G(2d,p)	−604.227 02 (5.98)	

	total energy[a]		
level	SO_2	NH_3	TMA
HF/6-31G(d)	−547.169 01	−56.184 36	−173.269 30
HF/6-31G(d,p)	−547.169 01	−56.195 53	−173.282 98
HF/6-311G(d)	−547.224 90	−56.200 94	−173.303 27
HF/6-31+G(d)	−547.175 70	−56.189 44	−173.272 89
HF/6-31+G(2d)	−547.191 97	−56.186 60	−173.270 39
MP2/6-31(d)	−547.672 86	−56.353 71	−173.827 58
MP3/6-31+G(2d,p)	−547.744 40	−56.420 21	
QCISD/6-31+G(2d,p)	−547.763 48	−56.422 47	
QCISD(T)/6-31+G(2d,p)	−547.789 82	−56.427 67	

[a] Based on HF/6-31G(d) geometry, in hartrees. [b] Numbers in parentheses refer to binding energy (ΔE) relative to amine and SO_2, in kcal mol^{-1}.

five excited states of $NH_3{\cdot}SO_2$ and the first excited state of $MA{\cdot}SO_2$, $DMA{\cdot}SO_2$, and $TMA{\cdot}SO_2$. Finally, vibrational frequencies of all complexes are summarized in Table IX and the corresponding IR spectra are given in Figure 4. Throughout this paper, bond lengths are given in angstroms and bond angles in degrees.

Structures and Energetics

The structures and energetics of the 1:1 amine·SO_2 complexes have been examined by several ab initio studies.[8] Previous theoretical findings were based on a variety of basis sets but only at the Hartree–Fock level. To gain some insight into the relative merits of various basis sets and the effect of electron correlation on the calculated geometries and binding energies of the amine·SO_2 complexes, we first performed a preliminary study of the geometries and binding energies of $NH_3{\cdot}SO_2$, $MA{\cdot}SO_2$, $DMA{\cdot}SO_2$, and $TMA{\cdot}SO_2$ calculated with the HF/STO-3G, HF/3-21G, HF/6-31G(d), and MP2/6-31G(d) levels of theory. Of the four 1:1 amine·SO_2 complexes considered here, only $TMA{\cdot}SO_2$ has complete experimental data on the structure and energetics in the gas phase. The N–S bond length of $TMA{\cdot}SO_2$, as determined by microwave spectroscopy, is 2.26 Å, and the corresponding dipole moment is 4.80 D.[2] The binding energy (ΔE) of $TMA{\cdot}SO_2$ is 9.2 kcal mol^{-1}.[4b,c] As evident from Table I, the use of STO-3G basis set yields greatly exaggerated N–S bond lengths and small binding energies. In addition, these minimal basis-set calculations predict all four 1:1 amine·SO_2 complexes to have essentially the same N–S equilibrium distance and stabilization energy. Significant changes in geometries and binding energies are observed in going from the minimal STO-3G basis set to the larger split-valence 3-21G basis set: the CT complexes are calculated to have considerably shorter N–S equilibrium distances and larger stabilization energies. The calculated N–S bond length of $TMA{\cdot}SO_2$ at the HF/3-21G level is closer to the experimental value; however, the calculated stability is drastically overestimated. Thus, the 3-21G basis set is not flexible enough to give reasonable estimates of the interaction energies. This is also reflected in exaggerated dipole moments (Table I). Addition of d-polarization functions on heavy atoms to the split-valence set also lead to results markedly different from the basis set lacking polarization functions. The N–S bond lengths derived from the polarized basis set (6-31G(d)) are 0.4–0.5 Å longer than those obtained from the 3-21G basis set, and the binding energies are about a factor of 2 smaller. These results suggest that a basis containing polarization functions is essential for the proper description of the amine·SO_2 molecular complexes. Similar findings have been reported for other donor–acceptor complexes and dimers.[8a] However, HF/6-31G(d) calculation yields a N–S bond length for $TMA{\cdot}SO_2$ 0.3 Å longer than the reported microwave value.[2] Electron correlation calculations at the MP2 level have differential effects on the structures and stabilities of the 1:1 complexes. Inclusion of electron correlation leads to a longer N–S bond in $NH_3{\cdot}SO_2$ but gives shorter N–S bonds for the larger complexes. The N–S distance of $TMA{\cdot}SO_2$ is shortened dramatically by 0.18

Table IV. Calculated Total Energies (hartrees), Zero-Point Energies (ZPE, kcal mol^{-1}), Thermal Corrections ($H - H_0$, kcal mol^{-1}), and Dipole Moments (μ, D) of Amine·SO_2 Complexes and Related Species

	total energy					
	HF/6-31G(d)	MP2/6-31G(d)	MP3/6-31+G(2d,p)	ZPE[a]	$H - H_0$[a]	μ[b]
NH_3	−56.184 36	−56.357 38	−56.420 21	23.22	1.79	2.19 (1.69)
MA	−95.209 83	−95.514 44	−95.604 54	43.24	2.09	1.53 (1.57)
DMA	−134.238 85	−134.678 10	−134.795 43	62.41	2.67	1.14 (1.16)
TMA	−173.269 30	−173.846 47	−173.990 97	81.27	3.27	0.74 (0.74)
SO_2	−547.169 01	−547.700 10	−547.744 40	5.03	1.89	2.19 (1.62)
$NH_3{\cdot}SO_2$	−603.365 06	−604.068 69	−604.174 91	29.91	4.16	3.76 (3.38)
$MA{\cdot}SO_2$	−642.391 49	−643.229 46	−643.362 92	49.89	4.60	3.86 (3.66)
$DMA{\cdot}SO_2$	−681.420 59	−682.394 57	−682.555 76	68.92	5.31	3.78 (4.01)
$TMA{\cdot}SO_2$	−720.451 35	−721.567 97	−721.755 75	87.91	5.85	3.89 (4.48)
$(NH_3)_2{\cdot}SO_2$	−659.557 87	−660.434 72	−660.602 85	54.32	6.73	1.70 (0.49)
$MA_2{\cdot}SO_2$	−737.610 09	−738.755 38	−738.977 33	94.12	7.71	2.48 (1.82)
$DMA_2{\cdot}SO_2$	−815.668 38			132.18	9.12	1.96
$TMA_2{\cdot}SO_2$	−893.729 35			169.94	10.31	2.49

[a] Calculated using the HF/6-31(d) optimized geometries. [b] HF/6-31G(d) values, with MP2/6-31G(d) value in parentheses.

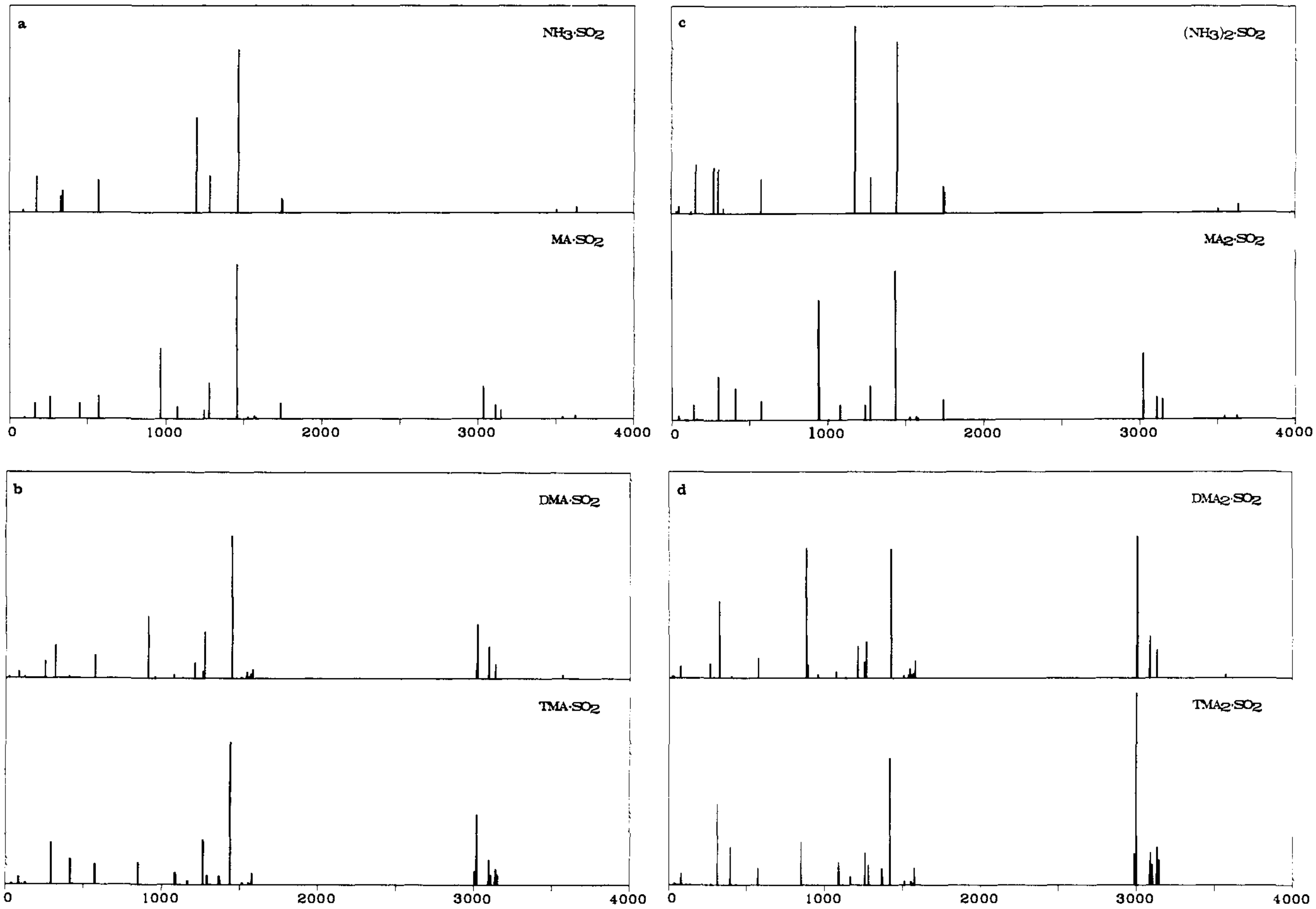

Figure 4. Computed IR spectra of the 1:1 and 2:1 amine$\cdot$SO$_2$ charge-transfer complexes: (a) $NH_3\cdot SO_2$ and $MA\cdot SO_2$; (b) $DMA\cdot SO_2$ and $TMA\cdot SO_2$; (c) $(NH_3)_2\cdot SO_2$ and $MA_2\cdot SO_2$; (d) $DMA_2\cdot SO_2$ and $TMA_2\cdot SO_2$.

Table V. Calculated Enthalpies of Complex Formation (ΔH,[a] kcal mol^{-1}) at Room Temperature (298 K)

molecules	HF/ 6-31G(d)	MP2/ 6-31G(d)	MP3/ 6-31+G(2d,p)	QCISD(T)/ 6-31+G(2d,p)
$NH_3\cdot SO_2$	5.37	5.06	4.49	4.00
$MA\cdot SO_2$	5.87	7.29	6.70	
$DMA\cdot SO_2$	5.91	8.19	7.93	
$TMA\cdot SO_2$	5.94	11.29	10.65	
$(NH_3)_2\cdot SO_2$	3.45	3.58	3.00	
$MA_2\cdot SO_2$	3.59	5.29	4.28	
$DMA_2\cdot SO_2$	3.90			
$TMA_2\cdot SO_2$	3.79			

[a] ΔH is obtained by adding scaled Δ(ZPE) and $\Delta(H - H_0)$ to ΔE (Table IV).

Å in going from the HF to MP2 levels of theory, and the calculated stabilization energy increases by 4 kcal mol^{-1}. The effect of electron correlation is progressively larger in going from $NH_3\cdot SO_2$ to $TMA\cdot SO_2$, indicating the danger of using the results of smaller complexes to estimate uncertainties for the larger systems. Large electron correlation effects have been reported for other donor-acceptor complexes, such as $BH_3\cdot CO$.[11] In summary, both basis set and electron correlation are found to have profound effects on the calculated geometries and stabilities of the amine$\cdot$SO$_2$ complexes.

The most stable geometries of the 1:1 and 2:1 molecular complexes between methyl-substituted amines and SO$_2$ are shown in Figure 1. All structures were found to favor a conformation with the SO$_2$ plane almost perpendicular to the N–S axis. The stabilities of the various conformations of $NH_3\cdot SO_2$ have been studied by Sakaki et al.[8a] The preference of a perpendicular coordination mode over the coplanar coordination mode was explained in terms of the unfavorable lone-pair repulsion in the coplanar coordination structure. The complete set of optimized structural parameters, except for the methyl hydrogens, for the 1:1 and 2:1 complexes at HF/6-31G(d) and MP2/6-31G(d) levels are collected in Table II. All complexes are characterized by long N–S equilibrium bond

Table VI. Calculated Atomic Charges[a,b]

atom[c]	$NH_3\cdot SO_2$	$MA\cdot SO_2$	$DMA\cdot SO_2$	$TMA\cdot SO_2$	$(NH_3)_2\cdot SO_2$	$MA_2\cdot SO_2$
S	2.652 (0.043)	2.647 (0.038)	2.635 (0.026)	2.614 (0.005)	2.686 (0.077)	2.680 (0.071)
O	−1.345 (−0.040)	−1.362 (−0.057)	−1.382 (−0.077)	−1.395 (−0.090)	−1.372 (−0.067)	−1.390 (−0.085)
N	−1.168 (−0.050)	−1.203 (−0.085)	−1.305 (−0.089)	−1.413 (−0.108)	−1.164 (−0.046)	−1.167 (−0.049)
H_1	0.397 (0.019)	−0.022 (0.032)	0.403 (0.051)	−0.059 (0.031)	0.391 (0.018)	−0.031 (0.024)
H_2	0.405 (0.032)	−0.064 (0.025)	−0.058 (0.029)	−0.010 (0.046)	0.401 (0.028)	−0.007 (0.012)
H_3		0.392 (0.032)	−0.011 (0.044)	−0.045 (0.032)		0.372 (0.012)
H_4			−0.048 (0.010)	−0.054 (0.002)		
H_5				−0.005 (0.051)		
C_1		0.615 (0.012)	0.634 (0.000)	0.617 (−0.019)		0.605 (−0.022)
C_2				0.627 (−0.009)		
CT[d]	0.038	0.077	0.129	0.176	0.029	0.050

[a] HF/6-31+G(d,p)//MP2/6-31G(d) wavefunctions. [b] Numbers in parentheses refer to charge changes as a result of complex formation. [c] Atomic labels are illustrated in Figure 1. [d] Total number of electrons transferred from amine to SO$_2$.

Table VII. Topological Properties (au) at N-S and S-O Bond Critical Points[a]

molecule	ρ_b	$\nabla^2\rho_b$	H_b	bo[b]	ϵ
		N-S Bond			
$NH_3\cdot SO_2$	0.021	0.058	0.001	0.123	0.026
$MA\cdot SO_2$	0.031	0.076	−0.001	0.186	0.023
$DMA\cdot SO_2$	0.044	0.090	−0.003	0.270	0.045
$TMA\cdot SO_2$	0.056	0.091	−0.008	0.382	0.091
$(NH_3)_2\cdot SO_2$	0.017	0.052	0.009	0.110	0.016
$MA_2\cdot SO_2$	0.025	0.066	0.002	0.165	0.031
		S-O Bond			
SO_2	0.273	1.234	−0.294	1.430	0.203
$NH_3\cdot SO_2$	0.274	1.230	−0.296	1.364	0.183
$MA\cdot SO_2$	0.274	1.203	−0.297	1.339	0.171
$DMA\cdot SO_2$	0.274	1.172	−0.299	1.308	0.152
$TMA\cdot SO_2$	0.273	1.128	−0.300	1.282	0.140
$(NH_3)_2\cdot SO_2$	0.274	1.223	−0.297	1.346	0.173
$MA_2\cdot SO_2$	0.273	1.186	−0.298	1.316	0.158

[a] HF/6-31+G(d,p)//MP2/6-31G(d) wavefunctions. [b] Covalent bond order.

lengths, 2.36–2.86 Å. The strength of the donor–acceptor interaction is reflected in the N-S bond length. Table II shows the progressive shortening of N-S distance in going from $NH_3\cdot SO_2$ to $MA\cdot SO_2$, to $DMA\cdot SO_2$, and to $TMA\cdot SO_2$. A similar trend of N-S bond length is predicted for the 2:1 adduct series. The calculated N-S equilibrium distances of the 2:1 complexes are longer, by about 0.2 Å, than those of the corresponding 1:1 complexes, suggesting that the intermolecular interactions in the 2:1 adducts are weaker. In accordance with the trend in N-S bond length, the calculated tilt angles of the SO_2 plane off the N-S axis (α) decrease with increasing numbers of methyl group in the CT complexes. The calculated structure of $TMA\cdot SO_2$ is in close agreement with the microwave data.[2]

A comparison of the geometries of the SO_2 subunit of the CT complexes with the SO_2 monomer reveals structural features which can be explained by the order of donor–acceptor interaction. It is clear from Table II that donation of electronic charge from amine to SO_2 leads to a longer S–O distance and a smaller OSO angle. The magnitude of the SO_2 perturbation in the 1:1 complex series follows closely the sequence of donor ability of amine established above. The results for the 2:1 adducts also follow the trend. When SO_2 accepts electrons from two amine donors, the changes in S–O bond length and OSO angle are greater in the 2:1 complexes than in the corresponding 1:1 adducts.

It is interesting to note that the hydrogens and methyl groups of the amine subunit are strongly tilted towards the SO_2 moiety. For instance, in $NH_3\cdot SO_2$ the hydrogens eclipsed to the SO_2 group have a significantly smaller bond angle (∠HNS = 105.2°) than that of the staggered hydrogen (∠HNS = 123.0°). In fact, short O···H contact distances, about 2.7 Å, are observed in $DMA\cdot SO_2$ and $TMA\cdot SO_2$. This suggests that the conformation of these amine·SO_2 complexes are in part determined by the favorable nonbonding O···H interactions. For example, $NH_3\cdot SO_2$ prefers an eclipsed conformation. This is readily explained by the fact that the eclipsed conformer has two favorable O···H interactions,

Table VIII. Calculated Vertical Transition Energies (TE, nm)[a]

	1st excited state			2nd excited state			3rd excited state			4th excited state			5th excited state		
molecule	TE	f[b]	sym	TE	f[b]	sym	TE	f[b]	sym	TE	f[b]	sym	TE	f[b]	sym
$NH_3\cdot SO_2$	283	0.024	A′	242	0.000	A″	188	0.113	A″	161	0.208	A′	147	0.064	A′
$MA\cdot SO_2$	274	0.036	A′	233	0.000	A″	184	0.092	A″	174	0.253	A′	158	0.002	A′
$DMA\cdot SO_2$	268	0.066	A′	222	0.000	A″	179	0.292	A′	179	0.081	A″	158	0.006	A′
$TMA\cdot SO_2$	258	0.088	A′	213	0.001	A″	180	0.351	A′	180	0.060	A″	151	0.064	A′
$(NH_3)_2\cdot SO_2$	270	0.035	B_2	230	0.000	A_2	182	0.102	B_1	182	0.010	A_1	153	0.483	B_2
$MA_2\cdot SO_2$	257	0.058	B_2	217	0.000	A_1	167	0.071	B_1	168	0.005	A_1	166	0.337	B_2

[a] CIS/6-311+G(d,p)//MP2/6-31G(d) values. [b] Oscillator strength.

Table IX. Calculated Harmonic Vibrational Frequencies[a]

molecule	frequency
$NH_3\cdot SO_2$	20 (A″), 95 (A″), 132 (A′), 186 (A′), 349 (A′), 2362 (A″), 604 (A′), 1262 (A′), 1352 (A′), 1543 (A″), 1837 (A″), 1844 (A″), 3690 (A′), 3824 (A′), and 3825 (A″)
$MA\cdot SO_2$	26 (A″), 100 (A″), 101 (A′), 169 (A′), 208 (A″), 274 (A′), 472 (A″), 601 (A′), 1017 (A′), 1061 (A″), 1130 (A′), 1311 (A′), 1345 (A′), 1476 (A″), 1533 (A″), 1607 (A′), 1650 (A′), 1661 (A″), 1829 (A′), 3195 (A′), 3277 (A′), 3313 (A″), and 3815 (A″)
$DMA\cdot SO_2$	24 (A″), 86 (A″), 89 (A′), 129 (A′), 192 (A″), 236 (A″), 266 (A′), 334 (A′), 429 (A′), 602 (A′), 959 (A′), 1006 (A′), 1133 (A″), 1193 (A″), 1274 (A″), 1330 (A′), 1340 (A′), 1525 (A″), 1589 (A″), 1621 (A′), 1626 (A″), 1637 (A″), 1652 (A′), 1661 (A′), 1664 (A″), 3175 (A″), 3181 (A′), 3254 (A″), 3302 (A′), 3303 (A″), and 3755 (A′)
$TMA\cdot SO_2$	41 (A″), 90 (A′), 111 (A″), 134 (A′), 204 (A″), 247 (A″), 283 (A″), 284 (A′), 308 (A′), 437 (A′), 458 (A1), 460 (A″), 602 (A′), 893 (A′), 1142 (A′), 1146 (A″), 1176 (A″), 1227 (A′), 1227 (A″), 1331 (A′), 1357 (A′), 1438 (A′), 1442 (A″), 1514 (A″), 1594 (A′), 1594 (A″), 1636 (A″), 1637 (A′), 1638 (A″), 1638 (A′), 1660 (A″), 1660 (A′), 1661 (A′), 3165 (A), 3165 (A″), 3178 (A′), 3256 (A″), 3261 (A′), 3274 (A′), 3302 (A″), 3306 (A′), and 3316 (A″)
$(NH_3)_2\cdot SO_2$	35 (B_1), 35 (A_2), 51 (B_1), 54 (A_1), 104 (A_2), 115 (A_1), 135 (B_2), 166 (B_2), 287 (A_1), 319 (B_1), 323 (A_2), 355 (B_2), 610 (A_1), 1239 (B_2), 1242 (A_1), 1348 (A_1), 1523 (B_1), 1838 (A_2), 1839 (B_1), 1846 (B_2), 1846 (A_1), 3692 (B_2), 3692 (A_1), 3826 (B_2), 3826 (A_1), 3827 (A_2), and 3827 (B_1)
$MA_2\cdot SO_2$	14 (A_2), 16 (B_1), 46 (B_1), 49 (A_1), 92 (A_1), 105 (A_2), 110 (B_2), 147 (B_2), 170 (A_1), 188 (B_1), 207 (A_2), 316 (B_2), 429 (A_2), 430 (B_1), 605 (A_1), 992 (B_2), 996 (A_1), 1059 (A_2), 1059 (B_1), 1136 (B_2), 1137 (A_1), 1305 (B_2), 1305 (A_1), 1340 (A_1), 1477 (A_2), 1478 (B_1), 1511 (B_1), 1607 (B_2), 1607 (A_1), 1650 (B_2), 1651 (A_1), 1661 (A_2), 1662 (B_1), 1831 (B_2), 1831 (A_1), 3182 (B_2), 3182 (A_1), 3272 (B_2), 3272 (A_1), 3311 (A_2), 3311 (B_1), 3731 (B_2), 3731 (A_1), 3815 (A_2), and 3815 (B_1)
$DMA_2\cdot SO_2$	16 (A_2), 24 (B_1), 35 (A_1), 39 (B_1), 72 (A_2), 73 (A_1), 79 (B_2), 129 (B_2), 142 (B_1), 168 (A_1), 195 (A_2), 242 (A_2), 242 (B_1), 280 (B_2), 304 (A_1), 343 (B_1), 425 (A_1), 426 (B_2), 606 (A_1), 931 (B_2), 940 (A_1), 1009 (B_2), 1010 (A_1), 1132 (A_2), 1132 (B_1), 1195 (A_2), 1195 (B_1), 1278 (A_2), 1278 (B_1), 1323 (A_1), 1323 (B_2), 1334 (A_1), 1390 (B_2), 1390 (A_1), 1503 (B_1), 1588 (A_2), 1589 (B_1), 1620 (B_2), 1621 (A_1), 1628 (A_2), 1630 (B_1), 1637 (A_2), 1638 (B_1), 1652 (B_2), 1652 (A_1), 1662 (B_2), 1663 (A_1), 1665 (A_2), 1665 (B_1), 3159 (A_2), 3159 (B_1), 3166 (B_2), 3166 (A_1), 3245 (A_2), 3245 (B_1), 3249 (B_2), 3249 (A_1), 3295 (A_2), 3296 (B_1), 3297 (B_1), 3297 (A_1), 3760 (B_1), and 3760 (A_1)
$TMA_2\cdot SO_2$	22 (A_2), 39 (B_1), 41 (A_1), 48 (B_1), 66 (A_1), 85 (B_2), 92 (A_2), 117 (B_2), 141 (A_1), 147 (B_1), 200 (A_2), 254 (A_2), 254 (B_1), 284 (B_2), 284 (A_1), 286 (A_2), 286 (B_1), 330 (B_2), 418 (B_1), 423 (A_1), 457 (A_1), 458 (B_2), 459 (B_1), 460 (A_2), 604 (A_1), 896 (B_2), 900 (A_1), 1146 (B_2), 1147 (A_1), 1150 (A_2), 1151 (B_1), 1175 (A_2), 1175 (B_1), 1228 (A_2), 1228 (B_1), 1228 (B_2), 1228 (A_1), 1326 (A_1), 1350 (B_2), 1350 (A_1), 1440 (B_2), 1440 (A_1), 1445 (B_1), 1445 (A_2), 1495 (B_1), 1593 (A_2), 1594 (B_2), 1594 (B_1), 1594 (A_1), 1636 (A_2), 1637 (B_2), 1637 (B_1), 1638 (A_1), 1639 (A_2), 1639 (B_2), 1639 (B_1), 1639 (A_1), 1660 (B_2), 1660 (A_2), 1660 (A_1), 1661 (B_2), 1661 (A_1), 3145 (A_1), 3145 (B_1), 3145 (A_2), 3145 (B_1), 3158 (B_2), 3159 (A_1), 3247 (A_2), 3247 (B_1), 3253 (B_2), 3253 (A_1), 3267 (B_2), 3268 (A_1), 3293 (A_2), 3293 (B_1), 3297 (B_2), 3298 (A_1), 3310 (A_2), and 3311 (B_1)

[a] Unscaled HF/6-31G(d) values.

whereas the staggered conformer only has one.

To further investigate the effect of basis set on the binding energies (ΔE) of amine$\cdot$SO$_2$ complexes, we have calculated the binding energies of both $NH_3\cdot SO_2$ and TMA$\cdot$SO$_2$ with a sequence of basis sets, 6-31G(d), 6-31G(d,p), 6-31+G(d), 6-31G(2d), and 6-311G(d),[11] at the HF level. Significant changes occur in going from 6-31G(d) to 6-31+G(d), i.e., inclusion of diffuse sp functions on heavy atoms and from 6-31G(d) to 6-31G(2d), i.e., expanding the basis set from one set of d-polarization functions to two. In particular, the use of a second set of d-polarization functions on heavy atoms leads to a lowering of binding energy by almost 2 kcal mol^{-1} (Table III). On the other hand, the effects of p-polarization functions on hydrogen atoms (6-31G(d) → 6-31G(d,p)) and increasing the basis set from double-ζ valence to triple-ζ valence (6-31G(d) → 6-311G(d)) are very small. Thus, the 6-31+G(2d,p) basis set should be adequate for electron correlation calculations. A similar conclusion has been reported for the sulfamic acid zwitterion ($NH_3\cdot SO_3$) complex.[19] As mentioned above, correction for electron correlation is more important for the larger amine$\cdot$SO$_2$ complexes. In going from the HF to MP2 levels of theory, ΔE of TMA$\cdot$SO$_2$ increases by 5.1 kcal mol^{-1}, whereas the ΔE value of $NH_3\cdot SO_2$ is almost unchanged (Table III).

The amine$\cdot$SO$_2$ complexes can be considered as donor–acceptor adducts of the amine with sulfur dioxide. The N–S bond in these molecules results from the donation of the lone pair electrons of amine to the empty 3p$_z$ orbital of sulfur dioxide. The actual strength of the N–S bond will depend on the electron donor ability of the amine, and the strength of the donor–acceptor interaction in these complexes can be determined by the following complex formation reactions:

$$\text{amine} + SO_2 \rightarrow \text{amine}\cdot SO_2 + \Delta H$$

$$\text{amine} + \text{amine}\cdot SO_2 \rightarrow (\text{amine})_2\cdot SO_2 + \Delta H$$

The calculated enthalpies of complex formation (ΔH, 298 K) at the MP3/6-31+G(2d,p)//MP2/6-31G(d) level are summarized in Table V. Our higher-level calculations confirm earlier theoretical findings by Douglas and Kollman on the order of 1:1 amine$\cdot$SO$_2$ affinities (TMA > DMA > MA > NH$_3$).[8b] The stabilization energies increase almost monotonically as a function of the number of methyl groups in the amine donor. In other words, the effect of successive replacement of hydrogen atoms of ammonia by methyl groups on the value of ΔH is almost additive. This is of course consistent with the chemical intuition that a methyl group is a much better electron-donating group than is a hydrogen. These results are also consistent with the experimental studies of the CT complexes between I$_2$ and amines in hydrocarbon solvents, which established the same order of strength of interaction for the methyl-substituted amines.[20] According to the frontier orbital theory,[21] the strength of the donor–acceptor interaction can be related to the energy of the highest occupied molecular orbital (HOMO) of the donor. An amine molecule with a higher-lying HOMO is a better donor and shows a larger stabilization energy compared to species with a lower HOMO. This is readily shown by a plot of the eigenvalues of the HOMO of amines against the computed stabilization energies relative to amine and SO$_2$ (Figure 2). The computed ΔH for TMA$\cdot$SO$_2$ (10.7 kcal mol^{-1}) agrees well with the gas-phase experimental value of 9.7 kcal mol^{-1}.[4b,c] However, our calculated ΔH value for $NH_3\cdot SO_2$ (4.5 kcal mol^{-1}) is significantly smaller than the experimental estimate (7.7 kcal mol^{-1}) in the solid phase.[8a] To obtain a more definitive theoretical estimate of the formation enthalpy of $NH_3\cdot SO_2$, we have also performed energy calculations with a higher-level treatment of electron correlation using quadratic configuration interaction with singles and doubles and with correction for triple excitation (QCISD(T)).[22] The higher-level QCISD(T) value (4.0 kcal mol^{-1}) is close to the MP3 estimate. The basis set superposition error was estimated for the $NH_3\cdot SO_2$ complex using the counterpoise method.[15] This is recognized to overestimate the correction for weakly bound complexes[23] but should provide an upper limit. Using the 6-31+G(2d,p) basis set, the correction was found to be 0.67, 1.41, and 1.37 kcal mol^{-1} at the HF, MP2, and MP3 levels of theory, respectively. Therefore the calculated binding energy after this correction is 3 kcal mol^{-1}. Thus, the difference between the calculated and experimental values can be attributed to medium effect on this CT complex.

As is evident in Table V, all the 2:1 CT complexes are calculated to be thermodynamically stable with respect to dissociation to amine and the corresponding 1:1 complex and are predicted to be experimentally observable. The trend of stability follows that in the 1:1 complex series. The existence of the smallest 2:1 complex has been demonstrated by a matrix infrared study at a high concentration of ammonia.[5] However, there is no evidence of the existence of the larger 2:1 adducts, in sharp contrast to the calculated stabilities for these species.

Finally, we note that all the 1:1 amine$\cdot$SO$_2$ complexes are very polar molecules with large calculated dipole moments (Table IV). Thus, the introduction of a polarizable dielectric medium would have a strong influence on the geometries and energies of these donor–acceptor complexes. Indeed, a strong medium effect has been observed for TMA$\cdot$SO$_2$: the N–S distance in the crystal structure[3] is 0.22 Å shorter than the gas-phase value,[2] and the measured formation enthalpy increases by 2 kcal mol^{-1} in going from the gas phase to heptane solution.[4] Further studies are in progress on the solvent effects on the structures and stabilities of these amine$\cdot$SO$_2$ charge-transfer complexes.[24]

Charge Distributions and Topological Properties

While the calculated structural parameters and binding energies account for most of the features found for the amine$\cdot$SO$_2$ charge-transfer complexes, the electron density analysis, defined within the framework of Bader's theory of atoms in molecules,[9] will provide further insight into the nature of the interaction between the complex components (amine donor and SO$_2$ acceptor). First, we consider the charge distributions of these donor–acceptor complexes. The atomic charges, given by the nuclear charges less the electron populations, are given in Table VI. As can be seen from the table, the S, O, and N atoms, as well as all the hydrogens and carbons adjacent to the N atom, bear relatively strong charges. In fact, these atoms form an alternating charge distribution on the O–S–N–H and/or O–S–N–C skeletons of all complexes considered. It thus appears that the stabilization of the N–S bond in the amine$\cdot$SO$_2$ complexes is in part due to the strong electrostatic attraction. These results are consistent with previous theoretical findings for the bonding characteristics of donor–acceptor complexes.[25]

The atomic charges given in Table VI may appear rather large. Those for S and O are about twice that found with the Mulliken population analysis, whereas those for the amine part are close to the Mulliken populations. The charges are the first term of a Taylor's series expansion which includes atomic dipoles, quadrupoles, and higher moments. Thus, in order to reproduce the molecular dipole moments one must use both the charges and the atomic dipoles which result from the fact that the center of charge distribution at an atom does not coincide with the nuclear position.[9] Unlike the Mulliken charges, those derived via numerical integration of the charge density have only a small sensitivity to the basis set used.[26] The atoms in molecules approach has been

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(26) Wiberg, K. B.; Wendoloski, J. J. *Proc. Nat. Acad. Sci.* **1981**, *78*, 6561. Isobutene provides a dramatic example of basis set dependency of the Mulliken population. Using the 6-31G* basis set the central carbon is calculated to have a +0.1 eV charge, and with the 6-311++G** basis set the charge increases to 1.0 eV.

Table X. Calculated SO_2 Fundamental Frequencies of Amine·SO_2 Complexes[a]

	ν_1			ν_2			ν_3		
molecule	calcd	expt[b]	shift[c]	calcd	expt[b]	shift[c]	calcd	expt[b]	shift[c]
SO_2	515	526		1182	1167		1365	1381	
NH_3·SO_2	524	530	9	1177	1038	−5	1343	1350	−22
MA·SO_2	523	538	8	1170		−12	1334	1338	−31
DMA·SO_2	524	527	9	1166		−16	1326	1309	−39
TMA·SO_2	524		9	1158	1120	−24	1317	1277	−48
$(NH_3)_2$·SO_2	530		15	1173		−9	1325	1310	−40
MA_2·SO_2	526		11	1165		−17	1315		−50
DMA_2·SO_2	527		12	1161		−21	1307		−58
TMA_2·SO_2	526		11	1153		−29	1301		−64

[a] HF/6-31G(d) values; scaled by 0.87. [b] From ref 5. [c] Calculated frequency change upon complex formation.

found to be very useful in the study of a variety of chemical problems.[10,27]

Next, we consider the effect of complex formation on the charge density distributions of the donor and acceptor subunits. The calculated changes in atomic charges in going from the reactants to the complex are summarized in Table VI. The main effect of donor–acceptor formation on SO_2 is to increase the electron population at the oxygen atoms. The trend of electron population increase at oxygens confirms the order of the electron-donating ability of amines (TMA > DMA > MA > NH_3). For the amine subunit, the nitrogen atom donates charge to the SO_2 acceptor but receives compensation from carbons and hydrogens. The net result is a building up of charge at nitrogen compared to its amine value, and all hydrogens and most carbons become more positive upon complex formation. In other words, both the donor and acceptor components show a larger degree of charge separation as a result of complex formation. Hence, substantial electrostatic intermolecular interactions would be expected between the amine donor and the SO_2 acceptor.

As pointed out by a previous Morokuma component analysis of the energetics of the complex formation between amine and SO_2,[8a,b] charge transfer is a very important term in determining the stability of the amine·SO_2 complexes. The smallest 1:1 complex, NH_3·SO_2, shows only a small amount of charge transfer (0.04 eV) from the NH_3 group to the SO_2 moiety. However, there is a progressive increase in the amount of charge transfer in going from NH_3·SO_2 to TMA·SO_2 (Table VI). For the large TMA·SO_2 complex, 0.18 eV is predicted for the amount of charge transfer, in good accord with the upper limit (0.2–0.3 eV) estimated from experimental dipole moment and the nitrogen nuclear quadrupole coupling constant.[2a] The CT values of the 2:1 complexes are smaller than those of the corresponding 1:1 complexes. There are strong correlations between the trends in N–S bond length, stabilization energy, and the CT values. In general, the stronger the N–S bond, the greater the extent to which the reactants' charge distributions are perturbed. Note that the degree of charge transfer is also reflected in the magnitude of S–O bond lengthening upon complex formation (Table II).

Finally, we consider the intermolecular interaction between amine and sulfur dioxide in terms of topological properties calculated at the N–S and S–O bond critical points. It has been shown that the investigation of the Laplacian ($\nabla^2\rho_b$) and local energy density (H_b) provides a useful means to distinguish between shared and closed-shell interactions.[28,29] The sign of the Laplacian of the charge density ($\nabla^2\rho_b$) indicates whether there is a local concentration ($\nabla^2\rho_b < 0$) or a local depletion ($\nabla^2\rho_b > 0$) of charge.[28] The local energy density (H_b) is defined as the sum of the local potential energy density (V_b) and local kinetic energy density (G_b). Since V_b is always negative and G_b is always positive, the sign of H_b reveals whether the accumulation of electron density at the bond critical point is stabilizing ($H_b < 0$) or destabilizing ($H_b > 0$). For a covalent bond, the local energy density at the bond critical point is always negative (stabilizing).[29] As is evident in Table VII, the N–S bonds of the amine·SO_2 complexes exhibit the characteristics of a closed-shell interaction. At the N–S bond critical point, $\nabla^2\rho_b > 0$ and $H_b \sim 0$, i.e., both the electrostatic and the energetic aspects of a shared interaction are not satisfied. Note that the weak N–S bonds of the CT complexes are readily reflected by the small values of ρ_b. In accordance with the trend of N–S bond length, greater covalent character is found for the N–S bond of the larger amine·SO_2 complexes. This is also reflected by the greater magnitude of ρ_b and smaller values of $\nabla^2\rho_b$ and H_b (Table VII). Significant bond ellipticity is also calculated for the N–S bond in these CT complexes. It is interesting to examine the effect of complex formation on the topological properties of the S–O bond critical point. First, we note that the changes in electronic density (ρ_b) and local energy density (H_b) are small. There is a significant increase of $\nabla^2\rho_b$ value in going from NH_3·SO_2 to TMA·SO_2. In contrast, the calculated ellipticity (ϵ) and bond order decrease with increasing number of methyl groups in the complexes. These results indicate that the electron density received from the amine donor is accumulated mainly at the oxygen atoms.

In summary, the N–S donor–acceptor bonds in the CT complexes are characterized by weak intermolecular interactions, dominated by strong electrostatic forces. The stabilities of these complexes are determined by the degree of charge transfer.

Ultraviolet Spectra

UV spectroscopy represents one of the most important experimental techniques for studying charge-transfer complexes.[1] For TMA·SO_2, it shows a characteristic strong absorption band, the so-called charge-transfer band, at the 270–280-nm region.[4] Here, we have calculated the first five transition energies of all the 1:1 complexes as well as the two smaller 2:1 complexes, $(NH_3)_2$·SO_2 and MA_2·SO_2, using the configuration interaction including all singly excited configurations (CIS) approach.[16] The 6-311+G(d,p) basis set was used for the CIS calculations, based on the MP2/6-31G(d) optimized geometries, and the results are summarized in Table IX. Recent studies on the CIS energies have shown that the use of two sets of diffuse functions on heavy atoms is important for the proper description of excited states.[16,30] However, a preliminary study on NH_3·SO_2 and TMA·SO_2 has shown that the change from using one to two sets of diffuse functions is very small. Hence, the 6-311+G(d,p) basis set should be adequate for reliable prediction of the lower transition energies for the amine·SO_2 complexes. The charge-transfer band of TMA·SO_2 measured by experiment corresponds to the first-excited-state transition. The calculated lowest transition energy for TMA·SO_2 is 258 nm, in good accord with the experimental value of 276 nm.[4b,c] The corresponding CT bands for NH_3·SO_2, DMA·SO_2, and DMA·SO_2 are predicted to be 283, 274, and 268 nm, respectively. The charge density distributions were calculated, and the differences from the ground-state distribution were ob-

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tained to gain additional information concerning the excited states of these CT complexes. Contour plots of the charge density differences are shown in Figure 3. It can be seen that the first-excited-state transition corresponds to a $n\rightarrow\pi^*$ transition. Thus, there is a progressive increase in the $n\rightarrow\pi^*$ energy gap in going from $NH_3{\cdot}SO_2$ to $TMA{\cdot}SO_2$. For $NH_3{\cdot}SO_2$ the second, third, and fourth excited states also correspond to $n \rightarrow \pi^*$ transitions. However, the fifth state strongly resembles a diffuse s orbital (Figure 3).

Vibrational Frequencies and Infrared Spectra

To facilitate future characterization of the 1:1 and 2:1 amine·SO_2 CT complexes in the gas phase, we have reported the complete set of calculated (unscaled) harmonic frequencies (Tables IX) and their computed infrared spectra (Figure 4). First, we note that the bending mode of SO_2 is the dominant band in all spectra. The calculated frequency changes of the antisymmetric (ν_1) and symmetric (ν_2) stretching and bending (ν_3) vibrations of the SO_2 subunit are presented in Table X. Vibrational frequencies of SO_2 calculated at the HF/6-31G(d) level are found to be an average ~15% greater than the experimental frequencies,[31] and therefore the fundamental frequencies of the SO_2 subunit calculated here are scaled by 0.87 for comparison with experiment. As can be seen in Table X, the calculated ν_1 shifts are at higher wavenumbers relative to the monomer SO_2, whereas both ν_2 and ν_3 shifts are at lower wavenumbers. These results are in good accord with the experimental data.[5] The frequency shifts for ν_1 are relatively constant. On the other hand, there is a progressive increase in the magnitude of ν_2 and ν_3 shifts in both the 1:1 and 2:1 series, with larger shifts predicted for the 2:1 series. The trend of the frequency shifts correlates well with the strength of the donor-acceptor interaction. The calculated ν_2 and ν_3 shifts are smaller than the experimental values. These differences are attributed to the deficiencies of the HF/6-31G(d) geometries. Frequencies calculated at the MP2/6-31G(d) level should provide better comparisons with experiment.

Conclusions

Several interesting points have been revealed by this study: (1) Inclusion of electron correlation is essential for the proper description of the N-S donor-acceptor bond in the amine·SO_2 complexes, especially for the larger complexes such as $TMA{\cdot}SO_2$. The calculated N-S bond lengths of $NH_3{\cdot}SO_2$, $MA{\cdot}SO_2$, $DMA{\cdot}SO_2$, and $TMA{\cdot}SO_2$ at the MP2/6-31G(d) level are 2.80, 2.62, 2.46, and 2.36 Å, respectively. The calculated geometry of $TMA{\cdot}SO_2$ is in close agreement with the microwave data. (2) The enthalpies of formation (ΔH, 298 K) of $NH_3{\cdot}SO_2$, $MA{\cdot}SO_2$, $DMA{\cdot}SO_2$, and $TMA{\cdot}SO_2$, computed using the MP3/6-31+G(2d,p)//MP2/6-31(d) procedure, are 4.5, 6.7, 7.9, and 10.7 kcal mol^{-1}, respectively. The calculated ΔH value of $TMA{\cdot}SO_2$ agrees well with the experimental value of 9.7 kcal mol^{-1}. The trends of binding energy and N-S bond length are in good accord with the chemical intuition that a methyl group is a stronger electron donor than hydrogen. (3) All the 2:1 CT complexes are predicted to be thermodynamically stable with respect to dissociation into the 1:1 complex and amine, with binding energies smaller than the corresponding 1:1 complexes. As $(NH_3)_2{\cdot}SO_2$ has been observed experimentally, the larger 2:1 complexes ($MA_2{\cdot}SO_2$, $DMA_2{\cdot}SO_2$, and $TMA_2{\cdot}SO_2$), with greater calculated formation enthalpies, should be experimentally accessible species. (4) The N-S bonds of the amine·SO_2 CT complexes exhibit characteristics of a weak closed-shell interaction, with strong electrostatic forces. The calculated amount of charge transfer correlates well with the stabilities of the amine·SO_2 donor-acceptor complexes. (5) The calculated charge-transfer band, corresponding to a transition of $TMA{\cdot}SO_2$ (at CIS/6-311+G(d,p) level), is 258 nm, in good accord with the experimental value of 276 nm. The corresponding CT bands for $NH_3{\cdot}SO_2$, $DMA{\cdot}SO_2$, and $DMA{\cdot}SO_2$ are predicted to be 283, 274, and 268 nm, respectively. (6) Significant frequency shifts are calculated for the fundamental vibrations of SO_2 subunit as a result of complex formation. The calculated frequency shifts for the 1:1 CT complexes are consistent with the experimental data.

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Solvent Effects on the Barrier to Isomerization for a Tertiary Amide from ab Initio and Monte Carlo Calculations

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Abstract: The effects of solvation on the free energies of activation for rotation about the carbonyl C-N bond in *N*,*N*-dimethylacetamide (DMA) have been examined through a combination of gas-phase ab initio calculations and solution-phase statistical mechanics simulations. The geometries of the planar ground state and the transition states with the nitrogen lone-pair anti and syn to the oxygen were optimized with the 6-31G(d) basis set. Subsequent calculations of the vibrational frequencies and correlation energies (MP4(fc)SDTQ/6-31G(d)//6-31G(d)) predict $\Delta G^{\ddagger}$'s of 14.6 and 18.7 kcal/mol for the anti and syn transition states at 298 K. NMR measurements have yielded a gas-phase $\Delta G^{\ddagger}$ of 15-16 kcal/mol. Solute-solvent potential functions were refined by fitting to results of 6-31G(d) calculations for the ground and transition states interacting with a water molecule in 17 low-energy orientations. These potentials were used in Monte Carlo simulations that yielded the changes in free energies in solvation in TIP4P water and the OPLS model of carbon tetrachloride. The observed ca. 2-kcal/mol increase in $\Delta G^{\ddagger}$ for water versus the aprotic solvent was reproduced; however, only a 0.4-kcal/mol barrier increase was computed for CCl_4 relative to the gas phase, while the experimental shift is 1-2 kcal/mol. The discrepancy may come from amide aggregation and variations in the transmission coefficient, whereas an explanation involving activation volumes is rejected. It is also predicted that the syn transition state becomes competitive with the anti in water, and hydrogen bonding analyses clarify the origin of the differential hydration.

Introduction

The importance of cis/trans isomerization about peptide bonds is emphasized by the role of proline isomerization in protein folding and by the recent findings that the binding proteins (immunophilins) for the immunosuppressive agents cyclosporin A, FK506, and rapamycin are peptidyl-prolyl cis/trans isomerases (rota-

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