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Structure of the Dimethyl Ether–Sulfur Dioxide Complex

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The microwave spectrum of the dimethyl ether–sulfur dioxide complex has been observed with a pulsed molecular beam Fourier transform microwave spectrometer. The rotational constants of $(CH_3)_2O{\cdot}SO_2$ are A = 4536.747 (12), B = 1865.147 (3), and C = 1457.853 (2) MHz. In addition to the normal isotopic form, the rotational spectra of the $(CH_3)_2O{\cdot}^{34}SO_2$, $(CH_3)_2O{\cdot}S^{18}OO$, $(CH_3)_2O{\cdot}S^{18}O_2$, and $^{13}CH_3OCH_3{\cdot}SO_2$ species were assigned. Only transitions with a- and c-dipole selection rules were observed. Stark effect measurements gave electric dipole components of μ_a = 1.880 (2), μ_c = 0.591 (1) and μ_{tot} = 1.970 (2) D. The dipole moment and moment of inertia data show that the complex has C_s symmetry. The two monomers are separated by 3.05 (1) Å (R_{cm}). The structure of the complex, determined by fitting the moments of inertia, has the planes of the two monomer units in an approximately parallel planes stacked configuration with the oxygen atom of the ether over the sulfur atom of SO_2. The O–C bonds eclipse the S–O bonds in SO_2.

Introduction

The complexes of sulfur dioxide have intrigued investigators for over 50 years.[1-4] Recent high-resolution spectroscopic studies have provided structural details for a variety of SO_2 complexes. These include charge-transfer complexes of SO_2 with trimethylamine[5] (TMA) and dimethylamine[6] (DMA) as well as weaker N–S complexes with pyridine[7] and HCN.[8] Various van der Waals complexes of SO_2 have also been investigated, including complexes with Ar,[9] ethylene,[10] acetylene,[11] benzene,[7a] H_2S,[12,13] and H_2O[13] and hydrogen-bonded complexes with the HX acids.[14] These complexes show a structural diversity which can be roughly categorized according to whether SO_2 is a lone-pair acceptor ($TMA{\cdot}SO_2$, $H_2O{\cdot}SO_2$), a π acceptor ($C_2H_4{\cdot}SO_2$), or a proton acceptor ($SO_2{\cdot}HX$). Of all of these, the only complex in which SO_2 interacts with an oxygen donor is $H_2O{\cdot}SO_2$. This complex has a stacked near-parallel planes configuration with eclipsing OH and SO bonds. Since there has been considerable interest in methyl group effects on the basicity of both amines and ethers,[15] we were motivated to study the dimethyl ether–sulfur dioxide complex (hereafter $DME{\cdot}SO_2$) both to determine the structural consequences when both hydrogens on water are replaced by methyl groups and to compare with our earlier work on the isoelectronic $DMA{\cdot}SO_2$ complex.

There are three previous reports on the $DME{\cdot}SO_2$ complex. Analysis of the temperature dependence of the second compressibility virial coefficient gave 3.6 kcal/mol for the dissociation energy of the complex.[16a] An equilibrium constant of 20(3) was determined for the association reaction from the IR spectrum of the liquid mixture at −40 °C.[16b] A photoelectron spectroscopic study indicated that the ionization energy of the lone-pair n_O electrons of $(CH_3)_2O$ were stabilized by 0.36 eV while the IE of the highest n_S electrons of SO_2 were destabilized by 0.89 eV, consistent with an O···S interaction in the complex.[17] This was confirmed by geometry-optimized ab initio (HF/SCF) calculations. The geometric results are summarized in Table I and show a wide variation in the S···O distance with basis set. In all these calculations, the complex was assumed to have C_s symmetry and the O–C bonds eclipsed the S–O bonds in SO_2. It is interesting that the short calculated S···O distances at the 3-21G/3-21G* level are nearly the same as the N···S distance obtained from the rotational spectrum of the isoelectronic $DMA{\cdot}SO_2$ complex.[6] However, one of the methyl groups staggers the two oxygens on the sulfur dioxide, and consequently, $DMA{\cdot}SO_2$ has no symmetry plane. The calculated S···O distances for $DME{\cdot}SO_2$ can also be compared to the reported S···O distance in $H_2O{\cdot}SO_2$ of 2.82 Å.[13] Finally, the dissociation energy reported for $DME{\cdot}SO_2$ (3.6 kcal/mol)[16a] compared to the measured value for $TMA{\cdot}SO_2$ (9.1 kcal/mol)[18] is consistent with the usual expectation that ethers are weaker Lewis bases than amines. These comparisons further stimulated us to obtain detailed structural data for the $DME{\cdot}SO_2$ complex.

Table I. Ab Initio Structural Parameters (Å, deg) for $(CH_3)_2O{\cdot}SO_2$[a]

	STO-3G	3-21G	3-21G*[,c]
d(S···O)[b]	2.796	2.349	2.355
α[b]	25.6	37.7	30.3
β[b]	91.7	86.9	85.1

[a] From ref 17. [b] See Figure 1 for definitions. [c] Includes d polarization functions on the S atom.

Experimental Section

A mixture of 1% dimethyl ether (Aldrich Chemical Co.) and 1% SO_2 (Matheson Co.) seeded in Ar carrier gas at a total pressure of 1–2 atm was used to form the complex in a molecular beam using a supersonic expansion. The enriched $^{13}CH_3OCH_3$ (90% ^{13}C, MSD Isotopes) was used without dilution by normal DME. The $SO^{18}O$ sample was obtained by first mixing equal amounts of SO_2 and $S^{18}O_2$ (99% ^{18}O, Alfa Products) in a glass bulb, where they quickly equilibriated. The spectrum of the ^{34}S isotopic species was observed in its natural abundance of 4%.

A Fourier transform microwave spectrometer was used to measure the rotational spectrum of the complex.[19] It operated between 7.0 and 18.0 GHz. The operating conditions parallel those described in the study of the $TMA{\cdot}SO_2$ complex.[5] The calibration[20] and measurement procedure for determining the second-order Stark effects have already been described.[5,21]

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Table II. Observed Transition Frequencies for the Isotopic Species of $(CH_3)_2O{\cdot}SO_2$

	normal		^{34}S		$^{18}O_{(S)}$		$^{18}O_{2(S)}$		^{13}C	
transition	ν_{obs}[a]	$\Delta\nu$[b]	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$
$2_{11}-1_{01}$	10 130.498	0	10 054.123	0	9 931.400	−1	9 737.387	−1	10 000.046	−2
$3_{12}-2_{02}$	14 077.103	−3			13 829.941	0			13 893.753	1
$2_{20}-1_{10}$	15 108.458	2								
$2_{21}-1_{11}$	15 472.802	−2								
$5_{05}-4_{13}$	10 468.200	−2								
$3_{03}-2_{02}$	9 799.828	0	9 704.007	−1	9 643.967	−3	9 496.868	−3	9 664.740	−3
$3_{13}-2_{12}$	9 330.696	−3	9 242.461	−1	9 179.168	−2	9 036.090	0	9 200.946	−3
$3_{12}-2_{11}$	10 549.586	1	10 432.710	−1	10 400.242	−3	10 262.770	1	10 405.793	−3
$3_{22}-2_{21}$	9 961.278	2	9 857.608	−1	9 811.828	1	9 672.756	3	9 824.202	3
$3_{21}-2_{20}$	10 130.050	−3	10 018.278	−2	9 987.128	−2	9 856.284	0	9 990.966	−1
$4_{04}-3_{03}$	12 887.088	4	12 767.140	4	12 673.649	1	12 470.511	0	12 709.088	−1
$4_{14}-3_{13}$	12 397.105	1	12 281.442	−3	12 193.555	−4	12 000.891	−2	12 224.628	−2
$4_{13}-3_{12}$	14 009.021	1	13 856.147	2	13 807.344	3	13 620.811	−1	13 817.985	1
$4_{23}-3_{22}$	13 248.840	4	13 112.205	3	13 048.282	3	12 861.231	2	13 066.466	2
$4_{22}-3_{21}$	13 652.571	1	13 497.350	3	13 466.314	−1	13 297.218	−1	13 465.405	−2
$4_{32}-3_{31}$	13 345.780	18			13 149.096	11			13 162.117	12
$4_{31}-3_{30}$	13 362.601	−19								
$5_{05}-4_{04}$	15 867.419	2	15 726.225	1	15 595.871	3	15 336.114	2	15 647.748	4
$5_{15}-4_{14}$	15 433.317	1	15 291.419	−1	15 176.993	0	14 933.804	−1	15 218.468	−1
$5_{14}-4_{13}$	17 410.767	0	17 225.056	−2	17 153.887	3	16 914.675	2	17 173.180	4
$5_{24}-4_{23}$	16 508.434	−2	16 340.175	−1	16 255.690	0	16 019.312	−3	16 281.104	−1
$5_{23}-4_{22}$	17 252.703	−3	17 052.593	−1	17 022.458	−2	16 814.200	−1	17 016.583	−1
$5_{33}-4_{32}$	16 705.910	−9			16 523.240	6			16 476.067	−14
$5_{32}-4_{31}$	16 764.150	10			16 460.440	−15			16 533.588	4

[a] Observed frequency (ν_{obs}) in MHz. [b] Observed − calculated frequency in kHz.

Table III. Spectroscopic Constants for the Isotopic Species of $(CH_3)_2O{\cdot}SO_2$

	normal[a]	^{34}S	$^{18}O_{(S)}$	$^{18}O_{2(S)}$	^{13}C
no. of lines	24	16	20	16	20
A/MHz	4536.747 (12)	4526.695 (3)	4411.140 (6)	4283.669 (3)	4481.877 (6)
B/MHz	1865.147 (3)	1843.016 (1)	1840.662 (2)	1818.499 (1)	1839.952 (1)
C/MHz	1457.853 (2)	1445.340 (1)	1432.561 (1)	1408.431 (1)	1437.349 (1)
D_J/kHz	−2.94 (3)	−2.61 (1)	−3.31 (1)	−3.92 (1)	−2.93 (1)
D_{JK}/kHz	347.1 (5)	333.6 (1)	354.5 (1)	366.5 (1)	346.1 (1)
D_K/kHz	−329.9 (27)	−329.9[b]	−329.9[b]	−329.9[b]	−329.9[b]
d_1/kHz	−0.79 (3)	−0.75 (1)	−0.83 (2)	−0.86 (1)	−0.80 (2)
d_2/kHz	−3.72 (1)	−3.49 (1)	−3.93 (1)	−4.22 (1)	−3.69 (1)
H_{JK}/kHz	0.025 (7)	0.025[b]	0.025[b]	0.025[b]	0.025[b]
H_{KJ}/kHz	−0.84 (1)	−0.84[b]	−0.84[b]	−0.84[b]	−0.84[b]
$\Delta\nu_{rms}$[c]/kHz	6.3	1.9	4.8	1.6	4.6

[a] The constants obtained using the Watson A reduction Hamiltonian: $A = 4536.709\ (12)$, $B = 1865.582\ (4)$, $C = 1457.449\ (2)$, in MHz; $\Delta_J = 4.51\ (4)$, $\Delta_{JK} = 302.7\ (5)$, $\Delta_K = -293.4\ (2.7)$, $\delta_J = 0.79\ (3)$, $\delta_K = 209.6\ (7)$, $\phi_{JK} = 0.056\ (7)$, $\phi_{KJ} = -0.94\ (4)$, in kHz. [b] Fixed to the value for the normal isotope. [c] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

Results and Discussion

Spectra. The initial search was performed carefully in the 8.0–12.0-GHz region. Many strong transitions were found which were likely to be the *a*-type R-branch transitions of the complex including transitions from the ^{34}S isotopic species. After enough transitions were found and some Stark splittings were observed, the transitions from the normal species and the ^{34}S species could be properly grouped and assigned. The spectrum for the normal isotopic species was characteristic of a near-prolate top with asymmetry parameter $\kappa = -0.74$; both *a*- and *c*-dipole selection rules were observed. The spectra of $(CH_3)_2O{\cdot}{}^{34}SO_2$, $(CH_3)_2O{\cdot}S^{18}OO$, $(CH_3)_2O{\cdot}S^{18}O_2$, and $^{13}CH_3OCH_3{\cdot}SO_2$ were readily assigned on the basis of predicted isotope shifts from a trial structure similar to the $H_2O{\cdot}SO_2$ complex. The observed transition frequencies are listed in Table II, and the spectroscopic constants, derived by using a Watson S-reduced Hamiltonian (I^r representation),[22] are given in Table III. Although two sextic distortion constants, H_{JK} and H_{KJ}, were used to fit the observed transitions, the $K_{-1} = 3$ transitions still deviated by 10–20 kHz and a negative D_J was obtained for every isotope. The unusual negative D_J is discussed in a later section.

There was no evidence for methyl group internal rotation splittings in these transitions, although such effects are prominent in the spectrum of free DME. Using an internal rotation program based on the method of Herschbach[23] and the direction cosines calculated from the structure (see below), a V_3 barrier of 600 cm^{-1} or lower would be needed to split the $J = 3-2$ transitions into resolvable components (≥10 kHz). This lower limit to the barrier is about 20% smaller than the observed barrier in free dimethyl ether.[24] The large changes in the moments of inertia from free DME are a factor contributing to the quenched internal rotation splittings.

Structure. The second moments $P_{bb} = (I_a + I_c - I_b)/2 = \sum_i m_i b_i^2$ for the normal and ^{34}S isotopic species are 93.549 and 93.546 amu·Å^2, respectively,[25] suggesting that the complex has an *ac* symmetry plane. These P_{bb} values are about 0.7 amu·Å^2 smaller than the sum (94.250 amu·Å^2) calculated from the structures of free DME[24] and SO_2[26] if they straddle a symmetry plane. This

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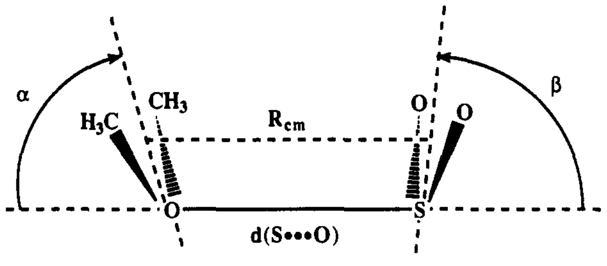

Figure 1. Structural parameters employed in the analysis. R_{cm} is the distance between the centers of mass of DME and SO_2. R_{cm} and d(S⋯O) are nearly parallel (they deviate by 0.5° from a parallel alignment). Angle α is formed by the C_2 axis of dimethyl ether and d(S⋯O), angle β is formed by the C_2 axis of SO_2 and d(S⋯O). The angles α and β are drawn to approximately represent the experimental values of 74 and 86°, respectively. The b axis is perpendicular to the plane of the page. The a axis makes an angle of about 3.8° with d(S⋯O).

Table IV. Structural Parameters (Å, deg) for $(CH_3)_2O{\cdot}SO_2$

	I[a]	II[b]	III[c]	$H_2O{\cdot}SO_2$[d]
R_{cm}	3.048 (1)[e]	3.051 (1)[e]	3.05 (1)	2.962 (5)
d(S⋯O)[f]	2.849 (1)	2.884 (2)	2.87 (3)	2.824 (16)
α[f]	72.6 (2.6)	76.1 (0.8)	74.3 (4.3)	63.5 (1.4)
β[f]	85.8 (5.7)	85.6 (1.6)	85.7 (5.7)	70.3 (1.0)

[a] Least-squares fit of moments of inertia of all isotopic data holding DME[22] and SO_2[24] geometries fixed. ΔI_{rms} was 0.491 amu·Å^2. [b] Least-squares fit of the second moments (P_{aa}, P_{cc}) of all isotopic data holding the DME and SO_2 geometries fixed. ΔP_{rms} for all the isotopes was 0.081 amu·Å^2. [c] Average of I and II with uncertainties sufficient to cover the uncertaintiy spread in I and II. [d] From ref 13. [e] Number in parentheses is the statistical uncertainty associated with the fitting process (1σ). [f] See Figure 1 for definition.

symmetry is also suggested by the observed selection rules and dipole moment components (see below). Assuming an ac symmetry plane and no changes in the structures of DME and SO_2 upon complexation, the moments of inertia of the five isotopic species were fit to three structural parameters. These three parameters are R_{cm}, the distance between the centers of mass of DME and SO_2, and the two tilt angles of the C_2 axes of the two monomers with respect to R_{cm}. However, it is more convenient to compare the intermolecular sulfur–oxygen distance d(S⋯O) and the tilt angles α and β between d(S⋯O) and the C_2 axes of the dimethyl ether and SO_2, respectively, as shown in Figure 1. Two different sets of inertial data were used to determine the structure of the complex. In fit I, the 15 observed moments of inertia of the five isotopic species were least-squares-fit to the three structural parameters, while in fit II, P_{bb} was ignored and only P_{aa} and P_{cc} of the five isotopic species were used. The structural parameters obtained from the two calculations are listed in Table IV and show significant differences between them.

In addition to the least-squares methods, the Kraitchman[27] coordinates of the sulfur and oxygen of the sulfur dioxide and the carbon of DME have been determined. These coordinates are listed in Table V as well as the coordinates from the least-squares fitting (fit I).

Table V. Heavy-Atom Coordinates for $(CH_3)_2O{\cdot}SO_2$ (Å) from Isotopic Data

	|a|		|b|		|c|	
	Kr[a]	I[a]	Kr	I	Kr	I
S	1.237	1.273	0.0	0.0	0.359	0.350
O[b]	1.278[c]	1.279	1.212[c]	1.235	0.419[c]	0.373
C	1.907	1.865	1.156	1.151	0.259	0.222

[a] Coordinate from Kraitchman (Kr) substitution method[27a] or least-squares fitting of moments of inertia (I). [b] Oxygen on sulfur dioxide. [c] From double ^{18}O substitution,[27b] 1.271, 1.213, and 0.426 Å were obtained.

Table VI. Stark Effect Data and Dipole Moments for $(CH_3)_2O{\cdot}SO_2$

transition	$\|M_J\|$	$\Delta\nu/E^2$[a]	(obs − calc)/%[b]
$3_{03}-2_{02}$	0	−0.7227	−0.08
$3_{03}-2_{02}$	1	−0.1014	−3.54
$3_{03}-2_{02}$	2	1.7487	−0.08
$3_{13}-2_{12}$	0	−0.8367	−0.11
$4_{04}-3_{03}$	0	−0.1527	−1.25
$4_{04}-3_{03}$	2	0.3211	1.48
$4_{04}-3_{03}$	3	0.9082	0.34

[a] Observed second-order Stark coefficient in units of 10^{-5} MHz/(V/cm)^2. [b] Calculated with dipole components of μ_a = 1.880 (2), μ_c = 0.591 (1) and μ_{tot} = 1.970 (2) D.

The precise meaning of the two derived structures in Table IV is unclear, compared to a well-defined structure such as the equilibrium structure (r_e), since the moments of inertia contain vibrational effects which have been ignored. Evaluating these effects requires more information about the intermolecular potential than is currently available. It might appear attractive to use the Kraitchman coordinates in Table V to derive the heavy-atom structural parameters, since some cancellation of vibrational effects is expected to occur with this procedure. The derived Kraitchman S–O distance in SO_2 (1.441 Å) is within 0.01 Å of free SO_2 but ∠OSO (114.5°) is about 5° smaller. It is unlikely that this signifies a real change in the SO_2 geometry; the complex is weak, and perturbations to the monomer geometries will be small or negligible. Hence, even the Kraitchman method is significantly perturbed by the vibrational content in the moments of inertia. Consequently, for comparison with other weak complexes where the structures are usually derived by least-squares techniques, the structural parameters in fit I with the statistical uncertainties may be preferred. This is an operational structure, i.e. the so called effective structure (r_0) in the ground vibrational state.[28] Because of the ambiguities in choosing whether I or II is the better structure, we also list their average as III in Table IV, along with uncertainties sufficient to encompass the statistical uncertainties from fits I and II. This is our best estimate of the structure with the present data.

The structure of the complex is very similar to that of the $H_2O{\cdot}SO_2$ complex, whose parameters are given in Table IV for comparison. The S⋯O distance appears shorter in $H_2O{\cdot}SO_2$ than in DME·SO_2 although the difference is not great. Vibrational amplitude data for the van der Waals stretch indicate a larger amplitude motion in the lighter $H_2O{\cdot}SO_2$ species (see below), suggesting that if vibrational corrections are made to the moments of inertia, the relative order of the S⋯O distances for DME·SO_2 and $H_2O{\cdot}SO_2$ is not likely to change. Considering the electron-releasing property of the methyl group and the higher polarizability of DME, this order may seem surprising. However, a competing effect arises from the larger dipole moment of H_2O (1.855 D)[29] compared to DME (1.30 D).[24b,29] Since the complexes are obviously oriented in a manner favorable for a dipole–dipole interaction, it would appear that this interaction is an important factor in any comparative analysis.[30] This point will be considered further in the next section. The contrast between the derived structure for DME·SO_2 and the ab initio calculated parameters in Table I will be discussed in the final section.

Dipole Moment. The electric dipole moment of the complex was determined from measurements of the second-order Stark effects ($\Delta\nu/E^2$) for seven M_J components from three transitions of the $(CH_3)_2O{\cdot}SO_2$ species. A least-squares fit of $\Delta\nu/E^2$ using

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(30) Effects from the higher multipole moments might also be involved, but they are difficult to consider, since experimental values for DME do not appear to be available.

Table VII. Comparison of the Pseudodiatomic Force Constants, Stretching Frequencies, and Binding Energies

	$(CH_3)_3N{\cdot}SO_2$[a]	$(CH_3)_2O{\cdot}SO_2$	$H_2O{\cdot}SO_2$[b]
τ_{bbbb}'/kHz	−3.92	−24.8	−98.8
k_s/mdyn·Å^{-1}	0.328	0.0675	0.0774
ω_s/cm^{-1}	134.5	65.4	96.7
ϵ/kcal·mol^{-1}	4.90	1.26	1.36
$\langle \Delta R_{cm}^2 \rangle^{1/2}$/Å[c]	0.064	0.098	0.111

[a] Reference 5. [b] Derived from data in ref 13. [c] Vibrational amplitude associated with ω_s.

the calculated second-order coefficients gave dipole components $\mu_a = 1.880$ (2), $\mu_c = 0.591$ (1) and $\mu_{tot} = 1.970$ (2) D. The value of μ_b was held to zero in the fitting due to the *ac*-symmetry plane in the complex (see the structure section). When μ_b^2 was not fixed to zero, the least-squares fit determined a value for it nearly equal to zero and negative ($\mu_b^2 = -0.000\,28$ D^2). The experimental values of $\Delta\nu/E^2$ are listed in Table VI. The μ_a dipole component is nearly parallel to d(S···O), making an angle of 1° with it.

The vector sum of the nearly opposed dipole moments of free SO_2 (1.633 D) and DME (1.30 D) predicts dipole components of $\mu_a = 0.483$, $\mu_c = 0.421$ and $\mu_{tot} = 0.640$ D for the complex. The difference between these and the observed values give induced dipole moment components of $\mu_a = 1.397$, $\mu_c = 0.169$ D. This overall induced moment (1.41 D) is almost aligned with the O···S bond vector, making it attractive to consider that it largely arises from electronic reorganization between oxygen and sulfur. If this reorganization is considered to arise from actual charge transfer, a transfer of 0.103 electron from the oxygen on dimethyl ether to the sulfur atom in sulfur dioxide is calculated. This can be compared to the upper limit of 0.32 electron transferred from the N to S in the TMA·SO_2 complex ($\mu_{tot} = 4.80$, $\mu_{induced} = 3.50$ D)[5] when the analysis is made in an identical manner.

Although the dipole moment of H_2O is 1.855 D,[29] which is about 0.55 D larger than that of DME, the dipole moment of the $H_2O{\cdot}SO_2$ complex[13] is almost the same as for DME·SO_2. The observed dipole moment for $H_2O{\cdot}SO_2$, $\mu_{tot} = 1.984(2)$ D, leads to induced dipole components of $\mu_a = 0.672$, $\mu_c = 0.321$ and $\mu_{induced} = 0.745$ D. The interaction distance and the force constants (see below) for the $H_2O{\cdot}SO_2$ and DME·SO_2 complexes suggest that the former is slightly more strongly bound with a smaller induced dipole moment. This appears to complicate any effort to identify a single property such as the dipole moments, induced dipole moments, or polarizabilities as the key to comparing the relative properties of the two complexes. On the other hand, the much greater stability of TMA·SO_2, the shorter N···S distance of 2.26 (3) Å, and the much larger induced dipole moment in that complex[5] suggest that the contribution from polarization and charge transfer are much more important when amines interact with SO_2.

Centrifugal Distortion Constants and Internal Dynamics. To explore whether the unusual negative sign for the centrifugal distortion constant D_J is the result of a pathological fit, the transitions in Table II were fit with an alternative Hamiltonian, namely the Watson A-reduced Hamiltonian (I^r representation).[22,31] The quality of the fit was virtually identical to that of the original fit; the constants are given in Table III. The distortion constants which contain different contributions from the vibrational motions can be used to calculate the more fundamental $\tau_{\alpha\beta\gamma\delta}$ distortion constants described originally by Kivelson and Wilson.[32] These are related to the inverse force constants (f^{-1}) and inertial derivatives ($J_{\alpha\beta}^{(i)} = \partial I_{\alpha\beta}/\partial r_i$) of the complex in the following way:

$$\tau_{\alpha\beta\gamma\delta} = -\tfrac{1}{2}\sum_{ij} J_{\alpha\beta}^{(i)}(f^{-1})_{ij}J_{\gamma\delta}^{(j)} \qquad (1)$$

The τ's calculated from the two sets of spectral distortion constants were identical within their estimated uncertainties. This indicates that the spectral distortion constants from the two fits are internally consistent, and the τ's do not depend on the Hamiltonian used to fit the spectrum. The value of $\tau_{bbbb}/h = \tau_{bbbb}'$ derived from these fits is given in Table VII.

The unusual negative D_J (but positive Δ_J) provides some insight into the out-of-plane vibrational motions in this complex. The relationships between the distortion constants D_J and Δ_J and the τ's are[31]

$$D_J = -\hbar^4(3\tau_{bbbb} + 3\tau_{cccc} + 2\tau_{bbcc} + 4\tau_{bcbc})/32 \qquad (2)$$

$$\Delta_J = -\hbar^4(3\tau_{bbbb} + 3\tau_{cccc})/8 \qquad (3)$$

Thus the differences in sign between D_J (=−2.94 kHz) and Δ_J (=4.51 kHz) arise from τ_{bbcc} and τ_{bcbc} and one or both of these two terms should be negative enough to make D_J negative. There are two possibilities. One of them involves a strong coupling between the van der Waals stretch and another vibrational mode in this complex. Indeed, there is a suggestion of a Coriolis-like interaction in this complex. The equal and opposite deviation in the fit of the $K_{-1} = 3$ transitions for the normal isotopic species suggests that the Hamiltonian may need a K-dependent term that is first order in P_a. This condition requires an accidental vibrational degeneracy, and coupled vibrational modes from the complex could be the source of this degeneracy. The second possibility could arise from a large-amplitude out-of-plane motion which contributes to τ_{bcbc}. In this regard, the eclipsing orientation of the methyl groups relative to the SO bonds may be noteworthy. In the trimethylamine[5] and dimethylamine[6] complexes with SO_2, where a methyl group staggers the SO bonds, it has been estimated that the difference in energy for the eclipsed vs staggered forms is less than 1 kcal/mol. Here, the difference is likely to be even less, considering the much smaller k_s force constant and longer interaction distance suggesting a low resistance to an out-of-plane vibrational motion.

For complexes with C_s symmetry, the force constant k_s associated with the van der Waals stretching along the center of mass line can be determined from τ_{bbbb}, if the internal vibrations of the subunits are neglected. For an *ac* symmetry plane, I_{bb}(complex) $= I_{aa}(SO_2) + I_{aa}(DME) + \mu R_{cm}^2$, where μ is the reduced mass $M_{SO_2}M_{DME}/(M_{SO_2} + M_{DME})$. Consequently, in the expression relating τ_{bbbb} to the force constant, all terms except the one involving k_s are zero.[33] Using $\partial I_{bb}/\partial R_{cm} = 2\mu R_{cm}$, eq 1 readily provides a value for $(k_s^{-1})_{R_{cm}}$. This leads to $k_s = 0.0675$ mdyn/Å. The associated vibrational frequency is 65.4 cm^{-1}. Assuming a harmonic vibration, the mean-squared amplitude for the van der Waals stretching mode is $\langle \Delta R_{cm}^2 \rangle^{1/2} = 0.098$ Å, which is reasonable considering the weak interaction in this complex. These parameters are listed in Table VII and compared to values for TMA·SO_2 and $H_2O{\cdot}SO_2$.

The values for the stretching force constant k_s, ω_s, and well depth ϵ for the complexes in Table VII clearly contrast the difference between DME·SO_2 and $H_2O{\cdot}SO_2$ and the much stronger TMA·SO_2. ϵ was estimated by assuming a Lennard–Jones 6–12 potential function which is clearly a poor approximation for TMA·SO_2.[5] The well depth ϵ, like the earlier evidence from the S···O distances, suggests that the water complex is slightly more stable than the ether complex.

Comparison with ab Initio Results. The SO_2 complexes with TMA, DMA, DME, and H_2O provide a related set to examine the effects of substitution of nitrogen with oxygen and replacement of hydrogen with methyl on their structures and energetics. Table VIII summarizes the experimental results (ER) and ab initio calculations (AIC) for this series. The AIC are taken from the literature or from calculations by us using GAUSSIAN86;[34,36] all the

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Table VIII. Comparison of Experimental and ab Initio Results

	$(CH_3)_3N\cdot SO_2$		$(CH_3)_2NH\cdot SO_2$		$(CH_3)_2O\cdot SO_2$		$H_2O\cdot SO_2$	
				Experimental				
$\Delta E_{diss}{}^a$/kcal·mol^{-1}	9.1				3.6			
ϵ^b/kcal·mol^{-1}	4.90		3.72		1.26		1.36	
d(S···X)/Å	2.26 (3)		2.34 (3)		2.87 (3)		2.82 (2)	
α (donor tilt)^c/deg	1 (3)		3 (3)		74 (4)		64 (1)	
β (SO_2 tilt)^d/deg	79 (3)		79 (3)		86 (6)		70 (1)	
μ_{tot}/D	4.80 (1)		4.39 (1)		1.97 (1)		1.98 (1)	
$\mu_{induced}{}^e$/D	3.50		2.78		1.4		0.78	
ref	5, 18		6		16,f		13	
				Ab Initio				
	3-21G*	3-21G	3-21G*	3-21G	3-21G*	3-21G	3-21G*	3-21G
ΔE_{diss}/kcal·mol^{-1}	17.2	17.2	16.6	16.6	21.3	22.1	12.7	13.7
d(S···X)/Å	2.19	2.26	2.24	2.32	2.40	2.46	2.48	2.53
α/deg	0	0	0	0	36.1	35.0	57.8	58.0
β/deg	81.2	83.1	82.0	84.2	86.8	90.9	90.8	95.5
μ/D	5.35	5.19	5.27	5.05	3.36	3.14	2.46	2.13
ref	6	6	6	6	36^g	36^g	36	36
	4-31G	STO-3G	6-31G	STO-3G	6-31G	STO-3G	6-31G	STO-3G
ΔE_{diss}/kcal·mol^{-1}	15.0	4.1	14.1	4.6	10.9	11.8	10.3	4.4
d(S···X)/Å	2.36	2.86	2.40	2.86	2.54	2.75	2.61	2.71
α/deg	0	0	0	0	16.8	16.2	34.8	36.5
β/deg	85	90	82.1	91.2	87.5	95.1	91.3	97.7
μ/D		2.2	5.15	2.39	3.90	1.95	3.21	1.58
ref	35a	35b	6	36	36	36^g	36	36

[a] ΔE for complex → donor + acceptor. [b] Well depth from pseudodiatomic approximation assuming a Lennard–Jones (6–12) potential. [c] For ether and H_2O, α is defined in Figure 1. For amines α is the tilt angle of the C_3 axis (or pseudo-C_3 axis for DMA) of the amine from the N···S distance. [d] See Figure 1. [e] Estimated from the difference between the observed dipole moment (μ_{tot}) and the dipole moment estimated from the unperturbed monomer dipole moments. [f] Present work. [g] These values for α, β, and d(S···O) differ slightly from similar calculations in the literature[17] where the structural parameters of the monomers were optimized as well. The methyl groups were assumed to have tetrahedral angles in these calculations.

calculations were at the HF/SCF level with no corrections for correlation effects or basis superposition errors. Our calculations employed fixed geometries for the monomers;[24,26] the distance between the monomers and the tilt angles, α and β, were varied, and the energy minimum was located.

Both the ER and AIC concur regarding the gross geometries of the complexes which are consistent with a lone-pair-donor, π-acceptor interaction. While this description in terms of familiar chemical concepts is appealing, it has been noted elsewhere,[18a,35,37,38] that these complexes are more accurately described as electrostatic complexes rather than charge-transfer complexes. An analysis of the bonding interaction as provided by the Morokuma energy decomposition procedure (4-31G basis set) partitions the calculated binding energy (kcal/mol) of −14.8 for TMA·SO_2 between electrostatic (−31.8), polarization (−4.9), charge-transfer (−14.1), and exchange repulsion (36.0) terms.[35a,39] Even though the electrostatic term is the largest attractive component, the amine complexes have traditionally been classified as prototype charge-transfer complexes in the literature.[18]

The ER indicate that the amine complexes are distinctly stronger than the DME and H_2O complexes. The interaction distances are about 0.5 Å larger and ΔE_{diss} and ϵ appear to be roughly one-third as large in the latter two complexes. These changes are expected on the basis of the well-known lower basicity of ethers compared to amines. However, the magnitude of the change in the interaction distance d(S···X) indicates a marked sensitivity to the small change (in absolute terms) in the binding energy. This sensitivity is considerably greater than observed in covalent bond distances for oxygen vs nitrogen substitution. It is also noteworthy that the sums of the van der Waals radii[40] for N and S (3.35 Å) and for O and S is (3.25 Å) are significantly longer than the observed distances.

Another indication of a difference in the strength of the interaction for the amines compared to ether/water is the magnitudes of the overall dipole moments and the estimated induced dipole moments in Table VIII. The Morokuma energy decomposition for TMA·SO_2 indicates that charge transfer is 3 times more important than polarization, providing a rationale for the large dipole moments in the amines.

The AIC provide a less consistent picture of the relative stabilities of the amine complexes compared to the DME and H_2O complexes. The DME·SO_2 complex appears to be more stable for all basis sets except the 6-31G. The $H_2O\cdot SO_2$ complex is less stable for all basis sets except the STO-3G. It is noted that d(S···X), α, and β for the amine complexes are in more reasonable agreement with experiment for most of the basis sets (STO-3G is an exception) in contrast to the case of the DME and H_2O complexes, where d(S···X) and especially α compare poorly with the experimental findings. This contrast suggests that little reliability should be attached to the ab initio estimated relative

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(36) The SCF energies (in au) for H_2O, DME, SO_2, $H_2O\cdot SO_2$, and DME·SO_2 are as follows:

	STO-3G	3-21G	3-21G*	6-31G
H_2O	−74.963 05	−75.585 42	−75.585 42	−75.983 98
DME	−152.117 99	−153.196 04	−153.196 04	−153.990 38
SO_2	−540.602 05	−544.246 33	−544.503 27	−546.903 39
$H_2O\cdot SO_2$	−615.572 13	−619.853 56	−620.109 00	−622.903 81
DME·SO_2	−692.738 86	−697.477 58	−697.733 20	−700.909 86

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(40) As pointed out by a reviewer, the large size of the exchange repulsion terms raises a question about the actual significance of the energy partitioning. Nevertheless, the decomposition procedure provides a means for comparing the relative magnitudes of the energy terms for related series of compounds and evaluating trends in electronic effects.

stabilities on the DME and H_2O complexes.

On the other hand, a comparison of the ER and AIC regarding the relative stabilities of the TMA and DMA complexes is more consistent. The results for d(S···N), ϵ, and ΔE_{diss} indicate that TMA·SO_2 is slightly more stable than DMA·SO_2, probably by about 0.5–1.0 kcal/mol (the STO-3G calculation is again an exception). The stabilizing effect from methyl substitution in amines has been discussed extensively in the literature and was summarized recently.[6] The Morokuma energy analysis indicates that increases in both the polarization and charge-transfer terms parallel the overall increase in stability with methyl substitution. While the evidence is not as compelling in the case of the ether/water complexes, it appears (from the experimental d(S···O) and ϵ) that the water complex may be slightly more stable than the ether complex. It was pointed out above (see structure and dipole sections) that competing effects occur here: the dipole moments of water (1.85 D) and DME (1.30 D) favor $H_2O \cdot SO_2$, while the increased polarizability of DME from methyl substitution (DME·SO_2, $\mu_{\mathrm{induced}} = 1.41$ D; $H_2O \cdot SO_2$, $\mu_{\mathrm{induced}} = 0.75$ D) favors DME·SO_2. This makes it difficult to qualitatively predict the more stable dimer. It is interesting that the difference in proton affinities favors DME by 22 kcal/mol over H_2O,[15a] which is not reflected in the experimental structures of their SO_2 complexes or in their stabilities, which appear roughly equal. In contrast, the difference in proton affinities for TMA and DMA of 4.2 kcal/mol[15a] favors TMA and is closer to the estimated differences in their binding energies (~1 kcal/mol) and the change in d(N···S) in their SO_2 complexes.

The ER and AIC concur that a methyl group staggers the SO_2 group in the amine complexes, while methyl groups eclipse the S–O bonds in DME·SO_2. One factor is the antiparallel orientation of the monomer dipoles in DME·SO_2, which will maximize the electrostatic interaction at the expense of the eclipsing arrangement. In the amine·SO_2 complexes, the dipole moments of the monomers are nearly perpendicular and eclipsing of the O–Me and S–O bonds is no longer a geometric consequence. Also, the short N···S and longer O···S interaction distances in the two types of complexes provide different interaction regimes; obviously, repulsive interactions between eclipsed groups may be more important in the amine complexes.

In summary, while the ER and AIC agree on many of the geometric and energetic trends, it is apparent that the AIC provide mixed results in terms of the energetics and structural parameters. The problem in calculating ΔE_{diss} is a well-known one, endemic to the problem of estimating a small number from the difference between two large numbers.[41] The neglect of correlation effects and basis set superposition corrections as well as the limited basis sets are the root of this difficulty. The observation that the gross geometries can be reasonably approximated by these HF-level calculations is gratifying. Nevertheless, regarding detailed geometries, the STO-3G calculations do reasonably well for d(S···O) in the ether/water complexes but poorly for the amine complexes, while the opposite is true for calculations at a higher level (such as 3-21G), which makes it difficult to propose any working hypothesis about choosing basis sets for new systems. More comparisons between theory and experiment for a broader set of complexes may serve to establish better guidelines for the reliability of such HF-level structural parameters for systems as complicated as these.

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Registry No. $(CH_3)_2O \cdot SO_2$, 42383-26-6; ^{34}S, 13965-97-4; ^{18}O, 14797-71-8; ^{13}C, 14762-74-4.

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Structural Dependence of the Luminescence from Bis(substituted benzenethiolato)(2,9-dimethyl-1,10-phenanthroline)zinc(II) Complexes

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Changes in luminescence spectra and lifetimes of crystalline samples of the title compounds at 77 K are correlated with phase changes of the solids. The ease of conversion among phases is a general property of this class of materials. For bis(benzenethiolato)(2,9-dimethyl-1,10-phenanthroline)zinc(II) complete structure determinations were made of both phases. The attendant changes of the optical properties are ascribed to rotation of the planes of the two thiol rings on a single zinc ion from an approximately perpendicular to a nearly face-to-face conformation as the slowly heated crystal undergoes the phase change. The relevance of these results to the problem of charge separation in solids is discussed.

Introduction

Luminescence from zinc complexes has been used extensively in this laboratory to monitor the effects of subtle structural changes upon the relative rates of radiative and radiationless processes in the crystals and solids. Of particular interest is the process of charge separation after optical excitation. Recently we extended our studies to the solid state where thermal barriers to radiationless processes have been observed.[1] In the course of these investigations, we have discovered that some of the complexes exhibit at least two crystalline phases and that the attendant luminescence properties are sensitive functions of the phase purity. Moreover, complete conversion to the high-temperature phase can be accomplished by heating to temperatures just below the melting point. Preliminary data on several complexes are described, and a detailed crystallographic study of two phases of the $\mathrm{Zn(PhS)_2(2,9\text{-}Me_2phen)}$ complex is reported.[2] For this latter system, the principal structural difference of the phases involves the relative orientation of the phenyl rings of the two coordinated thiols.

Experimental Section

Synthesis. To a solution of zinc acetate dihydrate (0.22 g, 1 mmol) dissolved in 100 mL of hot ethanol a solution of redistilled benzenethiol (0.21 mL, 2.1 mmol in 10 mL of ethanol) was added dropwise with stirring. As the second millimole was added, a white precipitate formed. After 5 min of continual stirring, 2,9-dimethyl-1,10-phenanthroline (0.21

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[1] Highland, R. G.; Crosby, G. A. *Chem. Phys. Lett.* **1985**, *119*, 454.

[2] Compounds are identified in Table V.

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