

comparison, the dipole moments of **10** and **11** are 3.48 and 4.39 D, respectively.

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## References and Notes

- (1) Cf. W. M. Jones and U. H. Brinker, "Pericyclic Reactions", Vol. 1, A. P. Marchand and R. E. Henr, Ed., Academic Press, New York, N.Y., 1977, Chapter 3; W. M. Jones, *Acc. Chem. Res.*, **10**, 353 (1977).
- (2) (a) C. P. Casey, T. J. Burkhardt, C. A. Bunnell, and J. C. Calabrese, *J. Am. Chem. Soc.*, **99**, 2127 (1977), and references cited; (b) C. P. Casey and S. W. Polichnowski, *ibid.*, **99**, 6097 (1977); (c) M. Brookhart and G. O. Nelson, *ibid.*, **99**, 6099 (1977).
- (3) For reviews, see D. J. Cardin, B. Centinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 487 (1972).
- (4) K. Öfele, *Angew. Chem., Int. Ed. Engl.*, **8**, 916 (1969).
- (5) K. Öfele, *J. Organomet. Chem.*, **12**, P 42 (1968).
- (6) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).
- (7) W. A. Herrmann, *Chem. Ber.*, **108**, 486 (1975).
- (8) Unpublished results of D. DeJohn, C. Mayor, and J. Morris, University of Florida.
- (9) Cf. B. F. Hullman and P. L. Pauson, *Chem. Ind. (London)*, 653 (1955); M. L. H. Green, M. Ishag, and T. Mole, *Z. Naturforsch.*, **20b**, 598 (1965); M. L. Green and T. Mole, *J. Organomet. Chem.*, **12**, 404 (1968); T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); L. Summers, R. H. Uloth, and A. Holmes, *J. Am. Chem. Soc.*, **77**, 3604 (1955); A. Eisenstadt, G. Scharf, and B. Fuchs, *Tetrahedron Lett.*, 679 (1971).
- (10) A. Sanders, L. Cohen, W. P. Giering, D. Kennedy, and C. V. Mogatti, *J. Am. Chem. Soc.*, **95**, 5430 (1973).
- (11) B. Föhlisch, P. Burgle, and D. Krockenberg, *Chem. Ber.*, **101**, 2717 (1968); B. Föhlisch and E. Haug, *ibid.*, **104**, 2324 (1971).
- (12) Attempts to separate individual isomers of **1** were not successful. <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) showed resonances at  $\delta$  2.15, 2.25, 2.62 (2H, t, d, satd CH), 4.65, 4.79, 4.84 (5H, s, s, s, Cp), 4.98–5.50, 5.78–6.83 (5H, br m, br m, vinyl). Their IR (neat) spectra showed carbonyl absorptions at 2020 and 1950 cm<sup>-1</sup> and a high resolution mass spectrum on the mixture gave *m/e* 268.01841 (calcd 268.01860).
- (13) C. P. Casey, S. W. Polichnowski, and R. L. Anderson, *J. Am. Chem. Soc.*, **97**, 7375 (1975).
- (14) To date, all attempts to isolate the  $\sigma$  complex **4** as a pure material have failed. For example, workup as described by Casey<sup>13</sup> for salts of methyl and phenyl pentacarbonyl tungstate invariably gave a mixture of **4** and regenerated **3** (identified by IR). The <sup>1</sup>H NMR of the mixture showed resonances (acetone-*d*<sub>6</sub>) at  $\delta$  2.76 (2H, d, *J* = 7.0 Hz), 5.0–5.4 (1H, m), 5.8–6.8 (4H, m), ~0.8–2.0, and 3.1–3.6 (tetrabutylammonium, 20 × 100% too intense for pure **4**).
- (15) E. S. Bolton, G. R. Knox, and C. G. Robertson, *Chem. Commun.*, 664 (1969).
- (16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, N.Y., 1972, p 687.
- (17) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); see also the series of works by Fisher, for example, E. O. Fisher, H. Hollfelder, P. Friedrich, F. R. Kreib, and G. Huttner, *Chem. Ber.*, **110**, 3467 (1977).
- (18) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
- (19) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973).
- (20) Complex **5** was measured in heptane and (CO)<sub>5</sub>WCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Me in THF. In polar solvents, the force constants showed a tendency to become smaller.
- (21) The uncertainty mainly arises from the low solubility of **5** in C<sub>6</sub>H<sub>6</sub>.

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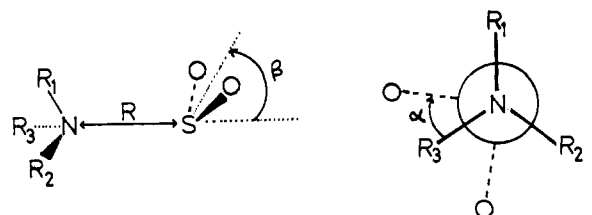
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## Trimethylamine-SO<sub>2</sub>, the Prototype Strong Charge-Transfer Complex

Sir:

Of all the charge-transfer complexes in the literature, trimethylamine (TMA)-SO<sub>2</sub> is among the best characterized. It is one of the few where one has an available x-ray structure<sup>1</sup> and gas phase energy of complex formation ( $\Delta E$ ).<sup>2</sup> It has the additional advantage that it is small enough that one can directly apply theoretical ab initio molecular orbital methods to it.

**Table I.** Amine-SO<sub>2</sub> Interaction Energies, Geometries, and Energy Components



	complex <sup>a</sup>			
	NH <sub>3</sub> -SO <sub>2</sub>	MA-SO <sub>2</sub>	DMA-SO <sub>2</sub>	TMA-SO <sub>2</sub>
Interaction energies and geometries				
$-\Delta E$ , kcal/mol	11.7	13.9	14.5	15.0
$R$ , Å <sup>b</sup>	2.63	2.45	2.40	2.36
$\beta$ , deg <sup>c</sup>	85	85	(85)	(85)
$\alpha$ , deg <sup>d</sup>	0	60	(60)	(60)
Energy components <sup>a,e</sup>				
$\Delta E^f$	-11.3	-13.7	-14.3	-14.8
$\Delta E_{es}^g$	-33.4	-33.1	-32.5	-31.8
$\Delta E_{pol}^h$	-3.4	-4.0	-4.5	-4.9
$\Delta E_{CT}^i$	-10.2	-12.3	-13.3	-14.1
$\Delta E_{ex}^j$	35.7	35.7	36.0	36.0

<sup>a</sup> The experimental monomer geometry for SO<sub>2</sub> and for the amines was used in the calculations, with the exception that all of the amines had tetrahedral RNR angles. A comparison of the ammonia-SO<sub>2</sub> results with  $\theta(\text{HNH}) = 106.7^\circ$  (experimental) and  $\theta(\text{HNH}) = \text{tetrahedral}$  showed negligible difference with the difference in  $\Delta E$  being 0.1 kcal/mol (NH<sub>3</sub>-SO<sub>2</sub> with experimental NH<sub>3</sub> geometry had a  $-\Delta E$  of 11.8 kcal/mol). In TMA,  $\theta(\text{CNC}) = 108.7^\circ$  experimentally. <sup>b</sup>  $R = R(\text{N-S})$ . <sup>c</sup>  $\beta$  is the tilt angle of the SO<sub>2</sub> off the N-S axis. <sup>d</sup>  $\alpha$  is the dihedral angle of rotation of amine relative to the SO<sub>2</sub>. In the Newman projection at the top of the page, for NH<sub>3</sub> ( $R_1 = R_2 = R_3 = \text{H}$ ), MA ( $R_1 = \text{Me}$ ;  $R_2 = R_3 = \text{H}$ ), DMA ( $R_1 = R_2 = \text{Me}$ ;  $R_3 = \text{H}$ ), and TMA ( $R_1 = R_2 = R_3 = \text{Me}$ ). <sup>e</sup> Energy components all evaluated at  $R = 2.45 \text{ \AA}$ ,  $\beta = 85^\circ$ ,  $\alpha = 180^\circ$  in kilocalories/mole. <sup>f</sup> Total interaction energy. <sup>g</sup> Electrostatic interaction energy. <sup>h</sup> Polarization energy. <sup>i</sup> Charge-transfer energy. <sup>j</sup> Exchange repulsion energy.

In fact, a set of ab initio calculations on H<sub>3</sub>N-SO<sub>2</sub> and TMA-SO<sub>2</sub> has appeared in this journal. Lucchese et al.<sup>3</sup> found H<sub>3</sub>N-SO<sub>2</sub> to be bound by 4.94 kcal/mol with  $R(\text{N-S}) = 2.86 \text{ \AA}$  and TMA-SO<sub>2</sub> bound by 4.06 kcal/mol with an identical  $R(\text{N-S})$ . These results are perhaps surprising when one realizes that the x-ray structure of TMA-SO<sub>2</sub> finds  $R(\text{N-S}) = 2.06 \text{ \AA}$ <sup>1</sup> and gas phase experiments find a  $-\Delta E$  for TMA-SO<sub>2</sub> of 9.7 kcal/mol.<sup>2</sup> Lucchese et al. carried out more extended basis set calculations (double  $\zeta$ ) on H<sub>3</sub>N-SO<sub>2</sub> and found that the interaction energy increased to 10.4 kcal/mol and  $R(\text{N-S})$  decreased to 2.70 Å. They did not study TMA-SO<sub>2</sub> at the double  $\zeta$  level.

These ab initio results are intriguing for a number of reasons. (1) Gas phase proton affinities of methyl substituted amines ( $\Delta E \sim -200 \text{ kcal/mol}$ ) follow the order TMA > DMA > MA > NH<sub>3</sub>;<sup>4</sup> gas phase Li<sup>+</sup> affinities ( $\Delta E \sim -40 \text{ kcal/mol}$ ) are in the order DMA > TMA > MA > NH<sub>3</sub>;<sup>5</sup> thus it may be reasonable<sup>6</sup> that, for the weaker Lewis acid SO<sub>2</sub>, NH<sub>3</sub> is a stronger Lewis base than TMA. However, studies on the closely related Lewis acid I<sub>2</sub> in hydrocarbon solvents indicate the strength of interaction in the order H<sub>3</sub>N < MA < DMA < TMA.<sup>7</sup> Is this latter a solvent effect and is it relevant to a gas phase study of amine-SO<sub>2</sub>? What is the correct order of the Lewis basicity for amine-SO<sub>2</sub> interactions? (2) What is the reason for the extremely large difference of 0.8 Å<sup>1</sup> between the STO-3G calculated<sup>3</sup> and experimental  $R(\text{N-S})$ ? It appears to be too great to be a crystal effect; yet STO-3G usually does well for structure predictions<sup>8</sup> and almost always *underesti-*

mates<sup>9</sup> the separation between molecules in intermolecular interactions.

In the hopes of shedding light on the above questions, we carried out ab initio calculations on the amine-SO<sub>2</sub> interactions using a valence shell "double  $\zeta$ " 431-G basis set.<sup>10</sup> We optimized the energy with respect to three intermolecular parameters for NH<sub>3</sub>-SO<sub>2</sub> and CH<sub>3</sub>NH<sub>2</sub>-SO<sub>2</sub> (MA) and then optimized only  $R(N-S)$  for (CH<sub>3</sub>)<sub>2</sub>NH(DMA)-SO<sub>2</sub> and TMA-SO<sub>2</sub>. The results of the geometry searches and Morokuma component analysis<sup>11</sup> at  $R(N-S) = 2.45$  Å are presented<sup>12</sup> in Table I. The results are interesting and help to answer the questions posed above. (1) The order of gas phase amine-SO<sub>2</sub> affinities is TMA > DMA > MA > NH<sub>3</sub>. We carried out a more complete geometry optimization of the SO<sub>2</sub> complex of NH<sub>3</sub> and MA than the SO<sub>2</sub> complexes of DMA and TMA; thus we expect that the order of interaction energies will be preserved upon complete geometry optimization. Further improvement of the basis set is likely (a) to increase the polarization energy and to increase the differences between the amines and (b) to decrease the electrostatic energies and to improve the overall agreement between the  $\Delta E$ (calculated) and  $\Delta E$ (experimental).<sup>13</sup> (2) The  $R(N-S) = 2.36$  Å for TMA-SO<sub>2</sub> is in much better agreement with the experimental value  $R(N-S) = 2.06$  Å. The calculated difference in energy between  $R(N-S) = 2.06$  and  $2.36$  Å is only 3 kcal/mol out of a total calculated  $\Delta E$  of -15 kcal/mol.<sup>14</sup> However, since the addition of polarization functions usually increases intermolecular separations in H-bonded complexes,<sup>9,13</sup> it isn't clear how definitive our calculated gas phase  $R(N-S)$  is. We hope that these results will stimulate microwave spectral studies on TMA-SO<sub>2</sub> in the gas phase. TMA-SO<sub>2</sub> also may be an example where correlation effects on the minimum energy structure are much larger than calculated for Li<sup>+</sup>OH<sub>2</sub>, F<sup>-</sup>OH<sub>2</sub>, and (H<sub>2</sub>O)<sub>2</sub>.<sup>15</sup>

Another fascinating finding is that the charge-transfer component (Table I) is the key to the methyl substituent effect in these systems, in contrast to the methyl substituent effect on proton affinities<sup>4</sup> (polarization key), amine vs. amide basicity (exchange repulsion key),<sup>6</sup> and most H-bond energies (electrostatic dominated).<sup>9,13</sup> Geometry optimization of the amine-Li<sup>+</sup> interactions at the 431-G level showed that, in that case,  $R(N-Li)$  was practically the same for all the amines.<sup>6</sup> The biggest difference between the relative magnitudes of the energy components of amine-Li<sup>+</sup> and amine-SO<sub>2</sub> interactions is the small size of the charge-transfer term in the former case and its significant contribution to the attraction in the latter case.

Further studies are in progress on these systems, in particular on amine-F<sub>2</sub> and amine-Cl<sub>2</sub> interactions, where STO-3G calculations predict NH<sub>3</sub> to be a stronger base than TMA.<sup>16,17</sup> Is that result real and are F<sub>2</sub> and Cl<sub>2</sub> very different Lewis acids than I<sub>2</sub>, or is this another example of the inability of STO-3G to correctly represent the methyl substituent effect in these prototype "charge-transfer" complexes? In addition, more complete geometry optimization on TMA-SO<sub>2</sub> with a more extensive basis set seems worthwhile to do.<sup>18</sup> However, even at this stage, the qualitative difference between amine-SO<sub>2</sub> and amine-Li<sup>+</sup> studied with double  $\zeta$  basis sets and the amine-SO<sub>2</sub> complex basis set dependence is very intriguing.

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## References and Notes

- (1) D. van der Helm, J. Childs, and S. D. Christian, *Chem. Commun.*, 887 (1968).

- (2) J. Grundnes and S. D. Christian, *J. Am. Chem. Soc.*, **90**, 2239 (1968).  
 (3) R. R. Lucchese, K. Haber, and H. F. Schaefer III, *J. Am. Chem. Soc.*, **98**, 7617 (1977).  
 (4) See theoretical calculations by Umeyama and Morokuma (*J. Am. Chem. Soc.*, **98**, 4400 (1976)) for the theoretical and experimental proton affinities of the amines.  
 (5) See R. L. Woodin and J. L. Beauchamp, *J. Am. Chem. Soc.*, **100**, 501 (1978).  
 (6) P. A. Kollman and S. Rothenberg, *J. Am. Chem. Soc.*, **99**, 1333 (1977).  
 (7) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).  
 (8) J. A. Pople in "Modern Theoretical Chemistry", Vol. IV, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977.  
 (9) For a review, see P. Kollman in "Modern Theoretical Chemistry", Vol. IV, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977.  
 (10) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).  
 (11) S. Iwata and K. Morokuma, *J. Am. Chem. Soc.*, **19**, 7563 (1973).  
 (12) We carried out the component analysis at a number of geometries, but report only the values at a common reference geometry here.  $R = 2.45$  Å was chosen because it was between the minima for NH<sub>3</sub> and TMA. All of the energy components are very distance dependent (much more so than the total energy) and increase in magnitude as  $R(N-S)$  decreases; thus, if one had used different  $R(N-S)$  for comparison of the different methyl amines, the interpretation of the results would have been much more ambiguous.  
 (13) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **99**, 1316 (1977). They found for (HF)<sub>2</sub> that the largest effect of addition of polarization functions to the basis set was the decrease in magnitude of the electrostatic energy. They also found an increase in polarization energy, but the total polarization energy for (HF)<sub>2</sub> (-0.3 kcal/mol with 431-G, -0.5 with 4-31G with d's on F) was quite small.  
 (14) This difference in  $R(N-S)$  appears a bit too large to be a crystal packing effect, since the TMA-SO<sub>2</sub> complexes form separated 1:1 complexes in the crystal. The difference in  $R(O\cdots O)$  for (H<sub>2</sub>O)<sub>2</sub> gas phase and H<sub>2</sub>O (ice) is only 0.2 Å, and this shortening in the crystal would be expected to be accentuated by the extended tetrahedral H-bonding network.  
 (15) G. Dierksen, W. Kraemer, and B. Roos, *Theor. Chim. Acta*, **36**, 249 (1975), and O. Matsuoka, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, **64**, 1361 (1976), find that correlation effects stabilize (H<sub>2</sub>O)<sub>2</sub> by ~1 kcal/mol and decrease O $\cdots$ O by ~0.1 Å.  
 (16) R. R. Lucchese and H. F. Schaefer, *J. Am. Chem. Soc.*, **97**, 7205 (1975).  
 (17) The limited results of ref 13 on H<sub>3</sub>N $\cdots$ ClF compared with CH<sub>3</sub>NH<sub>2</sub> $\cdots$ Cl-F suggest that ClF as a Lewis acid might form a stronger complex to NH<sub>3</sub> than TMA.  
 (18) In particular, it will be interesting to compare the observed (68°) and calculated  $\beta$  (we assumed the same value as in methylamine-SO<sub>2</sub>, 85°) as well as to look at changes in some of the intramolecular degrees of freedom upon complex formation. For example, in the crystal<sup>1</sup> complex, one C-N is 1.52 Å, the other two 1.48 Å; there is also significant asymmetry in the S-O bonds.

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## <sup>13</sup>C-<sup>1</sup>H Cross-Polarization in Liquids

Sir:

The observation of <sup>13</sup>C NMR spectra of organic solids using proton-carbon cross-polarization<sup>1-3</sup> yields remarkable improvements in resolution and sensitivity. We report here preliminary results which demonstrate the advantageous use of this pulse technique in <sup>13</sup>C NMR spectroscopy of organic liquids. In the cross-polarization experiment on liquid samples, spin-spin coupling is responsible for the magnetization transfer; hence we introduce the abbreviation JCP for  $J$  cross-polarization.

The JCP experiment contrasts with the pulsed <sup>13</sup>C FT NMR experiment in three important ways. First, pulse repetition rates are governed by the proton longitudinal relaxation times  $T_1$  rather than those of the carbon nuclei. Second, approximately a fourfold signal enhancement is predicted owing primarily to the ratio of the magnetogyric ratios for <sup>1</sup>H and <sup>13</sup>C. Third, the indirect spin-spin couplings,  $J_{CH}$ , modulate the amplitude of JCP spectra obtained as a function of cross-polarization time. The first two features are well known from the solid-state cross-polarization experiment. The third is a consequence of the mechanism of polarization transfer: in contrast