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CNDO CALCULATIONS ON THE IMIDES OF SULFUR DIOXIDE

J. R. GRUNWELL and W. C. DANISON, JR.
Department of Chemistry. Miami University. Oxford. Ohio 45056

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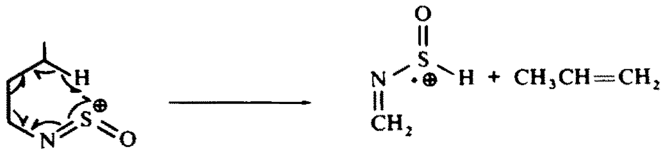
Abstract—The problem of geometrical isomerism associated with the imides of sulfur dioxide was discussed in terms of spectral data. The CNDO/2-SCFMO method was used to calculate the relative stabilities of the isomers. the barriers (inversion and rotation) to interconversion between the isomers. and the effect of alkyl substitution and inclusion of 3d orbitals on the relative stabilities and the barriers. The calculations show that the *cis. trans* sulfur di-imide (3) and the *trans*-N-sulfinylamine are the most stable. The effect of 3d orbitals is to stabilize any planar configuration in which the R-N-S angle is 180° (where R = H or Me) and to give nitrogen-sulfur bond distances in agreement with experimental values.

THE PROBLEM of geometrical isomerism in N-sulfinylamines and sulfur di-imides was suggested by the fact that pyrolysis of di-t-butyl sulfur-di-imide gives isobutene while no elimination reaction was observed for N-n-butylsulfinylamine.[1,2] If nitrogen and sulfur are sp^2 hybridized then there are three possible sulfur di-imide isomers—*cis. cis* (**1**). *trans. trans* (**2**). and *cis. trans* (**3**) and two potential N-sulfinylamines—*cis* (**4**) and *trans* (**5**). Only isomers **3** and **4** possess the geometry required for an E_i elimination reaction.

The mass spectrum of di-t-butylsulfur di-imide shows significant loss of isobutene *via* a McLafferty rearrangement while the mass spectrum of N-t-butylsulfinylamine shows a slight loss of isobutene. In addition. N-n-butylsulfinylamine fragments to an ion ($m/e = 77$) which arises from loss of propene (eq. 1). These data are consistent with isomers **3** and **5**. However. the microwave spectrum[3] of thionylimide has been assigned to the *cis*-isomer (**4**).



An X-ray diffraction[4] study shows that 4.4′-di-tolylsulfur di-imide has the *cis. trans* geometry. However. the NMR spectrum[5] of di-t-butylsulfur di-imide shows a singlet at δ 1·38 ppm. Only isomers **1** and **2** are consistent with the NMR data unless the t-butyl groups are rapidly exchanging at room temperature either through inversion at nitrogen or rotation about the nitrogen sulfur bond. This explanation is supported by the observation of a small inversion barrier for thio-oximes.[6] In addition. the calculated barrier[7] to inversion and rotation of carbodi-imide is about 8·0 kcal/mole while the measured barrier[8] is 6·6 kcal/mole.

In view of these results, we thought it would be useful to gain a theoretical insight into the relative stabilities of the various isomers, the energy of activation of each isomerization mechanism, the effect of including 3d orbitals in the basis set, and the effect of alkyl substitution.

METHOD OF CALCULATION

Pople's[9] CNDO/2 method[10] as formulated by Segal and Santry[11] for third row elements was employed. The molecules chosen for study were sulfur di-imide, dimethylsulfur di-imide,[12] thionylimide,[13] and N-methylthionylimide. In each case the N-S-N and the N-S-O angles were fixed at 120° and the energy was minimized with respect to the N-S, S-O, N-H, and N-C distances and the R-N-S angle. The interconversion mechanisms considered were rotation about the N-S bond and inversion at the nitrogen atom for *cis* to *trans*-thionylimides and for *cis, trans-* to *trans, trans-* and *cis, trans-* to *cis, cis*-sulfurdi-imides (Fig. 1).

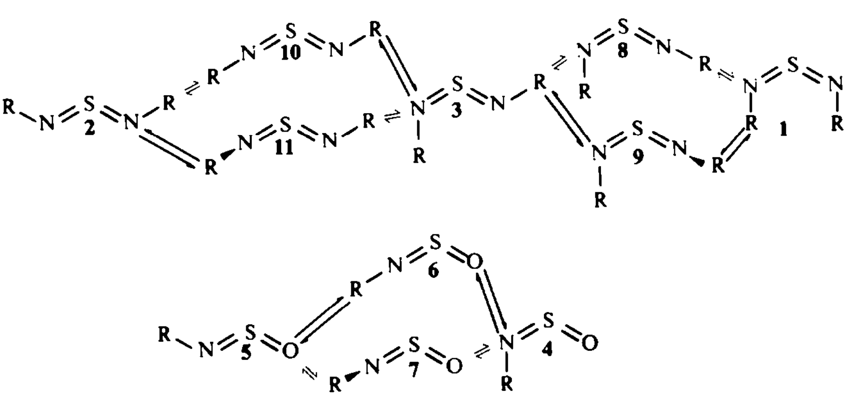


FIG 1. Interconversion mechanisms

RESULTS AND DISCUSSION

The experimental geometries for thionylimide and 4,4'-ditolylsulfur di-imide are shown in Fig. 2. Examination of Table I reveals a fairly good agreement with the calculated bond lengths for N-S and S-O provided 3d orbitals are included in the

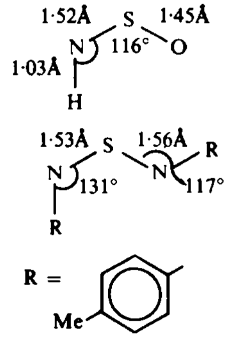


FIG 2. Experimental geometries

TABLE I. CALCULATED GEOMETRIES[a] Å

Isomer	R =	No. d Orbitals H	 Me[b]	With d Orbitals H	 Me[b]
1		1·76	1·76	1·56	1·55
2		1·77	1·78	1·55	1·56
3	a	1·78	1·76	1·55	1·52
	b	1·73	1·73	1·55	1·54
8	a	1·75	1·68	1·56	1·51
	b	1·72	1·67	1·51	1·47
9	a	1·72	1·75	1·56	1·53
	b	1·88	1·87	1·56	1·55
10	a	1·71	1·67	1·55	1·51
	b	1·69	1·66	1·51	1·48
11	a	1·72	1·77	1·55	1·57
	b	1·90	1·93	1·56	1·56
4	a	1·72	—	1·57	1·55
	b	1·49	—	1·49	1·42
5	a	1·74	—	1·56	1·56
	b	1·55	—	1·49	1·46
6	a	1·67		1·50	1·46
	b	1·49	—	1·44	1·37
7	a	1·92	—	1·58	1·60
	b	1·59	—	1·50	1·48

[a] For 3. 8. 9 (a) will be *cis* and for 3. 10. 11 (b) will be *trans*. For 4–7 (a) will be N=S and (b) S=O.

[b] *cis*-CH_3-N-S angle is 135°.

basis set. When d orbitals are excluded the N-S bond lengths are predicted to be about 0·2 Å longer than the experimental values.

The N-S bond lengths tend to shorten when the R-N-S angle is 180°. This suggests an increasing amount of double bond character for the N-S bond. When the R-N-S angle is 109 47′ and the dihedral angle is 90°. the N-S distance increases only if d orbitals are excluded. The longer bond is consistent with an increasing amount of single bond character for the N-S bond when d orbitals are not included.

Inspection of Table II shows that the *trans*-thionylimides are predicted to be more

TABLE II. RELATIVE ENERGIES (kcal/mole)

Isomer	R =	No. d Orbitals H	 Me	With d Orbitals H	 Me
3		0·00	0·00	0·00	0·00
1		-1·76	7·71	1·95	0·23
2		6·71	-4·71	4·52	-1·71
8		21·27	16·50	4·20	13·09
9		-13·36	-31·31	12·99	13·96
10		46·62	37·52	1·25	9·91
11		-11·11	-33·00	10·23	4·86
4		29·05	—	1·57	13·30
5		0·00	—	0·00	0·00
6		63·88	—	13·55	53·96
7		-18·45	—	13·36	10·98

TABLE III. ORBITAL POPULATIONS AND TOTAL CHARGE DENSITIES FOR THIONYLIMIDE

Atom	Orbitals	Pop.[5]	Dens.	Pop.[6]	Dens.	Pop[7]	Dens.
S	3s	1·8176	+0·495	1·8493	+0·359	1 8622	+0·388
	$3p_x$	1·3818		1 3376		0 9907	
	$3p_y$	1·5806		0·8288		1·7515	
	$3p_z$	0·7255		1·6257		1·0073	
O	2s	1·8989	−0·299	1·8855	−0·382	1·8801	−0·159
	$2p_x$	0·7189		0·7547		1·2121	
	$2p_y$	1·9816		1·7731		1·9602	
	$2p_z$	1·6995		1·9695		1·1070	
N	2s	1·6827	−0·264	1·6101	−0·130	1·7836	−0·277
	$2p_x$	1·1254		1·7659		1·4393	
	$2p_y$	0·8813		1·3489		0·8764	
	$2p_z$	1·5750		0·4048		1·1772	
H	1s	0·9311	+0·069	0·8461	+0·154	0·9524	+0·048

stable than *cis* isomers. However, the calculated dipole moment for *cis*-thionylimide is 1·29 debyes when d orbitals are included and is closer to the reported moment[3] for thionylimide (0·911 debyes) than the calculated moment for the *trans* isomer (4·25 debyes). Nevertheless, while the microwave spectrum of thionylimide seemed most consistent with the *cis* isomer the *trans* isomer could not be ruled out.

The *cis, trans* isomer (**3**) of sulfur di-imide is predicted the most stable, while the *trans, trans*-isomer (**2**) of dimethylsulfur di-imide is more stable than the *cis, trans* isomer by 1·71 kcal/mole when d orbitals are included.

TABLE IV. ORBITAL POPULATIONS AND TOTAL CHARGE DENSITIES FOR THIONYLIMIDE

Atom	Orbitals	Pop.[5]	Dens.	Pop.[6]	Dens.	Pop.[7]	Dens.
S	3s	1·8014	+0·371	1·8015	+0·345	1·8090	+0·429
	$3p_x$	0·8105		0·8060		0·8506	
	$3p_y$	0·9818		0·8337		1·0843	
	$3p_z$	0·7355		0·7124		0·5238	
	$3d_{z^2}$	0·0936		0·0989		0·0959	
	$3d_{xz}$	0·3408		0·3644		0·2854	
	$3d_{yz}$	0·1802		0·1955		0·1074	
	$3d_{x\ y}$	0·2868		0·4293		0·4263	
	$3d_{xy}$	0·3984		0·4136		0·3881	
O	2s	1·8087	−0·301	1·7908	−0·340	1·8102	−0·320
	$2p_x$	1·3623		1·4659		1·4054	
	$2p_y$	1·6154		1·6034		1·6765	
	$2p_z$	1·5145		1·4798		1·4282	
N	2s	1·5362	−0·210	1·3884	−0·148	1·5701	−0·261
	$2p_x$	1·0850		1·3620		1·3469	
	$2p_y$	1·3596		1·1493		1·2201	
	$2p_z$	1·2290		1·2479		1·1240	
H	1s	0·8604	+0·140	0·8573	+0·143	0·8478	+0·152

Table V. Orbital populations and total charge densities for sulfur di-imide

Atom	Orbitals	Pop.[2]	Dens.	Pop.[10]	Dens.	Pop.[11]	Dens.
S	3s	1·8342	+0·369	1·8270	+0·299	1·8694	+0·137
	$3p_x$	1·4747		0·6748		1·4843	
	$3p_y$	1·6633		1·6244		1·0100	
	$3p_z$	0·6589		1·5747		1·4993	
N	2s	1·7056	−0·246	1·6875	−0·398	1·6772	−0·026
	$2p_x$	1·1266		1·0496		1·2161	
	$2p_y$	0·7435		0·7035		1·5974	
	$2p_z$	1·6706		1·9571		0·5119	
H	1s	0·9382	+0·062	0·9641	+0·036	0·8849	+0·115
N[a]	2s	—	—	1·5627	−0·113	1·7818	−0·278
	$2p_x$	—		1·0922		0·3808	
	$2p_y$	—		1·9894		1·9293	
	$2p_z$	—		0·4683		1·1857	
H[a]	1s	—	—	0·8247	+0·175	0·9719	+0·028

[a] Atoms inverting or rotating.

Table VI. Orbital populations and total charge densities for sulfur di-imide

Atom	Orbitals	Pop.[2]	Dens.	Pop.[10]	Dens.	Pop.[11]	Dens.
S	3s	1·7788	+0·244	1·7944	+0·238	1·7894	+0·254
	$3p_x$	0·9175		0·7478		0·9689	
	$3p_y$	0·9494		0·9768		1·0241	
	$3p_z$	0·8147		0·7968		0·6893	
	$3d_{z^2}$	0·0868		0·0951		0·0899	
	$3d_{xz}$	0·3919		0·3996		0·2453	
	$3d_{yz}$	0·1893		0·1882		0·1771	
	$3d_{x^2-y^2}$	0·2824		0·2848		0·2779	
	$3d_{xy}$	0·3455		0·4782		0·4846	
N	2s	1·5243	−0·264	1·5400	−0·285	1·5448	−0·241
	$2p_x$	1·0671		1·0839		1·0966	
	$2p_y$	1·3702		1·3688		1·3942	
	$2p_z$	1·3021		1·2925		1·2052	
H	1s	0·8581	+0·142	0·8715	+0·128	0·8721	+0·128
N[a]	2s	—		1·3953	−0·224	1·5692	−0·289
	$2p_x$	—		1·0231		1·1189	
	$2p_y$	—		1·4829		1·4613	
	$2p_z$	—		1·3229		1·1392	
H[a]	1s	—		0·8573	+0·143	0·8523	+0·148

[a] Atoms inverting or rotating.

The barriers to interconversion for sulfur di-imides are small when d-orbitals are included. For dimethylsulfur di-imide. the lowest energy isomerization mechanism involves rotation of the N–S bond between the *cis. trans-* and *trans. trans-*isomers. However. the preferred mechanism for sulfur di-imide is inversion at nitrogen between 2 and 3. No distinction can be made between rotation and inversion for the *cis* to *trans* isomerization of thionylimide. but the barrier is small.

Since inclusion of d orbitals gives the best agreement with experimental geometries and the interconversion barriers are small. the configuration integrity of sulfur di-imides and thionylimides at room temperature should be compromised.

When d orbitals are excluded. the non-planar structures in which the R–N–S angle is 109° 47′ are the most stable. This suggests that there is little π stabilization due to overlap between sulfur's $3p_z$ and nitrogen's $2p_z$ orbitals. Examination of the populations of the $2p_z$ and $3p_z$ for nitrogen. oxygen. and sulfur (Tables III and V) shows that the N–S and S–O bonds are polar and possess only partial double character.

The effect of including d orbitals in the basis set is to stabilize geometries where the R–N–S angle is 180°. The mechanism of this stabilization is revealed by consideration of thionylimide. The xy plane is the molecular plane. With d orbitals included in the basis set. the sulfur atom gains 0·026 electrons when the H–N–S angle is 180° as compared to 120°. The gain is primarily in sulfur's 3dxy and $3d_{(x^2-y^2)}$ orbitals (Table IV). However. when d orbitals are neglected. sulfur loses 0·796 electrons from the $3p_x$ and $3p_y$ orbitals when the S–N–H angle is 180° as compared to 120° (Table III). With the inclusion of d-orbitals the nitrogen atom loses 0·358 electrons from the 2s and $2p_y$ orbitals when the H–N–S angle goes from 120° to 180°. Without d orbitals. nitrogen gains 0·4676 electrons in the $2p_y$ orbital.

Clearly as the H–N–S angle goes to 180° nitrogen becomes more electron withdrawing through the σ-bond. The effect of sulfur's $3d_{(x^2-y^2)}$ and $3d_{xy}$ orbitals is to offset the increased electron withdrawing power of sp hybridized nitrogen by back donation of electron density from nitrogen's 2s and $2p_y$ orbitals. thereby stabilizing the structure. This type of stabilization is known as π' bonding and has been postulated by others for cyclic phosphonitrilic halides[14, 15] and thiooximes.[6]

Finally. the Me group causes an increase in the inversion barrier when d orbitals are included. We have no obvious explanation for this effect. although the calculated N–S bond length is shorter for the linear structure when a Me group replaces a proton.

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REFERENCES

[1] J. L. Downie. R. E. Maruca. and J. R. Grunwell. *Chem. Comm.* 298 (1970)
[2] J. R. Grunwell. unpublished results
[3] W. Kirchhoff. *J. Am. Chem. Soc.* **91**. 2437 (1969)
[4] G. Leandri. V. Busetti. G. Valle. and M. Mammi. *Chem. Comm.* 413 (1970)
[5] D. Clemens. A. Bell. and J. O'Brien. *Tetrahedron Letters* 1491 (1965)
[6] C. Brown. B. T. Grayson. and R. F. Hudson. *Ibid.* 4925 (1970)
[7] M. S. Gordon and H. Fischer. *J. Am. Chem. Soc.* **90**. 2471 (1968)
[8] J. A. L. Anet. J. C. Jochims. and C. H. Bradley. *Ibid.* **92**. 2557 (1970)
[9] J. A. Pople and D. L. Beveridge. *Approximate Molecular Orbital Theory.* McGraw-Hill. New York (1970)

[10] Program 141. *Quantum Chemistry Program Exchange.* University of Indiana. Bloomington. Indiana

[11] D. P. Santry and G. A. Segal. *J. Chem. Phys.* **47**. 158 (1967)

[12] B. Cohen and A. G. MacDiarmid. *Angew. Chem.* **75**. 207 1963): *Angew. Chem. Internat.* Ed. **2**. 151 (1963)

[13] P. W. Schenk. *Ber. Chem. Dtsch. Ges.* **65**. 94 (1942)

[14] D. W. J. Cruickshank. *J. Chem. Soc.* 5486 (1961)

[15] D. P. Craig and N. L. Paddock. *Ibid.* 4118 (1962)