Ab Initio Molecular Orbital Study of the Geometric and Electronic Structure of Dimethylsulfurdiimine

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The (E,Z) and (E,E) forms of dimethylsulfurdiimine were fully optimized by ab initio STO-3G calculations. The (E,Z) conformation is predicted to be more stable than the (E,E) conformation by ca. 41 kJ/mol, in agreement with experimental data. The sulfur 3d orbitals play a crucial role in describing the structural characteristics of the molecule. 4-31G and equivalent 31G core-less calculations have been employed to obtain atomic charge densities, bond overlap populations and molecular orbital energies. A good agreement was obtained between the results of all-electron and pseudo-potential calculations.*

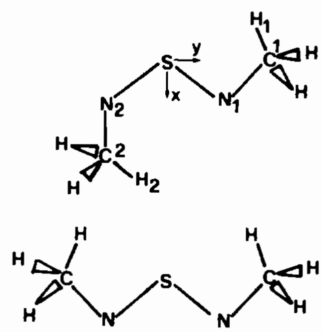

Fig. 1. (E,Z) and (E,E) forms of dimethylsulfurdiimine.

Introduction

Dimethylsulfurdiimine is a prototype of cumulative S–N bond systems R–N=S=N–R, which serve as ligands for various transition metals [1]. The molecular geometry of this system has been investigated by N.M.R. [2, 3], X-ray [4] and electron diffraction measurements [5]. The results indicate that the (E,Z) conformation is generally more stable than the (E,E) conformation, the (Z,Z) structure being hindered on steric grounds. E.S.R. experiments suggest [1] that in the R–N=S=N–R radical anions the two nitrogen atoms are magnetically equivalent, a result in accord with the (E,E) structure being the most stable (Fig. 1).

Previous theoretical investigations on the R–N=S=N–R system include HF Slater X_α calculations using a double zeta basis set and semi-empirical CNDO/2 and INDO calculations [1, 6–9]. The molecular geometry of the closely related sulfurdiimine H–N=S=N–H was previously studied at the CNDO/2 level [10]. It was found that (E,E), (E,Z) and (Z,Z) forms are energetically very close, the (Z,Z) conformation being slightly favoured over the (E,Z) one when sulfur *3d* orbitals are taken into account.

Although semi-empirical calculations have been usefully applied to support experimental findings [1, 7, 8], an *ab initio* investigation on the conformational preference and on the electronic structure of the simple CH_3–N=S=N–CH_3 compound seems to be appropriate by considering the current interest in the properties of S–N compounds [11] and, specifically, the role of the R–N=S=N–R system in coordination chemistry. One main object of the work deals with the use of pseudopotentials for core electrons to treat specifically the chemically-significant valence region of the molecule.

Calculations

Fully optimized geometries of dimethylsulfurdiimine were determined by assuming C_s and C_{2V} symmetry for the (E,Z) and (E,E) forms respectively. The calculations were carried out with the program HONDO, which uses analytic gradient techniques [12] by using a minimal STO-3G or STO-3G* basis set. The largest component of the energy gradient was less than 0.004 a.u. Further calculations on the optimized geometries were carried out with the split valence 4-31G and 4-31G + *5d* bases [13]

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TABLE I. Pseudo-potential Parameters for S, C and N. Atoms.

Atom	l	α	n_i	a_i
S	0	2.34149	−2	0.14375
			0	27.45100
			2	−15.83253
	1	2.65388	−1	4.30265
			0	7.61981
			2	0.84505
	2	1.13649	−1	−0.74309
C	0	5.33046	−1	1.36925
	1	14.06116	0	−6.05201
N	0	7.56515	−1	1.73126
	1	19.51709	0	−7.06106

(five *d* atomic functions contracted from six Cartesian Gaussians, *3d* exponent 0.45). Valence electron calculations were performed by using the pseudo-potential operator [14] successfully applied to many molecular systems [15]:

$$W_{l,c}(r) = \Sigma_i a_i r^{n_i} \exp(-\alpha r^2)$$

The calculations utilize a 31G basis set, optimized at atomic level by a pseudo-potential version of the ATOM program [16]. The pseudo-potential parameters and the 31G basis set for S, C and N atoms are reported in Tables I and II respectively. The Huzinaga 31G basis set was used for H [17]. The calculations were carried out running the RSHONDO program [18] on a Vax-11/780 computer.

Results and Discussion

The optimized structure parameters of the (E,Z) and (E,E) forms of dimethylsulfurdiimine are reported in Table III. The inclusion of sulfur *3d* orbitals in the basis set considerably reduces bond distances and increases N–$\hat{S}$–N and S–$\hat{N}$–C angles, making them comparable with the experimental data in the vapour [5]. The geometric parameters of the (E,Z) and (E,E) forms differ very slightly from each other. Significant variations were encountered only in the valence angles at S and N(2) atoms. They decrease in the (E,E) form reflecting loss of repulsive non-bonding interactions between N(1) and the C(2)–H(2) bond. This figure was clearly revealed in the electron diffraction experiment [5].

At both levels of calculations (STO-3G and STO-3G*) the molecule is predicted to be planar, with the C(1)–H(1) and C(2)–H(2) bonds in the molecular plane. The (E,Z) conformation is more stable than the (E,E) conformation, by 41 KJ/mol. The present results contrast with CNDO/2 calculations

TABLE II. Orbital Exponents and Coefficients of the 31G Split Gaussian Basis Set.

Atom	Orbital	Exponent	Coefficient
S	*s*	4.35831	0.08528
		1.98013	−0.37082
		0.42588	0.65068
		0.15711	1.0
	p	1.83231	−0.11095
		1.10718	0.21233
		0.37322	0.56178
		0.12314	1.0
	d	0.45	1.0
C	*s*	2.38201	−0.24214
		1.44306	0.18526
		0.40585	0.59128
		0.13843	1.0
	p	8.60957	0.04365
		1.94355	0.20949
		0.54279	0.50276
		0.15249	1.0
N	*s*	3.69411	−0.17152
		1.27105	0.22173
		0.46773	0.58710
		0.17307	0.35270
	p	9.74937	0.06262
		2.26966	0.25939
		0.67806	0.49678
		0.20226	1.0

[6], which predict that the (E,E) form is slightly more stable than the (E,Z) form when sulfur *d* orbitals are present, while non-planar structures become highly favoured by excluding them.

The charge densities and overlap populations of the (E,Z) form of dimethylsulfurdiimine are reported in Table IV. A very dramatic effect of the sulfur *d* orbitals is evident: at 4-31G level the S–N bonding interaction is very small or vanishes. On the contrary, with S *3d* orbitals present the overlap population rightly indicates a double bond character for S–N. An analysis of σ- and π-electron charges shows that the electron redistribution is principally within the σ-system, although significant d_π–p_π interactions operate.

Clearly the sulfur *3d* orbitals play a crucial role in the description of the geometric and bonding characteristics of this molecule, as found in other hypervalent N–S compounds [19].

The population analysis obtained by pseudo-potential calculations is in qualitative agreement with that computed from all-electron wave functions. The absence of core electrons cause a substantial decrease in the S–N and C–N bond polarity. Both methods however give comparable charge distribution within the molecule, as is shown by the computed dipole moment values reported in Table V.

TABLE III. Comparison of Calculated and Experimental Structural Parameters of Dimethylsulfurdiimine. Distances are given in Å, angles in degrees.

Structure	(E,Z)			(E,E)
	STO-3G	STO-3G*	Exp.[a]	STO-3G*
$r(S-N_1)$	1.643	1.494	1.532	1.500
$r(S-N_2)$	1.612	1.481		1.500
$r(N_1-C_1)$	1.505	1.488	1.464	1.492
$r(N_2-C_2)$	1.493	1.487		1.492
$r(C-H)$	1.092	1.092	1.110	1.092
$\alpha(N_1-S-N_2)$	110.7	116.7	113.6	112.0
$\alpha(S-N_1-C_1)$	109.1	116.8	116.5	116.2
$\alpha(S-N_2-C_2)$	118.2	122.0	124.3	116.2
$\alpha(N_1-C_1-H_1)$	115.7	113.7	107.8	114.0
$\alpha(N_2-C_2-H_2)$	116.2	111.4		114.0
Other valence angles at C	108.1	108.4	107.8	109.3
E_{total}(a.u.)	−578.77603	−578.96155		−578.94582

[a]Ref. 5.

TABLE IV. Charge Densities and Overlap Populations for Dimethylsulfurdiimine ((E,Z) form).

	4-31G		4-31G + 5*d*		Pseudo-potential 31G		Pseudo-potential 31G + 5*d*	
	π	total	π	total	π	total	π	total
S	+0.804	+1.248	$+0.851(3p_z)$ $-0.025(3d_{xz})$ $-0.176(3d_{yz})$	+0.426	+0.852	+0.890	$+0.844(3p_z)$ $-0.027(3d_{xz})$ $-0.185(3d_{yz})$	+0.173
N_1	−0.431	−0.932	−0.333	−0.507	−0.401	−0.768	−0.317	−0.377
N_2	−0.400	−0.889	−0.334	−0.496	−0.511	−0.712	−0.445	−0.318
C_1	−0.133	−0.254	−0.108	−0.137	0	−0.077	−0.005	−0.106
C_2	−0.118	−0.288	−0.088	−0.149	−0.119	−0.119	−0.117	−0.120
$S-N_1$	0.004		0.748		−0.064		0.840	
$S-N_2$	0.200		0.880		0.234		0.810	
N_1-C_1	0.360		0.534		0.454		0.538	
N_2-C_2	0.320		0.438		0.416		0.448	

TABLE V. Dipole Moment of Dimethylsufurdiimine ((E,Z) form).

	4-31G	4-31G + 5*d*	Pseudo-potential 31G	Pseudo-potential 31G + 5*d*
μ_x	−0.66	−0.52	−0.53	−0.41
μ_y	1.91	1.68	1.93	1.75
μ_{total}	2.02	1.76	2.00	1.79

The calculated ionization energies (IE, Koopmans' theorem) of dimethylsulfurdiimine are reported in Table VI. The UV photoelectron spectrum of this compound has been obtained by Schouten and Oskam [8]. Their results are also included in Table VI for comparison. At all the theoretical levels there are no inversions in the ordering of the valence orbitals. The sequence of the four highest occupied orbitals is predicted to be π, σ, σ, π, in agreement with the results of CNDO/2 and X_α calculations [8].

TABLE VI. Valence Molecular Orbital Energies (eV) and S–N Overlap Populations of Dimethylsulfurdiimine ((E,Z) form).

Orbital	Energy	4-31G $E_T = -584.66901$ Overlap population S–N₁	S–N₂	Energy	4-31G + 5*d* $E_T = -584.78210$ Overlap population S–N₁	S–N₂	Pseudo-potential 31G Energy	Pseudo-potential 31G + 5*d* Energy	Exp.[a]
6a″(LUMO, π*)	1.87	−0.954	−0.970	2.43	−0.734	−0.712	1.64	2.28	
5a″(HOMO, π)	−8.95	−0.010	0.010	−9.38	0.106	0.114	−9.01	−9.43	9.16
19a′	−10.52	−0.242	−0.482	−10.72	−0.112	−0.166	−10.56	−10.76	9.86
18a′	−11.83	−0.352	0.262	−11.76	−0.090	0.148	−11.89	−11.77	10.55
4a″(π)	−14.20	0.138	0.118	−13.96	0.164	0.148	−14.32	−13.98	11.91
17a′	−14.44	0.004	−0.056	−14.28	0.066	−0.042	−14.53	−14.29	
16a′	−15.67	0.040	−0.064	−15.65	0.010	−0.006	−15.72	−15.67	12.85
3a″(π_{CH_3})	−16.08	−0.010	0.016	−16.09	−0.006	0.030	−16.13	−16.10	
2a″(π)	−17.13	0.136	0.120	−16.94	0.116	0.094	−17.22	−16.95	
15a′	−17.57	0.020	0.102	−17.44	0.062	0.120	−17.68	−17.46	
14a′	−17.65	0.140	−0.026	−17.58	0.046	−0.068	−17.73	−17.63	
13a′	−20.35	−0.410	−0.278	−20.16	−0.268	−0.146	−20.44	−20.19	
12a′	−25.41	0.072	0.088	−25.28	0.112	0.128	−25.52	−25.39	
11a′	−26.99	−0.038	−0.094	−26.77	−0.012	−0.022	−27.12	−26.87	
10a′	−32.64	0.106	0.142	−32.32	0.208	0.222	−32.88	−32.48	
9a′	−36.70	0.340	0.332	−35.86	0.342	0.336	−37.03	−35.77	

[a]Ref. 8.

A useful bonding picture may be obtained by examination of the orbital overlap population shown in Table VI. Many valence orbitals show non-bonding or anti-bonding character, a feature common to other S–N compounds [20]. The S–N bonding character is greatly increased by the presence of S 3*d* functions; their effect on Koopmans' IE, however, appears to be not important, except on the HOMO and LUMO which are significantly stabilized. This is particularly evident in the STO-3G results. The 4a″ and 5a″ π-orbitals are essentially localized on the S and N atoms respectively, while the 2a″ and 3a″ orbitals represent the symmetric combination of the heavy atoms p_z orbitals and the π_{CH_3} orbital respectively. The agreement between experimental and Koopmans' ionization potential values is not particularly good, especially on going to inner orbitals. This may be traced to a deficiency in the basis set as well as to substantial relaxation effects accompanying ionization, by considering the relatively high localization of the outermost orbitals.

The agreement between the IEs from all-electrons and pseudo-potential calculations is surprisingly good. The IE figures agree within 0.1 eV.

The pseudo-potential model used in the present work appears to be reliable and may thus be safely used in larger S–N molecules.

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