Ab Initio Calculations of the Molecular Structures and the Electronic Properties of Sulfur-containing Compounds: III. Thioacrolein ($CH_2=CH-CH=S$) and Thioglyoxal ($S=CH-CH=S$)

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Results of ab initio SCF calculations on thioacrolein ($CH_2=CH-CH=S$) and thioglyoxal ($S=CH-CH=S$) are reported. The geometries are optimized by the analytical gradient method using the double zeta (DZ) basis set. The trans conformers of these molecules are calculated to be more stable than the cis conformer by 2.06 and 4.31 kcal/mol, respectively.

1. Introduction

Recently we have reported ab initio calculations of molecular structures and electronic properties of sulfur-containing transient species of the type R–B=S (R=H, CH_3, NH_2, OH, F and Cl) [1] and of the type RHC=S (R=H, CH_3, NH_2 and OH) [2] molecules, for which experimental studies are partly available from microwave, IR and photoelectron spectroscopies. A recent study of unstable thiocarbonyls by microwave spectroscopy by Georgiou and Kroto [3] in the products of high-temperature pyrolysis of hexamethyl-s-trithiane confirmed a further transient species, the trans-thioacrolein (trans-2-propenethial) molecule, whose structure and dipole moment are reported. The microwave spectrum of the corresponding carbonyl species, trans-acrolein, is previously well known [4] and while the search of the cis conformer seems to be unsuccessful as yet, the trans-cis interconversion energy has been estimated as 1.63 ± 0.17 kcal/mol in a recent matrix IR study of Blom et al. [5].

In the present study, we report ab initio SCF calculations of the trans and cis conformers of thioacrolein ($CH_2=CH-CH=S$) and also of the thioglyoxal molecule ($S=CH-CH=S$) whose spectroscopic detection is not reported as yet. The electronic structures have been studied in terms of charge distributions and molecular properties calculated by gaussian orbital basis set of double-zeta (DZ) quality.

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2. Details of Calculation

Ab initio SCF calculations of structures and properties of $CH_2=CH-CH=S$ and $S=CHCH=S$ have been carried out employing gaussian basis set of Huzinaga's (9s, 5p) set [6], contracted to a double zeta (4s, 2p) according to Dunning's scheme [7] for C. The Huzinaga's (12s, 8p) set [8] has been contracted to a (6s, 4p) set according to Dunning and Hay [9] for S. A (4s) gaussian expansion of hydrogen 1s orbital with a scale factor of 1.2 was similarly contracted to a (2s) set for hydrogens [7]. The molecular geometries were optimized by the force gradient method with analytical gradient [10] as implemented in MONSTERGAUSS 80 program [11].

3. Results and Discussion

The atomic arrangements and labelling of the thioacrolein and thioglyoxal molecules are shown in Figure 1. The calculated SCF energies with the DZ basis set for the fully optimized molecular geometries for these molecules in their trans, perpendicular and cis conformers are listed in Table 1. The trans conformer refers to the trans conformation of the C1=C2 and C3=S double bonds about the C2–C3 single bond for thioacrolein. The cis-

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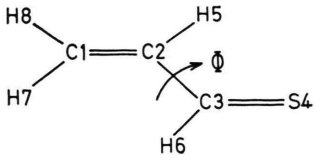
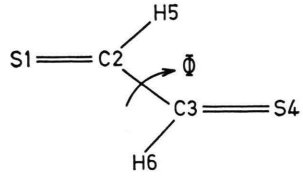


(1) Thioacrolein



(2) Thioglyoxal

Fig. 1. Numbering of atoms in thioacrolein and thioglyoxal; trans: $\Phi = 0°$, perpendicular: $\Phi = 90°$ and cis: $\Phi = 180°$.

Table 1. Calculated SCF energies and energy differences in conformers of thioacrolein and thioglyoxal[a].

	SCF energies	Energy differences
Thioacroleine		
trans:	− 513.32367	0.0
perpendicular:	− 513.30882	9.31
cis:	− 513.32038	2.06
Thioglyoxal		
trans:	− 871.77116	0.0
perpendicular:	− 871.75943	7.35
cis:	− 871.76428	4.31

[a] SCF energies in a.u. and energy differences in kcal/mol.

trans separation energies were found to be 2.06 kcal/mol and 4.31 kcal/mol and the internal rotation barriers with respect to the minimum trans conformer were calculated as 9.31 kcal/mol and 7.35 kcal/mol, respectively. For thioacrolein, the calculated cis-trans energy is comparable to the experimental value of 1.63 ± 0.17 kcal/mol [5] and the calculated value of 1.51 kcal/mol [12] for acrolein itself. The calculated cis-trans energy separation for thioglyoxal is also similar to various calculated values for glyoxal [13]. The calculated rotational barrier for thioglyoxal is found to be also similar to the previously calculated value for glyoxal [13] and the rotational barrier for thioacrolein is found to be about 2 kcal/mol larger than that of the thioglyoxal molecule.

The optimized geometries determined by the DZ SCF calculations are listed for thioacrolein and thioglyoxal in Table 2. A comparison between the calculated values and experiment is only possible for trans thioacrolein for which previous microwave study determined the r_s structure for the skeleton of $CH_2{=}CH{-}CH{=}S$ [3]. Except for the C=S double bond distance, the calculated geometrical parameters are in excellent agreement with the experimental ones. The C=S bond distance is overestimated by about 0.04 Å in the calculation. This is mainly due to the lack of the polarization func-

Table 2. Optimized geometries of thioacrolein ($CH_2{=}CH{-}CH{=}S$) and thioglyoxal ($S{=}CH{-}CH{=}S$) using the DZ basis set[a].

Molecules	Thioacrolein ($CH_2{=}CH{-}CH{=}S$)			Thioglyoxal ($S{=}CH{-}CH{=}S$)		
	trans	perpendicular	cis	trans	perpendicular	cis
Bond lengths						
C1−C2	1.340 (1.341)	1.331	1.340	—	—	—
S2−C2	—	—	—	1.646	1.642	1.644
C2−C3	1.459 (1.455)	1.485	1.466	1.465	1.479	1.473
C3−S4	1.652 (1.610)	1.646	1.657	1.646	1.642	1.644
C2−H5	1.083	1.089	1.084	1.087	1.086	1.086
C3−H6	1.089	1.090	1.088	1.087	1.086	1.086
C2−H7	1.086	1.086	1.085	—	—	—
C1−H8	1.083	1.084	1.084	—	—	—
Bond angles						
< C1C2C3	122.4 (122.9)	124.9	124.9	—	—	—
< S1C2C3	—	—	—	123.7	125.4	127.8
< C2C3S4	125.4 (125.5)	125.0	128.0	123.7	125.4	127.8
< H5C2C1	120.7	120.0	119.4	—	—	—
< H6C3S4	119.3	118.7	118.0	120.7	120.0	118.6
< H5C2S1	—	—	—	120.7	120.0	118.6
< H7C1C2	121.9	122.3	121.6	—	—	—
< H8C1C2	121.4	120.9	121.0	—	—	—

[a] Bond lengths in Å units and bond angles in degrees. Values in parentheses are available experimental ones of [3].

Table 3. Calculated rotational constants of thioacrolein and thioglyoxal[a].

	Thioacrolein (CH_2=CH−CH=S)	Thioglyoxal (S=CH−CH=S)
trans:		
A	46397.0 (45947)	51757.5
B	2729.0 (2794)	1673.4
C	2577.4 (2633)	1621.0
cis:		
A	13697.4	17908.4
B	2393.5	3678.1
C	2037.5	3051.4

[a] In MHz units.
[b] Values in parentheses are experimental ones of [3].

tions in the basis set employed in the calculation, as was also shown in previous theoretical studies [1, 2]. It is worthwhile to compare bond distances and bond angles among trans, perpendicular and cis conformers in both molecules. Among geometrical parameters the C2—C3 single bond distance, and the < C1C2C3 and < S1C2C3 bond angles in CH_2=CH−CH=S and S=CH−CH=S are found to be those which change more significantly due to internal rotations along the C2—C3 single bond. In the perpendicular conformer the C2—C3 single bond distance becomes appreciably larger due to the lack of π-conjugation, as expected. The calculated rotational constants are listed in Table 3 and compared with experimental values for trans thioacrolein [3]. The calculated rotational constants for cis thioacrolein and for thioglyoxal may be served as a guidance for future experimental studies of detection and conformation of these species.

Of interest is the ordering of the higher lying MO's of trans thioacrolein and glyoxal. In both molecules, the HOMO is found to be the lone pair orbital of the sulfur atom with 9.43 eV (trans acrolein) and 10.17 eV (trans glyoxal), respectively. The separation between the HOMO and the next lying MO's which is of π-symmetry is calculated to be rather small; 0.21 eV (thioacrolein) and 0.28 eV (thioglyoxal). In thioacrolein, these two MO's (n and π) are distinctively separated from the next lying MO's (π-type) by 3.2 eV. As in the case of glyoxal [13], the ordering of four higher lying MO's of trans thioglyoxal is found to be n, π, n and π, though the separation between the three MO energies (10.17 eV, 10.45 eV and 10.50 eV) is calculated as very small. Future photoelectron spectroscopical studies for these species would be of interest with respect to the ordering and magnitude of the calculated MO energies.

The calculated net charges and overlap populations are summarized in Table 4. Of interest is the overlap population of the C2—C3 bond in both molecules. It is shown that the C2—C3 overlap population in the trans thioacrolein molecule is

Table 4. Net charges and overlap populations of thioacrolein and thioglyoxal.

Molecules	Thioacrolein (CH_2=CH−CH=S)			Thioglyoxal (S=CH−CH=S)		
	trans	perpendicular	cis	trans	perpendicular	cis
Net charges						
C1	− 0.290	− 0.280	− 0.245	—	—	—
C2	0.029	− 0.060	− 0.021	− 0.344	− 0.363	− 0.378
C3	− 0.494	− 0.469	− 0.474	− 0.344	− 0.363	− 0.378
S4	0.037	0.065	0.030	0.125	0.112	0.175
H5	0.175	0.191	0.148	0.220	0.252	0.205
H6	0.193	0.226	0.194	0.220	0.252	0.205
H7	0.177	0.166	0.174	—	—	—
H8	0.173	0.161	0.194	—	—	—
Overlap populations						
C1—C2	1.213	1.348	1.260	—	—	—
C2—C3	0.300	0.196	0.234	0.100	− 0.125	− 0.034
C3—S4	0.686	0.892	0.784	0.676	0.824	0.779
C2—H5	0.734	0.750	0.726	0.756	0.721	0.760
C3—H6	0.740	0.718	0.740	0.756	0.721	0.760
C1—H7	0.712	0.756	0.720	—	—	—
C1—H8	0.722	0.752	0.710	—	—	—

appreciably larger than those of the perpendicular and cis conformers. In thioglyoxal, the same trends persists though it is much smaller in magnitude than for thioacrolein. It is worthwhile to note that the overlap populations in the perpendicular and cis conformers are calculated to be slightly negative. Accordingly, the overlap population for the C3=S4 double bond in both molecules becomes much larger in the perpendicular and cis conformers compared to the trans conformer.

It is well known that the calculated net charges and overlap populations are dependent upon the basis set employed in the calculation. A previous ab initio study of the >C=S species [2] showed that the overlap populations calculated with basis set including polarization functions became much larger than those from the DZ basis set, while the qualitative trends persisted. In general, the DZ basis set has the tendency to overestimate the polarity of a bond and hence the calculated net charges from the DZ plus polarization functions are expected to be smaller in magnitude than those from the DZ basis set. Specifically, the charges of the C3 atom are expected to be smaller in magnitude and those of the S4 atom might become slightly negative in the DZ plus polarization function basis set, according to previous theoretical study for the >C=S species, where a comparison had been made between DZ and DZ plus polarization basis sets.

Table 5. Molecular electronic properties of thioacrolein and thioglyoxal.

Molecules	Thioacrolein (CH_2—CH—CH=S)		Thioglyoxal (S=CH—CH=S)	
	trans	cis	trans	cis
Dipole moment[a]				
μ	3.025 (2.61)[c]	2.876	0.0	2.756
Quadrupole moment[b]				
Q_{xx}	0.5202	— 0.5821	3.2315	— 5.0798
Q_{yy}	— 2.3805	— 2.7228	3.0020	0.9843
Q_{zz}	1.8603	3.3049	— 6.2334	4.0955
$\langle r^2 \rangle$	— 71.3990	— 70.6733	— 91.4317	— 87.2925

[a] Debye units. [b] Principal axis system.
[c] Experimental value of [3].

The calculated dipole and quadrupole moments are listed in Table 5. The calculated dipole moment for the trans thioacrolein of 3.025 Debye is approximately 20% larger then the experimental value of 2.61 Debye of [3]. The $\langle r^2 \rangle$ value may be served as a measure of the extent of the charge distribution. It is shown that the calculated $\langle r^2 \rangle$ values are larger in magnitude for the trans conformers in both molecules.

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