Theor Chim Acta (1988) 74:259-267

Theoretica Chimica Acta

Ab initio study of the methyl internal rotation and aldehyde hydrogen wagging of thioacetaldehyde in the X^1A' and a^3A'' states*

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Received June 1, revised December 21/Accepted December 23, 1987)

Ab initio SCF calculations have been performed for the methyl internal rotation and for aldehyde hydrogen wagging of thioacetaldehyde in the first triplet excited state, a^3A'', as well as in the singlet ground state, X^1A'. The preferred conformations for these states are the anti-eclipsed and the eclipsed ones, respectively. The calculated barrier heights to methyl rotation (118.3 and 455.6 cm^{-1} for a^3A'' and X^1A', respectively) are in good agreement with the available experimental data. The singlet ground state and the triplet excited state exhibit a planar and pyramidal configuration, respectively. The inversion barrier of the pyramidal configuration is found to be very low 67.4 cm^{-1}. Finally, the change of conformation and structure with the transition is explained by a change of hydridization of the aldehyde carbon atom due to an $n \rightarrow \pi^*$ excitation.

Key words: Internal rotation—Aldehyde hydrogen wagging—Potential energy functions—Conformation in triplet excited state

1. Introduction

Thioacetaldehyde, CH_3–CHS, is an unstable molecule which was first isolated and characterized by photoelectron spectroscopy in the pyrolysis products of 1,3,5-trimethyltrithiane, $(CH_3–CHS)_3$ [1]. The ground state structure of this

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

molecule, dipole moment, and internal rotation barrier, were determined by Kroto et al. by microwave spectroscopy [2]. Its infrared and Raman spectra have not yet been measured.

The low-lying electronic states of thioacetaldehyde have been investigated by Judge et al. [3]. The spectrum of this molecule is similar to those of thioformaldehyde and thioacetone [4-7]. It shows six transitions in the 190-700 nm region. These absorption bands have been assigned to the intravalence singlet and triplet $n \rightarrow \pi^*$ and singlet $\pi \rightarrow \pi^*$ transitions, and to three Rydberg singlet transitions. As far as we know, the electronic ground and excited states of thioacetaldehyde have never been studied theoretically.

Recently, the phosphorescence excitation and emission spectra of thioacetaldehyde have been investigated by Judge et al. [8]. From the torsional structure of the spectra, these authors deduced the rotational barriers of the methyl group for both singlet ground state and triplet excited state. An analysis of the data of isotopic species showed that the torsional motion in the triplet state should be coupled to the large amplitude wagging of the aldehyde hydrogen.

The oxygen analogue, acetaldehyde, provided them with a useful model against which thioacetaldehyde results could be compared. Acetaldehyde had been previously investigated experimentally and theoretically as well, by Noble et al., and Baba et al. [9-11]. These authors had found two long progressions, in its singlet-singlet spectrum, that were attributed to the two large amplitude out of plane modes, V'_{14} and V'_{15}, corresponding to the aldehyde hydrogen wagging and to the methyl torsion, respectively. The existence of the two progressions was explained, on the basis of Franck-Condon arguments, assuming that the equilibrium positions of the two vibrational modes were very different in the two combining electronic states. The aldehyde hydrogen, which is coplanar in the ground state, should adopt a pyramidal structure in the excited state. In the same way, the methyl group, in an eclipsed conformation in the ground state, should have an anti-eclipsed conformation in the excited state. The conclusions were confirmed theoretically in an *ab initio* SCF (self consistent Field) calculation performed by Baba et al. [12].

In the same way, Judge et al. investigated the phosphorescence spectra of the thioacetaldehyde homologue, thioacroleine, both theoretically and experimentally [13]. Trans-thioacroleine was found to be more stable than the cis form in the ground state, while in the triplet state the cis form was favoured.

In the present work, *ab initio* conformational calculations for large amplitude modes of thioacetaldehyde have been carried out, in both ground states and first triplet excited state, in order to verify Judge's hypothesis. It is found that thioacetaldehyde hydrogen will adopt a coplanar geometry in the ground state and a pyramidal geometry in the first triplet states. In the same manner, it is seen that the methyl group will exhibit an eclipsed, and anti-eclipsed conformation, in the two states.

2. Method

Since the SCF calculations performed by Baba et al., using a RHF (restricted Hartree-Fock) scheme, for both ground and first singlet excited states of acetaldehyde, seemed to yield reasonable results, the same level of approximation is adopted in the present paper [12]. The calculations presented here for thioacetaldehyde were thus carried out by means of the standard Monstergauss program, the RHF and UHF (Unrestricted Hartree-Fock) schemes being used for the singlet ground state, and triplet excited state, respectively [14]. The UHF model was seen to furnish relatively good energy values for the lowest triplet state, even better than a configuration interaction calculation limited to mono-excitations [15].

The basis set employed through all the calculations was 4-31G, to which six d-type gaussian orbitals with exponent $a = 0.39$ and centered on the sulphur atom were added. The standard 4-31G basis set, without d-type orbitals, however, was used in the geometry optimization of the triplet state, because of the limitation of the Monstergauss program.

The geometrical parameters reported by Kroto and Landsberg for the thioacetaldehyde ground state were used in the conformational calculation of this state [2]. They are given in Fig. 1. The geometry of the tiplet state was partially optimized using an analytical gradient procedure. In order to select which were the geometrical parameters to be optimized, we assumed that the transition $(n \rightarrow \pi^*)$ will mainly induce a change of hybridization in the carbonyl carbon atom. The geometry optimization was thus limited to the C=S bond length, the C-C-S bond angle and the wagging of the hydrogen atom around an axis lying in the plane of the molecule perpendicular to the C-H bond and passing through the carbon atom. The other parameters were assumed to be those of the singlet state. The following parameters were found $r(\text{C=S}) = 1.80$ Å, $A(\text{CCS}) = 122°$ and $\alpha(\text{wagging}) = 7°$, in relatively good agreement with the theoretical values

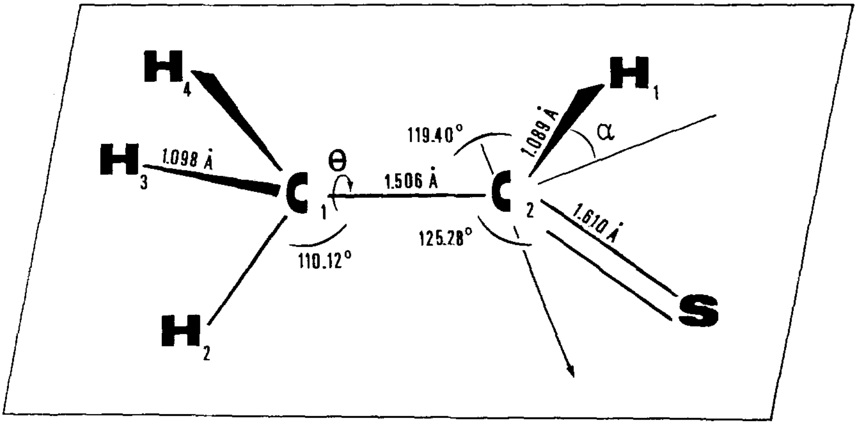

Fig. 1. Geometric parameters and rotation axes of thioacetaldehyde, in its eclipsed conformation

found for thioformaldehyde [16, 17]. The CS theoretical bond length, however, seems to be ~0.1 Å too long when compared with the experimental value [4].

Using this geometry calculations were performed for both singlet ground and first triplet excited states, where the methyl group was rotated about the C-C bond by an angle of θ (up to 30°) from the eclipsed conformation. Simultaneously the wagging angle of the hydrogen atom (α) was modified from $-35°$ to $+35°$ for the singlet, and from $-60°$ to $+60°$ for the triplet state.

In order to determine the potential energy functions for the two vibrational modes, the results of these calculations for each state were plotted in a symmetry adapted double Fourier expansion in terms of θ and α. The symmetry was introduced in this expansion by taking into account the invariance properties of the potential energy function under the operations of the non-rigid symmetry group of the molecule [18, 19].

As is easily verified, the non-rigid symmetry group for the torsion and wagging in thioacetaldehyde is a group isomorphic to the symmetry point group C_{3v}. This group contains the identity, the internal threefold rotations of the methyl group, $\hat{C}_3$ and $\hat{C}_3^2$, and the double exchange operations, $\hat{V}$, $\hat{C}_3\ \hat{V}$ and $\hat{C}_3^2\hat{V}$.

The $\hat{V}$ operation is defined as follows:

$$\hat{V}f(\theta, \alpha) = f(-\theta, -\alpha)$$

As a result, the potential energy function takes the simple form:

$$V(\theta, \alpha) = \sum_{KL} [A_{KL} \cos 3K\theta \cos L\alpha + B_{KL} \sin 3K\theta \sin L\alpha] \tag{1}$$

which is indeed invariant under all the operations ($\hat{E}$, $2\hat{C}_3$ and $3\hat{V}$) of the group. The fitting of the theoretical results to this symmetry adapted function was carried out by means of the multiple linear regression procedure BMDP1R of the package BMDP83 [20].

3. Results and discussion

Singlet ground state

The total energy values found for the singlet ground state of planar thioacetaldehyde as a function of the conformational angle of the methyl group (θ), are given in Table 1. It is seen that the preferred conformation is the eclipsed one ($\theta = 0°$), and the anti-eclipsed one ($\theta = 60°$) is less favourable. The calculated barrier height is $V_3 = 455.6\ \text{cm}^{-1}$, which is in relatively good agreement with the experimental values of $V_3 = 549.6\ \text{cm}^{-1}$, measured by microwave spectroscopy [2], and $V_3 = 535.3\ \text{cm}^{-1}$ obtained from vibrational analysis of the phosphorescence spectrum [8].

In the same table, the corresponding energy values obtained for the triplet geometry are given. Here again, the eclipsed and anti-eclipsed conformations are respectively the most and least favourable. The corresponding barrier height is $V_3 = 398.1\ \text{cm}^{-1}$.

Table 1. Energy values, in a.u., obtained in the SCF calculations for the methyl rotation in thioacetaldehyde

θ	S (S geo.)	S (T geo.)	T (planar)	T (pyramidal[a])
0°	−475.017863 min	−474.996210 min	−474.984146 max	−474.983822
15°				−474.983585 max
30°	−475.016828	−474.995307	−474.984426	−474.983829
45°				−474.984409
60°	−475.015787 max	−474.994396 max	−474.984685 min	−474.984992
75°				−474.985237 min
90°	−475.016828	−474.995307	−474.984426	−474.984994

[a] $\alpha = 20°$ (S geo mean singlet geometry)

The energy values found for the singlet ground state of thioacetaldehyde, in its eclipsed conformation, are plotted versus the wagging angle, α, of the aldehyde hydrogen in Fig. 2. It is seen that the most stable configuration is the planar one ($\alpha = 0°$). The same result is found for thioacetaldehyde in its anti-eclipsed conformation.

These results were adjusted, by means of the multiple linear regression procedure mentioned above, to the symmetry adapted potential energy function (1). The following expression was found (in kcal/mol):

$$V(\theta, \alpha) = 59.21452 - 58.59543 \cos \alpha + 0.21826 \cos 3\theta \cos \alpha$$
$$-0.86427 \cos 3\theta \cos 2\alpha + 1.87939 \sin 3\theta \sin \alpha$$

with a very good correlation factor, 0.9999, and standard deviation, 0.0348 kcal/mol.

This expansion provides a good analytical description of the potential energy function. Because of the presence of mixed terms it is apparent that the coupling between the two torsional modes is not negligible in the singlet ground state.

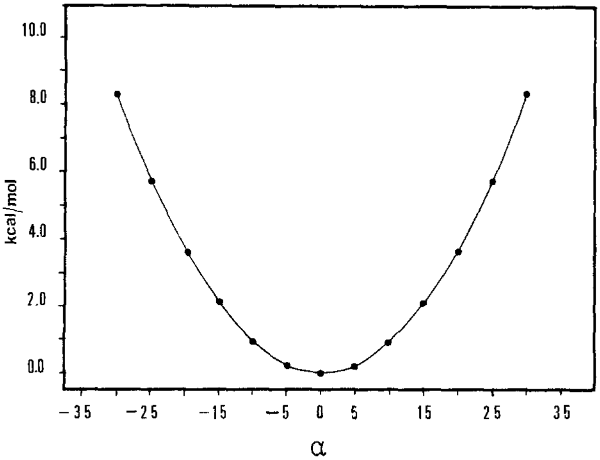

Fig. 2. Potential energy curves ($\theta = 0°$) in kcal/mol, for the aldehyde hydrogen wagging of thioacetaldehyde, in its eclipsed conformation and singlet ground state X^1A'. (1 kcal/mol = 349.64 cm^{-1})

An analysis of the SCF singlet wavefunction shows that the highest occupied molecular orbital (HOMO) is a typical *n* orbital mainly centered on the sulphur atom. In contrast, the lowest unoccupied molecular orbital (LUMO) is a π^* antibonding orbital mainly localized on the thiocarbonyl bond.

Triplet excited state

The total energy values obtained for the first triplet excited state of planar thioacetaldehyde as a function of the conformational angle of the methyl group are also given in Table 1. Notice that some convergence difficulties were met in the UHF-SCF calculations, especially at large α values, because of the proximity of the b^3A' ($\pi \rightarrow \pi^*$) state.

It is seen that the preferred conformation is not the anti-eclipsed one, whereas, the eclipsed one is the less favourable. The calculated barrier height is $V_3 = 118.3\ \mathrm{cm}^{-1}$ which is in very good agreement with the experimental value, $V_3 = 94.2\ \mathrm{cm}^{-1}$, evaluated by torsional analysis of the phosphorescence spectrum using a planar model [8].

This change of conformation between the single ground state and the first excited state can be explained on the basis of hyperconjugation, as Judge and Baba proposed [8, 12].

The energy values found for the triplet state of thioacetaldehyde versus the wagging angle are plotted in Figs. 3 and 4, for the eclipsed and anti-eclipsed conformations, respectively. It is seen that thioacetaldehyde exhibits a preferred pyramidal configuration with a wagging angle, $\alpha = 20°$, although the potential energy curves seem to be very flat between $-30°$ and $+30°$. The inversion barrier

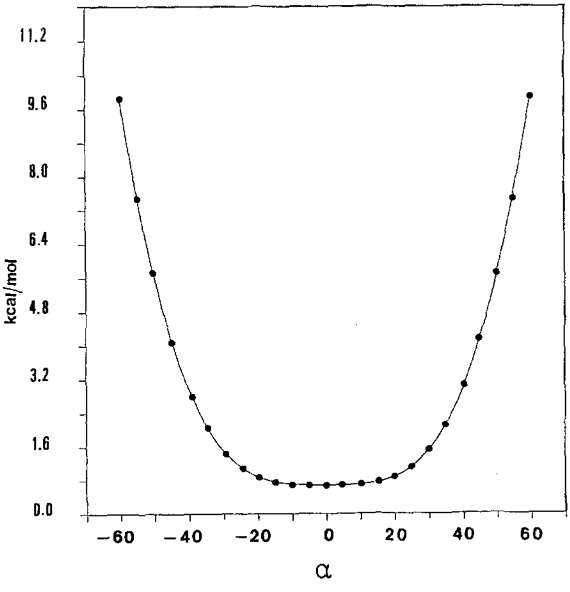

Fig. 3. Potential energy curves ($\theta = 0°$) in kcal/mol, for the aldehyde hydrogen wagging of thioacetaldehyde, in its eclipsed conformation and triplet first excited state a^3A''

height is indeed very low $V_i = 67.4\ \mathrm{cm}^{-1}$, when compared to that of acetaldehyde $V_i \approx 500\ \mathrm{cm}^{-1}$ [11].

The total energy values obtained for the triplet state of pyramidal thioacetaldehyde versus the rotational angle of the methyl group are also listed in Table 1. It is found that the preferred conformation is now roughly a gauche one ($\theta = 75°$). The calculated barrier height is now $V_3 = 362.6\ \mathrm{cm}^{-1}$.

These results were also adjusted by means of a multiple linear regression procedure to the symmetry adapted potential energy function (1). The following expression was encountered, after smoothing, (in kcal/mol):

$$\begin{aligned} V(\theta, \alpha) = {} & 28.11636 - 31.49741 \cos \alpha + 3.87966 \cos 3\alpha \\ & + 1.49301 \cos 3\theta \cos \alpha - 1.40930 \cos 3\theta \cos 2\alpha \\ & + 0.08605 \cos 3\theta \cos 3\alpha \\ & - 0.03067 \sin 3\theta \sin \alpha + 0.45733 \sin 3\theta \sin 3\alpha \end{aligned}$$

with a very good correlation factor, 1.0000, and standard deviation: 0.0252 kcal/mol.

The presence of large mixed terms in this expansion suggests the existence of a large coupling between both vibrational modes in the triplet state.

An analysis of the SCF (UHF) triplet wavefunction of planar thioacetaldehyde shows that the two highest unpaired occupied orbitals are respectively an n orbital centered on the sulphur atom, and a π antibonding orbital localized on the thiocarbonyl bond. As a result, it may be concluded that the electronic

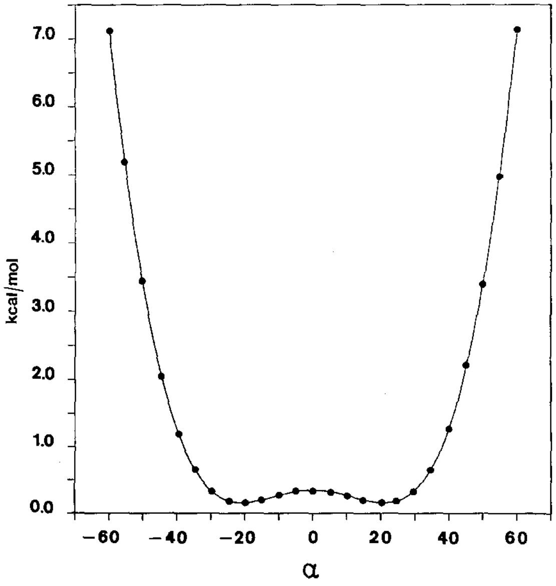

Fig. 4. Potential energy curves ($\theta = 60°$) in kcal/mol, for the aldehyde hydrogen wagging of thioacetaldehyde, in its anti-eclipsed conformation and triplet first excited state a^3A''

Table 2 Spin density distributions for triplet state of planar and pyramidal thioacetaldehyde for ($\theta = 0°$)

Atom	T (planar)	T (pyramidal)[a]
C_1	−0.1714	−0.1604
H_n	0.0345	0.0328
C_2	1.1650	1.1442
S	0.9856	0.9930
H_1	−0.0826	−0.0752

[a] $\alpha = 20°$

transition, from the singlet ground state to the triplet excited state, is actually an $n \rightarrow \pi^*$ transition. This induces a change of hybridization in the thiocarbonyl carbon atom, and a change of structure.

In order to confirm this conclusion, the spin density distribution encountered, in the planar configuration of the thioacetaldehyde triplet state, is given in Table 2. It is seen that the unpaired electrons are mainly situated on the sulphur and carbon atoms of the thiocarbonyl bond. The thiocarbonyl bond is then not a double bond anymore, but a single bond, in the triplet state, with a change of hydridization from sp^2 to sp^3. The spin density distribution obtained in the pyramidal configuration is also given in the same Table. It confirms the above conclusions.

Conclusions

The present calculations show that there are important configurational and structural changes between the singlet ground state and the first triplet excited state of thioacetaldehyde, such as those observed in the case of acetaldehyde. As a result, the emission and absorption electronic spectra of thioacetaldehyde must also exhibit large band structures, because of the Franck-Condon principle. In fact, they were actually observed [8].

In the present work, the potential energy surfaces for the methyl internal rotation and aldehyde hydrogen wagging, in thioacetaldehyde have been calculated for the singlet ground state, X^1A', and the triplet first excited state, a^3A''. The calculated barrier heights to internal rotation are in good agreement with the known experimental data [2, 8]. The singlet ground state and triplet state exhibit a planar and pyramidal configuration, respectively. The inversion barrier, however, in the triplet state, is very low, so that large amplitude motions must be expected.

An analysis of the analytical forms of the potential energy functions obtained in the present calculations suggest a large coupling between the two vibrational modes, especially in the triplet state. At the present time, calculations are in progress in our laboratory to solve the two dimensional motion equation using the symmetry adapted potential following [17]. From the solutions, the vibrational structure of the electronic spectrum will be determined.

Finally, the change of conformation and structure with the transition is explained by a change of hybridization of the thiocarbonyl carbon atom due to an $n \rightarrow \pi^*$ excitation.

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