Infrared spectroscopic evidence for an attractive intramolecular 1,5-CH···O interaction in 1-methoxy-2-(methylthio)ethane

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An attractive intramolecular 1,5-CH··O interaction is evidenced in a conformer of 1-methoxy-2-(methylthio)ethane, in which the distance between a hydrogen atom of the SMe group and the oxygen atom is significantly shorter than the van der Waals separation.

In 1992, we showed the importance of an intramolecular 1,5-CH··O interaction for determining the conformational stabilities of 1,2-dimethoxyethane (DME) in an argon matrix.[1] Since this work was reported, a considerable number of theoretical studies have been published, which dealt with the conformational properties of this molecule by paying special attention to this peculiar interaction.[2–6] These theoretical studies have shown the importance of this interaction in the conformational stabilisation of the DME molecule, in agreement with the experimental results by gas-phase electron diffraction[7] and matrix-isolation and gas-phase IR spectroscopy.[1,8] These experimental findings for the intramolecular 1,5-CH··O interaction were, however, not necessarily decisive because of the complexity involved in the analysis of the experimental data owing to the presence of many conformers. Here we report definitive detection by matrix-isolation IR spectroscopy of a conformer of 1-methoxy-2-(methylthio)ethane (MMTE), $MeOCH_2CH_2SMe$, which is stabilised by an intramolecular 1,5-CH··O interaction. The characteristics of this intramolecular interaction should be similar in many respects to those of the well-recognised intermolecular CH··O interactions in organic crystals.[9]

The matrix-isolation IR spectra of MMTE were measured by depositing the premixed gases (Ar/MMTE = 2000) onto a caesium iodide plate kept at 11 K. Further experimental details are the same as described previously.[10] *Ab initio* molecular orbital calculations were performed using the GAUSSIAN 94 program[11] on all of the 14 possible conformers of MMTE by the second-order Møller–Plesset perturbation theory (MP2) using the 6-31G* basis set to evaluate the energies, optimized structures, partial charges, vibrational wavenumbers and IR intensities. The calculated wavenumbers were scaled by a uniform factor of 0.95 in the light of the previous systematic studies dealing with a large number of experimental wavenumbers.[12,13]

The IR spectrum of MMTE in an argon matrix at 11 K is shown in Fig. 1. The intensity behaviour of the bands with varying temperature has revealed that the spectrum consists of the bands arising from two conformers. To identify these conformers, the observed spectrum was critically compared with the *ab initio* calculated theoretical spectra of all the possible conformers. The observed bands coincide only with the bands of the TGG′ and TTG conformers.† The theoretical spectra of these conformers are shown in Fig. 1, in comparison with the observed spectrum. The existence of the TGG′ and TTG conformers in an argon matrix agrees with the calculated energies given in Table 1, corresponding as they do to the two lowest-energy conformers of MMTE.

It is noted that the TGG′ conformer, whose optimized structure is shown in Fig. 2, is highly stabilized in the isolated state. In this conformer, the distance (indicated by dots) between one of the hydrogen atoms of the SMe group and the oxygen atom is 0.244 nm, which is significantly shorter than the expected van der Waals separation of *ca.* 0.270 nm. It is obvious that an attractive intramolecular 1,5-CH··O interaction occurs between these non-bonded atoms and greatly stabilizes the TGG′ conformer. The H··O distance in MMTE is shorter than the corresponding distance in DME by 0.002 nm, indicating that the interaction in the former molecule is stronger than in the latter.

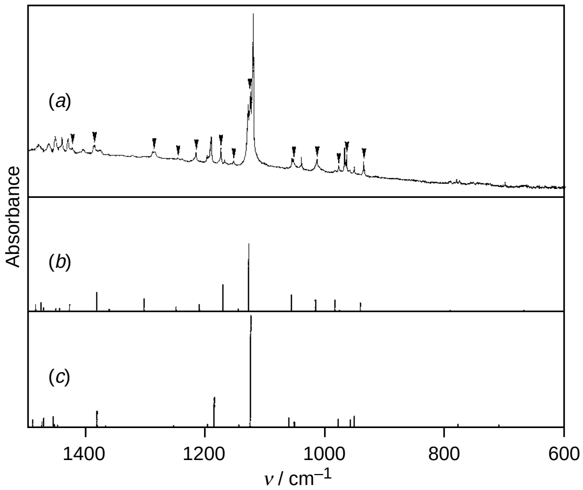

Fig. 1 Observed and calculated IR spectra of MMTE: (*a*) observed matrix-isolation spectrum at 11 K, (*b*) calculated spectrum of the TGG′ conformer and (*c*) calculated spectrum of the TTG conformer. In the observed spectrum, the bands which are assigned exclusively to the TGG′ conformer are marked with an arrow.

The calculated partial charges of atoms are shown in Fig. 2. It is noteworthy that the methyl carbon atom bonded to the sulfur atom carries a large negative charge (−0.63 *e* units), which is comparable to the partial charge (−0.62 *e*) of the oxygen atom. The positive partial charge (+0.22 *e*) of the methyl hydrogen atom that interacts with the oxygen atom is larger than the partial charges (+0.18 and +0.19 *e*) of other hydrogen atoms

Table 1 Energies of the 14 possible conformers of 1-methoxy-2-(methylthio)ethane (MMTE)

Conformer[a]	Energy/ kJ mol^{-1} [b]	Conformer[a]	Energy/ kJ mol^{-1} [b]
TGG′[c]	0.000	GGG	8.633
TTG	3.042	GTG	8.647
TTT	5.848	GGT	8.851
GGG′[c]	6.167	GTT	11.094
TGT	6.514	G′GG[d]	13.447
G′TG	7.662	G′GT[d]	14.745
TGG	7.688	G′GG′[c,d]	—[e]

[a] Conformation around the MeO–CH_2–CH_2–SMe bonds (T = *trans*, G = *gauche*). [b] Relative energies with respect to the energy of the TGG′ conformer, calculated at the MP2/6-31G* level. [c] 1,5-CH··O interaction is involved. [d] 1,5-CH··S interaction would be possible. [e] Transformed into the TGG′ conformer during structure optimization.

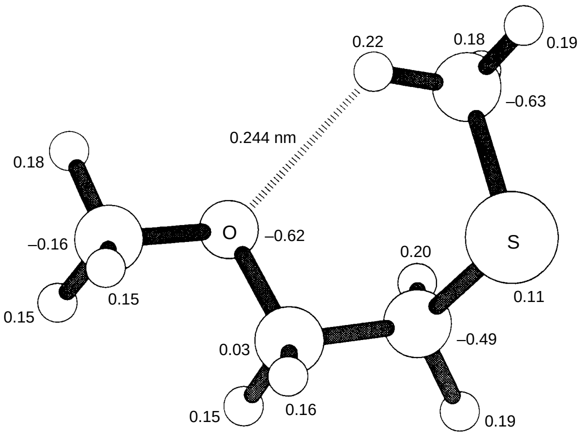

Fig. 2 Optimized structure of the TGG′ conformer of MMTE. The intramolecular 1,5-CH··O interaction occurs between the methyl hydrogen atom and the oxygen atom as indicated by dots; the H··O distance is 0.244 nm and the C–H··O angle is 118.0°. The values shown are the partial charges of atoms in *e* units.

belonging to the same methyl group. These results indicate that the (S)C–H bond in the TGG′ conformer is like an alcoholic O–H bond in respect of partial charges and interacts attractively with the oxygen atom; this electrostatic interaction can therefore be described as $C^{\delta-}$–$H^{\delta+}\cdots O^{\delta-}$. In the MMTE molecule, an analogous intramolecular interaction may be anticipated to occur between one of the hydrogen atoms of the OMe group and the sulfur atom. The calculated energies (Table 1) indicate, however, that conformational stabilisation by this interaction is unlikely to occur.

The salient result in this work is that we have convincingly detected a conformer, TGG′, of MMTE which is highly stabilised by an intramolecular 1,5-CH··O interaction. Before the importance of this interaction was recognized, the conformers such as TGG′ of MMTE were thought to be unstable owing to apparent heavy steric repulsions between the relevant atoms which are in close proximity to each other. The comparison of the results for MMTE and DME indicates that the (S)CH··O interaction is stronger than the (O)CH··O interaction. The substituent atom, sulfur or oxygen, bonded to the C–H bond may change the strength of the 1,5-CH··O interaction.

Footnotes and References

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† T = *trans*, G = *gauche*. Conformation around the MeO–CH_2–CH_2–SMe bonds.

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