Conformational Stability of 1,2-Dimethoxyethane in the Gas Phase Studied by Infrared Spectroscopy: Importance of an Intramolecular 1,5-CH···O Interaction

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The gas-phase infrared spectra of 1,2-dimethoxyethane measured at various temperatures gave a value of 0.31±0.04 kcal mol^{-1} for the energy difference between the *trans–gauche–gauche'* and *trans–trans–trans* conformers, the latter being more stable. This value is in good agreement with the results of high-level *ab initio* calculations. The present experimental finding gives definitive evidence for the importance of an intramolecular 1,5-CH···O interaction in the stabilization of the *trans–gauche–gauche'* conformer in the gas phase.

The conformational stability of 1,2-dimethoxyethane (DME) $CH_3OCH_2CH_2OCH_3$ has been one of the most disputing subjects in the field of experimental and theoretical structural chemistry in these years. In 1992 we reported the matrix-isolation infrared spectra of DME and showed that the *trans–trans–trans* (TTT) conformer is the most stable in an argon matrix.[1] In the same work, we emphasized the importance of an intramolecular 1,5-CH···O interaction which stabilizes the *trans–gauche–gauche'* (TGG') conformer. The existence of this interaction was suggested already in 1979 by Astrup[2] in his electron diffraction study of DME in the gas phase. There had been no direct observations, however, of the conformational stabilization by this interaction until we reported the matrix-isolation infrared spectra.[1]

Following our experimental work, several theoretical studies on DME have been developed[3–5] and the conformational properties associated with the 1,5-CH···O interaction have been elucidated. In spite of these theoretical developments, there is no definitive experimental evidence for the significance of this interaction in DME in the gas phase. In a previous study,[6] the infrared and Raman spectra of gaseous DME have been measured, but spectral changes with temperature were not examined. These circumstances have urged us to study the infrared spectra of DME in the gas phase at different temperatures and to evaluate energy differences between relevant conformers.

The infrared spectra of gaseous DME were measured at various temperatures ranging from 290 K to 350 K with a sample pressure of 5.0 kPa using a gas cell of 10 cm path length with KBr windows. The spectra were recorded on a Nicolet Impact 400 spectrometer equipped with a DTGS detector by the co-addition of 200 scans at a resolution of 4 cm^{-1}. The temperature was monitored by a copper–constantan thermocouple with its end placed inside the cell. For measuring the area intensities of the absorption bands, the spectral profiles in the 800–1100 cm^{-1} region were analyzed by fitting with resolved Gaussian components. Although the observed bands showed a partly resolved rotational structure, the band shape was approximated to the Gaussian.

The infrared spectra of DME in the gaseous state at different temperatures along with the spectrum in the liquid state are shown in Figure 1. The observed bands were assigned to the relevant conformers on the basis of a previous normal coordinate analysis utilizing *ab initio* molecular orbital calculations.[1] A spectral comparison shows that, in going from the liquid state to the gaseous state, the relative intensity of the 573-cm^{-1} band due to the TGT conformer decreases, while that of the 542-cm^{-1} band due to the TGG' conformer increases. This spectral observation indicates that the TGG' conformer is more populous in the gaseous state than in the liquid state relative to the TGT conformer. It is thus evident that the intramolecular 1,5-CH···O interaction is more important in the gas phase, in good agreement with a recent theoretical prediction by molecular dynamics simulations.[7]

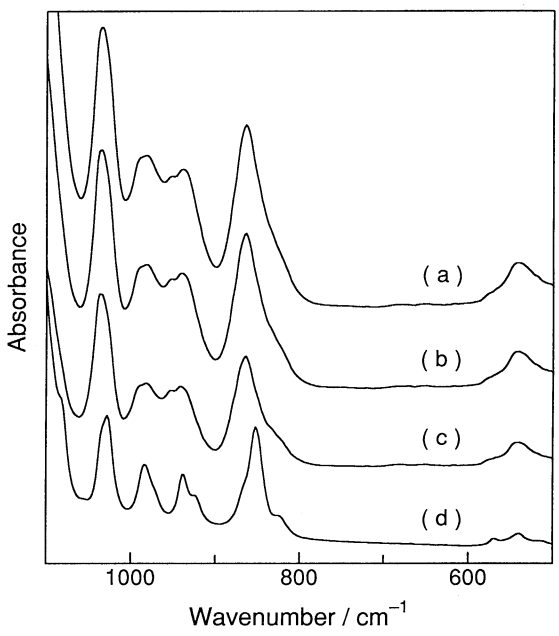

Figure 1. Infrared spectra of 1,2-dimethoxyethane in the gaseous state at (a) 348 K, (b) 320 K, and (c) 291 K and (d) in the liquid state at 300 K.

The infrared bands at 986 and 946 cm^{-1} in the gas phase are assigned to the TGG' and TTT conformers, respectively.[1] From the temperature dependence of the intensity ratio of these bands as plotted in Figure 2, the energy difference between the two conformers was evaluated. Several spectral measurements gave a value of 0.31±0.04 kcal mol^{-1} for this energy difference, the TTT conformer being more stable. The quantitative determination of the energy difference between the TGG' and TGT conformers, on the other hand, was not possible, because the band at 573 cm^{-1} due to the TGT conformer was observed only as an ill-defined shoulder. It appears, however, that the relative intensities of these bands do not change appreciably with temperature, suggesting that the energy difference between these conformers is not large.

The present experimental value of the energy difference between the TGG' and TTT conformers is now compared with

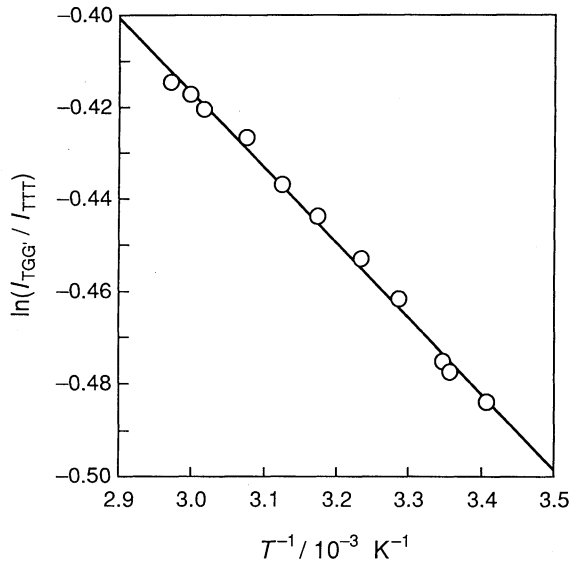

Figure 2. Logarithmic intensity ratio $\ln(I_{TGG'}/I_{TTT})$ of 1,2-dimethoxyethane as a function of reciprocal temperature.

the theoretical values from *ab initio* calculations, as summarized in Table 1. The restricted Hartree–Fock calculations with the 6-31G basis set[1] and the 6-311G** basis set[8] gave an energy of the TGG' conformer higher than that of the TTT conformer by 1.44 kcal mol^{-1} and 1.46 kcal mol^{-1}, respectively. The calculations including electron correlation effects, on the other hand, yielded an energy of 0.53 kcal mol^{-1} for the TGG' conformer relative to that for the TTT conformer at the MP3/6-311+G*//HF/6-311+G* level[3] and of 0.23 kcal mol^{-1} at the MP2/D95+(2df,p) level.[4] Our experimental energy difference between the TGG' and TTT conformers in the gas phase, 0.3 kcal mol^{-1}, is in good agreement with the results of the high-level calculations. These calculations also gave an energy difference between the TGG' and TGT conformers of less than 0.1 kcal mol^{-1}. This result is again consistent with the temperature dependence of the infrared spectra as mentioned above.

The conformational properties of DME in the gas phase have been studied previously by the NMR method.[9] Rotational isomeric state simulations of the observed vicinal coupling constants gave an energy for the *gauche* conformation of the OC–CO bond, E_σ, of –0.4 kcal mol^{-1} relative to the energy for the *trans* conformation. The same NMR data were later reanalyzed on the basis of the *ab initio* calculations at the MP2 level, and the experimental coupling constants were reproduced with a value of 0.1 kcal mol^{-1} for E_σ.[4] The previous[2,9] and present experimental observations of the conformational properties of DME in the gas phase now appear to be consistent with one another and are well correlated with the results of the high-level *ab initio* calculations including electron correlation effects.

Table 1. Calculated and experimental relative energies of four low-energy conformers of 1,2-dimethoxyethane

Conformer	Relative energy/kcal mol^{-1}				
	HF[a]	HF[b]	MP3[c]	MP2[d]	Exptl[e]
TTT	0.00	0.00	0.00	0.00	0.00
TGT	2.62	1.32	0.51	0.14	
TGG'	1.44	1.46	0.53	0.23	0.31
TTG	1.89	1.93	1.65	1.43	

[a]HF/6-31G level.[1] [b]HF/6-311G** level.[8] [c]MP3/6-311+G*//HF/6-311+G* level.[3] [d]MP2/D95+(2df,p) level.[4] [e]Infrared spectra in the gas phase (present work).

A salient result of the present infrared spectroscopic study of DME in the gas phase is that the energy of the TGG' conformer lies only 0.3 kcal mol^{-1} above that of the TTT conformer. This experimental finding gives definitive evidence for the importance of the 1,5-CH···O interaction in the stabilization of the TGG' conformer in the gas phase.

References and Notes

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