

The vibrational and NMR spectra, conformations and ab initio calculations of methoxymethylene- and 1-methoxyethylidene- propanedinitrile

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Abstract

The IR and Raman spectra of methoxymethylene-propanedinitrile [$\text{H}_3\text{C}-\text{O}-\text{CH}=\text{C}(\text{CN})_2$] and 1-methoxyethylidene-propanedinitrile [$\text{H}_3\text{C}-\text{O}-\text{C}(\text{CH}_3)=\text{C}(\text{CN})_2$] as a solid, liquid and solute in various solvents have been recorded in the region $4000-50\text{ cm}^{-1}$. NMR spectra of both compounds in various solvents at different temperatures were also obtained.

Semiempirical (AM1, PM3, MNDO, MINDO3), ab initio using DZP basis sets and DFT calculations using B3LYP with 6-31G** basis sets were carried out for both compounds. These calculations support the idea on the existence of two conformers with a planar $\text{C}=\text{COC}$ moiety and with the methyl group oriented as *anti* and *syn* towards the $\text{C}=\text{C}$ double bond. The calculated small energy difference between them suggests the presence of both in the samples at room temperature.

In contrast with the calculations, only one conformer has been found in the liquid vibrational and NMR spectra. Complete assignments of the vibrational spectra for the compounds mentioned were made with the aid of normal coordinate calculations employing scaled ab initio and DFT force field constants. The scaled ab initio and DFT frequencies indicate that the conformer present in the liquid (solutions) and solid phases is *anti*. © 1997 Elsevier Science B.V.

Keywords: Vibrational and NMR spectra; Conformational analysis; Alkyl vinyl ethers; Semiempirical and ab initio calculations

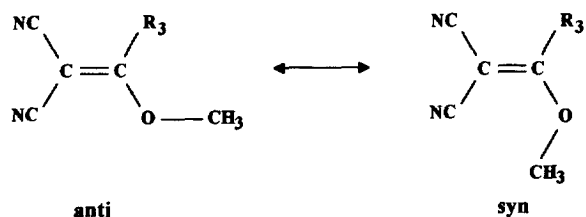
1. Introduction

Alkoxy-methylenes of general formula $\text{R}_1\text{O}-\text{CR}_3=\text{CXY}$, where R_1 and R_3 are H, alkyl or (hetero)aryl and X and Y are electron-withdrawing groups, as readily accessible and highly reactive compounds are very important in a number of syntheses. Their reactions with aliphatic, aromatic or heteroatomic amines give the corresponding N-(un)substituted amino-methylene/ethylidene compounds. The latter are used as materials for pharmaceutical, dye, polymer and other syntheses [1–4]. Both alkoxy-methylenes

and enamines with $\text{Y} = \text{Z} = \text{CN}$ represent a group of compounds that are also widely used in organic syntheses [5]. Despite their wide use in the organic syntheses, a sound theoretical study of the physical and physico-chemical properties of these compounds has not yet been carried out. Aminomethylene propanedinitrile and (1-aminoethylidene) propanedinitrile and their N-methyl derivatives have been recently studied by vibrational and NMR spectroscopy and ab initio calculations [6,7]. These studies have shown that (methylamino)methylene propanedinitrile and (1-methylamino)ethylidene propanedinitrile exist

in two conformational forms with methyl group oriented *anti* and *syn* toward the C=C double bond. This work also represents the continuation of the studies in Refs. [6,7] for the alkoxy compounds.

The conformational possibility for methoxymethylene propanedinitrile (MEM) ($R_1 = \text{CH}_3$, $R_3 = \text{H}$) and 1-methoxyethylidene propanedinitrile (MEE) ($R_1 = R_3 = \text{CH}_3$) is determined by rotation around the =C–O single bond. Assuming a planar C=COC moiety, both compounds can exist in two conformational forms with the methyl group oriented as *anti* and *syn* towards the C=C double bond:



A nonplanar *gauche* conformer results from rotation around the =C–O single bond from either the *anti* or the *syn* positions.

From previous studies on the closely related simple alkyl vinyl ethers it has been established that the most stable molecular conformation for these compounds is the planar *syn* one. The simplest methyl vinyl ether [$\text{H}_3\text{C}-\text{O}-\text{CH}=\text{CH}_2$] has been widely studied by vibrational spectroscopy [8–11], microwave spectroscopy [12], infrared matrix isolation spectroscopy [13] and electron diffraction [14]. These studies have clearly demonstrated that methyl vinyl ether exists in two spectroscopically recognizable conformers in the fluid phases. From the band shapes and rotational fine structure in the gas phase and from the spectra in solvents with different polarity it was suggested that the less polar and planar *syn* conformer is more stable and the less stable one is the more polar and probably nonplanar *gauche* conformer. The dipole moment of the *syn* conformer is 0.96 D [12] and the enthalpy difference between the conformers was found to be $4.8 \pm 1.0 \text{ kJ mol}^{-1}$ in the gas phase and $2.8 \pm 0.8 \text{ kJ mol}^{-1}$ in 1,1,2-trichloroethane [8]. From the matrix isolation study using a Knudsen cell, an enthalpy difference of $6.6 \pm 0.4 \text{ kJ mol}^{-1}$ was measured [13]. The same conclusion has been reached from infrared spectra of ethyl vinyl ether [15] and the

enthalpy difference $3.3 \pm 0.8 \text{ kJ mol}^{-1}$ in 1,1,2-trichloroethane was estimated.

The conformational structure of 2-methoxypropene [$\text{H}_3\text{C}-\text{O}-\text{C}(\text{CH}_3)=\text{CH}_2$] has been studied by vibrational spectroscopy [16,17]. The spectra reveal the presence of two conformers in the fluid phase with an enthalpy difference 3.6 kJ mol^{-1} in the liquid state. From the vapour phase spectra it has been found that the more stable conformer has a planar configuration of the heavy atoms.

In the aforementioned studies on alkyl vinyl ethers, the multiplicity of C=C bond stretching vibrations in the region $1600\text{--}1660 \text{ cm}^{-1}$ is highly indicative of the presence of a second conformer. By studying the change in relative intensities of these bands with increasing temperature and solvent polarity, it was found that the more stable and less polar *syn* conformer has a C=C frequency lower by about $20\text{--}30 \text{ cm}^{-1}$. This fact has been confirmed by studying the infrared spectra and conformations of *trans* and *cis* methyl propenyl ethers [$\text{H}_3\text{C}-\text{O}-\text{CH}=\text{CH}-\text{CH}_3$] [18]. For the *trans* compound, a multiplicity in the region of the C=C bond stretching vibrations was found and two conformers were determined; for the *cis* compound the *syn* conformer is inconvenient for steric reasons and only one conformer (probably slightly nonplanar from *anti* structure), without a multiplicity in the C=C bond stretching region, was found. For all the above-mentioned alkyl vinyl ethers, the multiplicity of some characteristic vibration modes of ethylene hydrogens also support this conclusion.

2. Experimental

The purity and identity of both samples were checked by differential scanning calorimetry using a Perkin–Elmer DSC-7 and by mass and NMR spectroscopy. Mid-IR spectra were recorded on Bruker model IFS 88 and on Philips model PU9800 FT–IR spectrometers. Raman spectra in the region $4000\text{--}50 \text{ cm}^{-1}$ were measured on a Bruker RFS 100 instrument. The ^{13}C NMR spectra in chloroform and acetone, cooled to -60 and -80°C respectively, were run with a Varian VXR-300 spectrometer and no evidence of separate spectra arising from restricted rotation was obtained.

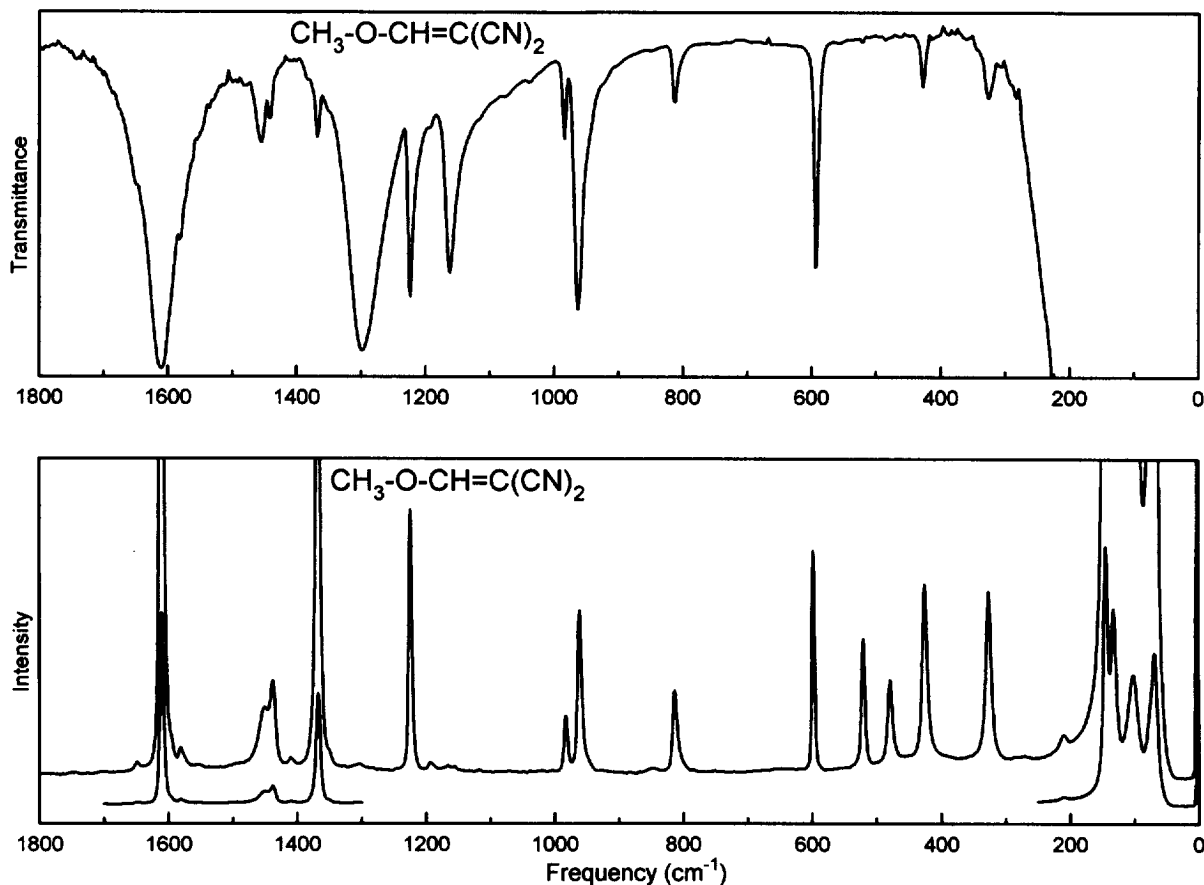


Fig. 1. IR (top) and Raman (bottom) spectra of solid MEM at room temperature.

3. Results and discussion

A mid-IR survey spectrum of MEM as a KBr pellet and a corresponding Raman spectrum as a solid powder are shown in Fig. 1. Infrared and Raman curves of the acetonitrile, dichloromethane and chloroform solutions and of the solid MEM between $1700\text{--}1520\text{ cm}^{-1}$, shown in Fig. 2, demonstrate the occurrence only of one band in this region of the spectra. Mid-IR and Raman spectra of liquid MEE are given in Fig. 3. Comparison of the solid and liquid spectra indicates that for MEM as well as for MEE the same conformer is present in both phases.

Semiempirical (AM1, PM3, MNDO and MINDO3) methods were employed using the MOPAC program. For the ab initio Hartree–Fock SCF calculations the HONDO-like program and the standard Huzinaga DZP basis set were employed. To improve the accuracy

of the ab initio energies, MP2 corrections were carried out without reoptimization of the geometry of the molecules at MP2/SCF level. Also standard molecular orbital DFT calculations were carried out using the GAUSSIAN 94 program package for both conformers of MEM and MEE. Fully optimized geometries and vibrational spectra were calculated at B3LYP/6-31G** level. Table 1 summarizes the calculated energies.

All these calculations, except the PM3 and MNDO methods for MEE, give a planar structure for the C=COC moiety of both conformers for both compounds. Since no experimental data regarding the structure are reported, we will next assume planar *anti* and *syn* conformers for MEM and MEE. PM3 and MNDO methods give a planar structure for the *syn* conformer of MEE but a slightly nonplanar structure for second conformer (6° and 27° from *anti* orientation, respectively).

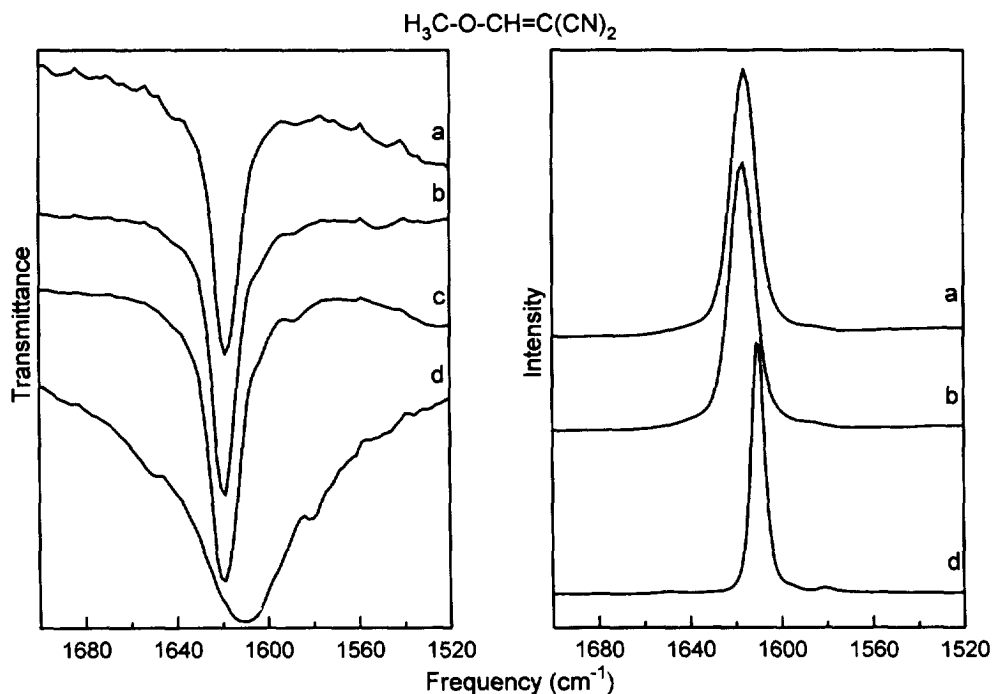


Fig. 2. IR (left) and Raman (right) spectra of MEM as a solute in (a) acetonitrile, (b) dichloromethane and (c) chloroform, and (d) as a solid, at room temperature.

While the results obtained by semiempirical methods are very different, the *ab initio* and DFT methods agree in suggesting for MEM *anti* and for MEE *syn* as a more stable conformer. The calculated *ab initio* and DFT energy differences imply that at

room temperature, both compounds exist as two conformers in the gas phase (from 20 up to 40% of the less stable conformer). Unfortunately, because of the very small vapour pressure, the gas phase vibrational spectra could not be obtained. On the other hand, in

Table 1
Calculated energy differences for *anti* and *syn* conformers of MEM and MEE

Method	MEM $\Delta(\text{syn} - \text{anti})$ (kJ mol ⁻¹)	MEE $\Delta(\text{syn} - \text{anti})$ (kJ mol ⁻¹)
Semiempirical		
AM1	-5.97	-4.29
PM3	0.41	3.65
MNDO	9.55	1.85
MINDO3	14.95	7.48
<i>Ab initio</i> (DZP)		
SCF	4.20	-1.77
MP2	-3.59	-0.89
ZPE	1.74	0.74
SCF + MP2 + ZPE	2.35	-1.92
DFT (6-31G**)		
B3LYP	1.91	-1.26
ZPE	1.72	0.34
B3LYP + ZPE	3.63	-0.92

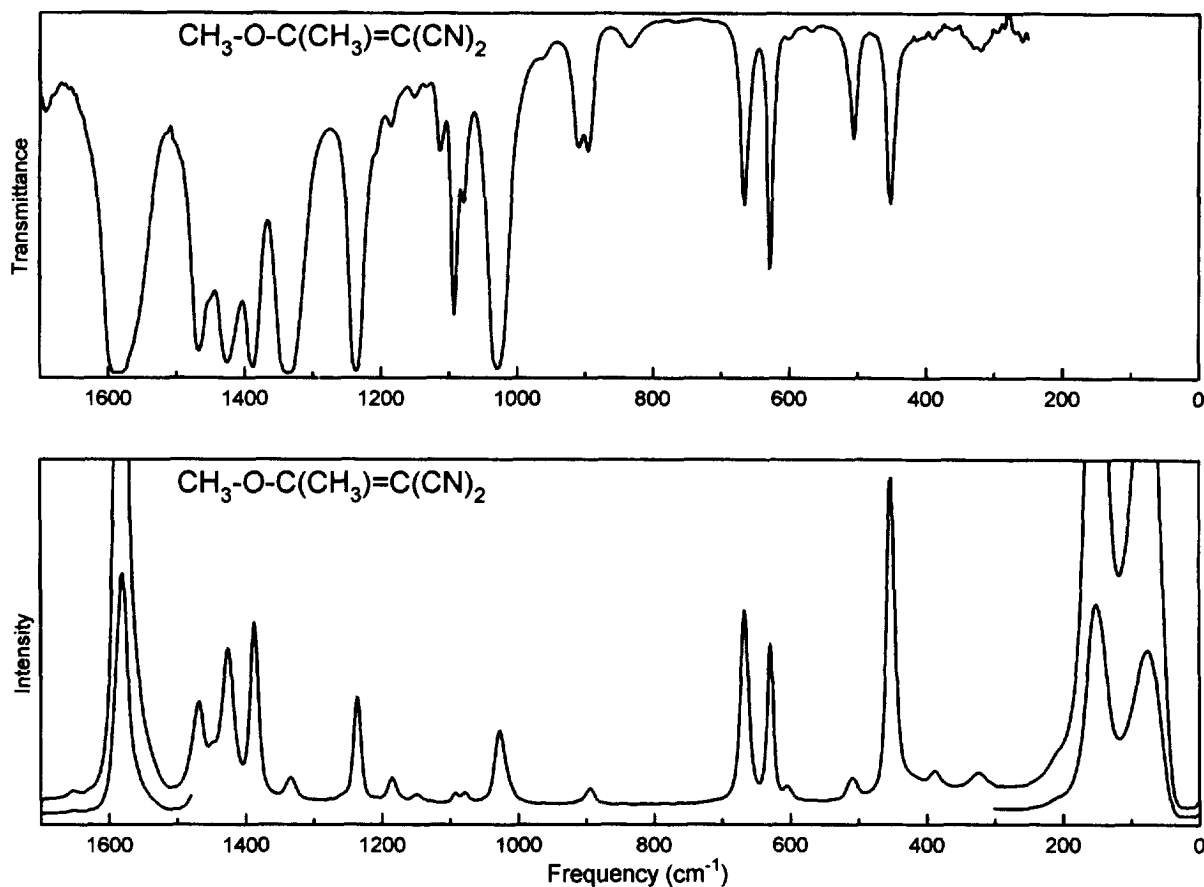


Fig. 3. IR (top) and Raman (bottom) spectra of liquid MEE at room temperature.

vibrational spectra between $1350\text{--}300\text{ cm}^{-1}$ (below the -CH_3 deformation modes and above the torsion modes and four low frequency modes associated with the =C(CN)_2 group), 14 and 17 vibrational modes can be expected for MEM and MEE, respectively. Simple counting of the number of bands in this region from MEM solution spectra and from MEE liquid spectra suggests that only one conformer is present. The same conclusion can be drawn also from the missing multiplicity of the aforementioned highly indicative C=C bond stretching vibration band of alkyl vinyl ethers around 1600 cm^{-1} (Figs. 2 and 3). A slight low frequency asymmetry of this band in the liquid spectra of MEE might be an indication of the small amount of the second conformer. But despite the calculated energies it can be concluded in any case that in both compounds one conformer is dominant.

According to our experience the arrays of frequencies calculated for the individual conformers are of much greater utility for conformational analysis than are the calculated energy differences between them [19]. Therefore, we compared the ab initio and DFT frequencies of *anti* and *syn* conformers with the frequencies of solid MEM and liquid MEE. It is well known that the ab initio SCF results in different basis sets systematically overestimate the force field, and therefore the force fields in internal coordinates were scaled according to the type of internal coordinates, using the scheme $F_{ij}(\text{scaled}) = F_{ij}(\text{ab initio}) (x_i x_j)^{1/2}$, where x_i and x_j are scaling factors for diagonal constants [20]. The scale factors from similar aminomethylene propanedinitrile and its *N*-methyl derivatives [6], where an excellent agreement between calculated and experimental frequencies was achieved,

Table 2
Comparison of observed and calculated vibrational frequencies for MEM

No.	<i>anti</i>			<i>syn</i>			Obs. ^b
	ab initio	scaled ^a	DFT	ab initio	scaled ^a	DFT	
ν_{12}	1426	1307	1317	1460	1340	1330	1297
ν_{13}	1343	1226	1241	1339	1219	1232	1224
ν_{14}	1286	1172	1187	1273	1158	1174	1161
ν_{15}	1280	1164	1174	1270	1158	1167	1161
ν_{16}	1114	1025	1008	1111	973	961	984
ν_{17}	1093	957	937	1032	950	940	960
ν_{18}	875	796	822	866	789	813	813
ν_{19}	713	645	640	716	648	640	598
ν_{20}	659	594	602	674	607	617	598
ν_{21}	578	522	526	637	580	587	520
ν_{22}	547	486	486	554	494	494	478
ν_{23}	457	412	421	496	442	445	425
ν_{24}	350	315	321	403	365	369	326
ν_{25}	340	308	304	284	258	268	326
ν_{26}	218	200	198	246	229	210	209
ν_{27}	153	137	135	206	188	183	144
ν_{28}	129	120	121	179	162	166	131
ν_{29}	128	116	116	162	145	144	101
ν_{30}	63	59	44	74	69	69	68

^a Calculated using scaling factors mentioned in text.

^b Observed frequencies are from solid spectra.

were also used for MEM and MEE. A comparison of the observed and ab initio scaled and DFT vibrational frequencies for MEM is given in Table 2.

It is interesting to note that the ab initio scaled frequencies are very close to the DFT frequencies. Comparison of both with the frequencies of solid MEM and liquid MEE imply that, for MEM as well as for MEE, the more stable conformer is the *anti* form. Several attempts to optimize the mentioned scale factors to experimental frequencies always gave better results for the *anti* conformer. A higher occurrence of the *anti* conformer in polar liquid phase as given by ab initio and DFT calculations can be explained by its higher polarity: dipole moments calculated by ab initio/DFT methods are 7.77/7.31 D for *anti* and 5.76/5.46 D for *syn* MEM conformers and 8.65/8.06 D for *anti* and 6.28/5.93 D for *syn* MEE conformers, respectively.

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