

Raman and infrared spectra, conformations and *ab initio* calculations of 3-methoxymethylene-2,4-pentanedione

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Abstract: The IR (4000–400 cm⁻¹) and Raman (4000–50 cm⁻¹) spectra of 3-methoxymethylene-2,4-pentanedione [H₃C—O—CH=C(COCH₃)₂] as a liquid and solutes in various solvents of different polarity have been recorded at ambient temperature. Additional IR and Raman spectra were obtained for amorphous and crystalline solid state at low temperature. The vibrational spectra revealed that the compound exists at least in two dominant conformers of different polarity and that the conformer present in the solid phase is less polar. NMR spectra in various solvents at different temperatures were also obtained.

The compound can exist in several conformers due to the rotation around O—C= and both =C—C bonds with planar or nonplanar arrangements of heavy atoms. *Ab initio* MP2 and DFT calculations using a wide scale of basis sets were carried out. According to these calculations six conformational structures of the eight theoretically possible conformational structures with the methoxy group oriented as *anti* or *syn* and carbonyl groups oriented as *Z* or *E* towards the C=C double bond were obtained at potential energy surface. It has been shown that the conformers with the *E* orientations of both acetyl groups are not the stable ones. The calculated *ab initio* MP2 and DFT energies of all found conformers in vacuum suggest the most stable *Z**E**a* conformer where *Z* and *E* regard to the *trans* and *cis* acetyl groups, respectively and *a* denotes the orientation of the methoxy group. The *E**Z**a* conformer was calculated as the second most stable one with the energy by at least 10 kJ mol⁻¹ higher. Corrections of the relative energies of single conformers obtained in vacuum on the polar surroundings were done by including the solvent effect into the calculations using IEF Polarizable Continuum Model.

Assignments of the vibrational spectra for the studied compound were made with the aid of normal coordinate calculations employing scaled *ab initio* force field. The scaled *ab initio* frequencies as well as calculated energies indicate that *Z**E**a* is the conformer present in the solid phase.

Keywords: Raman and Infrared spectra, NMR spectra, conformational analysis, alkoxy methylenes and diacetylenes, *ab initio* MP2 and B3LYP calculations.

Introduction

Alkoxy methylenes of general formula R—O—CH=—CXY, where R are alkyl or (hetero)aryl electron-donor groups and X and Y are electron-withdrawing groups, represent simple push-pull compounds. As relatively easy accessible and highly reactive compounds they are very important in a number of syntheses. Their reactions with aliphatic, aromatic or heteroatomic amines give the corresponding N-(un)substituted aminomethylene compounds which are used as starting materials for many pharmaceuticals, dyes, polymers and other products (Cook, 1969; Dyke, 1973; Albrecht, 1977; Bouzard, 1990).

The studied 3-methoxymethylene-2,4-pentanedione [H₃C—O—CH=C(COCH₃)₂] (MMP) has R=CH₃ and X=Y=COCH₃. The first conformational pos-

sibility of MMP is given by the rotation around the O—C= single bond with the methyl group in the *anti* or *syn* orientation towards the C=C double bond. The simplest model for such conformational possibility is methyl vinyl ether as a parent compound for MMP and its conformers are at Fig. 1. Methyl vinyl ether has been widely studied by vibrational spectroscopy (Owen, 1964; Ignatyev, 1981; Cadioli, 1982), electron diffraction (Owen, 1970; Samdal, 1975; Pyckhout, 1983), microwave spectroscopy (Cahill, 1968) and infrared matrix isolation spectroscopy (Beech, 1985). These studies have shown that methyl vinyl ether in the fluid phases exists in two conformers: the less polar and planar *syn* conformer is more stable and the less stable one is the more polar and probably nonplanar *anti* conformer. The enthalpy difference between the conformers was

found to be 4.8 ± 1.0 kJ mol⁻¹ in the gas phase and 2.8 ± 0.8 kJ mol⁻¹ in 1,1,2-trichloroethane (Owen, 1964). In the liquid phase the enthalpy differences of 6.0 ± 0.7 kJ mol⁻¹ and 6.2 ± 0.5 kJ mol⁻¹ were obtained, respectively (Cadioli, 1982; Sakakibara, 1976). From the matrix isolation study the enthalpy difference of 6.6 ± 0.4 kJ mol⁻¹ was measured (Beech, 1985).

The similar conclusion has been done from the conformational study of 2-methoxypropene [H3C-O-C(CH3)=CH2] by vibrational spectroscopy (Diallo, 1981; Gallinella, 1983). The spectra revealed the presence of two conformers with the enthalpy difference of 3.6 kJ mol⁻¹ in the liquid state and it has been found from the vapour phase spectra that the more stable conformer has a planar structure and a *syn* configuration of heavy atoms.

On the other side the substitution of both ending ethylene hydrogens by some electron-withdrawing groups support the *anti* orientation of the methoxy group as it has been shown by vibrational and conformational studies of methoxymethylene-propanedinitrile [H3C-O-CH=C(CN)2] and 1-methoxyethylidene-propanedinitrile [H3C-O-C(CH3)=C(CN)2] (Gatjal, 1997, Gatjal, 2004).

The additional conformational possibility for MMP is given by the rotation of both acetyl groups around the =C—C single bond. The simplest compound demonstrating the conformational possibility of the vinyl and acetyl groups is methyl vinyl ketone H2C=CH-COCH3 (Bowles, 1969, Durig, 1981, de Smedt, 1989). For its two conformers all heavy atoms are located in a plane and are denoted as the *s-trans* (*E*) and *s-cis* (*Z*) with respect to the orientation of the two C=C and C=O double bonds (Fig. 2). The *s-trans* conformer is more stable by 2.4 ± 0.2 kJ mol⁻¹ (Bowles, 1969) and 2.1 kJ mol⁻¹ (Durig, 1981) in the gas and liquid phases, respectively, and by 1.9 ± 0.1 kJ mol⁻¹ in the CS₂ solution (de Smedt, 1989).

The conformational possibilities of MMP are given by the rotation of both acetyl groups and the stable conformers can have the orientation of the carbonyl oxygen towards or away from the C=C double bond marked as *Z* or *E* orientations. Therefore, MMP can

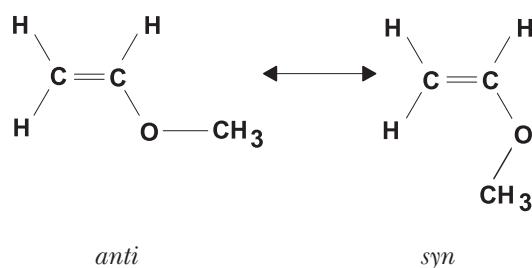


Fig. 1. Conformers of methyl vinyl ether.

have theoretically four orientations of both acetyl groups *ZZ*, *ZE*, *EZ* and *EE* where the first letter expresses the orientation of the *trans* acetyl group and the second one the orientation of the *cis* acetyl group. Additionally the third letters *a* or *s* will denote the orientation of methoxy group. Therefore, MMP can theoretically exist as *ZZa*, *ZEa*, *EZa*, *EEa*, *ZZs*, *ZEs*, *EZs* and *EEs* conformers. The conformations of both acetyl groups strongly depend on the possibility to create stabilizing intramolecular hydrogen bond between the electron-donor group, e.g. amino group H₂N— (Gróf, 2007) or alkylamino group R—NH— (Gatjal, 2015) and carbonyl of the *cis* acetyl group. The conformers with such bond belong to the most stable ones. On the other side for compounds without the possibility to create such an intramolecular hydrogen bond, e.g. compounds with dialkylamino group R¹R²N— (Gatjal, 2011) or alkoxy group R—O— (Gatjal, 1999), also other conformers can belong to the most stable ones.

Planarity favoured by the conjugation of studied alkoxy methylenes can often be difficult to achieved for steric reasons due to the substituent size of both the X, Y groups or the size of the R—O— alkoxy group. Therefore for MMP one or both carbonyls may lie out of ethene plane, or alternatively the whole molecule may twist along the axis of the carbon double bond. Due to the steric effects a nonplanar *gauche* conformation of acetyl group can result from the rotation around the =C—C single bond from either the *s-trans* or *s-cis* positions. The three double bonds of MMP represent a cross-conjugated system. In hydrocarbon frameworks the simplest cross-conjugated molecule is 3-methylene-1,4-pentadiene (Almenningen, 1988) where electron diffraction, in agreement with the *ab initio* calculations, revealed that the most stable conformer has two double bonds coplanar with the *s-trans* arrangement and the third one is twisted from *s-cis* positions by 40 degrees.

Experimental and computational details

The purity and identity of the compound were checked by mass and NMR spectroscopy. Mid-IR

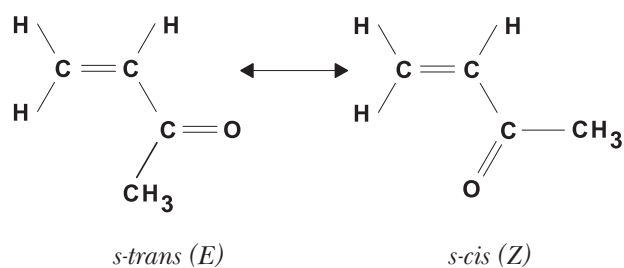


Fig. 2. Conformers of methyl vinyl ketone.

spectra in the 4000–400 cm^{-1} region were recorded on Bruker model IFS 88 and on Nicolet model NEXUS 470 FT-IR spectrometers at room temperature. The solution IR spectra in chloroform and acetonitrile were measured in a Specac cell equipped with KBr windows. Cryostats cooled with liquid nitrogen and with windows of CsI and polyethylene were used in solid IR measurements. Raman spectra in the 4000–50 cm^{-1} region were measured on Bruker RFS 100 Raman spectrometer with Nd^{3+} : YAG laser at the wavelength of 1064 nm. The Raman spectra of the solutions were obtained at room temperature. A liquid capillary of 3 mm inner diameter surrounded by a Dewar and cooled by a flow of cold nitrogen gas was used for Raman solid state measurements.

NMR spectroscopy was performed in the solutions of dimethylsulfoxide (DMSO) and chloroform (CDCl_3) in order to confirm the identity of the sample. ^1H NMR and ^{13}C NMR spectra were recorded at room temperature with both Varian VXR-300 and INOVA 600 spectrometers. The ^{13}C and ^1H NMR spectra in DMSO at room temperature and in chloroform and acetone, cooled to -60 and -80 $^\circ\text{C}$, respectively, were run with a Varian VXR-300 spectrometer and no evidences of separate spectra due to restricted $\text{O}-\text{C}=\text{C}$ or $=\text{C}-\text{C}$ rotations were obtained.

Ab initio MP2 (Møller, 1934) and DFT B3LYP (Becke, 1988; Lee et al., 1988; Becke, 1993) computations were performed using the Gaussian03 (Frisch et al., 2003) and Gaussian09 (Frisch et al., 2009) program packages. Standard basis sets 6-31G**, 6-311G**, 6-311++G**, cc-pVDZ, aug-cc-pVDZ and cc-pVTZ were used for both methods. Solvent effects in the solvents of different polarity were approximated by Integral Equation Formalism Polarizable Continuum Model (IEF PCM) (Cossi, 1996; Mennucci, 1997) and a full conformational analysis of the MMP

was performed. A vibrational analysis was used to confirm that the optimal geometry corresponds to the energy minimum (no imaginary vibrations) and to obtain the vibrational spectra.

Results and discussion

Quantum-chemical calculations

In order to understand the conformational behavior of MMP and to interpret the experimental results we have supported our study by theoretical calculations. The numbering and structure of the studied compound is depicted in Fig. 3. In the first step we have tried to find all stable conformers from the eight theoretically possible *ZEa*, *ZEs*, *ZZa*, *ZZs*, *EZa*, *EZs*, *EEa* and *EEs* ones. Table 1 and Table 2 summarize the calculated MP2 and DFT B3LYP relative energies of MMP conformers as well as their dipole moments for an isolated molecule (in vacuum) in several basis sets. The calculated energies for all methods and basis sets show that the most stable conformer is *ZEa*.

According to these calculations all other found conformers have much higher energy in vacuum and their appearance in a liquid phase at room temperature seems not probable. However on the other side the calculated dipole moments of the found conformers have a broad range and therefore the appearance of the next possible conformers in polar solutions can be expected. Some calculated geometrical parameters at the *ab initio* MP2 level in 6-311++G** basis set are collected in Table 3.

The relative energies of single conformers obtained in vacuum were corrected by including solvent effect into the calculations using IEF Polarizable Continuum Model (PCM) at *ab initio* MP2 levels in 6-311++G** and cc-pVTZ basis sets. The energy differences between the conformers of MMP are collected in Tables 4a and 4b and depicted in

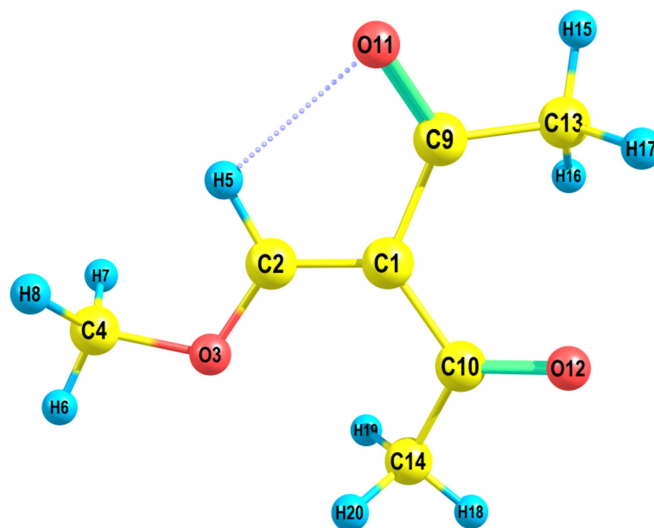


Fig. 3. Structure and numbering of atoms in MMP for *ZEa* conformer.

Tab. 1. Calculated MP2 relative energies including ZPE correction (kJ mol^{-1}) of MMP stable conformers in different basis sets in vacuum. Calculated dipole moments (in Debye) are in parentheses.

Conformer	MP2					
	6-31G**	6-311G**	6-311++G**	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ
<i>ZEa</i>	0.00 (4.65)	0.00 (4.61)	0.00 (4.98)	0.00 (4.50)	0.00 (4.95)	0.00 (4.74)
<i>ZEs</i>	22.98 (3.11)	20.99 (3.00)	18.42 (3.28)	a	a	a
<i>ZZa</i>	20.34 (1.47)	18.55 (1.57)	14.45 (1.63)	21.72 (1.41)	15.82 (1.76)	18.07 (1.44)
<i>ZZs</i>	22.67 (2.79)	21.06 (2.69)	16.89 (2.58)	23.51 (2.67)	13.97 (2.92)	19.42 (2.69)
<i>EZa</i>	14.34 (5.68)	12.47 (5.66)	7.84 (5.93)	16.12 (5.21)	8.14 (6.11)	10.57 (5.78)
<i>EZs</i>	14.93 (3.44)	14.40 (3.34)	10.91 (3.62)	15.83 (3.36)	6.58 (3.88)	11.38 (3.69)
<i>EEa</i>	a	a	a	a	a	a
<i>EEs</i>	a	a	a	a	a	a

a – conformer not found.

Tab. 2. Calculated DFT B3LYP relative energies including ZPE correction (kJ mol^{-1}) of MMP stable conformers in different basis sets in vacuum. Calculated dipole moments (in Debye) are in parentheses.

Conformer	B3LYP					
	6-31G**	6-311G**	6-311++G**	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ
<i>ZEa</i>	0.00 (4.96)	0.00 (5.02)	0.00 (5.22)	0.00 (4.87)	0.00 (5.15)	0.00 (5.02)
<i>ZEs</i>	30.41 (3.59)	30.33 (3.59)	27.15 (3.76)	32.81 (3.51)	a	a
<i>ZZa</i>	22.74 (1.37)	21.86 (1.61)	17.11 (1.90)	24.83 (1.37)	16.52 (1.58)	17.98 (1.58)
<i>ZZs</i>	28.09 (2.68)	27.96 (2.71)	24.86 (2.84)	30.91 (2.61)	23.79 (2.79)	26.23 (2.69)
<i>EZa</i>	18.44 (5.60)	17.30 (5.85)	12.33 (6.25)	19.40 (5.42)	11.06 (6.14)	12.15 (5.91)
<i>EZs</i>	20.60 (3.44)	20.56 (3.56)	17.25 (3.79)	22.23 (3.36)	16.34 (3.75)	18.16 (3.63)
<i>EEa</i>	a	a	a	a	a	a
<i>EEs</i>	a	a	a	a	a	a

a – conformer not found.

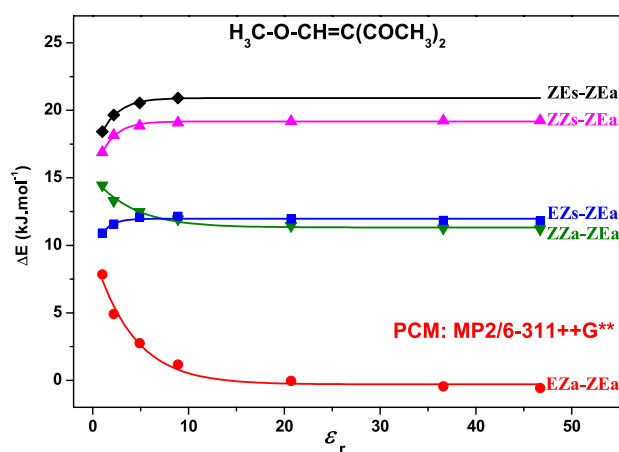


Fig. 4. Energy difference between isomers and conformers of MMP as a function of relative permittivity of surroundings calculated by IEF PCM model at *ab initio* MP2 level with 6-311++G** basis set.

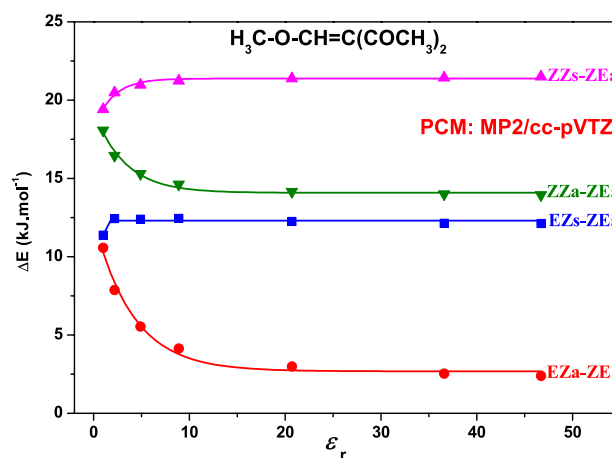


Fig. 5. Energy difference between isomers and conformers of MMP as a function of relative permittivity of surroundings calculated by IEF PCM model at *ab initio* MP2 level with cc-pVTZ basis set.

Figs. 4 and 5. From these results we can see that *ZEa* conformer remains the most stable one also in very polar surroundings. As the second most stable

conformer remains *EZa* one but its energy drops down from the values of 8–10 kJ mol^{-1} for vacuum to the value of about 2–0 kJ mol^{-1} in very polar sur-

Tab. 3. Some geometric parameters of stable MMP conformers calculated at *ab initio* MP2 level with 6-311++G** basis set in vacuum.

Coordinate ^a	<i>ZEa</i>	<i>ZE_s</i>	<i>ZZa</i>	<i>ZZ_s</i>	<i>EZa</i>	<i>EZ_s</i>
<i>Bonds (Å)</i>						
C ₁ =C ₂	1.360	1.358	1.356	1.362	1.354	1.364
C ₂ —O ₃	1.339	1.342	1.336	1.334	1.343	1.334
O ₃ —C ₄	1.434	1.433	1.431	1.430	1.429	1.432
C ₁ —C ₉	1.506	1.505	1.491	1.501	1.477	1.486
C ₁ —C ₁₀	1.489	1.501	1.500	1.497	1.512	1.503
C ₉ =O ₁₁	1.226	1.223	1.226	1.224	1.229	1.229
C ₁₀ =O ₁₂	1.227	1.223	1.222	1.225	1.219	1.224
C ₉ —C ₁₃	1.512	1.514	1.517	1.517	1.519	1.519
C ₁₀ —C ₁₄	1.514	1.516	1.521	1.517	1.508	1.513
<i>Angles (°)</i>						
C ₁ =C ₂ —O ₃	124.9	130.1	123.1	131.9	121.7	131.7
C ₁ =C ₂ —H ₅	118.6	118.5	119.4	117.7	122.3	119.4
C ₂ —O ₃ —C ₄	114.2	118.4	114.6	119.4	114.6	120.1
C ₂ =C ₁ —C ₉	114.1	115.8	116.9	114.3	122.1	118.8
C ₂ =C ₁ —C ₁₀	124.8	125.7	120.6	127.4	119.9	125.6
C ₁ —C ₉ =O ₁₁	120.6	121.8	122.1	122.2	119.8	119.5
C ₁ —C ₁₀ =O ₁₂	119.8	122.0	121.5	122.4	120.4	120.4
C ₁ —C ₉ —C ₁₃	118.5	116.8	116.9	116.3	119.4	120.2
C ₁ —C ₁₀ —C ₁₄	119.4	115.8	117.7	116.2	116.0	118.1
<i>Dihedral angles (°)</i>						
C ₁ =C ₂ —O ₃ —C ₄	-174.8	20.3	-172.8	7.7	-164.4	10.5
O ₃ —C ₂ =C ₁ —C ₉	-178.9	-174.3	-178.6	-178.8	-176.3	-175.7
O ₃ —C ₂ =C ₁ —C ₁₀	0.8	8.9	3.1	7.1	4.5	10.1
H ₅ —C ₂ =C ₁ —C ₉	-1.1	4.3	-1.1	-0.7	1.3	2.3
H ₅ —C ₂ =C ₁ —C ₁₀	178.6	-172.4	-179.4	-174.7	-177.9	-171.9
C ₂ =C ₁ —C ₉ =O ₁₁	22.3	-0.7	12.9	27.4	180.0	-174.1
C ₂ =C ₁ —C ₁₀ =O ₁₂	-158.9	-115.5	53.9	57.2	68.7	51.4
C ₂ =C ₁ —C ₉ —C ₁₃	-155.1	179.2	-165.4	-147.8	-0.7	5.6
C ₂ =C ₁ —C ₁₀ —C ₁₄	20.9	70.3	-124.7	-121.6	-110.4	-129.4

^aNumbering of atoms according to Fig. 3.

roundings in DMSO. Therefore in polar solutions the presence of the *EZa* conformer is possible.

Due to problems with finding some conformers with the *EE* orientation of both acetyl groups we have studied the dependence of the potential energy for the transition between *ZEa* and *EEa* conformers by the rotation of the *trans* acetyl group for several fixed dihedral angles of the *cis* acetyl group. This dependence is depicted at Fig. 6. It is clear that *EE* orientation of both acetyl groups has much higher energy and it is evident that this dependence for the *cis* acetyl group being in the plane of ethylene group (dihedral angle 180.0°) has no minimum. For fixed dihedral angles of the *cis* acetyl group outside of the plane of ethylene group the potential energy dependence has otherwise a minimum on the opposite side of the plane of ethylene group but after the optimization of all geometrical parameters always one of acetyl groups turned into the *Z* position. A similar situation occurs when the *trans* acetyl group is fixed and the *cis* acetyl group rotates (Fig. 7).

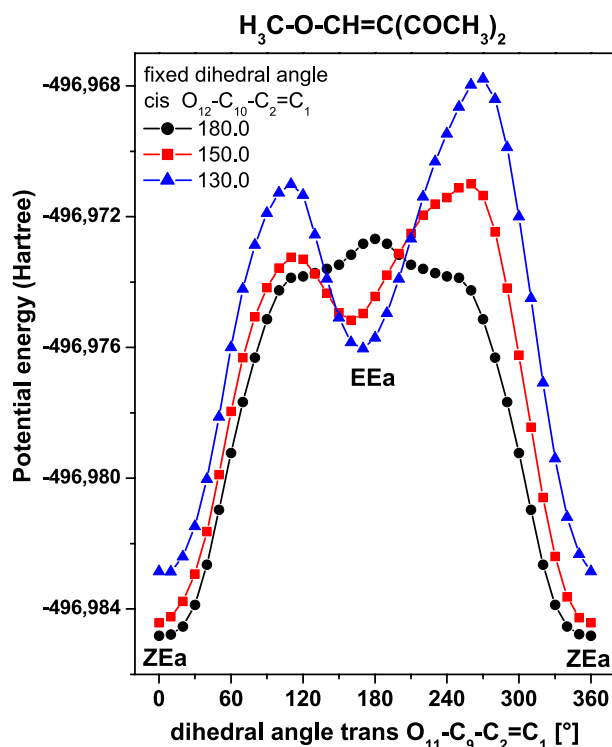


Fig. 6. Dependence of potential energy of MMP on the dihedral angle of *trans* acetyl group for fixed dihedral angle of *cis* acetyl group at *ab initio* MP2 level with cc-pVDZ basis set.

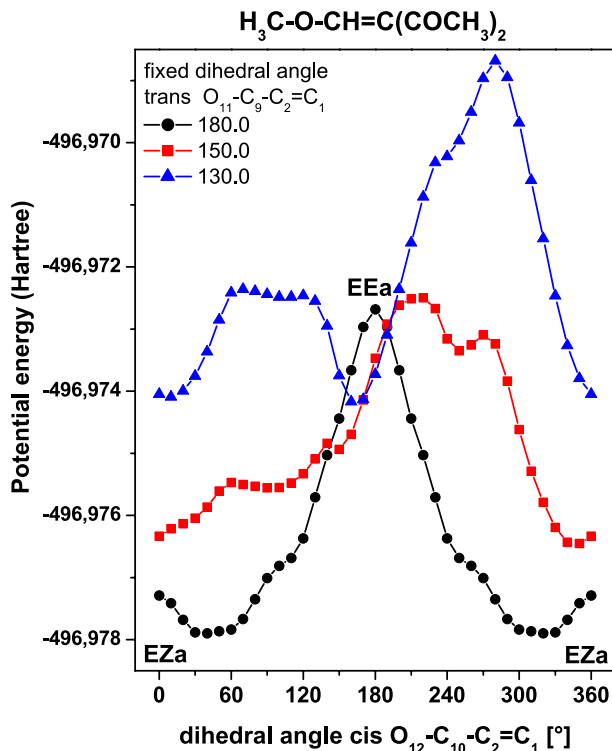


Fig. 7. Dependence of potential energy of MMP on the dihedral angle of *cis* acetyl group for fixed dihedral angle of *trans* acetyl group at *ab initio* MP2 level with cc-pVDZ basis set.

Tab. 4a. Calculated MP2 relative energies in 6-311++G** basis set (kJ mol^{-1}) for MMP conformers in the gas phase ($\epsilon_r = 1$), in CCl_4 ($\epsilon_r = 2.2$), in chloroform ($\epsilon_r = 4.7$), in dichloromethane ($\epsilon_r = 8.9$), in acetone ($\epsilon_r = 20.5$), in acetonitrile ($\epsilon_r = 35.7$) and in DMSO ($\epsilon_r = 46.8$) solutions according to IEF PCM solvent model.

Conformer	MP2/6-311++G**						
	$\epsilon_r = 1.0$	$\epsilon_r = 2.2$	$\epsilon_r = 4.7$	$\epsilon_r = 8.9$	$\epsilon_r = 20.5$	$\epsilon_r = 35.7$	$\epsilon_r = 46.8$
<i>ZEa</i>	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>ZEs</i>	18.42	19.66	20.55	20.92	a	a	a
<i>ZZa</i>	14.45	13.30	12.48	11.94	11.44	11.26	11.20
<i>ZZs</i>	16.89	18.17	18.86	19.09	19.19	19.24	19.25
<i>EZa</i>	7.85	4.92	2.76	1.17	-0.04	-0.44	-0.57
<i>EZs</i>	10.91	11.58	12.09	12.16	11.96	11.85	11.80
<i>EEa</i>	a	a	a	a	a	a	a
<i>EEs</i>	a	a	a	a	a	a	a

a – conformer not found.

Tab. 4b. Calculated MP2 relative energies in cc-pVTZ basis set (kJ mol^{-1}) for MMP conformers in the gas phase ($\epsilon_r = 1$), in CCl_4 ($\epsilon_r = 2.2$), in chloroform ($\epsilon_r = 4.7$), in dichloromethane ($\epsilon_r = 8.9$), in acetone ($\epsilon_r = 20.5$), in acetonitrile ($\epsilon_r = 35.7$) and in DMSO ($\epsilon_r = 46.8$) solutions according to IEF PCM solvent model.

Conformer	cc-pVTZ						
	$\epsilon_r = 1.0$	$\epsilon_r = 2.2$	$\epsilon_r = 4.7$	$\epsilon_r = 8.9$	$\epsilon_r = 20.5$	$\epsilon_r = 35.7$	$\epsilon_r = 46.8$
<i>ZEa</i>	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>ZEs</i>	a	a	a	a	a	a	a
<i>ZZa</i>	18.07	16.46	15.30	14.62	14.15	14.00	13.95
<i>ZZs</i>	19.42	20.48	20.98	21.24	21.38	21.43	21.50
<i>EZa</i>	10.57	7.88	5.55	4.14	3.00	2.54	2.39
<i>EZs</i>	11.38	12.43	12.40	12.45	12.25	12.14	12.12
<i>EEa</i>	a	a	a	a	a	a	a
<i>EEs</i>	a	a	a	a	a	a	a

a – conformer not found.

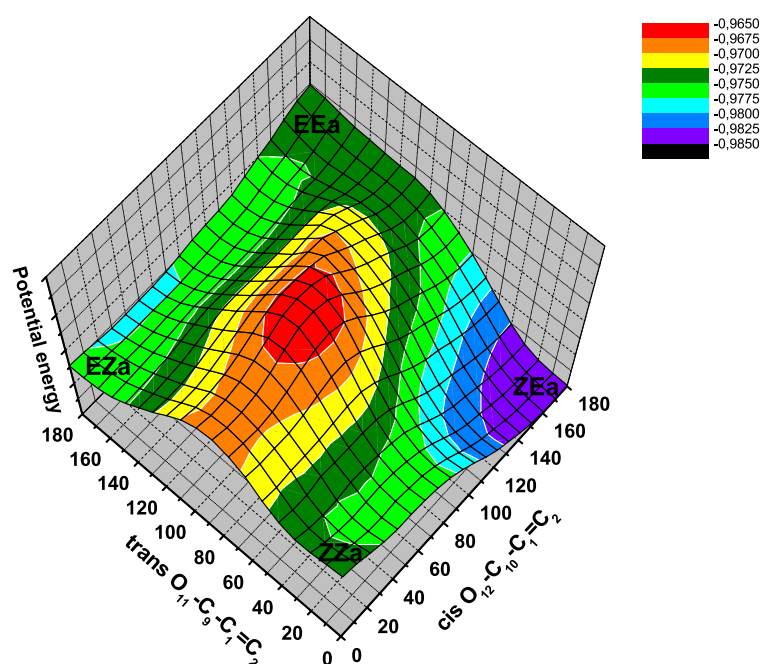


Fig. 8. Dependence of potential energy of MMP (in Hartree, related to the $-497,0000$ Hartree value) on relevant dihedral angles (in degrees) at *ab initio* MP2 level with cc-pVDZ basis set.

Therefore we can conclude that the *EE* orientation of both acetyl groups is not stable probably due to the charge repulsion of both carbonyl oxygens which disfavours the *EE* arrangement of both acetyl groups. To test such conclusion we have calculated the potential energy surface (PES) for fixed dihedral angles of both acetyl groups of MMP with the *anti* orientation of the methoxy group and results are depicted at Fig. 8. From the analysis of the PES we can see that the energy of the *EE* arrangement is the highest one and that the PES has not a global minimum for such an arrangement.

NMR spectra

The ^1H NMR spectra of MMP in chloroform and DMSO solutions are presented in Fig. 9. The comparison of the ^{13}C NMR spectra of MMP in chloroform and DMSO solutions with the calculated NMR spectra at *ab initio* MP2 level with cc-pVTZ basis set using IEF PCM solvation model for the *Z**E**a* and *E**Z**a* conformers are shown in Fig. 10. The hydrogen and carbon experimental chemical shifts are given in Table 5. We can observe in the ^1H NMR spectrum the signals of two acetyl methyl groups (at 2.1–2.4 ppm), the signals of methoxy groups (at 4.0 ppm) and the signals of the olefinic hydrogen (at 7.6–7.7 ppm). None of the mentioned observed hydrogen signals are split to indicate the

free rotation of the above groups at room temperature. The number of carbon resonances in chloroform (bottom) as well as in DMSO (top) spectrum in Fig. 10 corresponds to the presence of only one entity in both solutions. Such situation is also in the acetone solution at the temperature of $-80\text{ }^\circ\text{C}$. This can imply that MMP exists in these solutions as only one conformer or that the coalescence temperature for the rotation around the $\text{O}-\text{C}=\text{C}$ or $=\text{C}-\text{C}$ bonds is below this temperature. The middle spectrum compares the calculated resonances for *Z**E**a* and *E**Z**a* conformers at MP2 level with cc-pVTZ basis set using IEF PCM solvation model with chloroform as a solvent.

Experimental resonances of C_1 and C_2 in the ethylenic group and of C_4 in the methoxy group are very similar in chloroform as well as in DMSO solution. On the other side the experimental C_9 and C_{10} carbonyl resonances and C_{13} and C_{14} methyl carbon resonances for both acetyl groups are more separated in DMSO solution. The calculated differences of chemical shifts of C_9 and C_{10} carbonyl resonances and C_{13} and C_{14} methyl carbons resonances in chloroform solution for *E**Z**a* conformer are higher in comparison with the same ones for *Z**E**a* conformer (the middle spectrum at Fig. 10). This can indicate that the abundance of the more polar *E**Z**a* conformer in the DMSO solution is higher than in the chloroform solution.

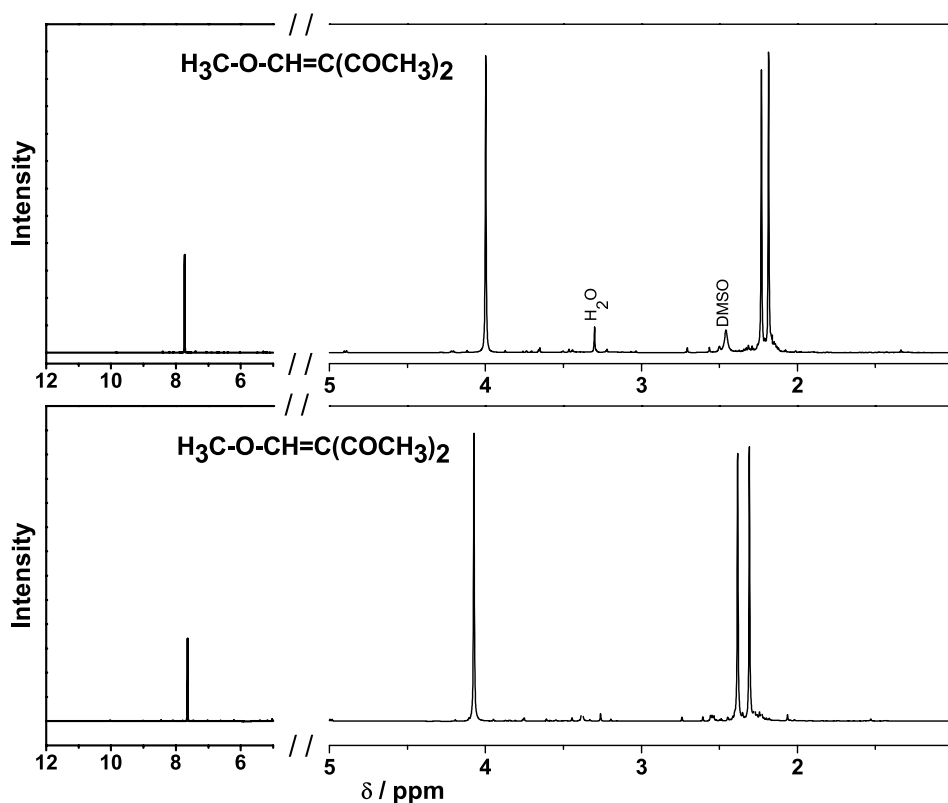


Fig. 9. ^1H NMR spectra of MMP in CDCl_3 (bottom) and in DMSO (top) at room temperature.

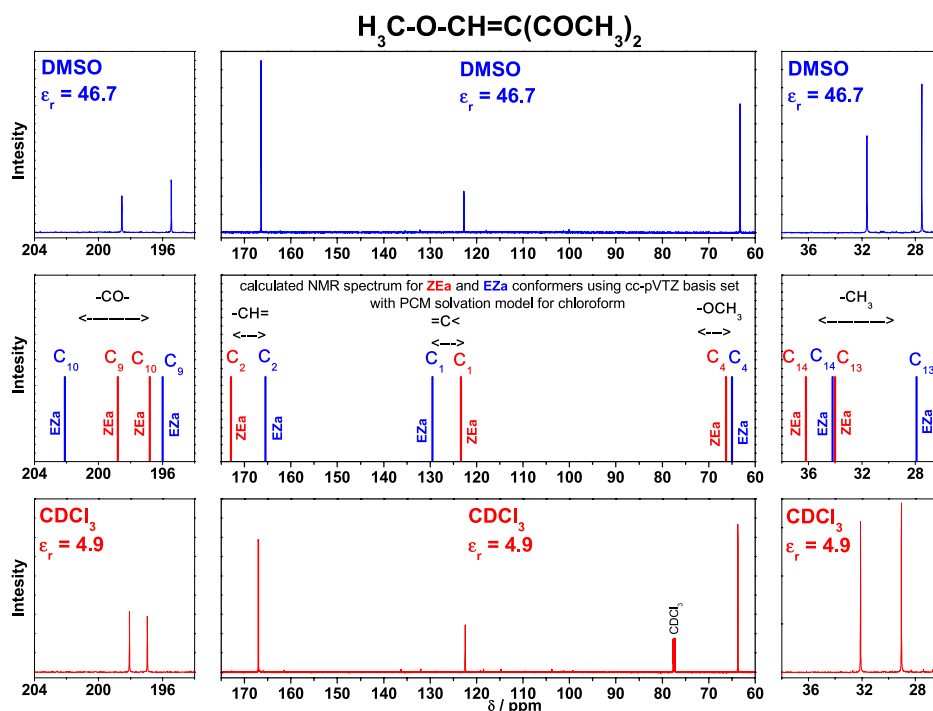


Fig. 10. ¹³C NMR spectra of MMP in CDCl₃ (bottom) and in DMSO (top) at room temperature. In the middle the calculated spectra for both *Z Ea* and *E Za* conformers are depicted.

Tab. 5. Measured NMR spectral data of 3-methoxymethylene-2,4-pentanedione (MMP).

Carbon spectra	Chemical shifts (ppm)	
	DMSO	CDCl ₃
>C=	122.74	122.44
—CH=	166.41	167.01
CH ₃	63.25	63.75
C=O	198.54	198.07
C=O	195.45	196.95
CH ₃	31.63	32.10
CH ₃	27.51	29.04
Hydrogen spectra		
CH ₃	2.19	2.31
CH ₃	2.23	2.38
OCH ₃	4.00	4.04
=C—H	7.73	7.64

Vibrational spectra

Since the sample has a small vapour pressure, only the measurements as a pure liquid and in solvents of different polarities at room temperature and in a solid phase at low temperature have been performed. The survey mid-infrared and Raman liquid and solid phase spectra of MMP are depicted in Fig. 11 and experimental frequencies are collected in Table 6. Disappearing of several bands from IR as well as Raman liquid phase spectra in comparison with the solid phase spectra support the assumption that MMP exists in the liquid phase as a mixture of at least

two conformers. The comparison of the liquid phase Raman spectra of MMP with those measured in CCl₄, chloroform, dichloromethane and acetonitrile solutions in the most significant 1775–1525 cm⁻¹ region, where the C=O and C=C double bond stretching vibrations can be expected, are shown in Figs. 12. These studies confirm the presence of at least two conformers with very different dipole moments in solutions of different polarity. The bands denoted with the asterisk increase their intensity in more polar solvents and disappeared in solid phase what means that less stable second conformer is more polar and that more stable less polar conformer in liquid phase is also present in the crystallized solid phase.

Experimental spectra in Figs. 13 and 14 are compared with the calculated ones for *Z Ea* and *E Za* conformers at MP2 level with cc-pVTZ basis set. Calculated vibrational frequencies were scaled by the scale factor of 0.96 according to [Merrick, 2007] and calculated Raman scattering activities were recalculated on the Raman scattering cross sections which are proportional to the Raman intensities. For the depicting of the calculated spectra the Lorentzian band shape with the halfwidth of 4 cm⁻¹ for IR and Raman spectra has been used. The MP2/cc-pVTZ force field was transformed from Cartesian coordinates to a set of suitable internal coordinates and the potential energy distribution (PED) was calculated for each mode. The comparison of the calculated and observed vibration frequencies of MMP conformers and PED for *Z Ea* conformer is in Table 7.

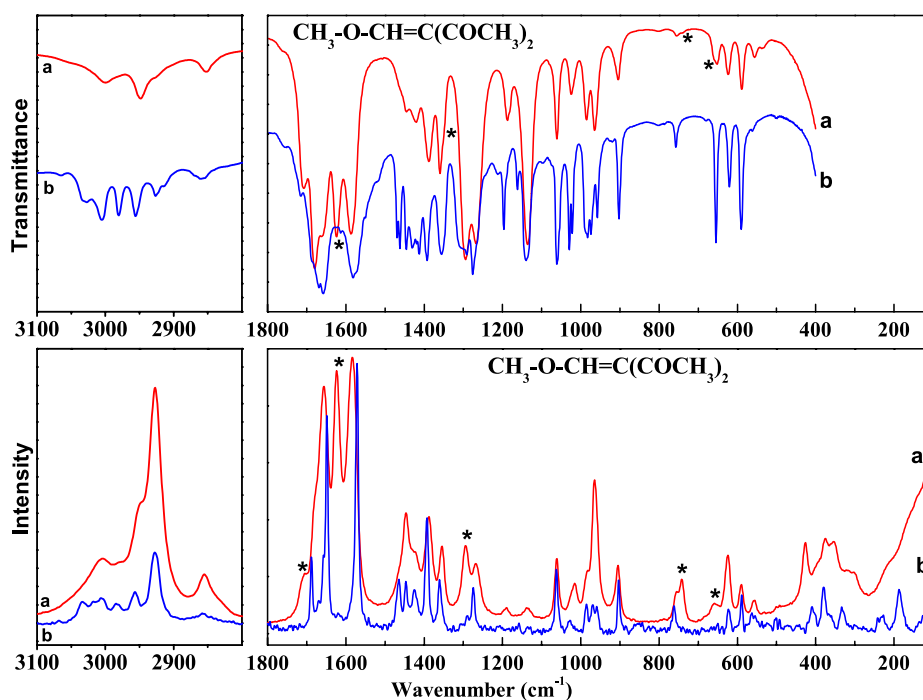


Fig. 11. IR (top) and Raman (bottom) spectra of MMP as a neat liquid (curve a) at room temperature and in the solid state (curve b). * denote bands vanishing in the solid phase.

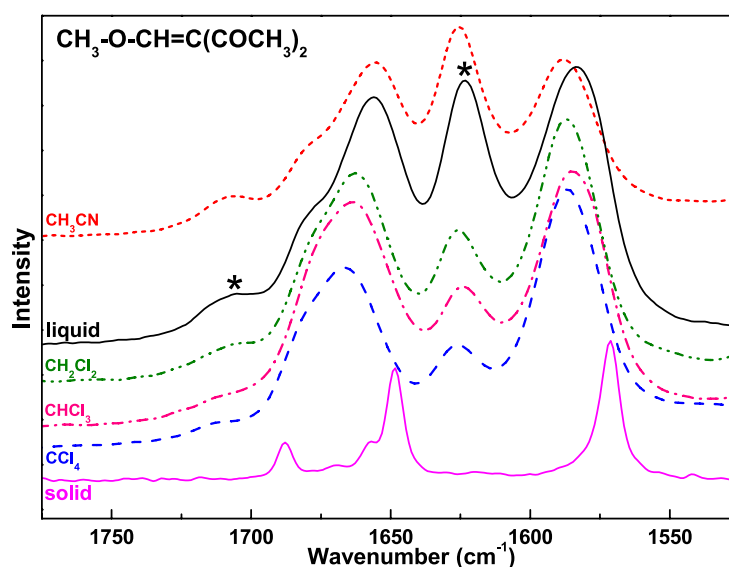


Fig. 12. Raman spectra of MMP as a neat liquid (top solid line) and in solvents of different polarity at room temperature and in the solid state (bottom solid line). * denote bands vanishing in solid phase.

Three bands above 1580 cm^{-1} therefore belong to the C=O and C=C stretching modes. The assignment of the C=O stretching modes for *ZEa* and *EZa* conformers is opposite according to the PED. Because for *ZEa* conformer the calculated higher frequency band at 1672 cm^{-1} can be assigned to the C=O stretch vibration of the *trans* acetyl group with the *Z* orientation of C=O/C=C bonds (55 *trans* C=O s, 11 C=C s) and the lower frequency band at 1650 cm^{-1} to the C=O stretch of the *cis*

acetyl group with the *E* orientation of C=O/C=C bonds (72 *cis* C=O s), thus for *EZa* conformer the calculated higher frequency band at 1685 cm^{-1} can be assigned to the C=O stretch vibration of the *cis* acetyl group with the *Z* orientation of C=O/C=C bonds (80 *cis* C=O s) and the lower frequency band at 1640 cm^{-1} to the C=O stretch vibration of the *trans* acetyl group with the *E* orientation of C=O/C=C bonds (75 *trans* C=O s). The C=C stretch vibrations were according to PED clearly calculated

Tab. 6. Measured infrared and Raman spectral data^a for 3-methoxymethylene-2,4-pentanedione (MMP).

Infrared		Raman		Interpretation	
Liquid	Solid	Liquid	Solid	<i>ZEa</i>	<i>EZa</i>
3056 ^b vw, sh	3065 vw		3068 w	V ₁	
	3034 w		3033 m	V ₂	
	3028 w		3029 m	V ₃	
	3015 vw,sh		3017 w	V ₄	
3000 vw	3006 w	3004 s	3006 m	V ₅	
2980 vw,sh	2981 w	2978 w	2983 w	V ₆	
2948 w	2956 w	2947 vs,sh	2956 m	V ₇	
2927 vw,sh	2926 vw	2927 vvs	2927 s	V ₈	
	2914 vw			V ₉	
2852 w	2860 vw	2854 s	2858 w	V ₁₀	
	1715 vw				
1708 m	*	1706 m	*		V ₁₁
1679 vs	1687 w,sh	1677 s,sh	1687 m	V ₁₁	
	1668 s		1669 vw		
1660 m,sh	1657 s	1656vs	1657 m,sh	V ₁₂	
			1648 vs		
1624 s		1623 vs	*		V ₁₃
	1581 s				
1586 s	1571 s,sh	1584 vs	1571 vs	V ₁₃	
	1469 m		1471 vw	V ₁₄	
1463 w,sh	1462 m	1464 w,sh	1464 m	V ₁₅	
1445 w	1446 m	1446 m	1445 m	V ₁₆	
	1430 w	1429 w		V ₁₇	
1420 m	1426 w	1422 w	1425 w	V ₁₈	
	1419 vw		1419 w	V ₁₉	
	1412 m		1411 vw,sh	V ₂₀	
1396 w,sh	1397 w,sh	1397 w,sh			
1388 s	1392 s	1388 s	1393 s	V ₂₁	
1359 s	1355 vs	1354 s	1361 m	V ₂₂	
1349 w,sh		1349 w,sh	1355 vw,sh	V ₂₃	
	1305 s,brd		1307 vw,brd		
1294 vs	1291 w	1294 s	1290 w	V ₂₄	
1268 vs	1276 vs	1268 s	1274 m	V ₂₅	
	1265 m,sh				
1187 w	1196 m	1189 w	1184 vvw	V ₂₆	
1181 w	*?				V ₂₆
	1162 w		1161 vw	V ₂₇	
1135 vs	1140 s	1135 w	1135 vw	V ₂₈	
	1135 s,sh				
1061 m	1061 s	1061 m	1062 m	V ₂₉	
	1054 m,sh				
1024 w	1029 m	1024 w,sh	1028 w	V ₃₀	
1016 vw,sh	1022 m	1015 w	1022 vw,sh	V ₃₁	
	988 m				
986 m	982 m	982 m,sh	986 w	V ₃₂	
	974 m		969 w	V ₃₃	
964 m	957 w	964 s	959 w	V ₃₄	
914 vw,sh	*	914 w,sh	*		V ₃₄
905 w	903 m	905 m	903 m	V ₃₅	
754 w	757 w	754 w,sh	761 w	V ₃₆	
740 vw	*	742 m	*		V ₃₆
659 w	*	658 w	*		V ₃₇
652 w,sh	654 m	651 w	652 vw	V ₃₇	
623 w	621 w	624 m	623 w	V ₃₈	
589 m	590 m	590 w	590 w	V ₃₉	
556 w	561 vw	555 w	562 vw	V ₄₀	
536 vw	*	532 vw,brd	*		V ₄₀
		426 w	408 w	V ₄₁	
		390 vw,sh			
		375 w	379 w	V ₄₂	
		354 w	362 vw	V ₄₃	
		319 vw,brd	333 w	V ₄₄	
		303 vw,brd		V ₄₅	
			242 vw	V ₄₆	
		220 w,sh	227 vw	V ₄₇	
			187 w	V ₄₈	
		163 w,sh		V ₄₉	
		128 w,sh		V ₅₀	
			101 m	V ₅₁	
			85 m		
		77 s	73 m	V ₅₂	
			62 m	V ₅₃	

^aWeak bands in 4000–3100 and 2800–1800 cm⁻¹ regions have been omitted.^bAbbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; brd, broad.

Tab. 7. Comparison of calculated and observed vibration frequencies of MMP conformers at ab initio MP2 level with cc-pVTZ basis set in vacuum.

No.	Calculated		Observed ZEa/EZa	Fundamental	PED (ZEa) ^a
	ZEa	EZa			
v ₁	3088	3086	3056	CH ₃ asym stretch	95 (O)CH ₃ as
v ₂	3078	3076	3034	CH ₃ asym stretch	99 (t) CH ₃ as
v ₃	3077	3076	3028	CH ₃ asym stretch	97 (c) CH ₃ as
v ₄	3056	3052	3015	CH ₃ asym stretch	22 (t) CH ₃ as
v ₅	3050	3041	3000	=C—H stretch	98 =C—H s
v ₆	3047	3040	2980	CH ₃ asym stretch	97 (c) CH ₃ as
v ₇	3045	3031	2948	CH ₃ asym stretch	99 (O)CH ₃ as
v ₈	2970	2958	2927	CH ₃ sym stretch	99 (t) CH ₃ ss
v ₉	2964	2954	2914	CH ₃ sym stretch	98 (c) CH ₃ ss
v ₁₀	2957	2947	2852	CH ₃ sym stretch	94 (O)CH ₃ ss
v ₁₁	1672	1685	1677/1706	C=O stretch	55 (t) C=O s, 11 C=C s
v ₁₂	1650	1640	1656/	C=O stretch	72 (c) C=O s
v ₁₃	1596	1619	1584/1623	C=C stretch	48 C=C s, 11 =C—H ρ, 10 =C—O s
v ₁₄	1461	1461	1469	CH ₃ asym bend	87 (O)CH ₃ aδ
v ₁₅	1456	1455	1463	CH ₃ asym bend	91 (O)CH ₃ aδ
v ₁₆	1430	1437	1445	CH ₃ asym bend	73 (c)CH ₃ aδ
v ₁₇	1429	1432	1430	CH ₃ sym bend	54 (O)CH ₃ sδ, 30 (tc)CH ₃ aδ
v ₁₈	1426	1429	1420	CH ₃ asym bend	71 (t) CH ₃ aδ
v ₁₉	1412	1427	1419	CH ₃ asym bend	79 (c) CH ₃ aδ
v ₂₀	1408	1416	1412	CH ₃ asym bend	84 (t) CH ₃ aδ
v ₂₁	1369	1367	1388	=C—H rock	31 =C—H ρ, 16 =CC ₂ as
v ₂₂	1341	1329	1359	CH ₃ sym bend	74 (t) CH ₃ sδ
v ₂₃	1330	1320	1349	CH ₃ sym bend	73 (c) CH ₃ sδ
v ₂₄	1267	1276	1294	=C—O stretch	37 =C—O s, 18 =C—H ρ
v ₂₅	1253	1250	1268	CC ₂ asym stretch	30 CC ₂ as
v ₂₆	1170	1168	1187/1181	CH ₃ rock	46 (O)CH ₃ ρ
v ₂₇	1140	1140	1162	CH ₃ rock	93 (O)CH ₃ ρ
v ₂₈	1123	1132	1135	O—C stretch	16 O—CH ₃ s, 15 =C—O s
v ₂₉	1047	1048	1061	CH ₃ rock	18 (c) CH ₃ ρ, 23 O—CH ₃ s
v ₃₀	1007	1004	1024	CH ₃ rock	33 (c) CH ₃ ρ, 29 (t) CH ₃ ρ
v ₃₁	1003	1001	1016	CH ₃ rock	33 (t) CH ₃ ρ, 26 (c) CH ₃ ρ
v ₃₂	981	963	986	CH ₃ rock	23 (t) CH ₃ ρ, 14 (c) CH ₃ ρ
v ₃₃	938	951	974	C—CH ₃ stretch	18 (t)C—CH ₃ s, 24 (t) CH ₃ ρ
v ₃₄	933	892	964/914	=C—H wag	67 =C—H ω
v ₃₅	892	878	905	C—CH ₃ stretch	29 (c) C—CH ₃ s, 12 (t) C—CH ₃ s,
v ₃₆	735	721	754/740	CC ₂ sym stretch	18 CC ₂ ss, 15 C=C—O δ, 12 CC ₂ δ
v ₃₇	632	637	652/659	C=O wag	20 (c) C=O ω, 14 (c) C=O ω
v ₃₈	597	603	623	C=O rock	13 (c) C=O ρ, 12 (t) C=O ρ
v ₃₉	568	532	589	C=O rock	34 (t) C=O ρ, 23 (c) C=O ρ
v ₄₀	539	505	556/536	C=O wag	45 (t) C=O ω, 15 (c) C=O ω
v ₄₁	389	452	426	=CC ₂ rock	14 =CC ₂ ρ, 14 CO ρ, 21 =CC ₂ s
v ₄₂	383	409	375	C—C—C deformation	26 (t) C—C—C δ, 14 C—O—C δ
v ₄₃	359	333	354	C—C—C deformation	28 (c) C—C—C δ, 20 (t) C—C—C δ
v ₄₄	338	331	319	C—O—C deformation	21 C—O—C δ, 15 (t) C—C—C δ
v ₄₅	318	280	303	C=C torsion	30 C=C τ, 23 (c) C—C—C δ
v ₄₆	223	186	242	=CC ₂ deformation	58 =CC ₂ δ
v ₄₇	219	169	220	=CC ₂ wag	36 =CC ₂ ω, 12 C=C τ
v ₄₈	193	132	187	C—CH ₃ torsion	78 (c) C—CH ₃ τ
v ₄₉	167	126	163	C—CH ₃ torsion	68 (t) C—CH ₃ τ
v ₅₀	145	120	128	C=C—O deformation	30 C=C—O δ, 33 CC ₂ ρ
v ₅₁	129	114	101	O—CH ₃ torsion	47 O—CH ₃ τ, 16 =C—O τ, 22 CC ₂ ω
v ₅₂	65	68	73	=C—O torsion	43 =C—O τ, 34 O—CH ₃ τ
v ₅₃	53	49	62	C—COCH ₃ torsion	25 (c) =C—C τ, 28 (t) =C—C τ
v ₅₄	31	32		C—COCH ₃ torsion	41 (t) =C—C τ, 29 (c) =C—C τ

^as, symmetric; a, asymmetric; (t) *trans* acetyl; (c) *cis* acetyl; s, stretch; δ, deformation; ρ, rocking; ω, wagging; τ, torsion.

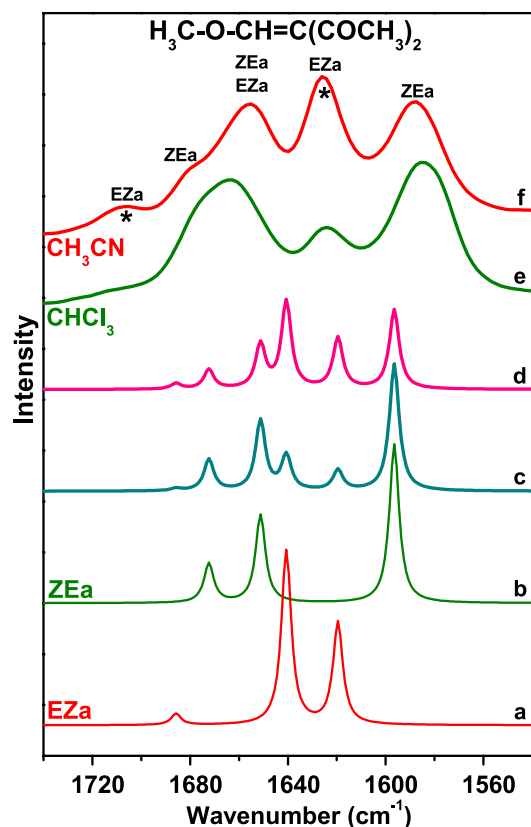


Fig. 13. Calculated Raman spectra of individual *Z Ea* and *E Za* MMP conformers (curves b and a, respectively) at MP2 level in cc-pVTZ basis set. Calculated Raman spectra of MMP with 80 % of *Z Ea* and 20 % of *E Za* conformers (curve c) and with 50 % of *Z Ea* and 50 % of *E Za* conformers (curve d). Curves e and f are experimental Raman spectra of MMP in chloroform and acetonitrile solutions at room temperature, respectively.

at 1596 cm^{-1} and at 1619 cm^{-1} for *Z Ea* and *E Za* conformers, respectively.

According to [Oelichmann, 1982] for the *Z* orientation of C=O and C=C double bonds the difference of their vibrational band frequencies is usually over 60 cm^{-1} whereas for the *E* orientation it is lower than this value. For our compound we calculated this difference of 76 and 54 cm^{-1} for the *Z* and *E* orientation of *trans* and *cis* acetyl groups, respectively, of the *Z Ea* conformer and of 66 and 21 cm^{-1} for the *Z* and *E* orientation of *cis* and *trans* acetyl groups, respectively, for the *E Za* conformer. The corresponding experimental differences obtained from the bands in Raman acetonitrile solution spectra are of 89 and 67 cm^{-1} for the *Z Ea* conformer and 80 and 29 cm^{-1} for the *E Za* conformer, respectively. Therefore in the light of the calculated wavenumbers in this region as well as in other regions we can argue for the assignment of the measured IR and Raman spectra as a mixture of *Z Ea* and *E Za* conformers.

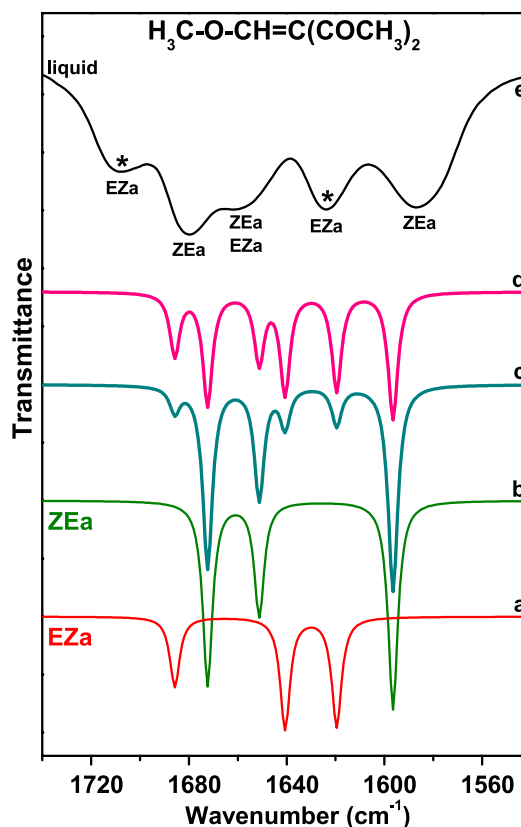


Fig. 14. Calculated IR spectra of individual *Z Ea* and *E Za* MMP conformers (curves b and a, respectively) at MP2 level in cc-pVTZ basis set. Calculated IR spectra of MMP with 80 % of *Z Ea* and 20 % of *E Za* conformers (curve c) and with 50 % of *Z Ea* and 50 % of *E Za* conformers (curve d). The curves e is an experimental IR spectrum of a neat liquid MMP at room temperature.

To support this conclusion we have calculated IR and Raman band intensities in the region of C=O and C=C bonds for the mixture of 80 % of *Z Ea* and 20 % of *E Za* conformers and 50 % of *Z Ea* and 50 % of *E Za* conformers (Figs. 13 and 14) and increasing band intensities in more polar surroundings can be explained by the increasing amount of the more polar *E Za* conformers in the mixture. The calculated IR and Raman band intensities show relatively well agreement with the experimental spectra in this region which cannot be achieved with the opposite assignment.

Conclusion

The analysis of NMR and vibrational spectra supported by theoretical calculations in vacuum and in the environment of various polarities revealed the existence of two structural forms of MMP. The studied compound exists in the solid state as the

ZEa conformer and similarly predominate in a less polar environments, e.g. CCl₄ or chloroform. In the more polar environments (such as dichloromethane, acetonitrile, DMSO) conformational equilibrium of MMP is visibly shifted towards the *EZa* conformer and MMP exists in these solutions as a mixture of two *ZEa* and *EZa* conformations. Conformational equilibrium of neat liquid MMP approaches to the conformational equilibrium in the acetonitrile solution.

Such experimental behaviour has been supported also by the solvent effect calculations at *ab initio* MP2 and DFT B3LYP levels using IEF PCM model. The assignment of normal vibrational modes of MMP based on PED calculations was performed.

Based on the measured vibrational and NMR spectra and quantum-chemical calculations we can conclude that MMP exists as a mixture of both *ZEa* and *EZa* conformers with *Z* and *E* orientations of both acetyl groups and with the *anti* orientation of the methoxy group. This study so extends the spectroscopic and structural information about the push–pull compounds without intramolecular hydrogen bonds.

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