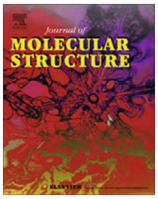
Journal of Molecular Structure 924–926 (2009) 54–61

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Conformational studies of aminomethylene-malonic acid dimethylester and its *N*-methyl derivatives using vibrational spectroscopy, X-ray analysis and *ab initio* calculations

M. Gróf[a], A. Gatial[a,*], P. Matějka[b], J. Kožíšek[a], V. Milata[c], N. Prónayová[d]

[a] Department of Physical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, SK-81237 Bratislava, Slovakia
[b] Department of Analytical Chemistry, Institute of Chemical Technology, CZ-16628 Prague, Czech Republic
[c] Department of Organic Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, SK-81237 Bratislava, Slovakia
[d] Central Laboratories, Faculty of Chemical and Food Technology, Slovak University of Technology, SK-81237 Bratislava, Slovakia

ARTICLE INFO

Article history:
Received 10 September 2008
Received in revised form 27 October 2008
Accepted 30 October 2008
Available online 6 November 2008

Keywords:
Vibrational spectra
Conformational analysis
Push–pull compounds
Ab initio calculations
Solvent effect calculations

ABSTRACT

The IR and Raman spectra of aminomethylene-malonic acid dimethylester (AMDME) [NH_2—CH=C($COOCH_3$)$_2$] and its *N*-methyl derivatives (MAMDME and DMAMDME) were measured in solid phase and in different solvents at various temperatures. X-ray analysis revealed that AMDME exists in solid phase as *EZ* conformer, MAMDME as *ZZa* conformer and DMAMDME as *ZE* conformer (the first and second *E* or *Z* letters express the orientation of the carbonyl oxygen to the C=C double bond for *trans* and *cis* methylester group, respectively, and the third letter *a* denotes *anti* position of methylamino group with respect to the C=C double bond). In less polar solutions dominantly two *ZZ* and *EZ* conformational forms of AMDME and *ZZa* and *EZa* of MAMDME are observed, whereas in more polar environments a third conformational form (*ZE* and *ZEa*, respectively) also appeared.

The behaviour of DMAMDME is different because there is no intramolecular hydrogen bond and in less polar solutions exists in two *ZZ* and *ZE* conformational forms. Very weak indications of a third conformational form (probably *EZ* conformer) were observed only in more polar surroundings. From the solution IR temperature dependent spectra the energy difference between *ZE* and *ZZ* conformers of $\Delta H = 1.8 \pm 0.5$ kJ mol^{-1} in chloroform and $\Delta H = 4.2 \pm 0.5$ kJ mol^{-1} in acetonitrile was estimated with the *ZZ* one being more stable.

The geometries and relative energies of the possible conformers of all three compounds were evaluated using *ab initio* MP2 and DFT B3LYP methods in 6-31G** basis set with PCM solvent effect inclusion. The influence of environment polarity on the conformational equilibrium is discussed.

1. Introduction

Push–pull ethylenes form a specific group of organic compounds characterized by the presence of different electron nature substituents on each side of the C=C double bond. They are highly reactive compounds of the general formula $R^1X—CR^2=CR^3R^4$ with electron donor groups at one end and strong electron acceptor groups at the other end of ethylenic C=C double bond. Very often R^2 = H and for X=NH or NR^1 and X=O as the electron donor groups R^1 can be hydrogen, alkyl, cycloalkyl, aryl or hetero(aryl) groups. On the other side as the electron acceptors R^3, R^4 are the groups such as —CN, —COR, —COOR, —SO_2CH_3, —NO_2. Mainly enamines (X=NH, NR^1) are frequently used as reactants or intermediates in chemical syntheses of drugs, polymers and dyes [1–3]. Alkoxymethylenes (X=O) are also often used in organic synthesis [4,5]. In this type of compounds with the bigger donor or acceptor substituents the polar character of push–pull ethylenes, the electronic interactions between substituents and the double bond are responsible for their non-linear optical properties and their use as possible novel electro-optics materials [6–12].

Despite the large interest in this type of compounds, there are not too much works devoted to the interpretation of their vibrational spectra or the interpretation was restricted only to some vibrational bands. In the case when both R^3, R^4 groups are identical the compound exists in one isomeric form and the conformational possibilities are caused by the electron donor or acceptor R^1 and R^3, R^4 groups, respectively. Thus theoretical and experimental study and interpretation of vibrational spectra of aminomethylene-propanedinitrile [$H_2N—CH=C(CN)_2$] (AMPDN) and its *N*-methyl derivatives has been performed [13] and for *N*-methyl substituted compound the conformers with *anti* and *syn* orientation of the methylamino group towards C=C double bond were found. The conformational analysis of methoxymethylene-propanedinitrile

---

[*] Corresponding author. Tel.: +421 2 59325460; fax: +421 2 52926032.
E-mail address: anton.gatial@stuba.sk (A. Gatial).

0022-2860/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2008.10.051

[$H_3C—O—CH{=}C(CN)_2$] (MMPDN) has been also performed [14,15] and only *anti* orientation of methoxy group was found.

The conformational analysis of 3-methoxymethylene-2,4-pentanedione [$H_3C—O—CH{=}C(COCH_3)_2$] (MMPDO) has shown that this compound exists in CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3CN solutions at least in two conformational forms and that the conformational equilibria are changed with the solvent polarity [16]. According to the results from semiempirical and *ab initio* calculations and from vibrational spectra, MMPDO exists as *ZEa* and *EZa* conformer (*a* represents the *anti* orientation of the methoxy group to the C═C double bond and *E*, *Z* express the orientation of the carbonyl oxygen with respect to the C═C double bond consecutively for *trans* and *cis* acetyl group).

The conformational study of 3-aminomethylene-2,4-pentanedione [$H_2N—CH{=}C(COCH_3)_2$] (AMPDO) revealed that this compound exists in solid phase as well as in more polar surroundings as *EZ* conformer (*E* denotes the away orientation of the carbonyl oxygen from the C═C double bond, *Z* implies the towards orientation of the carbonyl oxygen to the C═C double bond, again consecutively for *trans* and *cis* acetyl group) [17]. However, in less polar solvents we have observed the presence of two conformers of AMPDO, *EZ* and *ZZ*, which are both stabilized by an intramolecular hydrogen bond.

The previous study of some push–pull aminodiesters [18,19] showed that these compounds exist in solid phase in *EZ* conformation (*E* and Z denote again the orientation of the carbonyl oxygen with respect to the C═C double bond for *trans* and *cis* ester groups). In less polar surroundings *ZZ* conformer was observed too. However, in more polar environments a third conformational form (*EZ* conformer) also appeared. These compounds are in the case of amino or methylamino electron donor group stabilized by the intramolecular hydrogen bond between the amino hydrogen and the carbonyl oxygen of the ester group in *cis* position.

The conformational possibilities of AMDME and DMAMDME are the same and are given by the rotation of the both ester groups around the single C—C bond with respect to the C═C double bond. The orientation of the carbonyl oxygen can be towards (*Z*-conformer) or away (*E*-conformer) from the C═C double bond and thus, AMDME and DMAMDME can theoretically exist in four conformational forms *ZZ*, *EZ*, *ZE* and *EE*, where the first and second letters denote the position consecutively for *trans* and *cis* ester group, respectively. The difference between these compounds is that AMDME can be stabilized by an intramolecular hydrogen bond. In the case of MAMDME, which can be also stabilized by an intramolecular hydrogen bond, an additional conformational possibility arises from the rotation of the methylamino group around the N—C═ bond which can be *anti* (i.e. the methyl group is oriented away from the C═C double bond) or *syn* (i.e. the methyl group is oriented towards the C═C double bond) oriented. Thus, MAMDME can theoretically exist in eight conformational forms *ZZa*, *EZa*, *ZEa*, *EEa*, *ZZs*, *EZs*, *ZEs* and *EEs*.

In the case of all the mentioned conformers of the three studied compounds we consider the *syn* orientation of the methoxy group in both ester groups (i.e. the methyl group is oriented towards the carbonyl oxygen) because the *anti* position is energetically very disadvantageous.

2. Experimental and computational details

AMDME, MAMDME and DMAMDME were prepared by the reactions of dimethyl 3-methoxymethylenemalonate in methanol with an aqueous solution of ammonia, methylamine and dimethylamine, respectively. The slightly warmed mixture was stirred overnight at room temperature. The reaction mixture was then briefly heated to reflux. After ensuring that no starting derivative remained, the reaction mixture was evaporated on a vacuum evaporator and chromatographed on silica gel. The obtained product was recrystallized from the minimal amount of chloroform and n-hexane mixture in refrigerator.

X-ray diffraction data were recorded using Oxford Diffraction GEMINI R diffractometer. The requirement for the collection of these data was the preparation of appropriate single crystals. All measurements were carried out at the temperature of 100 K. The MoKα type of radiation was used in all experiments.

The infrared spectra in the region 4000–400 cm^{-1} were recorded with a Nicolet model NEXUS 470 FTIR spectrometer at room temperature. The solid phase measurements were performed after mixing the powdered sample with KBr and pressing into a pellet. The far infrared spectra in the region 600–50 cm^{-1} were recorded with a Nicolet model 5700 FTIR spectrometer in a polyethylene pellet at room temperature. The solution IR spectra of the three compounds in acetonitrile and chloroform were measured in a Specac temperature cell equipped with KBr windows. Raman measurements were performed using Bruker RFS 100 Raman spectrometer with Nd^{3+}: YAG laser at the wavelength of 1064 nm. The Raman spectra of the powdered solid as well as of the solutions were obtained in the region 4000–50 cm^{-1} at room temperature.

NMR spectroscopy was performed in the solutions of dimethylsulfoxide (DMSO) and deuterated chloroform ($CDCl_3$) to confirm the identity of the samples. The ^1H NMR and ^{13}C NMR spectra were recorded at room temperature with both Varian VXR-300 and INOVA 600 spectrometers. Purity of the samples was checked using differential scanning calorimetry with Perkin-Elmer DSC-7 calorimeter and melting points were 126, 64 and 57 °C for AMDME, MAMDME and DMAMDME, respectively.

Ab initio MP2 computations and the DFT ones employing B3LYP functional were performed using Gaussian 03 program [20]. The 6-31G** basis set was used in the both MP2 and DFT calculations and calculated energies were corrected with zero point energy (ZPE). The self-consistent reaction field (SCRF) theory via polarizable continuum model (PCM) including the effect of environment [21,22] was applied to correct the relative ground state energies obtained for isolated molecules.

3. Results and discussion

3.1. X-ray analysis, IR and Raman spectra

X-ray analysis of AMDME and MAMDME revealed that these compounds exist in solid phase with different orientation of *trans* ester group. While AMDME exists in solid phase as *EZ* conformer [23], MAMDME is present as *ZZa* conformer [24]. The single crystal of MAMDME turned out to be a non-merohedral twin. Furthermore, there are two pairs of independent molecules of MAMDME in the unit cell. The former X-ray study of DMAMDME [25] revealed that this compound exists in solid phase in *ZE* conformation with the carbonyl of *cis* methylester twisted by 68° to the plane formed by the other two C═C and C═O double bonds.

The comparison of infrared and Raman spectra of AMDME measured in the solvents of different polarity and in solid phase revealed the possible existence of more than one conformer of AMDME in less polar surroundings as well as in more polar solvents (Fig. 1). The temperature dependence of the conformational equilibrium of AMDME in acetonitrile solution is depicted in Fig. 2 together with the deconvolution of the measured spectra into individual bands. We can expect three bands for each conformer in the region of 1780–1580 cm^{-1} (two for the C═O stretching vibration and one for the C═C stretching vibration). There are more than three bands in the solution spectra in this region. Some of them disappear from the solid phase spectrum and their intensity

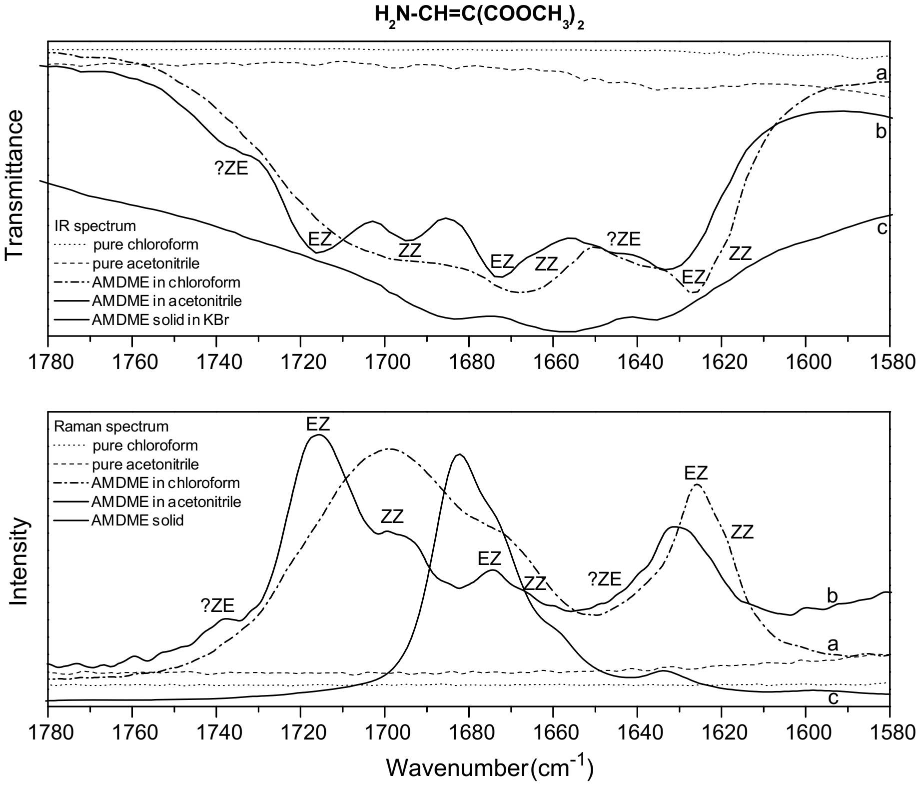


Fig. 1. IR (top) and Raman (bottom) spectra of AMDME in chloroform (curve a), in acetonitrile (curve b) and as solid (curve c). Dotted line is pure chloroform and dashed line is pure acetonitrile.

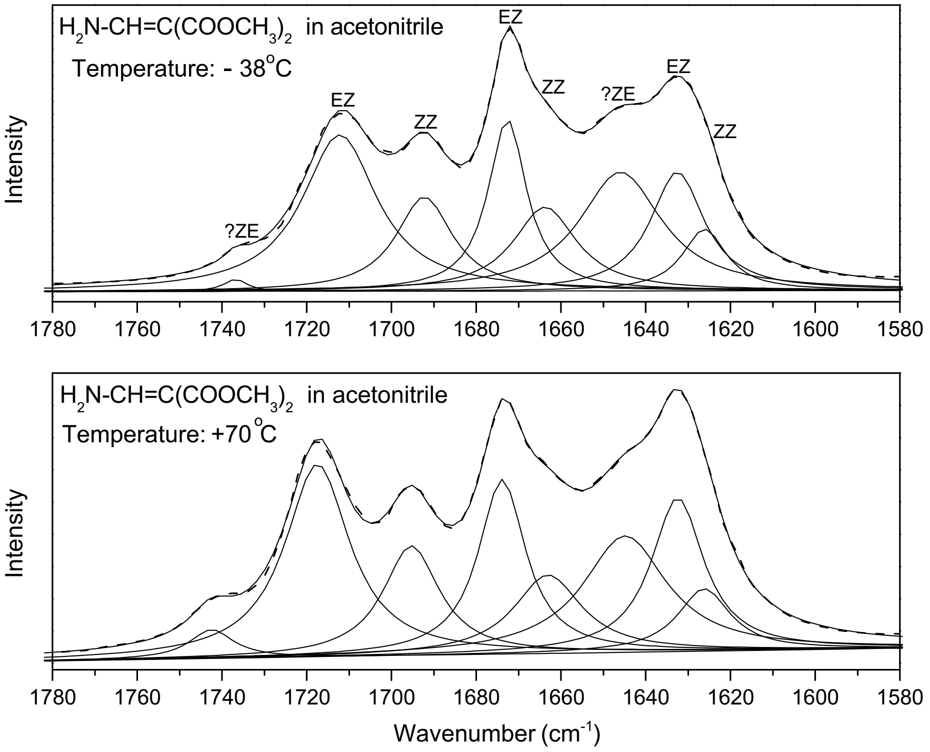


Fig. 2. IR spectra of AMDME in acetonitrile at −38 °C (top, dashed line) and at +70 °C (bottom, dashed line). Solid IR spectrum is obtained as the sum of the deconvoluted bands.

depends on the polarity of the solvent as well as on the temperature. Their assignment is based on the theoretical calculations of the conformer energies in polar surrounding and on the vibrational frequencies of individual conformers.

The infrared and Raman spectra of MAMDME measured in solid phase as well as in solvents of different polarity have a similar nature with those of AMDME. The spectra point out the possible existence of more than one conformer in less polar solvents as well as in more polar surroundings (Fig. 3). In the solution spectra there are again more than three bands in the C=O and C=C double bonds stretching vibrations region. Some of them disappear in the solid phase spectrum and their intensity depends again on the polarity of the solvent and temperature.

Although the infrared and Raman spectra of DMAMDME measured in solvents of different polarity do not contain so many bands as the spectra of AMDME and MAMDME, their comparison with the spectra measured in solid phase also implies the existence of at least two conformers of DMAMDME in solution. The bands that disappear from the vibrational spectrum in solid phase (at 1714, 1678 and 1612 cm^{-1}) are less intense in the more polar acetonitrile (Fig. 4). This means that they belong to a conformer that is less polar than in the solid phase present *ZE* conformer. We observed only some very weak indications of a third conformational form in the spectrum measured in acetonitrile (very weak band at 1757 cm^{-1}). In addition, the intensity of bands shows also the temperature dependence in less polar chloroform as well as in more polar acetonitrile (Fig. 5).

3.2. Quantum-chemical calculations

For all calculations we consider the *syn* orientation of the methoxy groups with respect to the carbonyl oxygen in both ester groups because the *anti* position is energetically very disadvantageous. The total energies and dipole moments of the individual conformers of AMDME are included in Table 1. According to these calculations the most stable conformer is the *ZZ* one. The next most stable is *EZ* conformer which is by 2–4 kJ mol^{-1} less stable. The third and the fourth most stable conformers are *ZE* and *EE* conformers, whose MP2 energies are by 12 and 17 kJ mol^{-1} higher, respectively. The influence of the polar environment on the conformer energies is included by the PCM solvation model and the results for AMDME are depicted in Fig. 6. As we can see, the *ZE* and *EE* conformers remain energetically disadvantageous in less polar surroundings. However, the energy difference between *EZ* and *ZZ* conformer in a less polar environment is only of 1–2 kJ mol^{-1} what is in agreement with the trend observed in the vibrational spectra where we suppose the presence of these two conformers in the less polar chloroform. We suppose the presence of the third *ZE* conformer in the acetonitrile solution what is also in a good agreement with the results from the PCM solvation model. According to this model the *ZZ* and *EZ* conformers are of equal stability and the relative energy of the *ZE* conformer decreases to 5–6 kJ mol^{-1}. The presence of the *EE* conformer can be excluded due to its highest relative energy in the gas phase as well as in polar environment.

The total energies and dipole moments of individual conformers of MAMDME are included in Table 2. The calculated relative energies are similar as for AMDME and the most stable conformer is again the *ZZa* one. *EZa* conformer is by 3–4 kJ mol^{-1} less stable. The third and the fourth most stable conformers are *ZEa* and *EEa* conformers, whose MP2 energies are by 14 and 20 kJ mol^{-1} higher, respectively. We consider only the *anti* orientation of the methyl group bound on nitrogen as the *syn* position is energetically very disadvantageous (MP2 energies of *syn* conformers are by over 30 kJ mol^{-1} and DFT ones over 40 kJ mol^{-1} higher). The results of the solvation PCM model for MAMDME are depicted in Fig. 7. As we can see the *ZEa* and *EEa* conformers are very disadvantageous in less polar surroundings. However, the energy difference between *EZa* and *ZZa* conformer in a less polar environment is of 1–2 kJ mol^{-1} what is in agreement with the trend observed in the vibrational spectra where we suppose the presence of these

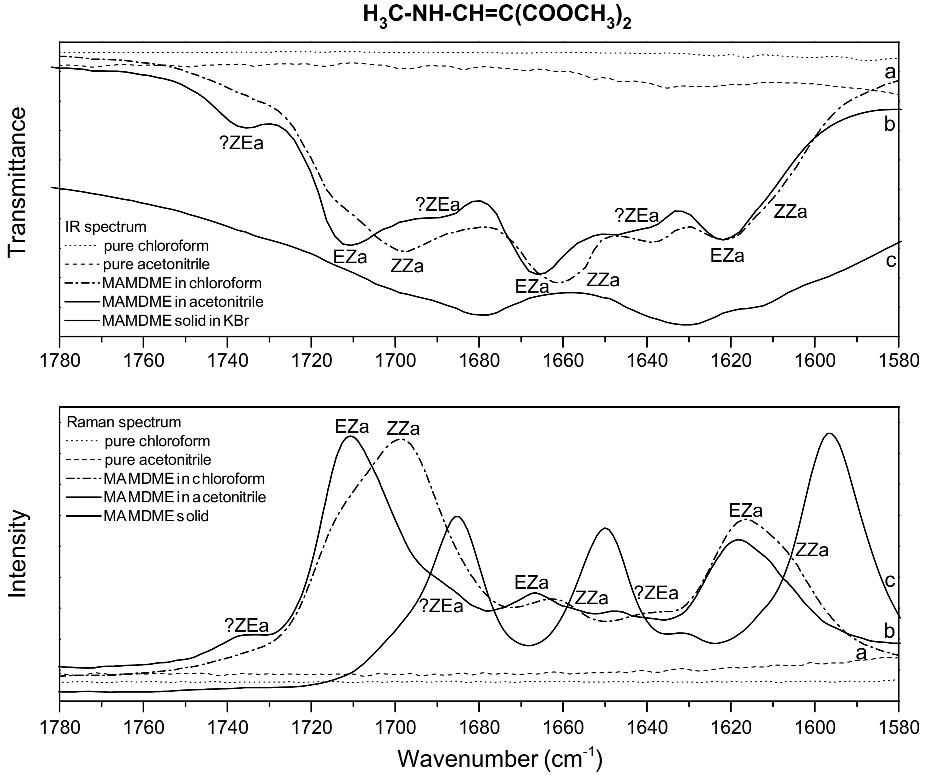


Fig. 3. IR (top) and Raman (bottom) spectra of MAMDME in chloroform (curve a), in acetonitrile (curve b) and as solid (curve c). Dotted line is pure chloroform and dashed line is pure acetonitrile.

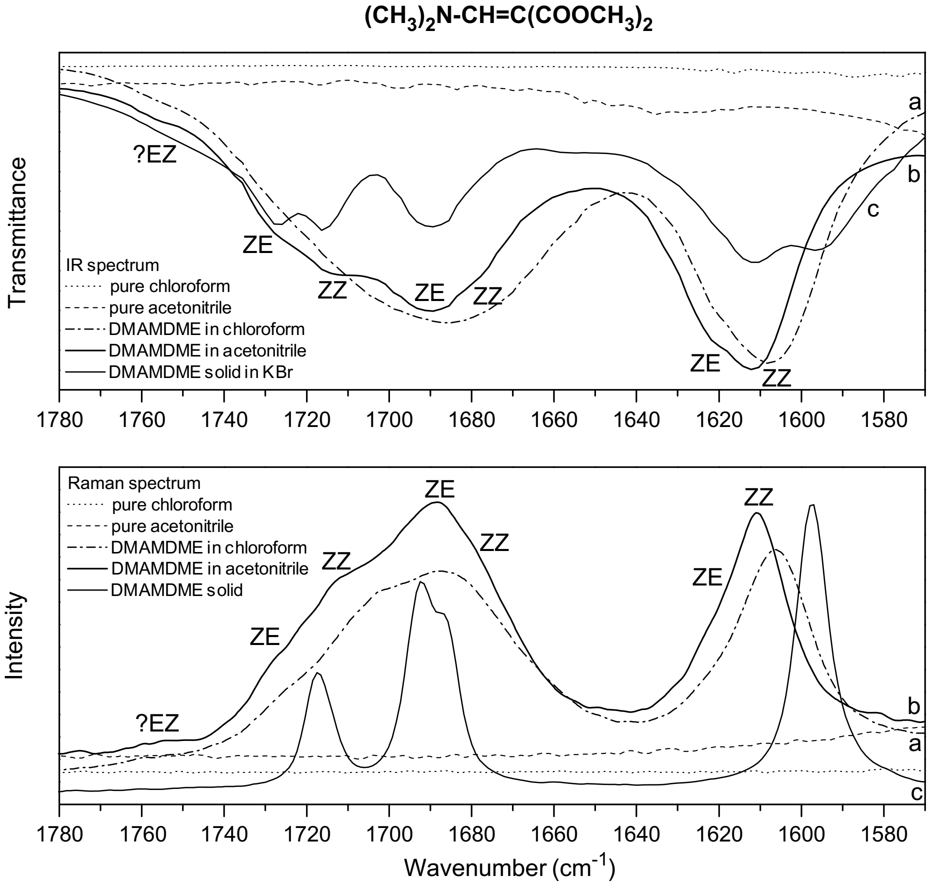


Fig. 4. IR (top) and Raman (bottom) spectra of DMAMDME in chloroform (curve a), in acetonitrile (curve b) and as solid (curve c). Dotted line is pure chloroform and dashed line is pure acetonitrile.

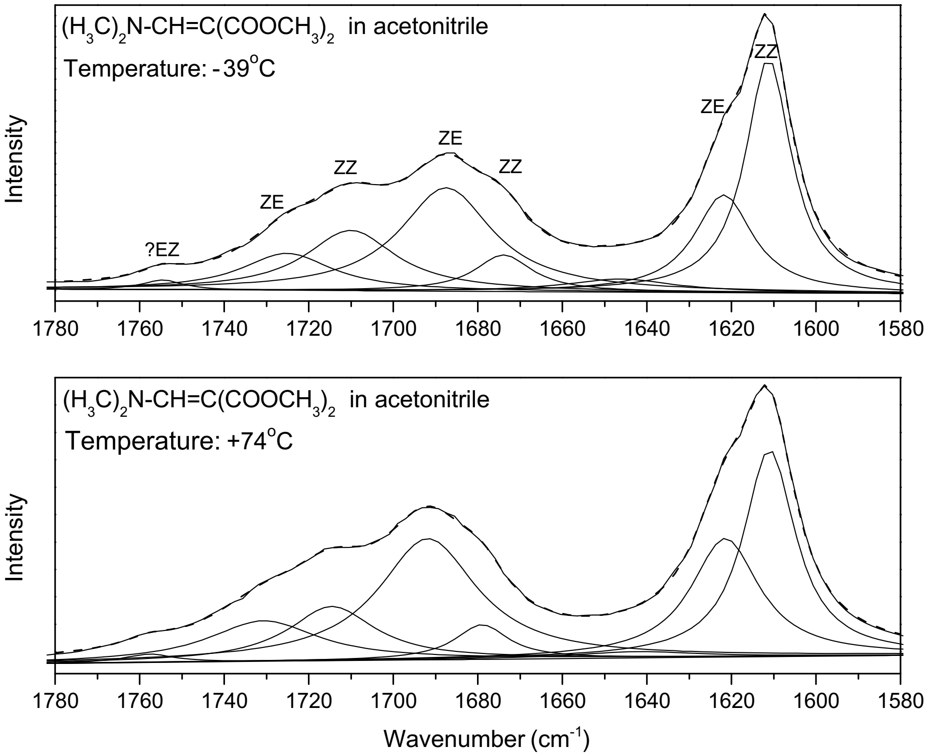


Fig. 5. IR spectra of DMAMDME in acetonitrile at −39 °C (top, dashed line) and at +74 °C (bottom, dashed line). Solid IR spectrum is obtained as the sum of the deconvoluted bands.

Table 1
Calculated MP2 and DFT total E and relative ΔE energies (with zero point energy correction) and dipole moments μ of individual conformers of AMDME.

Conformer	E (MP2) Hartree	ΔE (MP2) kJ mol^{-1}	μ_{MP2} D	E (B3LYP) Hartree	ΔE (B3LYP) kJ mol^{-1}	μ_{B3LYP} D
ZZ	−587.906606	0.00	1.50	−589.576604	0.00	1.48
EZ	−587.905685	2.42	3.36	−589.575107	3.93	3.58
ZE	−587.901858	12.46	4.17	−589.570627	15.69	4.37
EE	−587.899967	17.42	5.85	−589.567504	23.89	6.44

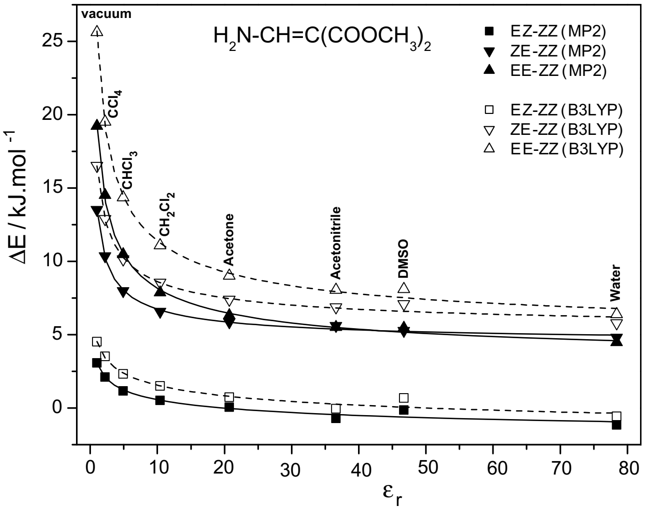


Fig. 6. Energy difference between the conformers of AMDME as the function of the relative permittivity of environment calculated using PCM model for different solvents at *ab initio* (MP2) and DFT (B3LYP) level in 6-31G** basis set.

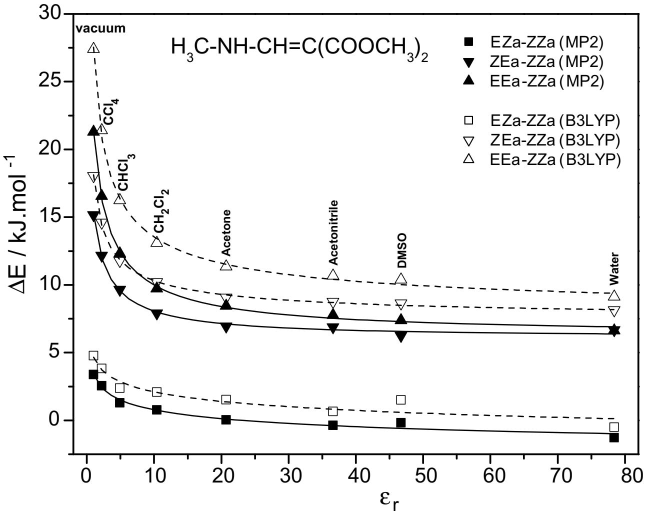


Fig. 7. Energy difference between the conformers of MAMDME as the function of the relative permittivity of environment calculated using PCM model for different solvents at *ab initio* (MP2) and DFT (B3LYP) level in 6-31G** basis set.

two conformers in the less polar chloroform. On the other hand, we suppose the presence of the third *ZEa* conformer in the acetonitrile solution what is also in a good agreement with the results of the PCM solvation model. According to this model the *ZZa* and *EZa* conformers are in more polar environment of equal stability and the relative energy of the *ZEa* (as well as *EEa*) conformer decreases to 7–9 kJ mol^{-1}.

The total energies and dipole moments of individual conformers of DMAMDME are included in Table 3. The situation is different from the trend calculated in the case of AMDME and MAMDME as the carbonyl oxygen in *cis* position is not bound with an intramolecular hydrogen bond. The most stable conformer is again the *ZZ* conformer. However, *EZ* and *ZE* conformers are both approximately of equal stability and their relative energy is by 4–5 kJ mol^{-1} higher than the energy of *ZZ* conformer. The least stable conformer is the *EE* conformer with relative energy of 11–14 kJ mol^{-1}. The results of the solvation PCM model for DMAMDME are depicted in Fig. 8. The situation differs from that calculated in the case of AMDME and MAMDME. In a less polar environment the energies of the both conformers with *E* orientation of the *trans* methylester group (i.e. *EZ* and *EE*) are higher than the energies of conformers with *Z* orientation of the methylester group in *trans* position (i.e. *ZZ* and *ZE*). The energy difference between *ZE* and *ZZ* conformers in a less polar solvent is only of 2–3 kJ mol^{-1} what is in agreement with the trend observed in the vibrational spectra where we suppose the presence of these two conformers in the less polar chloroform. However, in more polar surroundings the calculated energy differences between the mentioned conformers decrease below 2 kJ mol^{-1} and the relative energies of the third *EZ* conformer or the fourth *EE* conformer remain twice as large. According to the given results we can assign the indications of the presence of a third conformational form to the *EZ* conformer.

3.3. Conformational analysis

As has been shown by the theoretical calculations of AMDME in vacuum as well as in solvents of different polarity, we can assign the bands in less polar chloroform to the two most stable *ZZ* and *EZ* conformers with the *ZZ* conformer being the most stable one. The bands whose intensities increase in the more polar acetonitrile can be assigned to the more polar *EZ* conformer. The intensity of these bands seems also to increase with the temperature. Moreover such an assignment can be supported also by the trends of the calculated frequencies of all three bands in this region presented in Table 4. All three bands of *EZ* conformer in the double

Table 2
Calculated MP2 and DFT total E and relative ΔE energies (with zero point energy correction) and dipole moments μ of individual conformers of MAMDME.

Conformer	E (MP2) Hartree	ΔE (MP2) kJ mol^{-1}	μ_{MP2} D	E (B3LYP) Hartree	ΔE (B3LYP) kJ mol^{-1}	μ_{B3LYP} D
ZZa	−627.052932	0.00	2.01	−628.860371	0.00	1.94
EZa	−627.051890	2.74	3.91	−628.858838	4.02	4.06
ZEa	−627.047450	14.39	4.66	−628.853826	17.18	4.84
EEa	−627.045406	19.76	6.41	−628.850590	25.67	6.92

Table 3
Calculated MP2 and DFT total E and relative ΔE energies (with zero point energy correction) and dipole moments μ of individual conformers of DMAMDME.

Conformer	E (MP2) Hartree	ΔE (MP2) kJ mol^{-1}	μ_{MP2} D	E (B3LYP) Hartree	ΔE (B3LYP) kJ mol^{-1}	μ_{B3LYP} D
ZZ	−666.187895	0.00	2.56	−668.125998	0.00	2.57
EZ	−666.186213	4.42	4.22	−668.123986	5.28	4.56
ZE	−666.186168	4.53	4.22	−668.123415	6.78	4.53
EE	−666.183921	10.43	5.69	−668.120426	14.63	6.20

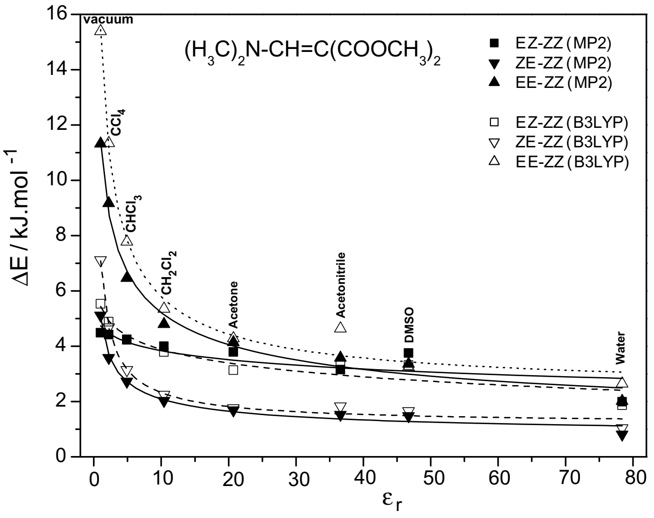


Fig. 8. Energy difference between the conformers of DMAMDME as the function of the relative permittivity of environment calculated using PCM model for different solvents at *ab initio* (MP2) and DFT (B3LYP) level in 6-31G** basis set.

bonds region are calculated at higher frequencies in comparison with the *ZZ* conformer. The bands present mainly in the vibrational spectrum of the more polar acetonitrile (marked with "?") could be then assigned to the *ZE* conformer (it is the third most stable conformer and it has a higher dipole moment than both more stable *ZZ* and *EZ* conformers).

The assignment of vibrational bands for MAMDME is very similar as for AMDME. According to the theoretical calculations in vacuum as well as in the solvents of different polarity, we can assign the bands in the less polar chloroform to the *ZZa* and *EZa* conformers with the dominance of *ZZa* conformer. The bands assigned to the *EZa* conformer increase their relative intensity in more polar solvents and at higher temperatures. Their assignment can be again supported by the calculated trends of vibrational frequencies for *ZZa* and *EZa* conformers in Table 4. The bands present mainly in the vibrational spectrum of the more polar acetonitrile (marked by "?") could be assigned to the *ZEa* conformer (it is the third most stable conformer and it has a higher dipole moment than *ZZa* or *EZa* conformer). The different nature of the solid phase spectrum of MAMDME in comparison with the solid phase spectrum of AMDME confirms the existence of a different conformer in solid phase (*EZ* and *ZZa* in the case of AMDME and MAMDME, respectively) and the split of each vibrational mode into two bands confirms the existence of two pairs of independent molecules in the unit cell.

The situation in the case of DMAMDME seems to be slightly simpler than for two former compounds. Experimental evidences for a third conformer are weak and in the interpretation of vibrational spectra we can consider two dominant conformers. According to the theoretical calculations, the bands that disappear from the solid phase spectrum can be assigned to the *ZZ* conformer, which is the most stable conformer and has a lower dipole moment than in the solid phase present *ZE* conformer. Also the calculated trends in the vibrational frequencies for all three bands are in excellent agreement with the experimental ones (Table 4). Such a simplification gave us the possibility to estimate the energy difference between the *ZE* and *ZZ* conformers from IR spectra measured at different temperatures. After the deconvolution of the measured IR spectra into the bands with Lorentz profile (Fig. 5) and using the band area for the band pairs of *ZE* and *ZZ* conformers at 1622 and 1612 cm^{-1} we have obtained using van't Hoff equation the energy difference $\Delta H(ZE - ZZ) = 4.2 \pm 0.5$ kJ mol^{-1} in chloroform and 1.8 ± 0.5 kJ mol^{-1} in acetonitrile. Temperature dependence IR spectra were measured in the interval from −46 up to +56 °C for chloroform and from −39 up to +74 °C for acetonitrile with the step of about 10 °C. These data are in very good agreement with the calcu-

Table 4
Comparison of the calculated (MP2 and B3LYP level of theory) and experimental vibrational frequencies of AMDME, MAMDME and DMAMDME conformers.

MP2			B3LYP			Experimental[a]		
AMDME								
ZZ	*EZ*	*ZE*	*ZZ*	*EZ*	*ZE*	*ZZ*	*EZ*	*ZE*
1791 (1734)[b]	1824 (1767)	1827 (1770)	1768 (1692)	1810 (1728)	1814 (1732)	1696	1717	1737
1755 (1697)	1759 (1700)	1789 (1733)	1719 (1648)	1728 (1659)	1767 (1691)	1663	1674	
1730 (1663)	1736 (1669)	1743 (1673)	1678 (1633)	1684 (1638)	1685 (1638)	1624	1634	1646
MAMDME								
ZZa	*EZa*	*ZEa*	*ZZa*	*EZa*	*ZEa*	*ZZa*	*EZa*	*ZEa*
1790 (1731)	1821 (1765)	1825 (1768)	1766 (1694)	1808 (1726)	1812 (1730)	1695	1712	1736
1749 (1688)	1760 (1694)	1788 (1730)	1711 (1647)	1722 (1666)	1766 (1694)	1646	1666	1689
1724 (1664)	1729 (1669)	1743 (1675)	1687 (1631)	1691 (1632)	1690 (1638)	1612	1622	1637
DMAMDME								
ZZ	*EZ*	*ZE*	*ZZ*	*EZ*	*ZE*	*ZZ*	*EZ*	*ZE*
1798 (1741)	1806 (1750)	1811 (1754)	1780 (1702)	1795 (1713)	1806 (1723)	1714	1757	1727
1781 (1726)	1782 (1727)	1795 (1740)	1754 (1675)	1767 (1689)	1775 (1697)	1678		1690
1734 (1660)	1735 (1660)	1738 (1663)	1662 (1609)	1668 (1616)	1671 (1616)	1612		1622

[a] Observed frequencies are from IR spectra in acetonitrile solution.

[b] Values in parenthesis are the corresponding scaled vibrational frequencies using the scale factors from [17].

lated values for both solvents using PCM solvation model (Fig. 8) predicting the decreasing energy difference between the conformers in more polar environments.

4. Conclusions

The three push–pull ethylenes – aminomethylene-malonic acid dimethylester and its *N*-methyl derivatives have been studied by means of X-ray analysis, infrared and Raman spectroscopy and theoretical computations. The obtained results can be summarized in the following conclusions:

- AMDME exists in solid phase as *EZ* conformer. We can observe the presence of *EZ* and *ZZ* conformers in less polar solvents. Additionally, in more polar environments also *ZE* conformer appears.
- MAMDME exists in solid phase as *ZZa* conformer. We can observe the presence of *ZZa* and *EZa* conformers in less polar solvents. Additionally, in more polar environments *ZEa* conformer appears as well. Thus the behaviour of this compound is analogous to that of AMDME.
- DMAMDME exists in solid phase as *ZE* conformer. We can observe the presence of *ZE* and *ZZ* conformers in less polar solvents. The energy difference between these conformers $\Delta H(ZE - ZZ) = 4.2 \pm 0.5$ kJ mol^{-1} in chloroform and 1.8 ± 0.5 kJ mol^{-1} in acetonitrile was estimated. Only a weak indication of a third conformational form (probably *EZ* conformer) was observed in more polar surroundings.

Acknowledgements

This work has been supported by Slovak Grant Agency (Projects VEGA No. 1/3566/06 and 1/0225/08) and by Science and Technology Assistance Agency under the contract No. APVV-20-0073-04. NMR experimental part of this work was facilitated by the support of Slovak National Research and Development Program No. 2003SP200280203.

References

[1] A.G. Cook (Ed.), Enamines: Synthesis Structure and Reactions, Marcel Dekker, New York, 1969.
[2] S.F. Dyke, The Chemistry of Enamines, Cambridge University Press, London, 1973.
[3] D. Bouzard (Ed.), Recent Progress in the Chemical Synthesis of Antibiotics, Springer-Verlag, München, 1990, p. 249.
[4] F. Freeman, in: LONZA Reaction of Malononitrile Derivatives, Synthesis, Georg Thieme Verlag, Stuttgart, 1981, pp. 925.
[5] V. Milata, Aldrichim. Acta 34 (2001) 20.
[6] D. Chemla, J. Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals, vol. 1, Academic Press, New York, 1987. pp. 123–187.
[7] H.S. Nalwa, T. Watanabe, S. Miyata, Nonlinear Optics of Organic Molecules and Polymers, CRC Press, Boca Raton, 1997. pp. 87–329.
[8] R.R. Pappalardo, R.M. Parrondo, P. Karafiloglou, E. Sanchez Marcos, J. Phys. Chem. 99 (1995) 6461.
[9] T. Kolev, Z. Glavcheva, D. Yancheva, M. Schürmann, D.C. Kleb, H. Preut, P. Bleckmann, Acta Crystallogr. E57 (2001) o760.
[10] T. Kolev, Z. Glavcheva, M. Schürmann, D.C. Kleb, H. Preut, P. Bleckmann, Acta Crystallogr. E57 (2001) o964. o966.
[11] T.M. Kolev, D.Y. Yancheva, B.A. Stamboliyska, Spectrochim. Acta A 59 (2003) 3325.
[12] T. Kolev, D. Yancheva, B. Shivachev, R. Petrova, M. Spiteller, Acta Crystallogr. E61 (2005) o550.
[13] A. Gatial, Š. Sklenák, V. Milata, P. Klaeboe, S. Biskupič, D. Scheller, J. Jurašková, Struct. Chem. 7 (1996) 17.
[14] .A. Gatial, Š. Sklenák, V. Milata, S. Biskupič, Ľ. Zalibera, R. Salzer, J. Mol. Struct. 435 (1997) 410–411.
[15] A. Gatial, V. Milata, S. Biskupič, J. Pigošová, K. Herzog, R. Salzer, Asian Chem. Lett. 8 (2004) 169.
[16] A. Gatial, K. Herzog, V. Milata, Ľ. Zalibera, S. Biskupič, R. Salzer, J. Mol. Struct. 482–483 (1999) 609.
[17] M. Gróf, A. Gatial, V. Milata, N. Prónayová, L. Sümmchen, R. Salzer, J. Mol. Struct. 843 (2007) 1.
[18] D. Smith, P.J. Taylor, J. Chem. Soc., Perkin Trans. II (1979) 1376.
[19] A. Gomez-Sanchez, E. Sempere, J. Bellanato, J. Chem. Soc., Perkin Trans. II (1981) 561.
[20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision A.1, Gaussian Inc., Pittsburgh, PA, 2003.
[21] M. Cossi, V. Barone, R. Cammi, J. Tomasi, Chem. Phys. Lett. 255 (1996) 327.
[22] B. Mennucci, J. Tomasi, J. Chem. Phys. 106 (1997) 5151.
[23] M. Gróf, J. Kožíšek, V. Milata, A. Gatial, Acta Crystallogr. E 64 (2008) o998.
[24] M. Gróf, J. Kožíšek, V. Milata, A. Gatial, Acta Crystallogr. E 64 (2008) o1133–o1134.
[25] U. Shmureli, H. Shanan-Atidi, H. Horwitz, Y. Shvo, J. Chem. Soc., Perkin Trans. II (1973) 657.