Journal of Molecular Structure 993 (2011) 232–242

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

# Isomerizational and conformational study of methyl-2-cyano-3-methoxyacrylate and methyl-2-cyano-3-aminoacrylate and its N-methyl derivatives

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

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

ARTICLE INFO

*Article history:*
Available online 28 November 2010

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

ABSTRACT

The isomers and conformers of four push–pull compounds: methyl-2-cyano-3-methoxyacrylate (MCMA) $H_3C—O—CH=C(CN)(COOCH_3)$, methyl-2-cyano-3-aminoacrylate (MCAA) $H_2N—CH=C(CN)(COOCH_3)$, methyl-2-cyano-3-methylaminoacrylate (MCMAA) $H_3C—NH—CH=C(CN)(COOCH_3)$ and methyl-2-cyano-3-dimethylaminoacrylate (MCDMAA) $(H_3C)_2N—CH=C(CN)(COOCH_3)$ have been studied experimentally by vibrational and NMR spectroscopy and theoretically by the ab initio calculations at MP2 level in 6-311++G** basis set. The IR and Raman spectra of all compounds as a solid and solute in various solvents have been recorded in the region 4000–50 $cm^{-1}$. The NMR spectra were obtained in chloroform, acetonitrile and DMSO at room temperature.

Because both electron-withdrawing groups are different, all studied compounds can exist as E and Z isomers and then conformational possibilities are given by the rotation of the methylester and methoxy or methylamino groups. NMR spectra revealed that both MCMA and MCDMAA compounds without the possibility of intramolecular hydrogen bonding were prepared as a pure E isomer whereas in the case of the compounds with the possibility of intramolecular bonding MCAA and MCMAA a mixture of both E and Z isomers was obtained.

X-ray analysis shows the presence of two EZ and EE conformers in solid MCMA. For this compound the possible second conformer was detected by NMR in more polar solvent DMSO. Vibrational spectra revealed the existence of two EZa and EEa conformers with Z and E orientation of methylester group and with *anti* orientation of dimethylamino group for MCDMAA. For MCAA and MCMAA the Z isomer with Z orientation of methylester group and with intramolecular hydrogen bond is the most stable one. In more polar surrounding (DMSO) the isomerization of ZZ or ZZa conformers of MCAA and MCMAA, respectively to E isomers occurred. These experimental findings have been supported by ab initio solvent effect calculations.



## 1. Introduction

Alkoxymethylenes as well as enamines and their N-alkylamino derivatives of the general formula $R^1O—CH=CXY$ and $R^1R^2N—CH=CXY$, where $R^1$ and $R^2$ are H, alkyl or (hetero)aryl and X and Y are electron-withdrawing groups such as —CN, —COR, —COOR, $—SO_2CH_3$, $—NO_2$ are push–pull ethylenes. They are easily available and highly reactive compounds with the wide use in a number of synthetic processes [1–4] and are useful as starting reactants or intermediates for pharmaceutical, dye, polymer and other syntheses [5–8]. The polar character of push–pull ethylenes, electronic interactions between substituents and the double bond are responsible for their non-linear optical properties and their use as new electro-optics materials [9,10]. Despite their wide use in the organic syntheses, a theoretical and experimental study of their conformers with the interpretation of vibrational spectra has not yet been carried out for many of them. We have studied by vibrational and NMR spectroscopy and by ab initio calculations the push–pull compounds of both types with the same electron-withdrawing groups where it is not necessary to consider the isomerization process: methoxymethylene-propanedinitrile (MEM) $H_3C—O—CH=C(CN)_2$ [11], aminomethylene-propanedinitrile (AM) $H_2N—CH=C(CN)_2$ and its N-methyl derivatives [12], 3-aminomethylene-2,4-pentanedione (AMP) $H_2N—CH=C(COCH_3)_2$ [13] and aminomethylene-malonic acid dimethylester (AMDME) $H_2N—CH=C(COOCH_3)_2$ and its N-methyl derivatives [14]. These studies have shown that MEM exists in the conformation with *anti* orientation of methoxy group, methylaminomethylene-propanedinitrile

* Corresponding author. Tel.: +421 2 59325 460; fax: +421 2 52926 032.
*E-mail address:* anton.gatial@stuba.sk (A. Gatial).

0022-2860/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2010.11.043

**Table 1**
Calculated ab initio energy at MP2 level with including ZPE and dipole moment for the isomers and conformers of studied compounds in 6-311++G** basis set.

| Compound | Isomer and conformer | Total energy (hartree) | Relative energy (kJ mol$^{-1}$) | Dipole moment (D) |
|---|---|---|---|---|
| MCMA | EZa | −511.891705 | 0.00 | 4.45 |
| | EZs | −511.890946 | 1.99 | 1.35 |
| | EEa | −511.889659 | 5.37 | 7.72 |
| | EEs | −511.888943 | 7.25 | 4.64 |
| | ZZa | −511.885944 | 15.13 | 4.09 |
| | ZZs | −511.883157 | 22.44 | 4.31 |
| | ZEa | −511.884117 | 19.92 | 7.23 |
| | ZEs | −511.879827 | 31.19 | 6.19 |
| MCDMAA | EZ | −531.205194 | 0.00 | 4.73 |
| | EE | −531.202346 | 7.48 | 7.67 |
| | ZZ | −531.198556 | 17.43 | 6.15 |
| | ZE | −531.194054 | 29.25 | 8.83 |
| MCAA | EZ | −452.889983 | 4.79 | 3.39 |
| | EE | −452.887853 | 10.38 | 6.57 |
| | ZZ | −452.891808 | 0.00 | 4.88 |
| | ZE | −452.886349 | 14.33 | 7.98 |
| MCMAA | EZa | −492.047906 | 7.42 | 4.05 |
| | EZs | −492.045296 | 14.28 | 4.21 |
| | EEa | −492.045780 | 13.01 | 7.11 |
| | EEs | −492.042700 | 21.09 | 7.23 |
| | ZZa | −492.050734 | 0.00 | 5.65 |
| | ZZs | −492.037813 | 33.92 | 5.62 |
| | ZEa | −492.044515 | 16.33 | 8.67 |
| | ZEs | −492.033409 | 45.49 | 8.26 |

$H_3C—NH—CH=C(CN)_2$ exists in two conformational forms with the methyl group oriented *anti* and *syn* toward the double C=C bond and that for AMP as well as AMDME preferred conformations are those with the intramolecular hydrogen bond between the amino hydrogen and carbonyl oxygen from the acetyl or methylester group, respectively.

For the push–pull compounds of both types with different electron-withdrawing groups, in addition to the conformational study, it is necessary to consider also the isomerization process. We performed such study for the compounds where one electron-withdrawing group is —CN and the second one is acetyl [15,16] or methylsulfonyl [15,16] group. This work represents the extension of such studies on the compounds where towards the cyano group as a second electron-withdrawing is the methylester group. Because of different electron-withdrawing groups, all studied compounds can exist as E (with methylester group in *trans* position towards the amino group) or Z (with *cis* position of mentioned groups) isomers. Therefore the first letter in labeling denotes the isomer of the studied compounds. The conformational possibilities for methylester group is given by the rotation around the =C—C single bond with the carbonyl group oriented away or towards the double C=C bond what is denoted by the second letter E or Z, respectively. The last conformational possibility of these compounds is given only for the methoxy and methylamino compounds where the methyl group bounded with oxygen or nitrogen can be oriented as *anti* or *syn* with respect to the C=C double bond what is denoted by small letters a or s, respectively.

The isomers and conformers of the next four compounds: methyl-2-cyano-3-methoxyacrylate (MCMA) $H_3C—O—CH=C(CN)(COOCH_3)$, methyl-2-cyano-3-aminoacrylate (MCAA) $H_2N—CH=C(CN)(COOCH_3)$, methyl-2-cyano-3-methylaminoacrylate (MCMAA) $H_3C—NH—CH=C(CN)(COOCH_3)$ and methyl-2-cyano-3-dimethylaminoacrylate (MCDMAA) $(H_3C)_2N—CH=C(CN)(COOCH_3)$ will be studied. To our knowledge no such study has been done till now and therefore we have decided to present basic experimental and theoretical information about the stable isomers and conformers of the mentioned compounds. Only NMR data for MCMA associated to the E isomer [17] and for MCAA [18] are presented. IR and NMR data are presented also for MCDMAA [19,20].

## 2. Experimental

### 2.1. Preparative

MCMA has been synthesized by recently improved method [21] by the reaction of trimethylortoformate and methyl cyanoacetate in equimolar solution of acetic anhydride:

$$HC(OCH_3)_3 + NCCH_2COOCH_3 \rightarrow H_3C—O—CH=C(CN)(COOCH_3) + 2CH_3OH$$

The reaction mixture was evaporated to dryness and purified by crystallization and chromatographically. The purity and melting point of MCMA was determined by differential scanning calorimetry using a Perkin-Elmer DCS-7 calorimeter. DSC records have shown that the purity of MCMA was better than 99% with melting point of 89 °C. MCMA was isolated as pure E isomers (with methoxy and methylester group, respectively in *trans* position).

Three amino compounds have been prepared from the MCMA according to the reaction scheme:

$$R^1R^2NH + H_3C—O—CH=C(CN)(COOCH_3) \rightarrow R^1R^2N—CH=C(CN)(COOCH_3) + CH_3OH$$

where $R^1$ and $R^2$ are H or $CH_3$. The corresponding pure E isomer of MCMA has been mixed with appropriate amine (water solution of amine or methanol solution of methylamine or ethanol solution of dimethylamine) at laboratory temperature. The reaction mixture was again evaporated to dryness and purified by crystallization and chromatographically. The purity and melting points of all three

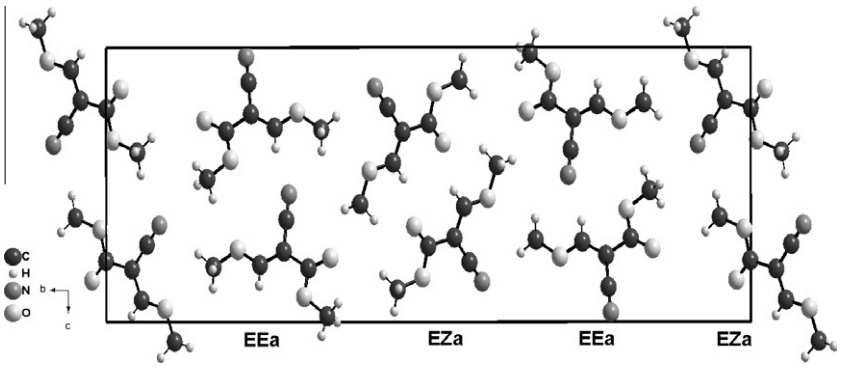


**Fig. 1.** Unit cell of MCMA.

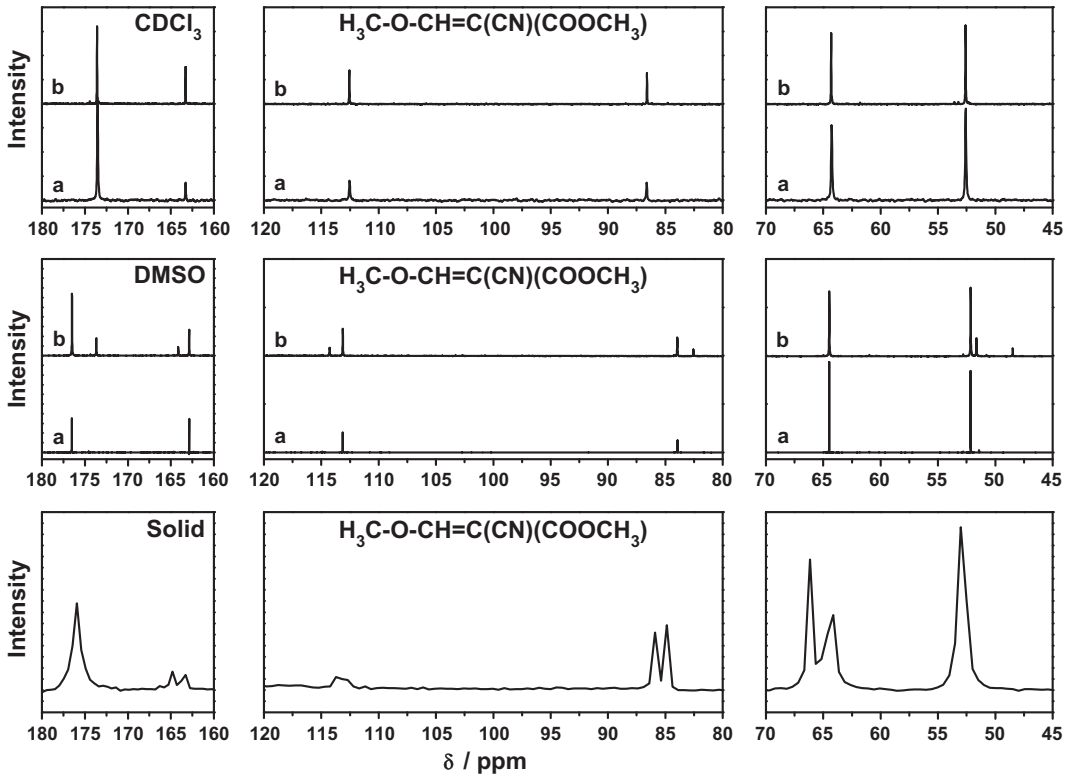


**Fig. 2.** $^{13}C$ NMR spectra of MCMA in $CDCl_3$ (top), in DMSO (middle) and in solid phase (bottom) at room temperature. The curve (a) is measured immediately after dissolving and curve (b) after 2 weeks.

solid amino samples were also determined by differential scanning calorimetry for every obtained chromatographic fraction. DSC records have shown that the purity of MCDMAA was better than 99% with melting point of 97 °C and was isolated as pure E isomer.

On the other side, for MCAA as well as for MCMAA two melting points have been observed at DCS record for each of them. Melting points are at 113 °C and 126 °C for MCAA and at 105 °C and 136 °C for MCMAA. DSC records for different chromatographic fractions indicate that both samples were probably obtained as a mixture of both Z and E isomers with different contents of both isomers in different chromatographic fractions.

### 2.2. Spectra

The $^1H$ and $^{13}C$ NMR spectra in chloroform, acetonitrile and DMSO were run at room temperature on both Varian VXR-300 and INOVA-600 spectrometers. The X-ray studies of MCMA, MCAA and MCDMAA have been performed with Oxford Diffraction GEMINI R diffractometer using Mo Kα radiation at the temperature of 293 or 100 K. Mid-IR spectra in the region 4000–400 $cm^{-1}$ were recorded on Nicolet model NEXUS 470 FTIR spectrometer. The mid-IR spectra at room temperature of all compounds were measured as KBr pellets. The IR spectra in solvents of different polarity ($CCl_4$, $CHCl_3$, $CH_2Cl_2$, $CH_3CN$ and DMSO) were measured in a cell equipped with KBr windows. To avoid the fluorescence, a Brucker RFS 100 Raman instrument equipped with near $Nd^{3+}$:YAG laser with wavelength 1064 nm was used. Raman spectra at room temperature of powdered solids as well as in chloroform and acetonitrile solutions were obtained in the region 4000–100 $cm^{-1}$.

### 2.3. Quantum chemical calculations

Quantum chemical calculations were performed at MO ab initio level with the Gaussian 03 program [22]. The calculations were carried out with full electron correlation by the perturbation method to second order MP2 [23] with fully optimized geometries at this level. The Berny analytical gradient method was used for optimizations. Stationary points with respect to the nuclear coordinates of isomers and conformers for all studied compounds were obtained by the simultaneous relaxation of all geometric parameters. Harmonic frequency calculations were carried out to characterize the stationary points and to determine zero point energy (ZPE). The total molecular energy at MP2 level including ZPE obtained for the individual conformers of all studied compounds in 6-311++G** basis set are given in Table 1 together with the calculated dipole moment at the same theory level using MP2 density. In order to explain the visible changes in the NMR and vibrational spectra of studied compounds in less and more polar solvents we have also done the solvent effect calculations for all their isomers and conformers. The solute–solvent interaction was taken into account via self-consistent reaction field (SCRF) theory. The molecular energy in the presence of a solvent was calculated with the Integral Equation Formalism Polarizable Continuum Model (IEFPCM) model [24]. This model was used in accordance with the routines included in the Gaussian 03 program. The calculations were done with the geometry optimized at MP2 level in the 6-311++G** basis set.

## 3. Results and discussion

### 3.1. Compounds without intramolecular hydrogen bonding

#### 3.1.1. Methyl-2-cyano-3-methoxyacrylate

X-ray measurements of MCMA were done on two different single crystals at laboratory temperature with the same result. Its structure is depicted in Fig. 1 and shows that in cell unit two EZa and EEa conformers of MCMA are present. MCMA crystallizes in the monoclinic space group $P2_1/c$. The cell parameters are

$a$ = 3.9797(5) Å, $b$ = 32.469(7) Å, $c$ = 11.0627(12) Å, $\alpha$ = 90.00, $\beta$ = 95.477(10), $\gamma$ = 90.00 with eight entities in cell. The refinement converged to $R_1$ = 0.0522 and $wR_2$ = 0.1258.

The $^{13}$C NMR spectra of MCMA in chloroform and DMSO solutions and in solid phase are shown at Fig. 2. Solutions spectra were measured immediately after dissolving (spectra a) and consequently after 2 weeks (spectra b). It is well known that in the case of push–pull substituted ethylene isomer an interconversion process can occur in a polar surroundings by the lowering of the barrier for internal rotation around the ethylenic C=C double bond due to polarization effect [25–30]. Therefore the NMR spectra in more polar acetonitrile were also measured. NMR spectra in all solvents measured immediately after dissolving at laboratory temperature according to the number of resonances point to the existence of only one molecular species despite the fact that in solid phase two conformers are present. This means that the sample exists in solutions as one conformer only, or if more conformers are present the laboratory temperature is above the coalescence temperatures. NMR spectrum even in very polar acetonitrile does not change even after several days indicating that there is no isomerization process in polar surroundings. However, in NMR spectra in even more polar DMSO the second entity has appeared after several days. It has been established in the previous conformational study of methoxymethylene-propanedinitrile $H_3C{-}O{-}CH{=}C(CN)_2$ [11] and methylaminomethylene-propanedinitrile $H_3C{-}NH{-}CH{=}C(CN)_2$ [12] that the vicinal coupling constant between olefinic hydrogen and cyano carbons $^3J$(C,H) are about 5 Hz and 10 Hz in *cis* and *trans* positions of both, respectively. Therefore the vicinal coupling constants between the olefinic hydrogen and cyano carbon have been measured for the isomer determination of studied MCMA and are depicted in Fig. 3. The measured values of 10.1 Hz confirm that MCMA exists even in very polar DMSO as E isomer and no isomeration process occurs. Therefore the second entity in DMSO can arise from the next E isomer conformer or due to some specific interaction of MCMA with DMSO.

IR and Raman spectra of MCMA in the double bonds stretching region 1800–1550 cm$^{-1}$ as a solid and solutions in chloroform and acetonitrile are depicted at Fig. 4. In this region we can expect two bands (C=O and C=C stretching) in IR and Raman spectra for MCMA. The splitting of bands in $^{13}$C NMR and Raman solid spectra of MCMA supports the X-ray analysis result about the presence of two EZa and EEa conformers in solid phase.

The behaviour of MCMA in solutions can be supported also by the solvent effect calculations. Fig. 5 represents the calculated energy difference (without ZPE) between the isomers and conformers of MCMA as a function of the surrounding relative permittivity for IEFPCM model in 6-311++G** basis set. As we can see, only the energy difference between EEa and EZa conformers (both conformers belong to the same E isomer) decreases in more polar surroundings in agreement with the calculated polarity of both conformers on the value that makes possible the presence of both conformers in solution at laboratory temperature. On the other side we can see that relative energies of Z-isomer conformers remain in more polar surroundings very high what makes the possible isomer interconversion process inconvenient. It is also interesting that relative

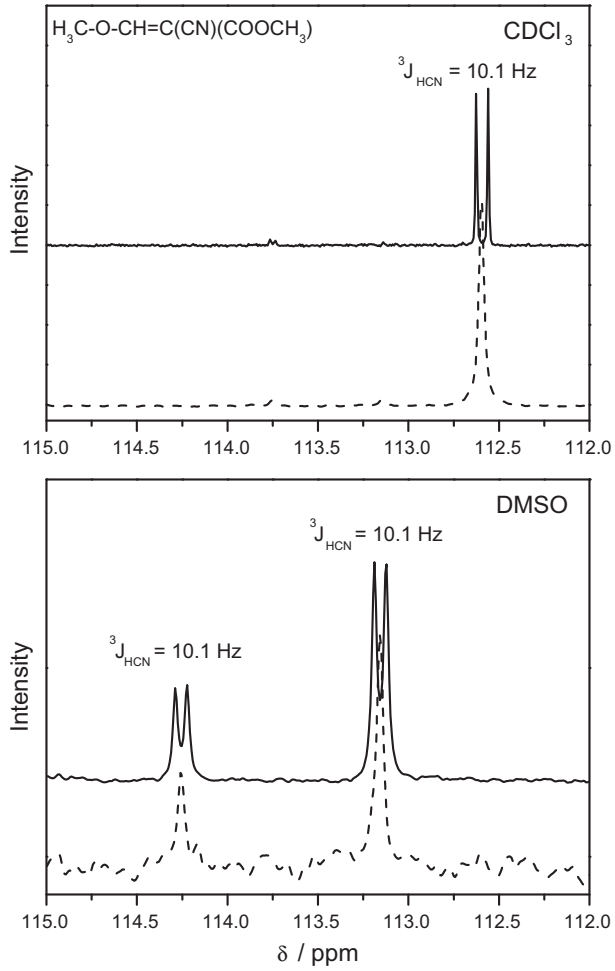


**Fig. 3.** Coupled (solid line) and decoupled (dashed line) $^{13}$C NMR spectra of MCMA in $CDCl_3$ (top) and in DMSO (bottom) at room temperature after 2 weeks.

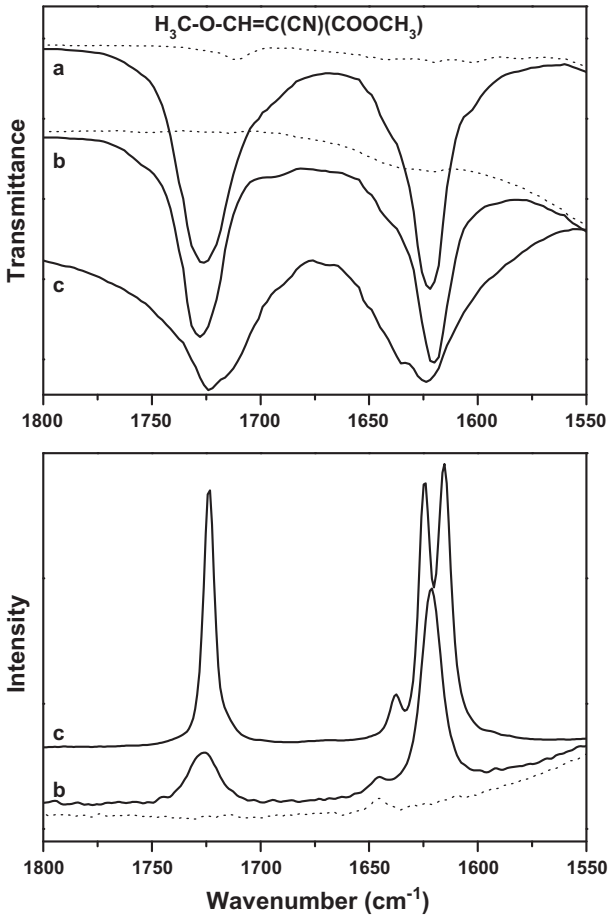


**Fig. 4.** IR (top) and Raman (bottom) spectra of MCMA at room temperature as a solution in chloroform (a) and acetonitrile (b) and as a solid (c). The dotted lines represent pure chloroform and acetonitrile.

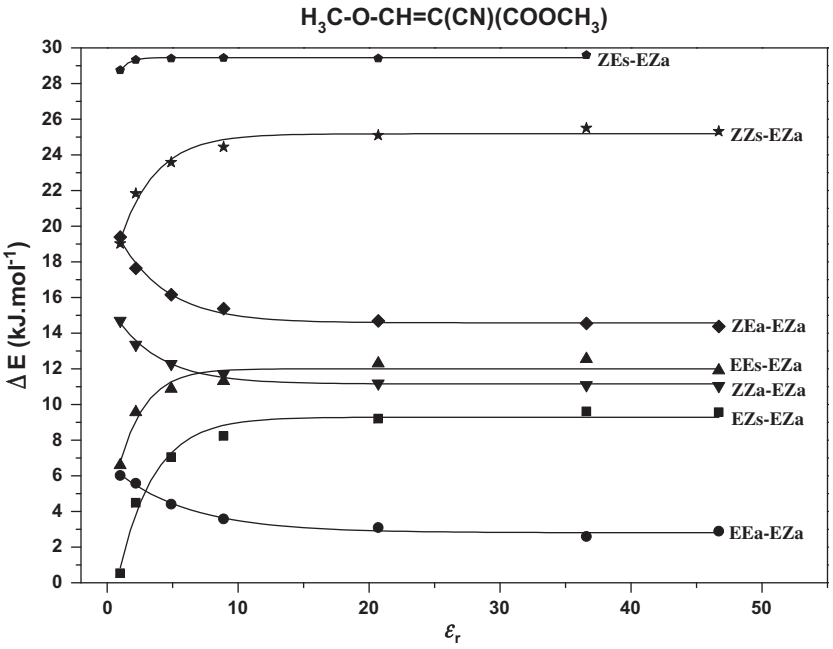


**Fig. 5.** Energy difference between isomers and conformers of MCMA as a function of relative permittivity of surroundings calculated by IEFPCM model at ab initio MP2 level with 6-311++G** basis set.

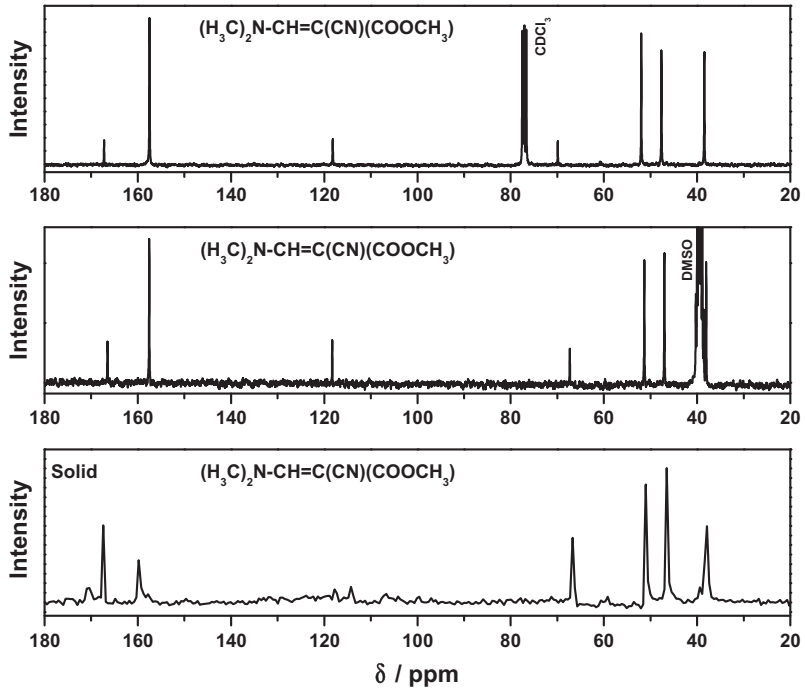


**Fig. 6.** $^{13}C$ NMR spectra of MCDMAA in $CDCl_3$ (top), in DMSO (middle) and in solid phase (bottom) at room temperature.

energy of all conformers with *syn* orientation of methoxy group increase in more polar environment.

### 3.1.2. Methyl-2-cyano-3-dimethylaminoacrylate

X-ray measurements of MCDMAA at laboratory temperature show that in unit cell there are present two entities both in EZ conformation. MCDMAA crystallizes in the triclinic space group P-1 with cell parameters $a = 7.1412(17)$ Å, $b = 7.8627(16)$ Å, $c = 8.2640(19)$ Å, $\alpha = 97.357(18)$, $\beta = 93.334(19)$, $\gamma = 115.91(2)$. The refinement converged to $R_1 = 0.0458$ and $wR_2 = 0.1355$.

The $^{13}C$ NMR spectra of MCDMAA in chloroform and DMSO solutions and in solid phase are shown at Fig. 6. These spectra indicate the presence of only one molecular entity. Its $^3J$(C,H) coupling constant of 10.4 Hz points out on E isomer. The spectra do not change even after several days thus excluding the isomerization process. On the other side IR and Raman spectra at Fig. 7 give arguments for the presence of two conformers in more polar solvents. According to the solvent effect calculations (Fig. 8), the presence of two conformers EZ and EE in polar environment is possible. It is in agreement with the calculated higher dipole moment of EE conformers and its decreasing energy in polar solvents.

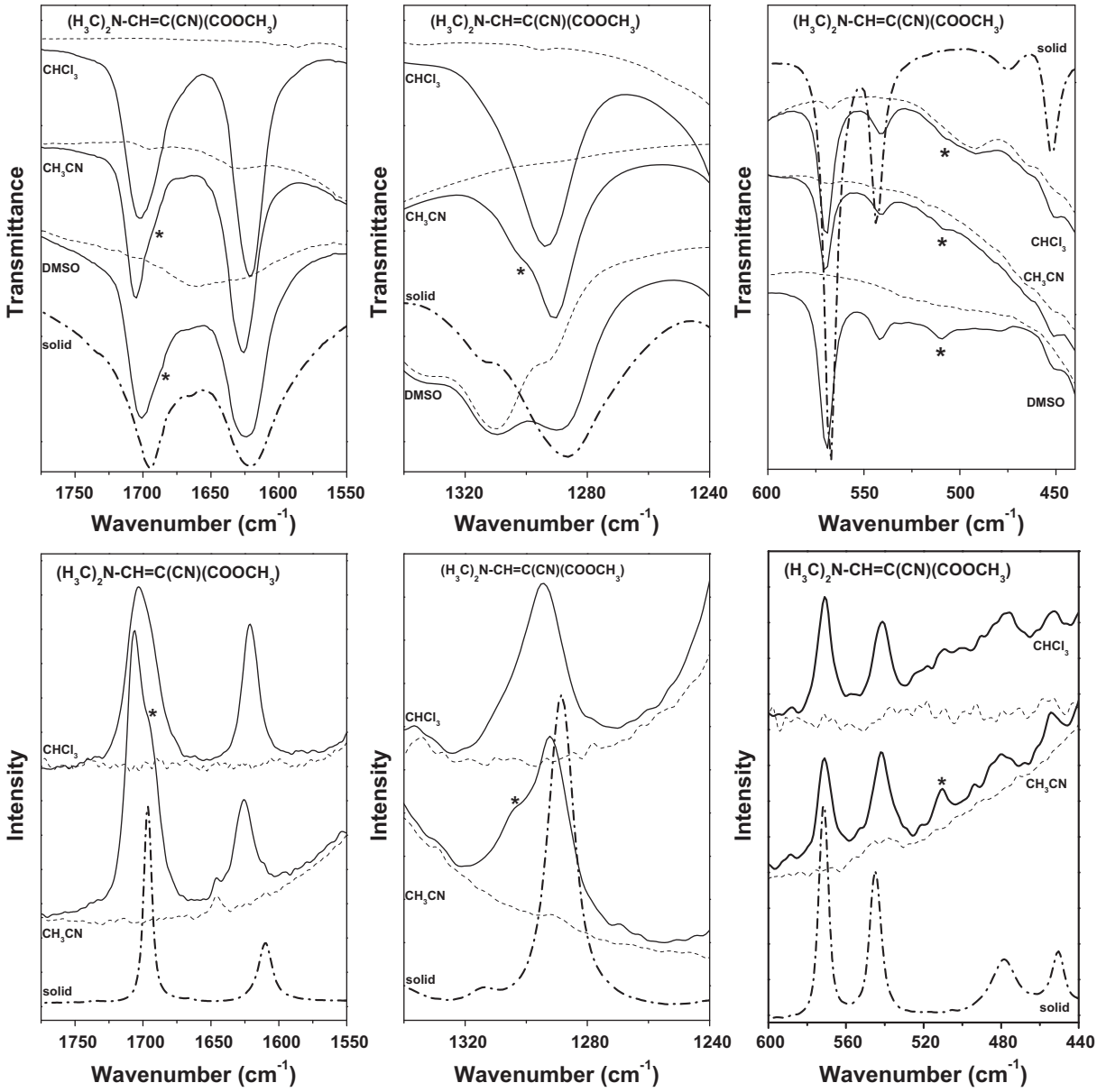


**Fig. 7.** IR (top) and Raman (bottom) spectra of MCDMAA solutions in chloroform, acetonitrile and DMSO (solid lines) and as a solid (dash-dot line). The dotted lines represent corresponding pure solvents.

### 3.2. Compounds with intramolecular hydrogen bonding

#### 3.2.1. Methyl-2-cyano-3-aminoacrylate

The DSC measurement has shown that MCAA was prepared as a mixture of two components and consequently this fact has been confirmed also by the NMR and vibrational spectroscopy. From the chromatography we were able to obtain the fraction with better than 97% of one component with the melting point of 126° C. NMR spectra of this fraction in less polar chloroform are at Fig. 9 (top) and confirm only small amount of the second component. The vicinal coupling constant between olefinic hydrogen and cyano carbons $^3J$(C,H) of 4.9 Hz confirms the presence of the dominant Z isomer in the chloroform solutions. This spectrum does not change even after several days thus excluding the isomerization process. The different situation is in more polar DMSO where NMR spectrum of the same fraction measured immediately after dissolution (Fig. 9 middle) is very similar to the NMR spectrum in chloroform, but in the spectrum measured after several days (3 weeks) the slight dominance of the second component is observed (Fig. 9 bottom). From its vicinal coupling constant between olefinic hydrogen and cyano carbons $^3J$(C,H) of 10.1 Hz is apparent that an isomerization process occurred and that the second component in the solutions is E isomer of MCAA.

X-ray measurement of the crystal from this fraction of MCAA was done at the temperature of 100 K [31] and indeed confirmed that MCAA crystallizes in the monoclinic space group $P2_1/n$ with four entities in the unit cell, all as ZZ conformer with the intramolecular hydrogen bond. This hydrogen bond stabilizes the Z isomer what is also in the agreement with the calculated energies for an isolated molecule in gas phase presented in Table 1.

According to the ab initio calculations, the energy differences between the most stable ZZ conformer and all other MCAA conformers are from 5 up to 15 kJ mol$^{-1}$ in nonpolar surrounding (Table 1). After including the solvent effect on their energy evaluation in polar surroundings the energy differences between them decrease (Fig. 10) and for the second most stable EZ conformer

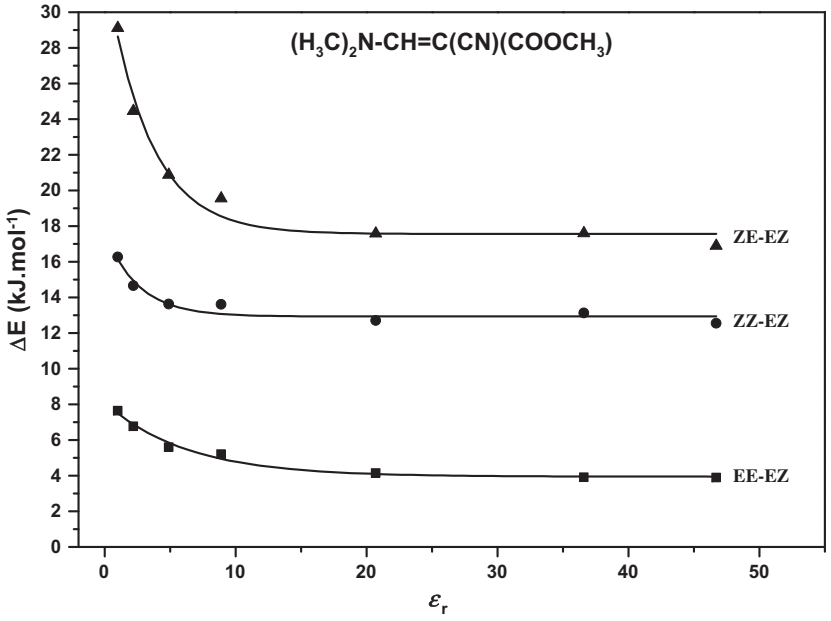


**Fig. 8.** Energy difference between isomers and conformers of MCDMAA as a function of relative permittivity of surroundings calculated by IEFPCM model at ab initio MP2 level with 6-311++G** basis set.

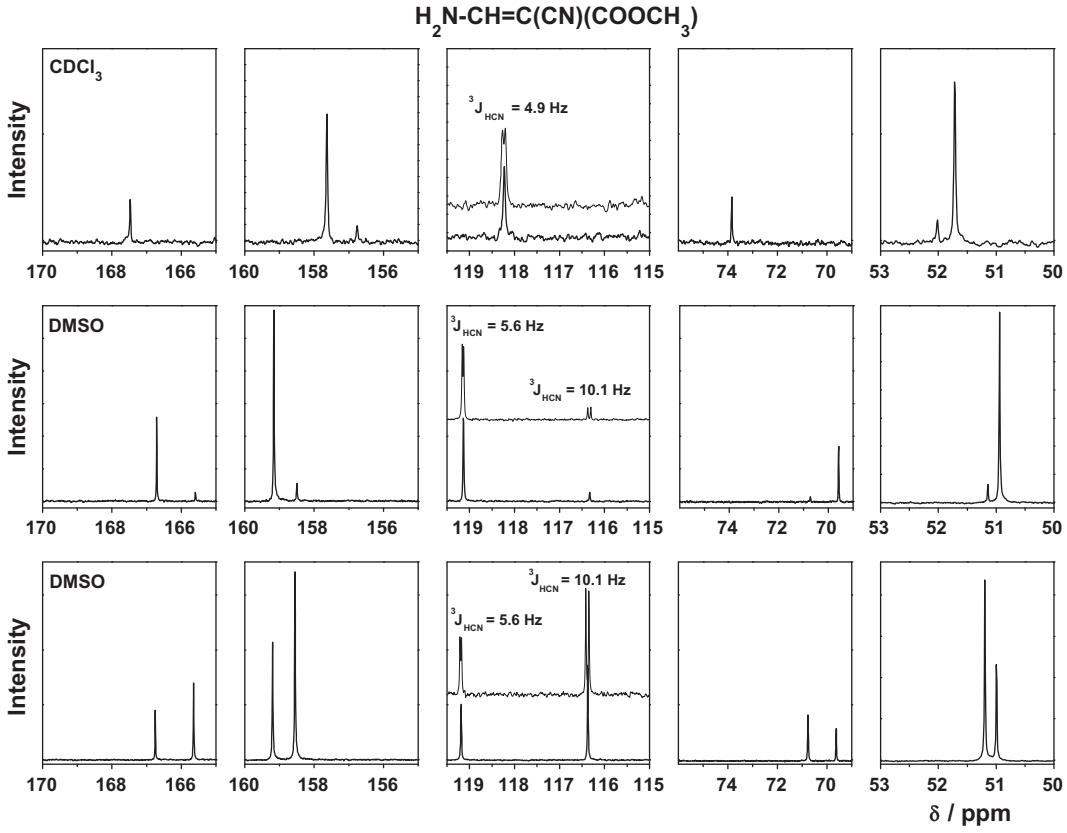


**Fig. 9.** $^{13}C$ NMR spectra of MCAA in $CDCl_3$ (top), in DMSO immediately after dissolving (middle) and in DMSO after 2 weeks (bottom) at room temperature (thick solid line). The thin solid lines represent corresponding coupled $^{13}C$ NMR spectra.

approach to the value of 2 kJ mol$^{-1}$. The low barrier and the small energy difference thus make the eventual isomer interconversion process in polar surroundings possible. The evidence of the presence EZ conformer in the IR spectrum of MCAA is possible to obtain from the comparison of the IR spectra of different chromatographic fractions of MCAA at Fig. 11, where are compared IR spectra in solid phase of chromatographic fraction with practically one ZZ conformer (curve a) and chromatographic fraction with higher amount of the second conformer (curve b).

### 3.2.2. Methyl-2-cyano-3-methylaminoacrylate

The DSC measurement of different chromatographic fractions has shown that MCMAA was also prepared as a mixture of two components. The melting point of the first melting component

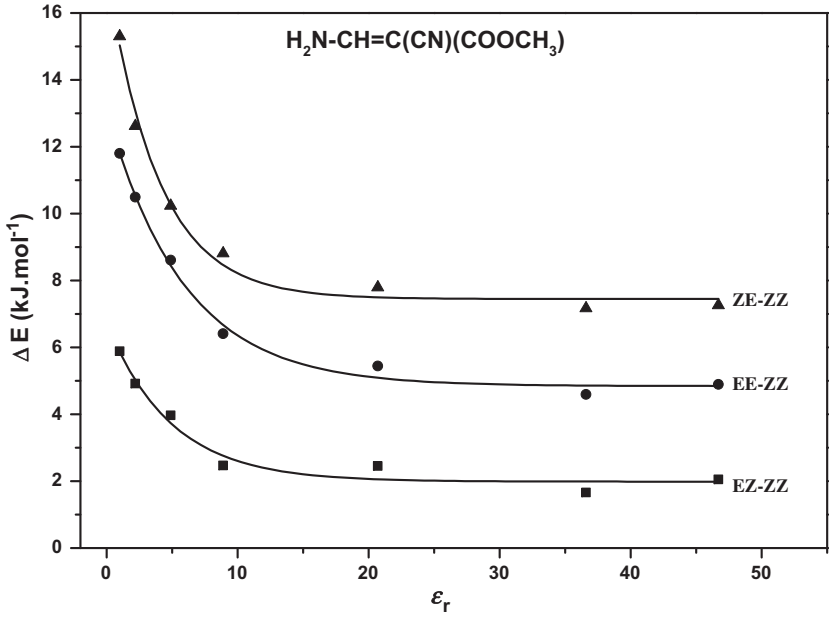


**Fig. 10.** Energy difference between isomers and conformers of MCAA as a function of relative permittivity of surroundings calculated by IEFPCM model at ab initio MP2 level with 6-311++G** basis set.

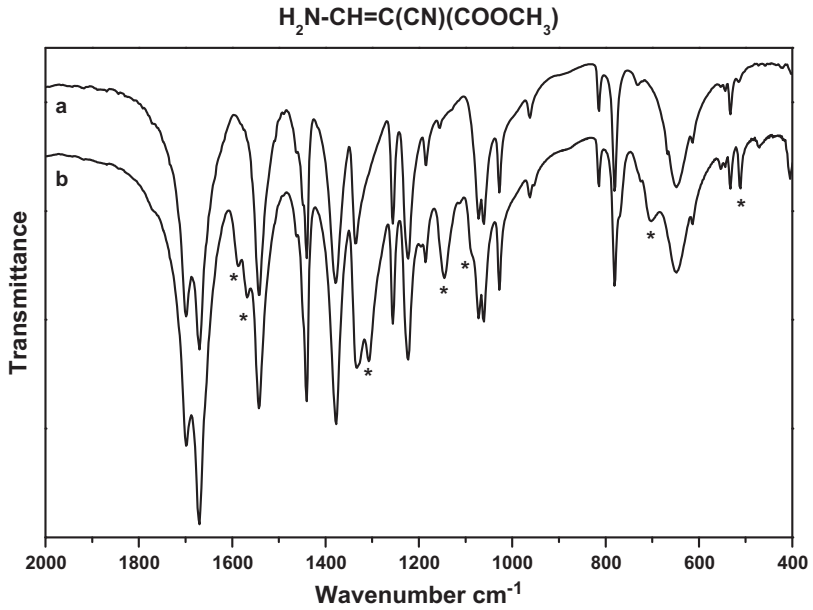


**Fig. 11.** Detail of IR spectra of different fractions of MCAA as a solid. Curve (a) denotes the fraction of MCAA with almost pure Z isomer and curve (b) denotes the fraction of MCAA with both isomers. Asterisks denote the bands which are not present in the fraction with almost pure Z isomer.

was at 105° C. As can be shown from the DSC record after the melting of the first component the isomerization occurs and consequently the second component was melting at 136° C. After the cooling and repeated annealing of the solid sample in DSC equipment the first melting component was practically not detected. It means that the first melting component is thermodynamically less stable and by annealing the chromatographic fractions on a temperature between both melting temperatures we were able to obtain almost the pure second melting component. This fact has been confirmed by the vibrational spectroscopy (Fig. 12) where are the IR and Raman spectra of the last chromatographic fraction with the higher contents of the first melting component before (curve a) and after annealing (curve b) on the temperature between both mentioned melting temperatures (20 min on 120° C). These spectra are compared with the IR and Raman spectra of the first chromatographic fraction (curve c) which contain practically only one second melting component. As we can see after the annealing of the last chromatographic fraction bands (marked with asterisk) disappeared and the spectra after annealing are very similar to the spectra of the first chromatographic fraction.

The mentioned facts from vibrational spectra are confirmed by the NMR spectra presented at Fig. 13. NMR spectrum of MCMAA in chloroform shows the presence of one dominant molecular species and small amount of the second component. The vicinal coupling constant between olefinic hydrogen and cyano carbons $^{3}J$(C,H) of the dominant component is 4.6 Hz what points out on Z isomer

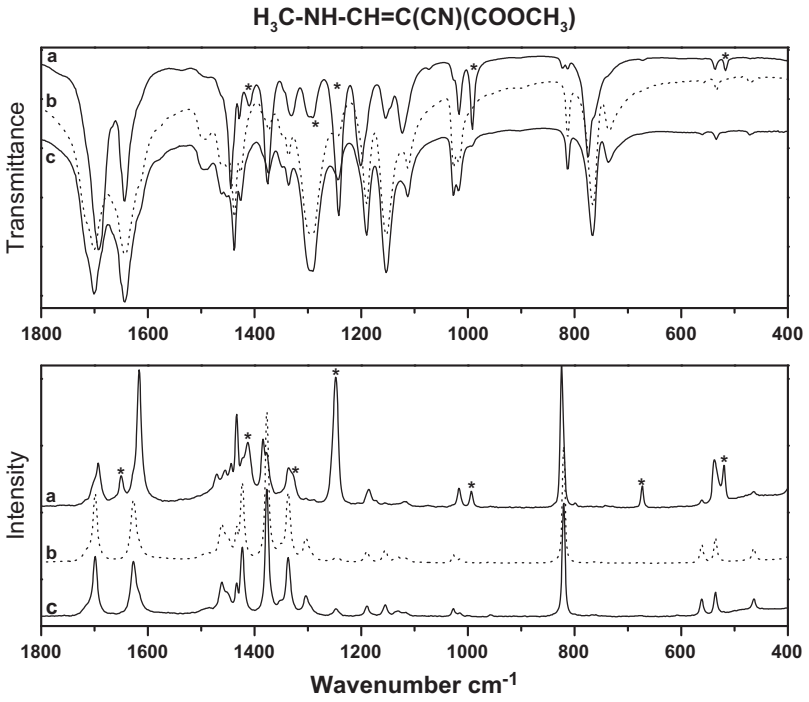


**Fig. 12.** IR (top) and Raman (bottom) spectra of MCMAA as a solid. Curve (a) denotes the fraction of MCMAA with both isomers, curve (b) the same fraction after 20 min annealing at 120° C and curve (c) the fraction of MCMAA with almost pure Z isomer. Asterisks denote the bands which are not present in the fraction with almost pure Z isomer and disappeared after annealing of the fraction with both isomers for 20 min at 120° C.

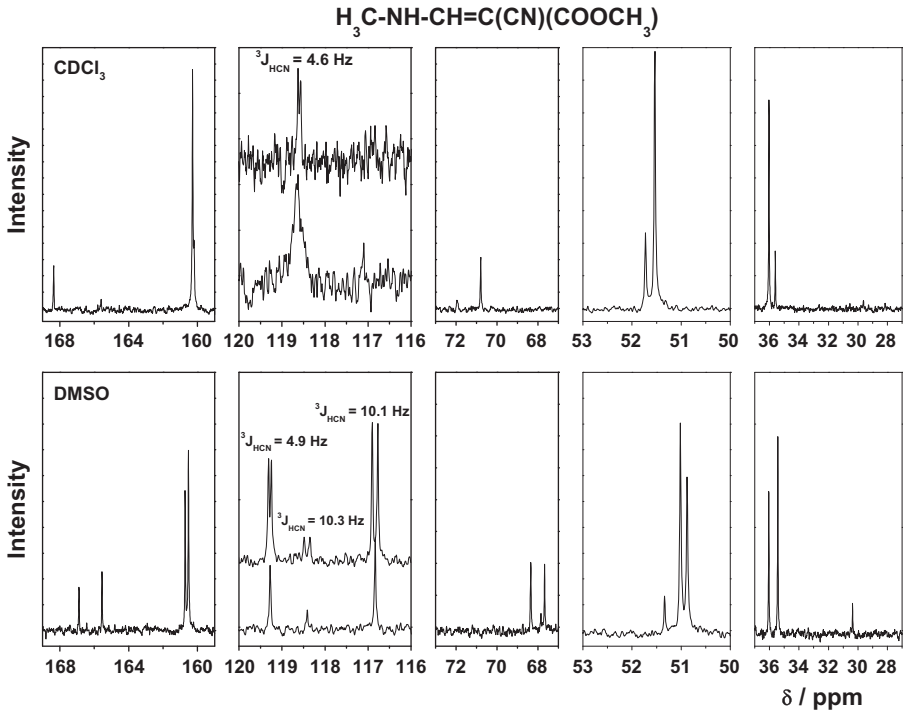


**Fig. 13.** $^{13}$C NMR spectra of the fraction of MCMAA with almost pure Z isomer in $CDCl_3$ (top) and in DMSO (bottom) at room temperature (thick solid line). The thin solid lines represent corresponding coupled $^{13}$C NMR spectra.

of MCMAA. However, the NMR spectrum of the same chromatographic fraction of MCMAA in DMSO has such amount of resonances for each carbon which hint the presence of three entities. The vicinal coupling constants between olefinic hydrogen and cyano carbons $^3J$(C,H) are 4.9 Hz for Z isomer and 10.1 and 10.3 Hz for two next two cyano carbon lines of MCMAA, respectively. It means that two entities of MCMAA in DMSO solution belong to E isomer and an isomerization process in more polar DMSO occurred. Such explanation is also in the agreement with the calculated ab initio energies (Table 1) where the energy of the ZZa conformer is markedly lower due to intramolecular hydrogen bond between amino hydrogen and carbonyl oxygen and also in the agreement with

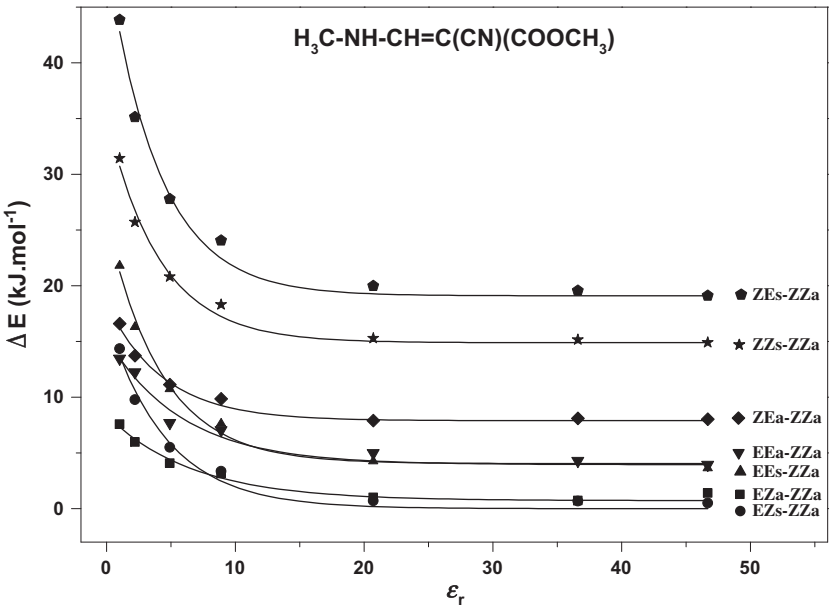


**Fig. 14.** Energy difference between isomers and conformers of MCMAA as a function of relative permittivity of surroundings calculated by IEFPCM model at ab initio MP2 level with 6-311++G** basis set.

the calculated energy difference between conformers in polar surroundings (Fig. 14). The energy difference between Z-isomer conformers ZEs–ZZa, ZZs–ZZa and ZEa–ZZa, respectively, decrease otherwise by 8–20 kJ mol$^{-1}$ but still remain high and over 10 kJ mol$^{-1}$. On the other side, the energy difference between all E isomer conformers and the most stable ZZa one (Fig. 14) decrease bellow 10 kJ mol$^{-1}$ and the energy of the E isomer conformers with Z orientation of the methylester group (EZa and EZs) in the polar surroundings approached to the energy of the ZZa conformer. Therefore their population could become noticeable at laboratory temperature if the isomer interconversion barrier is not very high and the isomer interconversion process can be under way. The presence of this conformers can be supported by the $^3J$(H,H) coupling constant between olefinic and amino hydrogens. The two most strong olefinic hydrogen resonances of MCMAA are doublets and the value of coupling constant of 15 Hz point out on the *anti* orientation of both hydrogens. Despite the third olefinic hydrogen resonance partly overlaps with one of the former ones, the half coupling constant of 7.5 Hz point out on *syn* orientation of both hydrogens.

## 4. Conclusions

Four push–pull compounds have been prepared. Two of them – MCMA and MCDMAA – without the possibility of intramolecular hydrogen bonding were prepared as pure E isomers and no isomerization process in polar surroundings have been observed. MCMA exists in solid phase as an equal mixture of EZa and EEa conformers but in less polar solutions only EZa conformer was detected. In DMSO solution after some time the second entity appeared which can arise from the next E isomer EEa conformer or due to some specific interaction of MCMA with DMSO.

MCDMAA exists in solid phase as EZ conformers. IR and Raman spectra and solvent effect calculation support the presence of the second more polar EE conformers in more polar solvents.

Next two compounds with the possibility of intramolecular hydrogen bonding – MCAA and MCMAA – were obtained in different isomer forms. For both the Z isomer with Z orientation of methylester group and with intramolecular hydrogen bond is the most stable one and from the chromatography we were able to obtain in the first fraction more than 97% of ZZ (for MCAA) or ZZa (for MCMAA) conformer. MCAA exists in solid phase as ZZ conformer and in more polar surrounding (DMSO) the isomerization of ZZ conformer to EZ conformer occurred. For MCMAA the interconversion of ZZa conformer to E isomer has been observed in more polar surrounding (DMSO) in higher extent than for MCAA and EZa and EZs conformers were detected by NMR spectroscopy. Ab initio solvent effect calculations are in agreement with these experimental findings. By the annealing of the solid mixture of Z and E isomers of MCMAA on a temperature between their melting temperatures the isomerization of E to Z isomer occurred.

## Acknowledgements

This work has been supported by Slovak Grant Agency (Projects VEGA Nos. 1/0127/08, 1/0817/08 and 1/0225/08). NMR experimental part of this work was facilitated by the support of Slovak National Research and Development Program No. 2003SP200280203.

## References

[1] V. Milata, Aldrichim. Acta 34 (2001) 20.
[2] S.F. Dyke, The Chemistry of Enamines, Cambridge University Press, London, 1973.
[3] A.G. Cook, (Ed.), Enamines: Synthesis, Structure and Reactions, second ed., Marcel Dekker, New York, 1988 (first ed., 1969).
[4] Z. Rappoport, The Chemistry of Enamines, Wiley, Chichester, 1994 (The Patai Series).
[5] R. Albrecht, Prog. Res. 21 (1977) 9.
[6] A.J. Fatiadi, in: LONZA New applications of Malononitrile in Organic Chemistry, Georg Thieme Verlag, Stuttgart, 1978; Synthesis (1978) 165.
[7] F. Freeman, in: LONZA Reaction of Malononitrile Derivatives; Georg Thieme Verlag, Stuttgart, 1981; Synthesis (1981) 925.
[8] D. Bouzard, in: Recent Progress in the Chemical Synthesis of Antibiotics, Springer-Verlag, Mnchen, 1990, p. 249.
[9] D. Chemla, J. Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals, vol. 1, Academic Press, New York, 1987. pp. 23–187.
[10] H.S. Nalwa, T. Watanabe, S. Miyata, Nonlinear Optics of Organic Molecules and Polymers, CRC Press, Boca Raton, 1997. pp. 87–329.
[11] A. Gatial, V. Milata, S. Biskupič, J. Pigošová, K. Herzog, R. Salzer, Asian Chem. Lett. 8 (2004) 169.
[12] A. Gatial, Š. Sklenák, V. Milata, P. Klaeboe, S. Biskupič, D. Scheller, J. Jurašková, Struct. Chem. 7 (1996) 17.

[13] M. Gróf, A. Gatial, V. Milata, N. Prónayová, L. Sümmchen, R. Salzer, J. Mol. Struct. 843 (2007) 1.
[14] M. Gróf, A. Gatial, P. Matějka, J. Kožíšek, V. Milata, N. Prónayová, J. Mol. Struct. 924 (2009) 54.
[15] J. Polovková, A. Gatial, V. Milata, P. Černuchová, N. Prónayová, T. Liptaj, P. Matějka, J. Mol. Struct. 785 (2006) 85.
[16] J. Polovková, A. Gatial, V. Milata, P. Černuchová, N. Prónayová, T. Liptaj, P. Matějka, J. Mol. Struct. 829 (2007) 8.
[17] C. Hametner, P. Černuchová, V. Milata, G. Vo-Thanh, A. Loupy, Magn. Reson. Chem. 43 (2005) 171.
[18] J. Kreutzmann, M. Michalik, B. Thomas, Zeit. Chem. (Stuttgart) 26 (1986) 404.
[19] Y. Shvo, H. Shanan-Atidi, J. Am. Chem. Soc. 91 (1969) 6689.
[20] L. Crombie, R.V. Dove, J. Chem. Soc. Perkin Trans. (1979) 686.
[21] J. Saloň, V. Milata, N. Prónayová, J. Leško, Monatsh. Chem. 131 (2000) 293.
[22] 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.
[23] C. Møller, M.S. Plesset, Phys. Rev. 46 (1934) 618.
[24] J.B. Foresman, T.A. Keith, K.B. Wiberg, J. Snoonian, M.J. Frisch, J. Phys. Chem. 100 (1996) 16098.
[25] J. Sandström, Top. Stereochem. 14 (1983) 83.
[26] R.R. Pappalardo, E.S. Marcos, M.F. Ruiz-Lopez, D. Rinaldi, J.-L. Rivail, J. Am. Chem. Soc. 115 (1993) 3722.
[27] T.J. Dwyer, P.G. Jasien, J. Mol. Struct. (Theochem) 363 (1996) 139.
[28] R. Benassi, C. Bertarini, E. Kleinpeter, F. Taddei, S. Thomas, J. Mol. Struct. (Theochem) 498 (2000) 201.
[29] I. Alkorta, C. Wentrup, J. Elguero, J. Mol. Struct. (Theochem) 585 (2002) 27.
[30] O. Červinka, Configuration, conformation and chiroptical properties of enamines, in: Z. Rappoport (Ed.), The Chemistry of Enamines, Wiley, Chichester, 1994, pp. 219–254 (Chapter 3, The Patai Series).
[31] M. Gróf, J. Kožíšek, V. Milata, A. Gatial, Acta Cryst. E63 (2007) 3338.