Accepted Manuscript

The conformational analysis of push-pull enaminones using Fourier transform IR and NMR spectroscopy, and quantum chemical calculations. V. α –Methyl –, Fluorine– β – *N*,*N* –Dimethylaminovinyl trifluoromethyl ketones

Sergey I. Vdovenko, Igor I. Gerus, Yuri I. Zhuk, Valery P. Kukhar, Gerd-Volker Röschenthaler

PII:	S1386-1425(14)00626-X
DOI:	http://dx.doi.org/10.1016/j.saa.2014.04.053
Reference:	SAA 12017
To appear in:	Spectrochimica Acta Part A: Molecular and Biomo- lecular Spectroscopy
Received Date:	24 December 2013
Revised Date:	7 March 2014
Accepted Date:	7 April 2014



Please cite this article as: S.I. Vdovenko, I.I. Gerus, Y.I. Zhuk, V.P. Kukhar, G-V. Röschenthaler, The conformational analysis of push-pull enaminones using Fourier transform IR and NMR spectroscopy, and quantum chemical calculations. V. α –Methyl–, Fluorine– β – *N*,*N* –Dimethylaminovinyl trifluoromethyl ketones, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2014), doi: http://dx.doi.org/10.1016/j.saa. 2014.04.053

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

The conformational analysis of push-pull enaminones using Fourier transform IR

and NMR spectroscopy, and quantum chemical calculations. V. α -Methyl-,

Fluorine– β –*N*,*N*–Dimethylaminovinyl trifluoromethyl ketones

Sergey I. Vdovenko,^{*a} Igor I. Gerus,^a Yuri I. Zhuk,^a Valery P. Kukhar,^a Gerd-Volker Röschenthaler^b

^a Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, ul. Murmanska 1, 02094, Kiev, Ukraine.

b Jacobs University Bremen gGmbH, School of Engineering and Science, Campus Ring 1, 28759 Bremen, Germany

ABSTRACT

IR Fourier spectra of two enaminoketones with general formula $F_3C-CO-CR=CH-N(CH_3)_2$, R = F (DMTFBN); $R = CH_3$, (DMTMBN) were studied in various pure solvents. For comparison results of earlier investigated enaminoketone R = H (DMTBN) was also presented. On the basis of NMR and IR spectra it was shown that enaminoketones DMTBN, DMTFBN and DMTMBN presented in solutions as equilibrium of two conformers, (*E-s-Z*) \longrightarrow (*E-s-E*) (for DMTFBN these conformers are denoted as (*Z-s-Z*) and (*Z-s-E*), respectively). DFT calculations were carried out to evaluate relative energy and dipole moment of each spatial form. It was shown that 'closed-ring' complex formation between (*E-s-Z*) and (*E-s-E*) conformers of DMTBN accounts for discrepancies between DFT calculations of conformer relative energies and experimentally evaluated enthalpies of (*E-s-Z*) \longrightarrow (*E-s-E*) equilibrium. In α -substituted DMTFBN and DMTMBN, where formation of 'closed-ring' complex was impossible we did not observe such discrepancies.

For both (*E-s-Z*) and (*E-s-E*) conformers of the DMTBN and DMTMBN the main influence on the \tilde{v} (C=O) vibrations has the solvent's hydrogen bond donor (HBD) acidity, whereas for the DMTFBN an influence of the solvent's polarity/polarizability dominated.

Keywords: NMR and IR-spectra; Conformational analysis; Enaminoketones; DFT calculations.

1. INTRODUCTION

Earlier [1-5] we investigated various enaminones with general formula R¹CO-CH=CH-NR²R³ and showed that all studied enaminoketones presented in solutions as an equilibrium of

two conformers, $(E-s-Z) \iff (E-s-E)$ where the ratio [(E-s-E)]/[(E-s-Z)] depended not only on R^1 , R^2 and R^3 substituents but also on solvent properties and total enaminone concentration. Particularly, we showed that the enaminone with $R^1 = H$ existed, mainly, as the (*E-s-E*) conformer (equilibrium constant at infinite dilution $K_{eq}(0) = 1.55$ [5]), whereas in the enaminoketone with $R^1 = CH_3$, the (*E-s-Z*) conformer prevailed and $K_{eq}(0)$ equaled 0.24 [6]. Further substitution of CH₃-group by CCl₃-group gave $K_{eq}(0) = 0.55$ [4], whereas in the enaminoketone with $R^1 = CF_3 K_{eq}(0) = 1.12$. Hence, the nature of R^1 substituent influenced not only on electron distribution in molecule, but also determined prevailing stereoisomeric form of the enaminoketone molecule. We also investigated the influence of the R^2 and R^3 substituents and showed [4] that the influence of these substituents on the conformer ratio is, mainly, due to steric interactions. From this point of view it was essential to investigate stereoisomeric composition of the enaminoketones with general formula F₃C-CO-CR=CH-N(CH₃)₂, where substituents were R = H, F and CH_3 . Thus, in this work we examined the stereoisomeric forms of the next three compounds: 4-(N,N-dimethylamino)-1,1,1-trifluorobut-3-en-2-one (CH₃)₂N-CH=CH(COCF₃) (DMTBN); 4-(N,N-dimethylamino)-1,1,1,3-tetrafluorobut-3-en-2-one F₃C-CO-CF=CH-N(CH₃)₂ (DMTFBN) and 4-(N,N-dimethylamino)-1,1,1-3-methylbut-3-en-2-one $F_3C-CO-C(CH_3)=CH-N(CH_3)_2$ (DMTMBN).

2. Experimental

2.1. General

Solvents (obtained from Aldrich) were purified using standard techniques and were dried over the appropriate drying agent before use. The enaminoketone DMTBN was obtained by the method described earlier [6]; enaminoketones DMTFBN and DMTMBN were synthesized, as was described in Experimental 2.2, distilled in vacuum, and stored under dry nitrogen at +4 °C.

2.2. Synthesis of studied enaminoketones DMTBN, DMTFBN, and DMTMBN.

¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a Bruker DRX-500 and Varian Unity Plus-400 instruments. Chemical shifts (δ) are given in ppm relative to TMS (using residual solvent signals at 7.27 ppm, ¹H; 77.16 ppm, ¹³C) or CFCl₃ (¹⁹F). Melting points were measured in the open capillary; the values are uncorrected. The enaminoketones DMTBN [2], DMTFBN, and DMTMBN have been obtained from the corresponding β -alkoxyvinyl ketones according to the Scheme 1. The starting compounds: (*E*)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one [1], and (*E*)-4-ethoxy-1,1,1-trifluoro-3-methylbut-3-en-2-one [7] were prepared as published previously by trifluoroacetylation of the corresponding alkyl vinyl ethers, and (*Z*)-1,1,1,3-tetrafluoro-4-

ethoxybut-3-en-2-one by the fluorination of α -unsubstituted (*E*)-4-ethoxy-1,1,1-trifluorobut-3en-2-one with xenon difluoride [8].

2.2.1. Typical procedure for the synthesis of enaminoketones DMTFBN, and DMTMBN.

Solution 0.454 g (4.0 mmol) of 40% Me₂NH in the water was added to a solution of 0.5 g (2.7 mmol) of corresponding alkoxyenone in 3 ml of acetonitrile under stirring at 0 °C and the mixture was stirred for 2 h at 20 °C. Then the solvents were evaporated in vacuum, the rest was extracted by DCM (2 x 10 mL), organic phase was dried with MgSO₄ and the solvent was evaporated in vacuum. The rest was distilled in vacuum.

2.2.2. 4-(*N*,*N*-Dimethylamino)-1,1,1,3-tetrafluorobut-3-en-2-one (DMTFBN)

The yield of enaminone DMTFBN was 0.42 g (85%) as yellow oil, b.p. 70-71 °C (1 mmHg). ¹H NMR (500.1 MHz, CDCl₃): δ = 3.22 (br. s, 6H), 6.88 (br. d, , *J* = 27.9 Hz, 0.47H), 7.11 (br. d, *J* = 26.9 Hz, 0.53H). ¹³C NMR (125.8 MHz, CDCl₃): δ = 38.8 (br. s), 39.2 (br. s), 46.6 (br. s), 47.2 (br. s), 117.1 (br. q, *J* = ~289.0 Hz), 136.0 (br. d, *J* = 228.9 Hz), 136.2 (br. d, *J* = 221.2 Hz), 136.5, 139.6, 168.0m, 169.7m. ¹⁹F NMR (376.3 MHz, CDCl₃): δ = -68.68 (br. d, *J* ~ 6 Hz, 1.44F), -75.13 (br. d, *J* = 17.5 Hz, 1.56F), -170.41 (br. dm, *J* ~ 27.5 Hz, 0.47F), -77.3 (br. dq, *J* ~ 27.0 and 18.0 Hz, 0.53F).

Anal. Calcd for C6H7F4NO: C, 38.93, H, 3.81, N, 7.57. Found: C, 46.63, H, 5.58, N, 7.61.

2.2.3. 4-(*N*,*N*-Dimethylamino)-1,1,1-trifluoro-3-methylbut-3-en-2-one (DMTMBN)

The yield of enaminone DMTMBN was 0.38 g (%) as yellow oil, b.p. 120 °C (12 mmHg). ¹H NMR (500.1 MHz, CDCl₃): δ = 2.04 (s, 3H), 3.20 (br. s, 6H), 7.34 (br. s, 1H). ¹³C NMR (125.8 MHz, CDCl₃): δ = 10.9, 43.8 (br. s), 100.1 (br. s), 118.4 (q, *J* = 292.5 Hz), 155.3, 178.1 (q, *J* = 30.5 Hz). ¹⁹F NMR (376.3 MHz, CDCl₃): δ = -66.4 (br. s).

Anal. Calcd for C7H10F3NO: C, 46.41, H, 5.56, N, 7.73. Found: C, 46.37, H, 5.62, N, 7.61.

2.3. Infrared spectra

Infrared spectra were recorded on a Bruker Vertex 70 FTIR spectrometer with KBr beamsplitter and RT-DLaTGS detector at ambient temperature $(20\pm1 \ ^{0}C)$. For all spectra 32 scans recorded at 2 cm⁻¹ resolution were averaged. Solution spectra were measured in carbon tetrachloride using standard NaCl cells with pathlengths 0.0103cm. Dilution measurements were carried out in carbon tetrachloride using standard NaCl cells with pathlengths 0.0022, 0.0063

0.01028, 0.0212, 0.0521, and 0.102 cm. Temperature measurements were carried out in thermostated (\pm 0.05 °C) NaCl cell with pathlength 0.01223 cm. The solutions were scanned at the same conditions as a background. The Bruker Opus software Version 6.0 was used for all data manipulation.

2.4. Quantum chemical calculations

Quantum chemical calculations of energies of formation for all possible conformers of the investigated enaminoketones DMTBN, DMTFBN, and DMTMBN were performed with a program HyperChem (Hypercube Inc., release 8.0.3) by DFT method, the hybrid B3LYP functional was combined with the 6-311G** basis set. The geometry of the conformers was optimized without fixing any parameter with the Polak-Ribiere algorithm in vacuum at RMS gradient 0.048 kJ mol⁻¹. Results are listed in Table 1.

3. Results

3.1. NMR spectra.

The ¹H, ¹⁹F, and ¹³C NMR spectra of studied enaminoketones are presented in Fig.S1 – S10. Both ¹H, ¹⁹F, and ¹³C NMR spectra reveal that DMTFBN exists as a mixture of two isomers (Z-s-E) and (Z-s-Z) with about equal ratio (53:47, correspondingly) in CDCl₃ solution at 293 °K (see Fig.S1-S5) and this ratio remains the same even in more polar solvent, DMSO-d₆. The Zconfiguration of the C=C double bond of DMTFBN is confirmed by the presence of two different signals of both olefinic substituents: hydrogen and fluorine atoms with nearly equal coupling constants ${}^{3}J_{\text{HF}}$ 26.9 and 27.9 Hz, which indicated a *trans*-orientation of the dimethylamino and CF₃CO groups – the common feature for push-pull acyclic enaminones. Doubled signals of both olefinic protons in ¹H NMR, and the olefinic fluorine atom and trifluoromethyl group in ¹⁹F NMR spectrum are a result of slow rotation of trifluoroacetyl group around the single C=C-C=Obond: two conformers (Z-s-E) and (Z-s-Z) of DMTFBN are detected by NMR spectrometry at room temperature. We suggest that the coupling constants between olefinic fluorine atom and trifluoromethyl group ${}^{4}J_{\text{FF}}$ 17.5 and ~6.0 Hz can be referred to (Z-s-E) and (Z-s-Z) conformers, correspondingly. It is worth to mention that in ¹H NMR spectra of DMTFBN Me₂N group demonstrates broadened signal in CDCl₃ and two overlapped signals in DMSO-d₆. Consequently, we observe slightly hindered rotation around C–N single bond, similar to that we have observed in NMR spectra of DMTMBN (Fig.S6) earlier. On the contrary, there are two

distinct separate signals of methyl groups in H¹ NMR spectra of DMTBN (see Fig.S9). Results of further NMR studies of DMTFBN and related compounds will be published elsewhere.

3.2. Attribution of the absorption bands in the region of the \tilde{v} (C=O) and \tilde{v} (C=C) vibrations.

In principle, push-pull β -dialkylamino vinyl trifluoromethyl carbonyl ketones are able to generate various spatial forms due to rotational isomerism around C=C double bond and =C-C single bond between vinyl and carbonyl group [1,9-14]. In general, eight stereoisomeric forms are to be anticipated for studied enaminoketones (Scheme 2). In view of symmetric substitution of dimethylamino group in studied compounds only four pairs of the \bar{v} (C=O) and \bar{v} (C=C) bands should be expected in IR-spectrum. However, in all studied cases the number of bands was less then four as a result of absence of some titled isomers or overlapping of some of their bands. It is worth to note that \bar{v} (C=O) and \bar{v} (C=C) vibrations of the enaminoketones are strongly coupled, possessing, in large measure, the character of out-of-phase and in-phase vibrational modes, respectively [15-17]. Nevertheless, as previously [4-6], we shall continue to use the \tilde{v} (C=O) and \tilde{v} (C=C) as a convenient form of shorthand.

In all IR-spectra of the DMTBN there were two pronounced \tilde{v} (C=O) bands at 1686 and 1672 cm⁻¹ (in CCl₄). Earlier [1,4,6] we ascribed \tilde{v} (C=O) band with higher wavenumber to the (E-s-Z), and that with lower wavenumber to the (E-s-E) conformer, respectively. The profile of the \tilde{v} (C=C) band for the DMTBN was characterized by a major very strong band at 1591 cm⁻¹ with a shoulder at 1622 cm⁻¹. In contrast to \tilde{v} (C=O) stretching vibrations \tilde{v} (C=C) is presented as single band in IR-spectrum. Previously [6] we revealed that this apparent single band is overall profile of two close highly overlapped bands: in the profile of this band for the deuterated derivative DMTBN-d₆ additional shoulder at 1562 cm⁻¹ appeared. We used 2Dshige version 1.3 [18,19] for calculation of 2D correlation spectra of DMTBN in region of \tilde{v} (C=C) stretching vibrations (see Fig.1) and simulated it in assumption that increase of total DMTBN concentration changes intensities of two close bands in opposite directions (see Fig. S11). It is well known that 2D IR spectrum consists of much sharper and better resolved peaks than the corresponding 1D spectrum [18]. The intensity changes, band shifts, and changes in band shapes are typical spectral variations observed under dilution and temperature changes for fluorinated enaminoketones [4-6, 20]. The effects of complex spectral feature variations, such as band shift and line intensity changing, are best visualized with simulated model data emphasizing the specific aspect of spectral changes. From Fig.1 it is clear that experimental and simulated spectra 2D spectra of DMTBN are very similar thus confirming our supposition. Minor discrepancies in shape of experimental and simulated 2D spectra we account for small band drift (~1cm⁻¹) to lower wavenumbers when concentration increased. Hence, we fitted this profile with three

Lorentz bands. Basing on concentration and temperature investigations we attributed the bands at 1588 and 1593 cm⁻¹ to the (*E-s-Z*) and (*E-s-E*) conformer, respectively [6].

In IR spectrum of DMTFBN we observed single broad band with relatively low intensity in the region of \tilde{v} (C=O) stretching vibrations and two very intensive bands in the region of \tilde{v} (C=C) stretching vibrations. In view of closeness of \tilde{v} (C=O) and \tilde{v} (C=C) bands we analyzed total profile of bands in region of double bond stretching vibrations. Similarly to DMTBN we assumed that \tilde{v} (C=O) profile consists of two bands intensity of which changed in opposite directions with increase of enaminoketone total concentration. As to \tilde{v} (C=C) bands, we observed such opposite changes in intensity with concentration variations. The same trend in band intensities we registered under temperature investigations. Using two pairs of \tilde{v} (C=O) and \tilde{v} (C=C) which intensity simultaneously changed (increasing for bands at 1704 and 1622 cm⁻¹ and decreasing for bands at 1694 and 1599 cm⁻¹) under dilution (Fig.S12), we simulated profile of DMTFBN spectrum at region of double bonds stretching vibrations. This simulation of DMTFBN 2D correlation spectra (Fig.S13) revealed that our representation of DMTFBN spectrum as a sum of two pairs of bands (namely, 1704 and 1622 cm⁻¹, 1694 and 1599 cm⁻¹) with inverse changes of intensities corresponds to the facts. Quantum chemical calculations (PM3 method) showed that pair of bands at 1704 and 1622 cm⁻¹ refers to (Z-s-E) conformer, whereas the pair at 1694 and 1599 cm^{-1} regards to (Z-s-Z) conformer.

In case of DMTMBN situation is more complicated: IR-spectrum of this enaminoketone in the region of double bond stretching vibrations has only one low-intensity broad band at 1672 cm⁻¹ and one very intensive band at 1605 cm⁻¹ with shoulder at lower frequency at 1564 cm⁻¹. To elucidate whether there is only one isomer, or respective \tilde{v} (C=O) and \tilde{v} (C=C) bands are profiles of strongly overlapped bands of two or more isomers, we calculated 2D correlation spectra of DMTMBN in the region of \tilde{v} (C=O) (Fig.S14) and \tilde{v} (C=C) vibrations (Fig.S15). Fig.S14 shows results of simulation studies of the case, where position shift of two bands is coupled with simultaneous intensity decrease of the band at 1692 cm⁻¹ and intensity increase of the band at 1660 cm^1 (similarly to those depicted in Fig.S16a). The same simulation was made for \tilde{v} (C=C) vibrations (using bands like those in Fig.S16b). It is apparent from the Fig.S14 and S15 that both \tilde{v} (C=O) and \tilde{v} (C=C) band consists of two overlapped bands which position and intensity varies during dilution, therefore we fitted the profile of \tilde{v} (C=O) and \tilde{v} (C=C) vibrations with two Lorentz bands. In contrast to bands at 1672, 1660, and 1605 cm⁻¹ the band at 1564 cm⁻¹ did not change in intensity under temperature or concentration variation, therefore, similarly to the DMTBN, we ascribed this band to the $\left[\tilde{v}\left(C-N\right)+\tilde{v}\left(C=C\right)\right]$ vibration which is shifted to lover wavenumbers in view of mass increase of CH=C(CH₃) moiety. Temperature rise resulted in intensity increase of the pair of bands at 1660 and 1605 cm⁻¹ with simultaneous

intensity decrease of the pair of bands at 1672 and 1598 cm⁻¹ The opposite trend was observed when passing from non polar carbon tetrachloride to polar acetonitrile: intensities of the bands at 1672 and 1598 cm⁻¹ increased, whereas intensities of the bands at 1660 and 1605 cm⁻¹ decreased [20]. Earlier, basing on concentration and temperature investigations, we attributed the bands at 1672 and 1598 cm⁻¹ to the \tilde{v} (C=O) and \tilde{v} (C=C) vibrations of the (*E-s-Z*) and the bands at 1660 and 1605 cm⁻¹ to the \tilde{v} (C=O) and \tilde{v} (C=C) vibrations of the (*E-s-E*) conformer, respectively [20]. It is worth to note that according to NMR data and results of quantum chemical calculations there is possibility for existence of a (*Z*) conformer, namely, the (*Z-s-Z*), to which we attributed the bands with very low intensity at 1698 cm⁻¹ and 1628 cm⁻¹ [20].

3.3. Results of DFT calculations

As it can be clearly seen from Table 1 the energy of the (E-s-E) conformer to be higher than the energy of the (E-s-Z) conformer for DMBN, DMTBN and DMTFBN (for the last enaminoketone hereinafter the (E-s-E) and (E-s-Z) conformers are denoted as (Z-s-E) and (Z-s-Z), respectively, *see* Scheme 2 and footnote (d) in Table 1), whereas energies of the (E-s-Z) and (E-s-E) conformer of DMTMBN are practically the same, although energy of the (E-s-E) conformer is somewhat higher. Energy of the (E-s-Z) conformer of enaminoketones DMBN, DMTBN and (Z-s-Z) conformer of DMTFBN is approximatly 13 kJ/mol lower than energy of the (E-s-E) conformers are much lower than RE of the (Z-s-E) and (Z-s-Z) isomer. The (E-s-Z) and (E-s-E) conformers of studied enaminoketones are practically planar, whereas the (Z-s-Z) and (Z-s-E) conformers are considerably distorted, especially the conformers of DMTMBN. Particularly the (Z-s-E) isomer of DMTMBN is significantly distorted (dihedral angle C=C-C=O is 139.3°).

According to experimental data for the enaminoketones DMBN, DMTBN and DMTFBN (as it was mentioned for the last enaminoketone denomination conformers is (Z-s-E) and (Z-s-E), respectively) the (E-s-E) conformer is more stable in comparison with the (E-s-Z) conformer (*see* enthalpies of *Trans-s-cis* \longrightarrow *Trans-s-trans* equilibrium in Table 1). In previous work [21] we showed that this discrepancy between results of spectroscopic measurements and quantum chemical calculations is a consequence of hydrogen bond formation between (E-s-Z) and (E-s-E) conformer (*see* Scheme 3). More detailed discussion of this problem is done in Discussion part of this work.

3.4. Solvent influence on IR spectra of the enaminoketones.

Solvent effects on the \tilde{v} (C=O) and \tilde{v} (C=C) bands were investigated in various solvents and we correlated obtained wavenumbers with solvatochromic parameters of Kamlet, Abboud and Taft [22] in accord with Eq. (1):

$$\tilde{\mathbf{v}} = \tilde{\mathbf{v}}_0 + (s\pi^* + d\delta) + a\alpha + b\beta + h\,\delta_{\mathrm{H}}^2 \tag{1}$$

where \tilde{v} is the vibration wavenumber of solute [such as \tilde{v} (C=O) and \tilde{v} (C=C) vibration] in pure solvent and \tilde{v}_0 is the regression value of the \tilde{v} (C=O) and \tilde{v} (C=C) vibration in cyclohexane as a reference solvent, π^* is an index of solvent's dipolarity/polarizability, δ is a discontinuous polarizability correction term for poly-chlorine substituted aliphatic and aromatic solvents, α is a measure of the solvent's hydrogen bond donor acidity, β is a measure of the solvent hydrogen bond acceptor basicity, and δ_H is the Hildebrand's solubility parameter. In Table 2 we presented the results of KAT correlations (Eqs.2-13) for all investigated enaminoketones.

3.5. Temperature investigations.

After band fitting the integrated intensity of each \tilde{v} (C=O) and \tilde{v} (C=C) band was calculated according to Eq. (14).

$$A = (c_s \times d)^{-1} \times \int_{band} \log(I_o/I) dv$$
(14)

where A (1 mol⁻¹ cm⁻²) is integrated intensity of the v(C=O) or v(C=C) band, c_s (mol/l) is the concentration of the given conformer in solution, d (cm) stands for the cell pathlength. The main problem was to evaluate the concentration of each stereoisomeric form c_s . Since all enaminoketones studied were presented as conformer equilibrium (*E-s-Z*) \rightleftharpoons (*E-s-E*) which depended on total concentration of enaminoketone and temperature, we used the method proposed earlier [6] for analysis of conformational equilibria assuming that the absorption coefficients of corresponding bands were temperature independent. We plotted integrals of \bar{v} (C=O) (*E-s-Z*) vs. integrals of appropriate \bar{v} (C=O) (*E-s-E*) at various total concentrations of the enaminoketone, c_{total} , provided the product $c_{total} \times$ pathlength was constant. Intercepts of this plot with axes were integrals of \bar{v} (C=O) bands of the (*E-s-Z*) and (*E-s-E*) conformer, respectively, but for all that the concentration of the conformer equaled the total concentration of enaminoketone, c_{total} . Knowing the cell pathlength and c_{total} , it was easy to calculate integrated intensities of the \tilde{v} (C=O) band of each conformer, and, hence, to evaluate from Eq. (14) the concentration of each stereoisomeric form, c_s , at given temperature. From temperature dependence of $\ln K_{eq} = f(1/T)$, where K_{eq} is an equilibrium constant, we calculated

thermodynamic parameters of the equilibrium $(E-s-Z) \iff (E-s-E)$. The results are listed in Table 1.

3.6. Evaluation of enaminoketone hydrogen-bond basicity.

Taft and co-workers [23] defined hydrogen-bond basicity pK_{HB} as log K_f for the 1:1 complexation of bases with 4-fluorophenol (4FP) in carbon tetrachloride at 298 K, [Eqs. (15)-(17)].

$$B + 4-FC_{6}H_{4}OH - 4-FC_{6}H_{4}OH - (15)$$

$$K_{f} = [Hydrogen-bond complex]/[B][4-FC_{6}H_{4}OH] - (16)$$

$$pK_{HB} = -\log_{10} (dissociation constant of the complex) = \log_{10} K_{f} - (17)$$

General equilibrium constant $K_{\rm f}^{\rm av}$ is defined by Eq. (18)

$$K_{\rm f}^{\rm av} = C_{\rm c}/C_{\rm a}C_{\rm b} = (C_{\rm a}^{\rm o} - C_{\rm a})/[C_{\rm a}(C_{\rm b}^{\rm o} - C_{\rm a}^{\rm o} + C_{\rm a})]$$
(18)

where C_c , C_b , C_a are the equilibrium concentrations of complex, base (enaminoketone) and acid (4FP), respectively, and C_a° and C_b° are initial concentrations determined by weight. C_a is obtained from the IR absorbance of the free OH band of (4FP) at 3614 cm⁻¹ (ϵ = 235 dm³ mol⁻¹ cm⁻¹ [24]). The equilibrium constants are taken as the mean of 9-10 values corresponding to 9-10 base concentrations. These concentrations are chosen such that the complex percentage is kept in the range 20–80% of the initial acid concentration. All measurements are carried out at the (4FP) concentration 7.4 × 10⁻³ mol dm⁻³ in order to avoid self-association. K_f is estimated to be accurate to within 5-10% and consequently pK_{HB} values are given to within ±0.02÷0.05 pK units. K_f evaluated thereby is average equilibrium constant which reflects general enaminoketone basicity without sharing it between the (*E-s-Z*) and (*E-s-E*) stereoisomeric forms. Method of estimation of equilibrium constants and enthalpies of hydrogen bond formation of individual stereoisomeric forms is described in [25]. Results are listed in Table 3.

4. Discussion

4.1. Conformer stability according to DFT calculations and experimental data.

From Table 1 it is obvious that calculated relative energies (RE) of individual conformers and enthalpies of equilibrium of these conformers are in good agreement with exception of DMTBN, where according to DFT calculation (*E-s-Z*) conformer is more stable than (*E-s-E*) one, whereas enthalpy of (*E-s-Z*) \longrightarrow (*E-s-E*) equilibrium testify to the effect that (*E-s-E*) conformer is more stable. As it is follows from Fig.2 the dipole moment of the DMTBN decreases with concentration increase although dielectric constant ε_r increases with increase of

total enaminone concentration. We interpreted this fact as evidence of H-complex formation between molecules of the enaminoketone. Moreover, as we have shown in [4] the dependence of band intensities on total DMTBN concentration was observed not only for v(C=O) and v(C=C) but also for v(C-H) and v(C-F) stretching vibrations. Analyzing all these phenomena we reached a conclusion that the (*E-s-Z*) and (*E-s-E*) conformers of DMTBN form 'closed-ring' hydrogen bonded complex as it is shown on Scheme 3. We revealed that complex formation occurs in two stages: at first, H-bond C_{α} – H···O=C arises with K = 214.4 M⁻¹ and Δ H = 27.48 kJ M⁻¹, and after that H-bond C_{α} – H···F–CF₂ is formed with K = 16.4 M⁻¹ and Δ H = 6.71 kJ M⁻¹. We assume that just this complexation accounts for discrepancy between enthalpies (Δ H) evaluated experimentally for conformer equilibrium (*E-s-Z*) — (*E-s-E*) and calculated relative energies (RE) of these conformers. Similar discrepancies were observed for many other β-alkylamino vinyl perfluoroalkyl ketones [4]. On the other hand, we did not observe such discrepancies for non-fluorinated DMBN and α -substituted enaminoketones DMTFBN and DMTMBN (*see* Table 1) where formation of 'closed-ring' hydrogen bonded complex is impossible.

4.2. Influence of α -substitution on hydrogen-bond basicity of enaminoketones.

 α -Substitution changes sharply of electron density distribution in enaminoketone conjugated system. This effect can be illustrated by comparison of hydrogen-bond basicity of DMBN, DMTBN and its α -F and α -CH₃ substituted derivatives (Table 3). It easy to notice that fluorination of methyl group in DMTBN diminishes drastically hydrogen-bond basicity and enthalpies of hydrogen bond formation ($-\Delta$ H) of both conformers due to electron withdrawal ability of CF₃ group [25]. Introduction of fluorine atom as α -substituent in DMFTBN lowers carbonyl hydrogen-bond basicity due to enhancement of electron withdrawal from carbonyl oxygen. At the same time introduction of electron donating CH₃ group into α -position strongly increases carbonyl hydrogen-bond basicity and negative value of enthalpy of complexation ($-\Delta$ H) becomes even higher than the one for non-fluorinated DMBN.

4.3. Solvent influence on IR spectra of studied enaminoketones.

Influence of α -substitution on distribution of electron density in conjugated enaminoketone system is more pronounced when spectra are compared in various solvents. Generally speaking solvent influence on IR spectra depends on distribution of electron density in solute molecule. The model equation of the linear solvation energy relationship (LSER) applied in infrared spectroscopy is shown as Eq. (1). Besides the dielectric effects, reflected by solvent polarity/polarizability term (π *) of Eq. (1), solvent molecules interact directly with the C=O and

C=C group by two kinds of attractive forces. The first of these forces is that the solvent molecule forms a hydrogen bond with oxygen of the carbonyl group (or with its π -system). The capability of solvent to donate proton in solvent-to-solute (enaminoketone) hydrogen bond is described by parameter α , solvent HBD acidity. The second is that the solvent molecule which has electronegative atoms O, N or other can form hydrogen bonds with a solute as proton donor. Parameter β describes the ability of a solvent to accept proton in solute-to-solvent hydrogen bond, i.e. its hydrogen bond acceptor capability with respect to a reference hydrogen bond donor. We correlated the wavenumbers of the \tilde{v} (C=O) and \tilde{v} (C=C) bands with solvatochromic parameters of various solvents according to Eq. (1) and presented the results in Table 2 as regression coefficients of parameters π^* , δ , α , β , and δ_{H^2} denoting each set of obtained coefficients as appropriate Eqs. (2) - (13) for stereoisomeric forms of studied enaminoketones. Only terms at the 0.95 significance level or higher were retained. The quality of multiple linear regressions is indicated by the standard error of the estimate (S.D., the smaller the better), the Fisher index of reliability (F, the larger the better), and the correlation coefficient (R, variance = R^2 , the closer to 1 the better) [22]. A correlation equation was considered as acceptable if the product correlation coefficient, R, indicates that the equation accounts for more than 80% of the variance $(R^2 \ge 0.80)$. From Eqs. (2) – (13) it followed that even conformers of the same studied enaminoketone differed notably in sensitivity to solvent influence, therefore it was reasonable to examine these multiple correlations for studied enaminoketones separately and then to compare the results obtained. Analysis of Table 2 revealed some general features: equations for all studied enaminoketones were statistically significant ($R^2 \ge 0.80$) with exception of the Eq. (3) where R^2 were much less then 0.8 (0.761), therefore we excluded this equation from consideration. Another similarity was that almost in all equations coefficients d of parameter δ (a discontinuous polarizability correction term) were insignificant, i.e. less then standard error of estimate (S.D.). Negligible contribution of the discontinuous polarizability correction term δ in Eq. 1 we noted earlier for multiple correlations of the \tilde{v} (C=O) and \tilde{v} (C=C) bands of DMBN [6].

4.1.1. Enaminoketone DMTBN

The detailed analysis of solvent influence on IR spectra of the DMTBN was done in our previous works [6,20]. Here we adduce general conclusions according to which main contribution to the \tilde{v} (C=O) and \tilde{v} (C=C) vibrations of both (*E-s-Z*) and (*E-s-E*) conformers made the solvent's hydrogen bond donor (HBD) acidity term (α) whereas solvent's polarity/polarizability (π *) influenced in much less extent [*see* Table 2, Eqs (2)-(5)]. Consequently, hydrogen bond formation determines the \tilde{v} (C=O) and \tilde{v} (C=C) bond shifts to lower wavenumbers. In case of (*E-s-E*) conformer contribution of the solvent's

polarity/polarizability term (π *) to the \tilde{v} (C=O) mode is greater than in the (*E-s-Z*) conformer due to the greater polarity/polarizability of carbonyl group in the (*E-s-E*) conformer. In so far as vibrational coupling takes place, therefore, the out-of-phase component will go to increase the wavenumber and decrease the intensity of the upper [\tilde{v} (C=O)] vibration, whereas the in-phase component will have the reverse effect on the \tilde{v} (C=C) [11].

4.1.2. Enaminoketone DMTFBN

In contrast to DMTBN the main influence on the \tilde{v} (C=O) and \tilde{v} (C=C) vibrations of both (*Z*-*s*-*Z*) and (*Z*-*s*-*E*) conformers has solvent's polarity/polarizability (π *) term [Eqs (6)-(9)]. Hence, shift of the \tilde{v} (C=O) and \tilde{v} (C=C) bands to lower wavenumbers is principally defined by dispersion interactions of this enaminoketone with solvent molecules. This fact confirms conclusion of lowered hydrogen-bond basicity of carbonyl oxygen in DMTFBN in comparison with DMTBN. Some exception has Eq.(7) where coefficients *s* and *a* are almost equal, that is influence of the solvent's polarity/polarizability (π *) and solvent's hydrogen bond donor (HBD) acidity term (α) on \tilde{v} (C=C) vibrations enhance each other. It is worth to note that influence of the solvent's polarity/polarizability (π *) term on \tilde{v} (C=O) band of the (*Z*-*s*-*Z*) conformer [Eq.(6)] is much higher than this influence on \tilde{v} (C=C) band [Eq.(7)], whereas for the (*Z*-*s*-*E*) conformer these values are almost the same [*cf*. coefficient *s* in Eq.(8) and (9)]. From this comparison it is follows that distribution of electron density in the (*Z*-*s*-*Z*) conformer is different than in the (*Z*-*s*-*E*) conformer.

4.1.3. Enaminoketone DMTMBN.

Solvent influence on the \tilde{v} (C=O) and \tilde{v} (C=C) vibrations of the (*E-s-Z*) and (*E-s-E*) conformers of the DMTMBN is very similar to that on corresponding conformers of the DMTBN. It is easy to notice from Table 2 [Eqs (10) and (12)] that the main influence on the \tilde{v} (C=O) vibrations of both conformers has the solvent's hydrogen bond donor (HBD) acidity term (α). The same is true for the \tilde{v} (C=C) vibrations of the (*E-s-Z*) conformer, whereas for the (*E-s-E*) coefficient *a* is twice as large as coefficient *s*, that is the solvent influence on the \tilde{v} (C=C) vibrations of the (*E-s-Z*) conformer is realized predominantly through solvent's polarity/polarizability. It is worth to note that in both the (*E-s-Z*) and (*E-s-Z*) conformer the solvent's hydrogen bond acceptor (HBA) basicity term (β) makes significant contribution

increasing the \tilde{v} (C=C) wavenumbers as a result of disturbance of the \tilde{v} (C=O) and \tilde{v} (C=C) vibration coupling.

Comparing the enaminoketones DMTBN and DMTMBN it is obvious that in both cases the solvent influence on the \tilde{v} (C=O) and \tilde{v} (C=C) vibrations is very similar and little discrepancies are caused by the fact that both conformers of the enaminoketone DMTPN are nonplanar (*see* Table 1).

5. Conclusions

1. All studied enaminoketones are TRANS isomers relatively to C=C double bond independently to α -substituent and solvent polarity and form *s*-*cis* and *s*-*trans* conformers relatively to C-C formally single bond.

2. *s-Cis* and *s—trans* conformers of DMTBN form 'closed-ring' hydrogen-bonded complex in two stages.

3. 'Closed-ring' complex formation of DMTBN is a root of discrepancies between results of DFT calculations of conformer stability and experimentally evaluated enthalpies of conformer equilibrium.

4. α -Substitution strongly influences on enaminoketone hydrogen-bond basicity. Electron withdrawing α -substitutuents lower hydrogen-bond basicity whereas electron-donating α -substitutuents increase it significantly.

5. Solvent influence on IR-spectra of studied enaminoketones strongly depends on electronic properties of α -substituent.

13

REFERENCES

- [1] S.I. Vdovenko, I.I. Gerus, M.G. Gorbunova, J. Chem. Soc., Perkin Trans.2 (1993) 559.
- [2] J. Wójcik, W. Domalewski, K. Kamieńska-Trela, L .Stefaniak, S.I. Vdovienko, I.I. Gerus, M.G. Gorbunova, Magn Reson. Chem. 31 (1993) 808.
- [3] I.I. Gerus, L.M.Kacharova, S.I. Vdovenko, Synthesis (2001) 431.
- [4]. S. I. Vdovenko, I. I. Gerus, O.V. Balabon, V.P. Kukhar, Trends in organic chemistry 16 (2012) 93.
- [5]. S.I. Vdovenko, I.I. Gerus, E.A. Fedorenko, Spectrochim. Acta Part A 74 (2009) 1010.
- [6]. S.I. Vdovenko, I.I. Gerus, V.P. Kukhar, Vibrational Spectroscopy 52 (2010) 144.
- [7]. I.S. Kondratov, V.G. Dolovanyuk, N.A. Tolmachova, I.I. Gerus, K. Bergander, R. Fröhlich, G. Haufe, Org. Biomol. Chem. 10, (2012) 8778.
- [8] I. I. Gerus, Y. I. Zhuk, L. M. Kacharova, G.-V. Röschenthaler, Book of Abstracts of 20th International Symposium on Fluorine Chemistry, Kyoto, Japan, July 22-27, 2012, 234.
- [9]. C.M. Kascheres, J. Braz. Chem. Soc. 14 (2003) 945.
- [10]. J. Dąbrowski, K. Kamieńska-Trela, Spectrochim. Acta, 22 (1966) 211.
- [11]. S.F. Tayyari, M. Fazli, F. Milani-nejad, J. Mol.Struct.(Theochem), 541 (2001) 11.
- [12]. M.Bugaj and K. Kamieńska-Trela, Polish J.Chem., 80 (2006) 1217.
- [13]. J. Wójcik, W. Domalewski, K. Kamieńska-Trela, L .Stefaniak, S.I. Vdovienko, I.I. Gerus, M.G .Gorbunova, Magn. Reson. Chem., 31(1993) 808.
- [14]. J. Wójcik, K. Kamieńska-Trela, M. Pecul, E. Bartoszak-Adamska, S.I. Vdovenko, I.I. Gerus, Chem. Phys. Phys. Chem., 5 (2004) 209.
- [15]. P.J. Taylor, Spectrochim. Acta, Part A 32 (1976) 1471.
- [16]. R.A. Nyquist, Interpreting Infrared, Raman, Nuclear Magnetic Resonance Spectra Vol.1, Academic Press, 2001.
- [17]. D. Smith and P.J. Taylor, Spectrochim. Acta, Part A 32 (1976) 1477.
- [18]. S. Noda, Yu. Ozaki, Two-dimensional Correlation Spectroscopy Applications in Vibrational and Optical Spectroscopy, John Wiley & Sones, Ltd, 2004.
- [19]. 2Dshige (c) Shigeaki Morita, Kwansei-Gakuin University, 2004-2005.
- [20]. S.I.Vdovenko, I.I.Gerus, H.A.Fedorenko, Spectrochim. Acta, Part A 103 (2013) 368.

- [21]. S.I.Vdovenko, I.I.Gerus, H.A.Fedorenko, V.P.Kukhar, ISRN Spectroscopy 2013, Article ID 640896, doi:20.5402/2012/640896.
- [22]. M.H. Abraham, R.M. Doherty, M.J. Kamlet, J.M. Harris, R.W. Taft, J. Chem. Soc. Perkin Trans.2 (1987) 913.
- [23]. D. Gurka, R.W. Taft, J. Am. Chem. Soc. 91 (1969) 4794.

- [24]. F. Besseau, M. Luçon, C. Laurence, M. Berthelot, J. Chem. Soc. Perkin Trans. 2 (1998) 101.
- [25]. S.I.Vdovenko, I.i.Gerus, E.A.Fedorenko, V.P.Kukhar, J.Mol.Struct. 977 (2010) 237.

Captions for figures

Fig.1. Synchronous (A) and asynchronous (B) spectrum of DMTBN under dilution in the region of v(C=C) stretching vibrations;
Simulated synchronous (C) and asynchronous (D) spectrum of DMTBN in the region of

v(C=C) stretching vibrations.

Fig. 2. Dependence of dipole moment $(\mu)vs.$ total concentration of DMTBN.

Scheme 1. Synthesis of studied enaminoketones.

Scheme 2. Possible stereoisomeric forms of the enaminoketones $CF_3CO-CR^1=CH-NR^2R^3$.

MAS

Scheme 3. Hydrogen bond cyclic complex formation between the (E-s-Z) and (E-s-E) conformers.



Fig.1. Synchronous (A) and asynchronous (B) spectrum of DMTBN under dilution in the region of v(C=C) stretching vibrations;

Simulated synchronous (C) and asynchronous (D) spectrum of DMTBN in the region of v(C=C) stretching vibrations.









Table 1. Calculated Total Energy, Relative Energy^a (RE), dipole moment (μ) and dihedral angle C=C–C=O (ϕ) of studied enaminones by DFT method and thermodynamic parameters of *Trans-s-cis* \longrightarrow *Trans-s-trans* equilibrium evaluated experimentally.

				Thermodynamic parameters				
Enaminone	Confor- mer		Basis set 6-3110	of Trans-s-cis Trans-				
						s-trans e	quilibrium	
		Energy,	RE,	μ, D	ф , °	ΔH ,	ΔS,	
		kJ dm3 mol ⁻¹	kJ dm3 mol ⁻¹			kJ mol ⁻¹	J mol ⁻¹ K ⁻¹	
h	E-s-E	-953473.99	11.93	5.75	179.3°	0.72+1.80	206 1+6 4	
DMBN[6] ⁰	E-s-Z	-953485.92	0	4.66 0		9.72±1.89	-200.1 ± 0.4	
DMTBN[6]	E-s-E	-1734386.52	12.74	7.0	180.0	-10 64+0 27	-210 8+0.9	
	E- s - Z	-1734399.26	0	7.0	0.5	-10.0410.27	-210.0±0.9	
	Z-s- E	NE ^c	-	-	- 6			
	Z-s-Z	-1734367.96	31.30	6.2	7.6			
	E-s-E	-1994268.34	64.66	6.5	156.7			
	E-s- Z	-1994302.11	31.63	6.3	4.1			
DMTFBN ^c	Z-s- E	-1994321.38	12.36	6.4	179.9			
	Z- s - Z	-1994333.74	0	6.3	0.8	11.76±1.06	-214±2.6	
	F-s-F	-1837019 56	-0	6.6	176.3			
DMTMBN[20]	L-3-L	-1057017.50	0	0.0	170.5	12.13±1.55	-204.0±5.4	
	E- s - Z	-1837018.47	1.09	6.6	0.3			
	Z-s- E	-1836989.31	30.25	5.3	139.3			
	Z- s - Z	-1837002.51	17.05	5.2	21.2			

^aRelative Energy (RE) – the difference of energies of the conformers;

^b 4-(dimethylamino)but-3-en-2-one

RCK

^c NE – "not exists": the conformer was transformed in ZZ-isomer under the geometry optimization;

^d Denomination Z-s-E and Z-s-Z corresponds to Trans-s-cis and Trans-s-trans, respectively, for enaminoketone

DMTFBN in accord with IUPAC demands.

Table 2. The coefficients (*s*, *d*, *a*, *b*, and *h*), error of estimate (S.D.), Fisher index of reliability (*F*), and correlation coefficients (R^2) of common correlation equation Eq. (1) for \tilde{v} (C=O) and \tilde{v} (C=C) bands of studied enaminoketones F₃C-CO-CR=CH-N(CH₃)₂. Solvatochromic parameters are from [20].

	Substituent R	Stereoisomeric form	Independent variable	Intercept ^a	S	а	b	d	h	N	S.D.	F	R^2	Eq. No.
1 Н		E-s-Z	ν̃ _(C=O)	1692	-1.814	-10.207	-4.766	5.483	-3.262	18	0.87286	20.494	0.903	2
	н		ν _(C=C)	1598	7.056	-11.051	-0.493 ^b	-1.650 ^b	-10.847	18	3.1461	13.590	0.761	3
	-	E-s-E	ν _(C=O)	1674	-4.574	-8.015	-0.748 ^b	0.090 ^b	-0.417 ^b	18	0.73229	124.17	0.981	4
			ν _(C=C)	1597	-3.335	-8.242	-4.218	1.860	-0.692 ^b	18	1.0656	76.969	0.970	5
		Z-s-Z	ν̃ (C=O)	1688	-36.654	-10.726	-2.758 ^b	-0.3610	8.961	21	3.7652	29.524	0.908	6
2	F		ν̃ (C=C)	1608	-11.383	-12.899	-4.761	0.4800 ^b	-2.403	21	2.030	69.905	0.9589	7
	L	Z-s-E	ν _(C=O)	1704	-22.787	-12.669	-1.183 ^b	-0.2788 ^b	3.281	21	1.7109	96.921	0.970	8
			ν _(C=C)	1631	-23.360	-14.533	-3.306 ^b	-0.0895 ^b	-1.588	21	1.4565	223.99	0.987	9
		E-s-Z	ν̃ (C=O)	1671	-7.906	-12.099	2.769 ^b	-1.117 ^b	-0.730 ^b	20	2.5017	24.612	0.905	10
3	CH ₃		ν _(C=C)	1598	-17.900	-24.678	6.500	-0.2371 ^b	7.197	20	2.3828	76.739	0.984	11
		E-s-E	ν̃ (C=O)	1669	-4.988	-10.259	-3.722	-0.2055	-8.689	20	3.7545	20.925	0.890	12
			$\tilde{v}_{(C=C)}$	1603	-23.733	-12.724	8.863	-0.2679 ^b	8.831	20	2.4835	30.153	0.921	13
^a Wavenumber, cm ⁻¹ . ^b Not significant.														

Table 3. Hydrogen bond basicity of the conformers (*E-s-Z*) and (*E-s-E*) (for DMTFBN these conformers are denoted as (*Z-s-Z*) and (*Z-s-E*)) of studied enaminoketones: frequency shifts Δv (OH), complex formation constants K_f, pK_{HB} values and enthalpies of hydrogen bond formation ($-\Delta$ H).

Enaminoketone	conformer	$\Delta v(OH), cm^{-1}$	K _f	рК _{НВ}	$-\Delta H$,(kJ/M)	
DMRN[25]	E-s-Z	334	230.5	2.363	20.53±5.41	
DIVIDIN[25]	E-s-E	457	633.1	2.801	35.70±4.11	
DMTBN[25]	E-s-Z	212	35.8	1.554	15.84±1.47	
	E-s-E	325	42.5	1.628	29.58±2.18	
DMTFBN	Z-s-Z	126	10.2	1.007	16.48±1.37	
	Z-s-E	156	30.8	1.488	22.30±2.14	
DMTMBN	E-s-Z	206	690.76	2.839	31.84±1.50	_
	E-s-E	253	553.35	2.743	40.82±2.11	

Represented equilibrium depends both on solvents and temperature.

ALP.

 α -Substitution strongly influences on enaminoketone hydrogen-bond basicity.



R = H (DMTBN); R = F, (DMTFBN); R = CH₃,(DMTMBN)

The conformational analysis of push-pull enaminones using Fourier transform IR and NMR spectroscopy, and quantum chemical calculations. V. α – Methyl, Fluorine– β –N,N–Dimethylaminovinyl trifluoromethyl ketones

Sergey I. Vdovenko, Igor I. Gerus, Yuri I. Zhuk, Valery P. Kukhar, Gerd-Volker Röschenthaler

Highlights

- 1. All studied enaminoketones are TRANS isomers wich form s-cis and s-trans conformers.
- 2. s-Cis and s-trans conformers of DMTBN form 'closed-ring' hydrogen-bonded complex.
- 3. α -Substitution strongly influences on enaminoketone hydrogen-bond basicity.
- 4. Solvent influence on IR-spectra of studied enaminoketones strongly depends on α-substituent.

24