α,β-Unsaturated Enamino-ketones with Trifluoromethyl Groups. Infrared Spectra and Structure

Sergei I. Vdovenko,* Igor I. Gerus and Marina G. Gorbunova
Institute of Bioorganic and Oil Chemistry, Academy of Sciences of Ukraine, Murmanskaya str. 1, Kiev, 252160, Ukraine

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The infrared spectra of two enamino-ketones containing the trifluoromethyl group, namely, 4-(*N*-methylamino)- **1** and 4-(*N*,*N*-dimethylamino)-1,1,1-trifluorobut-3-en-2-one **2** have been investigated in a number of solvents. It has been shown the title compounds possess spectral characteristics different from those of nonfluorinated analogues. Spatial and electronic structure features of these enamino-ketones are discussed.

It is known[1–5] that simple enamino-ketones of the type $O{=}C(R^1){-}CH{=}CH{-}NR^2R^3$ can exist in four distinct configurations (see Fig. 1).

Until now most spectroscopic investigations of the relationship between spatial structure and spectral parameters of α,β-unsaturated enamino-ketones have been carried out when R^1 = Alkyl. Introduction of a trifluoromethyl group as the R^1 substituent may be accompanied by changes in spatial and electronic structure and consequently affect the spectral parameters. For this reason the detailed study of α,β-unsaturated enamino-ketones containing a trifluoromethyl group as the R^1 substituent seemed desirable, especially since some spectral differences between enamino-ketones **1** ($R^1 = CF_3, R^2 = CH_3, R^3 = H$) and **2** ($R^1 = CF_3, R^2 = R^3 = CH_3$), and **1a** ($R^1 = CH_3, R^2 = C_2H_5, R^3 = H$) and **2a** ($R^1 = R^2 = R^3 = CH_3$) (see Fig. 1) were mentioned in a previous paper.[6]

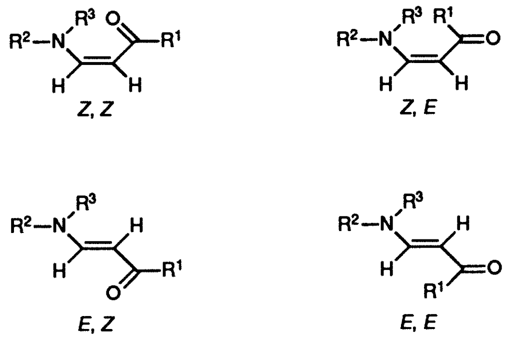

Fig. 1 Possible configurations of enamino-ketones

Results and Discussion

All spectral data are presented in Tables 1–4. Also representative spectra are depicted in Figs. 2 and 3. According to ^1H NMR data (see Table 1) enamino-ketone **1** exists in the *Z* form in nonpolar solvents (95–100%), while in highly polar media the percentage of the *E*-form increases considerably (76% in [$^2H_6$]DMSO: the total content of E_a and E_b rotamers, see Table 1) owing to $E \rightleftharpoons Z$ isomerization. The ability of *N*-alkyl α,β-unsaturated enamino-ketones like **1a** to undergo $E \rightleftharpoons Z$ isomerism has been described previously.[1a,3,7] In nonpolar solvents the infrared spectra of **1** exhibit a wide absorption band at 3230–3210 cm^{-1} with unvariable shape and intensity in the range of concentrations 0.005–0.5 mol dm^{-3} and temperatures 20–50 °C. The NH deuteriation of **1** leads to a low frequency shift of this band (from 3236 to 2408 cm^{-3}, in CCl_4), which we ascribed to the stretching vibrations of the NH-group being involved in intramolecular hydrogen bonding in the *Z,Z*-configuration (here and below designations of structures correspond to Fig. 1). In the skeletal vibration region spectra of **1** in the gaseous state and in nonpolar solvents exhibit individual $\nu_{C=O}$ and $\nu_{C=C}$ bands attributed to the *Z,Z* form (taking account of NMR data and the ability of **1** to form a strong intramolecular H-bond).

For comparison, in the spectrum of the chelate complex of **1** with Cu^{2+}, which is known to possess a rigid *Z,Z* configuration,† vibrational bands $\nu_{C=C}$ and $\nu_{C=C}$ lie at 1629 and 1561 cm^{-1}, respectively. Thus it is reasonable to assume that the bands near 1660 and 1600 cm^{-1} in nonpolar solvents ($\varepsilon_{C=O}/\varepsilon_{C=C}$ *ca.* 1) correspond to $\nu_{C=O}$ and $\nu_{C=C}$ of the *Z,Z* configuration. In the solid state, and in solvents of moderate polarity, an additional high frequency shoulder appears on contour of the $\nu_{C=O}$ band near 1680 cm^{-1}. Simultaneously a new band is observed at 3452–3436 cm^{-1}, the shape and position of which indicate that it belongs to free ν_{NH} vibrations of the *E* form; deuteriation shifts this band to lower frequencies (2548 cm^{-1} in CD_2Cl_2). The most considerable changes are observed in cases when polarity increases simultaneously with solvent proton accepting power, as can be seen from Fig. 2, where infrared spectra of **1** in mixtures of carbon tetrachloride and hexamethylphosphoramide (HMPA) are presented. Observed spectral changes are caused by $Z \rightleftharpoons E$ isomerization, and the presence of isosbestic points indicates on equilibrium of two forms only, *Z,Z* and *E,E*; the last form is additionally stabilized by intermolecular H-bond formation with HMPA (in proton accepting solvents the ν_{NH} band broadens and shifts to the region 3370–3310 cm^{-1}). Spectral characteristics and content of *Z,Z* and *E,E* forms in various solvents are listed in Table 2. As can be seen from Tables 1 and 2 there is good agreement between estimates of isomeric content, from NMR data and infrared spectra ($\nu_{C=O}$ bands). Concerning the $\nu_{C=C}$ stretching vibrations the situation is somewhat more complicated: it is likely that the bands of two forms coincide and the splitting of the $\nu_{C=C}$ band owing to the presence of *E* and *Z* isomers could not be observed in all cases.‡

The same effect was noted for β-halogenovinyl-ketones[9] and some α,β-unsaturated ketones.[10] Both $\nu_{C=O}$ and $\nu_{C=C}$ of the *Z,Z* form of **1** (Table 2) are somewhat higher than those of **1a** [1640 and 1580 cm^{-1}, respectively (ref. 3)], but values $\Delta\nu = \nu_{C=O} -$

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† According to ref. 8*a*, *b* and the absence of a ν_{NH} peak in the infrared spectrum of the complex.

‡ Existence of forms other than *Z,Z* or *E,E* (see Fig. 1) cannot be ruled out completely, but their presence is impossible to confirm in view of their very low content and the masking effects of other bands.

$\nu_{C=C}$ are almost the same, *ca.* 60 cm^{-1}. Taking into account the fact $\nu_{C=O}$ in **1** is lowered due to intramolecular H-bonding, and assuming this reduction to be approximately equal to the one in non-fluorinated α,β-unsaturated enamino-ketones (*i.e.* 30 cm^{-1}, from ref. 5), we have estimated the 'true' $\nu_{C=O}$ frequency of the *Z*,*Z* form of **1** to be *ca.* 1690 cm^{-1}. This result is consistent with the conclusions of Smith and Taylor[5] that $\nu_{C=O}(Z,Z) > \nu_{C=O}(E,E)$. In contrast to the *Z*,*Z* configuration, $\nu_{C=O}$ of the *E*,*E* form is more solvent sensitive: on passing from carbon tetrachloride to dimethyl sulfoxide this frequency falls by 19 cm^{-1} (1 cm^{-1} for *Z*,*Z*, see Table 2). It is clear that the carbonyl group in the *E*,*E* form is more 'exposed' to solvent, and the linear *E*,*E* alignment facilitates solvation as compared with the pseudo-aromatic ring of the *Z*,*Z* form. The presence of proton accepting groups (P=O, S=O, *etc.*) in solvent molecules promotes intramolecular H-bond breaking in the *Z*,*Z* form and formation of intermolecular H-bonds, thus stabilizing the *E*,*E* configuration. The temperature dependence of *E*,*E* and *Z*,*Z* content may be regarded as evidence for this assumption. Supposing the process to correspond to eqn. (1), this equilibrium has been studied in the temperature range 20–60 °C; [*Z*,*Z*] and [*E*,*E*••• HMPA] have been determined from infrared spectra.[11] According to eqn. (1) K_{eq} = [*E*,*E*•••HMPA]/{[*Z*,*Z*] × [HMPA]}, where

$$[Z,Z] + [\text{HMPA}] \underset{}{\overset{K_{eq}}{\rightleftharpoons}} [E,E]\cdots\text{HMPA}] \quad (1)$$

[HMPA] = [HMPA]$_0$ − [*E*,*E*•••HMPA], the concentration of non-bonded HMPA, [*Z*,*Z*] = concentration of *Z*,*Z* form, [*E*,*E*••• HMPA] = concentration of *E*,*E* in H-complex with HMPA; [*Z*,*Z*] + [*E*,*E*••• HMPA] = 5.2 × 10^{-2} mol dm^{-3}; [HMPA]$_0$ = 7.1 × 10^{-2} mol dm^{-3} (initial concentration of HMPA); K_{eq} = equilibrium constant in solution CCl$_4$.

The plot of [*E*,*E*••• HMPA]/[*Z*,*Z*] *versus* [HMPA] is linear

Table 1 ^{1}H NMR data[a] of **1** and **2** in various solvents

Isomer (substance)	Type of proton	Solvent CCl$_4$	CDCl$_3$	CD$_3$CN	(CD$_3$)$_2$SO
Z(**1**)	α-CH=, d[b]	5.27	5.36	5.24	5.18
	β-CH=, dd[b,c]	7.01	7.15	7.22	7.41
Z(**1**)	CH$_3$, d[d]	3.19	3.16	3.03	3.02
	NH, br, s	10.17	10.16	10.02	10.00
	Content[e] (%)	~99	96	73	24
E$_a$(**1**)	α-CH=, d[f]	5.34	5.39	5.36[g]	5.30[g]
	β-CH=, dd[f,h]	7.82	8.05	7.86[g]	7.86[g]
	CH$_3$, d[d]	2.91	2.91	2.76	2.74
	NH, br s	nd	nd	6.6	8.6
	Content[e] (%)	~1	4	~25	~66
E$_b$(**1**)	α-CH=, d[g,i]	nd	nd	5.38[g]	5.35[g]
	β-CH=, dd[g,i]	nd	nd	7.71[g]	7.86[g]
	CH$_3$, d[d]	nd	nd	2.94	2.96
	NH, br s	nd	nd	nd	8.9
	Content[e] (%)	nd	nd	~2	~10
E(**2**)	α-CH=, d[j]	—	5.28	—	5.28
	β-CH=, d[j]	—	7.88	—	7.95
	CH$_3$, 2 s	—	3.23; 2.96	—	3.22; 2.93

[a] Chemical shift in ppm, internal TMS, 0.05 mol dm^{-3}, T = 293 K. [b] $J(H_\alpha H_\beta)$ 6.9 ± 0.2 Hz. [c] $J(H_\beta NH)$ 13.5 ± 0.3 Hz. [d] $J(CH_3NH)$ 5 ± 0.1 Hz. [e] Estimated by the ratio of signal intensities of vinyl protons and methylamino group. [f] $J(H_\alpha H_\beta)$ 12.2 ± 0.2 Hz. [g] Signals overlap. [h] $J(H_\beta NH)$ 7.6 ± 0.2 Hz. [i] $J(H_\alpha H_\beta)$ ≈ 12 Hz. [j] $J(H_\alpha H_\beta)$ 12.15 ± 0.05 Hz.

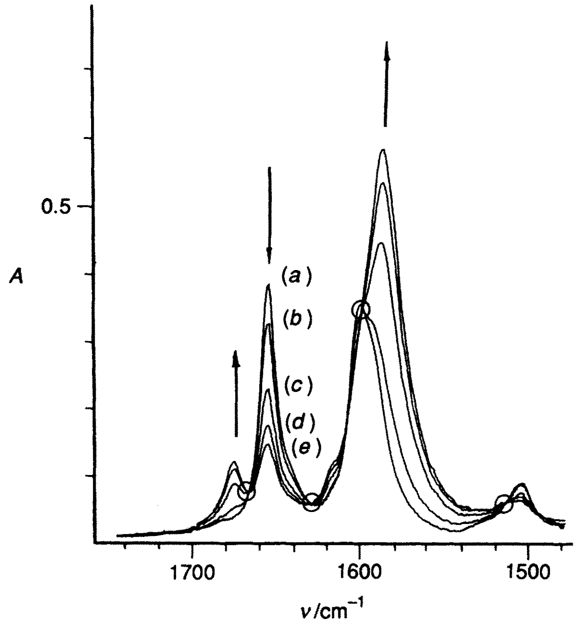

Fig. 2 Infrared spectra of enamino-ketone **1** in mixed solvent (volume ratio CCl$_4$:HMPA):(*a*) pure CCl$_4$; (*b*) 100:1; (*c*) 50:1; (*d*) 40:1; (*e*) 20:1. The isosbestic points are circled.

Table 2 Infrared spectra and content of isomeric forms in solutions of **1**

	$\nu_{C=O}$ band									
	Z,*Z*				*E*,*E*				$\nu_{C=C}$ band	
Solvent	ν/cm^{-1}	Δν$_{½}$/cm^{-1} mol^{-1}	ε$_a$[a]/dm^3 cm^{-1}	%[b]	ν/cm^{-1}	Δν$_{½}$/cm^{-1} mol^{-1}	ε$_a$[a]/dm^3 cm^{-1}	%[b]	ν/cm^{-1}	Δν$_{½}$/cm^{-1}
C$_7$H$_{16}$	1658	12	660	>99	*c*	*c*	*c*	<1	1606	16
c-C$_6$H$_{12}$	1657	12	660	>99	*c*	*c*	*c*	<1	1604	18
CCl$_4$	1655	11	610	97	1687	15	324	3	1602	23
CH$_2$Cl$_2$	1653	12	(600)	95	1680	17	330	5	1589	27
C$_2$H$_4$Cl$_2$	1653	13	(630)	93	1677	17	(330)	7	1590	27
CHCl$_3$	1654	17	570	96	1683	16	333	4	1588	30
c-C$_4$H$_8$O$_2$	1655	14	(630)	90	1687	20	(330)	7	1586	26
CH$_3$CN	1654	17	606	74	1671	18	(330)	26	1585	22
DMSO[d]	1654	13	620	24	1668	19	313	76	1583	30
HMPA[d]	1655	14	612	14	1670	19	300	86	1587	40

[a] Data in parentheses are mean values (see Experimental section). [b] Percentage content of title configuration. [c] Impossible to estimate owing to very low concentration. [d] DMSO = dimethyl sulfoxide, HMPA = hexamethylphosphoramide.

Table 3 Infrared spectra and content of conformers in solutions of **2**

	$\nu_{C=O}$ band									
	E,Z				*E,E*				$\nu_{C=C}$ band	
Solvent	ν/cm^{-1}	$\Delta\nu_{\frac{1}{2}}$/cm^{-1} mol^{-1}	$\varepsilon_a{}^a$/dm^3 cm^{-1}	%^{b}	ν/cm^{-1}	$\Delta\nu_{\frac{1}{2}}$/cm^{-1} mol^{-1}	$\varepsilon_a{}^a$/dm^3 cm^{-1}	%^{b}	ν/cm^{-1}	$\Delta\nu_{\frac{1}{2}}$/cm^{-1}
c-C_6H_{12}	1692	12	238	69	1673	12	354	31	1596	15
CCl_4	1687	12	203	70	1672	13	357	30	1591	15
c-$C_4H_8O_2$	1684	14	230	41	1672	12	372	59	1590	12
$CDCl_3$	1687	13	200	23	1669	13	360	77	1584	17
CH_2Br_2	1684	13	195	29	1667	12	369	71	1583	15
CH_3CN	1685	11	(185)	11	1668	13	(370)	89	1589	13
DMSO^c	*d*	*d*	*d*	*d*	1664	12	382	100	1586	15

[a] Data in parentheses are mean values, see Experimental section. [b] Percentage content of title conformer. [c] DMSO = dimethyl sulfoxide. [d] No traces found.

Table 4 Thermodynamic parameters of the $E,E \rightleftharpoons Z,Z$ equilibrium in solutions of **2**

Solvent	K_{eq}^{293}/dm^3 mol^{-1}	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$\Delta S°$/ J mol^{-1} K^{-1}
c-C_6H_{12}	2.2528	−2.0	11.7	47
CCl_4	2.3368	−2.1	10.5	43
CH_2Br_2	0.4005	+2.2	6.6	30
$CDCl_3$	0.3031	+2.9	9.6	23

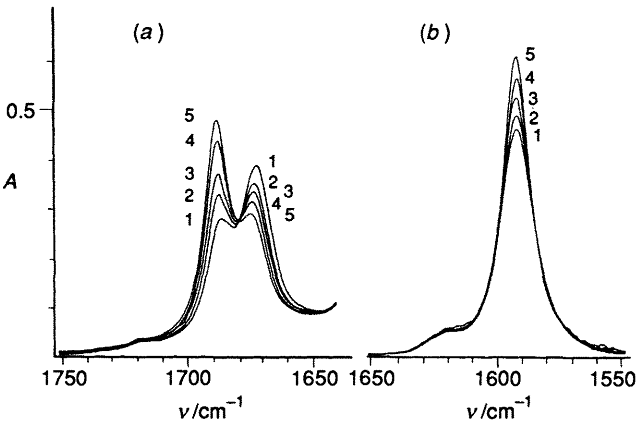

Fig. 3 Infrared spectra of enamino-ketone **2** in CCl_4. (*a*) Cell thickness × concentration = 2.0×10^{-3} mol dm^{-3} × cm; [**2**]/mol dm^{-3} = 0.67 (1), 0.16 (2), 0.09 (3), 0.04 (4), 0.02 (5). (*b*) Cell thickness × concentration = 2.5×10^{-4} mol dm^{-3} × cm; [**2**]/mol dm^{-3} = 0.165 (1), 0.12 (2), 0.08 (3), 0.03 (4), 0.01 (5).

in the range of investigated [HMPA],* thus verifying the 1 : 1 stoichiometry of the complex (*E,E*··· HMPA). The thermodynamic data obtained (*i.e.* K_{eq}^{293} = 14.28 dm^3 mol^{-1}; $\Delta G°$ = −6.5 ± 0.4 kJ mol^{-1}; $\Delta H°$ = −11.8 ± 0.4 kJ mol^{-1}; $\Delta S°$ = −18 ± 4 J mol^{-1} K^{-1}) also indicate that **1** exists predominantly as the complex (*E,E*··· HMPA). Compound **2**, like α,β-unsaturated dialkylaminovinyl-ketones,[7] is shown by NMR data (see Table 1) to exist in the *E*-stereomeric form. Infrared spectra of **2** in polar solvents are characterized by the presence of a very intensive band at 1584–1586 cm^{-1} and a band with moderate intensity at 1664–1669 cm^{-1}. As for **1**, and previously[6] for enamino-ketone **3**: R^1 = CF_3, R^2 = R^3 = C_2H_5, we ascribed the high frequency band to $\nu_{C=O}$, and the low frequency one to $\nu_{C=C}$ (see Table 3). The sensitivity of the $\nu_{C=O}$ contour to solvent polarity, concentration (Fig. 3) and temperature indicates the presence of equilibrium $E,Z \rightleftharpoons E,E$, noted for **2a** earlier.[2] Splitting of the $\nu_{C=C}$ band in **2** could in no case be observed, and only the $\nu_{C=C}$ intensity varied [Fig. 3(*b*)]. By analogy with non-fluorinated enamino-ketones,[1b,23] and applying the criteria of Smith and Taylor,[5] we have attributed the band at 1684–1693 cm^{-1} to the $\nu_{C=O}$ stretching vibration of the *E,Z* conformer, and the band at 1664–1674 cm^{-1} to that of the *E,E* form (Table 3). Values of $\Delta\nu = \nu_{C=O} - \nu_{C=C}$ of the *E,Z* form of **2** and **2a** are similar [95 ± 2 cm^{-1} and 95 ± 3 cm^{-1} (from ref. 2)], whereas for the *E,E* form the difference is significant [81 ± 4 cm^{-1} and 50 ± 10 cm^{-1} (from ref. 2), respectively]. In addition both $\nu_{C=O}$ bands of **2** demonstrate similar solvent sensitivity (6 cm^{-1} fall on passing from cyclohexane to dibromomethane, see Table 3), while for **2a** this is not the case.[2] According to Dabrowski *et al.*[2,4] this behaviour of **2a** is a consequence of coupling between the $\nu_{C=O}$ and $\gamma_{C=O}$ modes in the slightly non-planar *E,E* form. The index of conjugation of C=O and C=C bonds is the mean[5a,b] of $\nu_{C=O}$ and $\nu_{C=C}$, *i.e.* ν_m. In α,β-unsaturated enamino-ketones ν_m *ca.* 1570–1575 cm^{-1} (*E,E*) (from ref. 5a), whereas in **2** it equals 1631 cm^{-1}. Hence the double bond conjugation in **2** is higher than in **2a**, and so the decrease of resonance energy due to steric interactions in **2** is insignificant. Moreover, resonance enhancement in **2** can be illustrated by ^{1}H NMR spectra, where separate signals of the *N*-methyl groups of **2** are observed at ambient temperature (Table 1), whereas the signals of **2a** are broadened and almost overlapped under these conditions. The separation of the signals in **2a** has been observed at much lower temperatures.[4] Hindered rotation around the formally single C–N bond in **1** allows one to distinguish the separate forms E_a and E_b corresponding to two rotamers of the CH_3NH–CH=CH– fragment, which are indivisible in the infrared spectra. Furthermore, there is no contribution of $\gamma_{C=O}$ to the $\nu_{C=O}$ stretching vibration of **2** and the normal sensitivity of $\nu_{C=O}$ bands towards solvent action is observed. The enthalpy difference between *E,Z* and *E,E* form of **2** is higher than for **2a** [*cf.* Table 4 and 1.68 kJ mol^{-1} (from ref. 4)], but it is known[11] that the equilibrium ratio of conformers in solution depends on the free energy difference. ΔG of the conformers in **2** is comparable in absolute value with the one in **2a** [1.8 kJ mol^{-1} in 2,2-dichloroethene (from ref. 4)], but its sign depends on solvent polarity (see Table 4). It may be said in conclusion that the introduction of a CF_3-group as R^1 substituent in α,β-unsaturated enamino-ketones does not break the conjugation of C=O and C=C bonds (due to steric interaction with the α-hydrogen of vinyl group), and enhances polarization of whole conjugated system. As a result the spatial structure of the enamino-ketone is highly sensitive to solvent influence.

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* From the plot, K_{eq} = 13.7 ± 1.1 dm^3 mol^{-1}, [HMPA] = 0–0.3 mol dm^{-3}.

Experimental

α,β-Unsaturated enamino-ketones were synthesized from 1,1,1-trifluoro-4-ethoxybut-3-en-2-one and the appropriate alkylammonium chloride as described previously:[6] m.p.s 65 °C (**1**), 58 °C (**2**) (C_6H_{14}). The NMR spectra were all in accord with the structures. Chelate complex of **1** with Cu^{2+} was obtained by the method described earlier[13] and was purified by column chromatography, m.p. 90–91 °C. The deuteriation of **1** was carried out by adding a threefold D_2O excess to a solution of **1** (0.1 mmol) in CCl_4 (2 cm^3) and shaking the mixture for *ca.* 10 min. After D_2O separation the solution was partially dried over 3 Å molecular sieves (some D_2O traces are necessary to suppress opposite exchange). The spectral purity of $[^2H]$**1** was established by absence of a ν_{NH} vibration at *ca.* 3200 cm^{-1} and the presence of ν_{ND} at *ca.* 2400 cm^{-1}. In addition the control of α-position deuteriation in the vinyl fragment of $[^2H]$**1** was verified by ^1H NMR spectroscopy (intensity of δ_H 5.4), according to which α-deuteriated impurity was about 5–7%. ^1H and ^{19}F NMR spectra were obtained on a Bruker WP-200 spectrometer in solvents listed in Table 1. Infrared spectra were recorded on Specord Model 80 spectrophotometer, concentrations in all cases were 0.052 mol dm^{-3}, cell thickness 0.194 mm, unless stated otherwise. Temperature investigations were carried out in thermostatted (with accuracy ±0.05 °C) cells; all spectra were corrected for cell temperature dependence by multiplying by correcting coefficients (proportional to volume expansion of solutions with temperature).

Thermodynamic parameters of the investigated equilibria were calculated by the method described in ref. 11; ε_a values and percentage content of stereoisomeric forms were estimated by a conventional multicomponent analysis[14] procedure after $\nu_{C=O}$ band separation.[15] Data in parentheses (Tables 2 and 3) are mean values obtained by averaging the corresponding ε_a values in cases when they could not be estimated precisely from spectral data.

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