DIRECT DETERMINATION OF Z,E CONFIGURATION OF 4-ARYLIDENE-2-PHENYL(METHYL)-Δ^2-OXAZOLIN-5-ONES AND THEIR SOLVOLYSIS PRODUCTS BY ^{13}C NMR

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An important achievement in the asymmetric synthesis of α-amino acids has been the enantioselective catalytic reduction of the azlactones of α-acylaminoacrylic acids [1] and of the acids themselves [2]. To determine the mechanism and the stereochemistry of these reactions it is necessary to know the exact geometry of the chiral substrates. Various methods and approaches have been used over a long time to determine the Z,E configuration of unsaturated azlactones [3, 4]. Of these works [5] and [6], whose results seem the most reliable, and also [7] deserve to be singled out. In [5-7] the geometrical configuration of the solvolysis products of several azlactones were studied. The results on the geometry of the starting compounds were obtained with the assumption of a uniform configuration for the olefin bond of azlactones and of their solvolysis products. Furthermore, the Z,E assignment of solvolysis products in [6, 7] was based on a comparison of the chemical shift (CS) values of the olefinic protons in these compounds and in model compounds. In these cases, such an approach unavoidably involves certain assumptions. Only one substance was studied by x-ray diffraction analysis [5]. When all this is taken into account, the results on the Z,E configuration of azlactones obtained in these works cannot be considered conclusive.

In the present work the Z,E configuration of unsaturated azlactones and their solvolysis products has been established independently and without any assumptions concerning the value of the vicinal spin—spin coupling constants $^3J_{^{13}C,\ ^1H}$ measured in the ^{13}C NMR spectra.

DISCUSSION OF RESULTS

The ^{13}C resonance signals of unsaturated azlactones (I)-(X) were identified by their CS values (Table 1), the ^{13}C, ^1H ($J_{C,H}$) spin—spin coupling constants (SSCC) (Table 2), based on the shape of the monoresonance spectra of individual carbon atoms, and by comparison of the spectra so obtained. In assigning ^{13}C signals of the benzene ring at C^β, we also used published data on the effect of R^1 and R^2 substituents on the carbon atoms of monosubstituted benzenes [8].

Unambiguous assignment of known compounds as Z,E isomers, shown in Table 1, was carried out on the basis of the vicinal SSCC of the C=O carbon of the azlactone ring with the olefin proton H^β ($^3J_{CO,H\beta}$). It has previously been shown [9, 10] that for $^3J_{^{13}C^1H}$ in the $^{13}C—C=C—H$ fragment the condition $^3J^{trans}_{C,H} > {}^3J^{cis}_{C,H}$ is fulfilled. According to the data of [9], this inequality is manifested most strongly for carbons not subjected to the γ effect [11]. Due to the complete absence of γ effect on quaternary C atoms [11, 12], significant differences in $^3J_{CO,H\beta}$ can be expected for Z,E isomers in the cases observed. Actually, $^3J_{CO,H^\beta}$ is 5.5 and 12 Hz for Z and E isomers, respectively (see Table 2).

In all cases the C=O signals of the azlactone ring are doublets (164.6-168.2 ppm) due to the presence of $^3J_{CO,H\beta}$; this permits them to be distinguished from the nearby C=N signals (159.8-166.3 ppm) and from the C=O of the carbomethoxy group (168.5-168.9 ppm). When $R^3 = CH_3$, the C=N signals are quadruplets due to the interaction of ^2J with the methyl protons; when R^3 = Ph, they are triplets (at low signal—noise ratio they are unresolved multiplets) due to the interaction of ^3J with the two o-protons of the phenyl ring; while the C atom of the MeCOO group gives quadruplets due to the interaction of ^2J with the methyl protons of this group.

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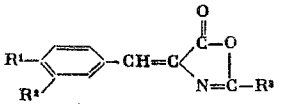
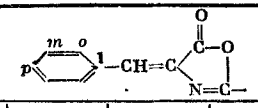
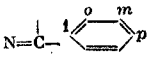
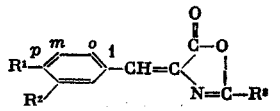
TABLE 1. ^{13}C Chemical Shifts (δ, ppm) for Azlactones 

Compound[a]	R^1[b]	R^2[b]												
			C=O	CH=	C=	C=N	1	o-	m-	p-	1	o-	m-	p-
R^3=CH_3 [c]														
Z-(I)	H	H	167,8	131,4	133,0	166,3	133,5	132,4	129,0	131,1	–	–	–	–
Z-(II)	MeCOO	H	167,7	130,1	132,6	163,3	130,9	133,5	122,2	152,7	–	–	–	–
Z-(III)	MeO	H	168,2	131,4	130,6	165,0	126,3	134,4	114,6	162,2	–	–	–	–
Z-(IV)	MeCOO	MeO	167,8	130,5	132,7	166,3	132,2	115,5[d] 125,9	123,2 151,5[e]	142,3	–	–	–	–
Z-(V)	MeO	MeCOO	167,9	130,3	131,3	165,5	126,5	126,2[d] 132,2	112,3 140,1[e]	153,8	–	–	–	
R^3=Rh														
Z-(VI)	H	H	167,6	131,8	133,4	163,7	133,7	132,6	129,0	131,3	125,8	(129,0	129,0	128,5)[f]
E-(VI)	H	H	164,6	140,1	134,4	161,5	(132,8	131,6	129,0	133,0	125,6	131,9	128,8	127,9)[f]
Z-(VII)	MeCOO	H	167,5	130,4	133,4	163,9	131,3	133,8	122,2	152,9	125,7	128,5	129,0	133,4
Z-(VIII)	MeO	H	167,9	131,8	131,2	162,5	126,6	134,7	114,6	162,3	126,0	128,2	128,9	133,0
E-(VIII)	MeO	H	165,1	140,3	132,5	160,6	126,3	134,5	114,7	162,0	126,3	127,9	129,0	132,6
Z-(IX)	MeCOO	MeO	167,3	130,8	133,4	163,7	132,5	115,6[d] 126,2	123,2 151,5[e]	142,5	125,7	128,3	129,1	133,3
Z-(X)[g]	HO	MeO	167,4	132,2	130,8	162,4	126,4	115,1[d] 128,4	115,7 150,7[e]	148,0	126,3	128,0	129,3	133,3
E-(X)[g]	HO	MeO	165,3	141,2	131,7	159,8	126,0	114,7 128,8	115,5 151,0	147,7	126,5	127,6	129,3	132,7

a) In $CDCl_3$, 0.4-0.7 mole/liter.
b) For acetate groups, δ CH_3 21.1 [Z-(II), Z-(VII)], 20.6 [Z-(IV), Z-(V), Z-(IX)], δC=O 168.9 [Z-(II)], 168.7 [Z-(IV), Z-(V)], 168.8 [Z-(VII)], 168.5 [Z-(IX)]; δCH_3O 55.4 [Z-(II), Z-(VIII)], 56.0 [Z-(IV), Z-(V), Z-(IX)], 55.6 [E-(VIII), Z-(X)], 55.7 [E-(X)].
c) δCH_3 15.5-15.7.
d) In position 2, relative to R^2.
e) In position 1, relative to R^2.
f) Assignments in parentheses uncertain.
g) In $(CD_3)_2CO$, 0.45 mole/liter.

TABLE 2. ^{13}C NMR Monoresonance Spectral Data for Azlactones

(I)-(X) 

Carbon atom	Form of spectrum	$J_{C,H}$, Hz or line width b_0, Hz
C=O	Doublet	$^3J_{vic}$ (=CH)=5,5 (Z isomers) 12,5 (E isomers)
CH=[c]	Doublet of triplets	^1J=152–157b, ^3J=5,0
C= E-(VIII), E-(X)	Doublet	^2J=5,0
(in remaining cases)[c]	Singlet	b_0~2,0
C=N (R³=CH₃)	Quadruplet	^2J=8,5
(R³=Ph)d	Triplet	^3J=5,0
1 (R²=H)e	»	^3J=8,0
(R²≠H)	Doublet	^3J=8,0
ortho[e]	Doublet of triplets	^1J=160–164, ^3J(o-H, =CH)= =6,5–7,5
meta (R²=H)[e]	Doublet of doublets	^1J=161–165, ^3J=5,0
(in position 3 rel. to R² ≠ H)	Doublet	^1J=161–163
(in position 1 rel. to R² ≠ H)	Multiplet	b_0 f 15–25
para E-(VI)	Doublet of triplets	^1J=163, ^3J=8,0
(in remaining cases)[e]	Multiplet	b_0f ~15–30
C=O (CH₃COO)	Quadruplet	^2J=7,0
CH₃ (CH₃COO)	»	^1J=130
CH₃O	»	^1J=144
CH₃ (R³)	»	^1J=131
Phg (R³) para	Doublet of triplets	^1J=161, ^3J=7,5

a) Protons interacting with carbon indicated in brackets.
b) ^{1}JZ-(VIII) — ^{1}JE-(VIII) = 155 — 152.5 = 2.5. ^{1}JZ-(X) — ^{1}JE-(X) = 156 — 153 = 3.
c) Exact form of spectrum and J not determined in (I) and (VI) due to overlapping lines.
d) Observed as multiplet with $b_0 \sim 7$ Hz in (VI), (VII), (X), due to low signal—noise ratio.
e) Exact form of spectrum and J not determined for C^1 in (VI), for o-, m-, p-C in (I) and (VI), due to overlapping lines and to deviation of spectra of these carbons from first order.
f) Not determined accurately due to low signal—noise ratio.
g) For p-C in (VI), for 1, o-, m-C in all compounds, see footnote e.

The Z configurations of Z-(XI) and the E configuration of E-(XI), obtained by alkaline hydrolysis of Z-(VI) and E-(VI) respectively, were determined analogously. The ^{13}C NMR data for Z-(XI) and E-(XI) are shown in Table 3. The $^3J_{COOH;H^\beta}$ values are 5 Hz for Z-(XI) and 10 Hz for E-(XI). The COOH signals are doublets, at 166.3 ppm for Z-(XI) in CD_3OD, and at 164.6 ppm for E-(XI) in $(CD_3)_2SO$. The neighboring NC=O signals are triplets due to interaction through three carbon bonds with the two phenyl o-protons. The $^3J_{COOH;H^\beta}$ values for Z-(XI) in $(CD_3)_2SO$ and E-(XI) in CD_3OD were not determined due to overlapping of the COOH

TABLE 3. Chemical Shifts and Spin—Spin Coupling Constants in ^{13}C NMR Spectrum of $PhCH{=}C(COOH)NHCOPh$ (XI)

Isomer	Solvent	δ, ppm			
		C=O	NC=O	CH=	=C, Ph
Z	CD_3OD	166,3 d $^3J_{COOH,H^\beta}$=5	167,8 t ^3J=3	134,5 d,t ^1J=157, ^3J=5 [a]	126,8; 127,7, 128,7; 128,9, 131,2, 133,2
E	$(CD_3)_2SO$	166,3 d $^3J_{COOH,H^\beta}$=10	163,9 t ^3J=3	120,3, 126,1, 126,4, 127,0, 127,1, 127,2, 128,9, 130,7, 132,1, 133,3	

a) Interaction with two o-protons of phenyl ring.

TABLE 4. Chemical Shifts of ^1H of Unsaturated Azlactones (I)-(X) (δ, ppm)

Compound	R^1	R^2	=CH[b]	o-C	m-C	p-	R^1	R^2	R^3[d]
				R^3=Me					
Z-(I)	H	H	7,02	7,13		8,07			2,27
Z-(II)	MeCOO	H	6,98	7,98	7,05	–	2,22	–	2,30
Z-(III)	MeO	H	6,97	7,93	6,82	–	–	3,88	2,27
Z-(IV)	MeCOO	MeO	6,95	7,41 7,80[e]	6,98	–	2,22	3,75	2,28
Z-(V)	MeO	MeCOO	6,92	7,70 7,88	6,88	–	2,23	3,77	2,28
				R^3=Ph					
Z-(VI)	H	H	7,10	7,17	–	8,20	–	–	7,17–8,20
E-(VI)	H	H	7,43	7,23	–	8,33	–	–	7,23–8,33
Z-(VII)	MeCOO	H	7,07	8,08	7,10	–	2,27	–	7,27–8,13
Z-(VIII)	MeO	H	7,07	8,03	6,87	–	–	3,77	7,23–8,05
E-(VIII)	MeO	H	7,43	8,13	6,89	–	–	3,78	7,33–8,08
Z-(IX)	MeCOO	MeO	7,05	7,47 8,00[e]	6,98	–	2,23	3,83	7,33–8,10
Z-(X)	HO	MeO	7,05	7,27 8,48	6,88	–	–	3,90	7,27–8,48
E-(X)	HO	MeO	7,45	7,28 8,48	6,87	–	–	3,90	7,28–8,48

a) In $CDCl_3$, 0.25 mole/liter.
b) In Z-(VI), E-(VI), Z-(VII), Z-(VIII), and Z-(IX), the assignment was confirmed by spectra at 200 MHz.
c) Assignment was made by calculating the known effect of R^1 and R^2 in monosubstituted benzenes on CS of ^1H, o, m, and p to these substituents. In Z-(II) to Z-(V), Z-(VII) to Z-(X), E-(VIII) to E-(X), $J_{H,H}(o) = 8.7$ Hz. In Z-(IV), Z-(V), Z-(IX), $J_{H,H}(m) = 1.8$-2.1 Hz.
d) In Z-(I) to Z-(V) the CH_3 lines are a doublet, J = 0.5 Hz, due to interaction of CH_3 and H^β (see text).
e) Proton in position 2 relative to R^2.

and NC=O lines. The data for Z-(VI), E-(VI), Z-(XI), and E-(XI) confirm the assumption of a uniform configuration for the olefin bond of unsaturated azlactones and their solvolysis products [3].

The CS of the olefinic C^β is 130.3-132.3 and 140.1-141.2 ppm in Z and E isomers, respectively. The spectrum of this carbon atom under monoresonance conditions, a doublet of triplets, and the values $^1J_{C,H} = 152$-157 and $^3J_{C,H} = 5$ Hz permit its signal to be distinguished from those of the neighboring benzene-ring carbons and the quaternary olefinic carbon. Thus the Z,E configuration of unsaturated azlactones can be identified from the C^β CS. An important factor in making the assignment is the number of resonance signals in the 135-151 ppm region. From the data in Table 1 it follows that when $R^2 = H$, the Z isomers have no resonance signals in this region, and the E isomers have one signal (due to C^β). When $R^2 \neq H$, the Z isomers have one signal in this region, which belongs to the phenyl carbon in position 1 relative to R^1, with CS values of 140.1 Z-(V), 142.3 Z-(IV), 142.5 Z-(IX), and 148.0 ppm Z-(X); the E isomers have two signals, one of which (at 147.7 ppm) also belongs to this same carbon, while the other (142.2 ppm) is C^β.

From the data for the PMR spectra of unsaturated azlactones (Table 4), it follows that the CS of H^β is characteristic for both isomers. In the Z isomers the values are 6.92-7.02 ppm (R^3 = Me) and 7.05-7.10 ppm (R^3 = Ph); in the E isomers they are 7.43-7.45 ppm (R^5 = Ph). The width of the H^β line is 2-2.5 Hz. The broadening appears to be due to allyl interaction of H^β with the o protons of the phenyl, while in Z-(I) to Z-(V) there is also a remote interaction with the protons of R^3 = Me, as showed by the dual resonance of $^1H-\{^1H\}$.

It is interesting to observe that in the unsaturated azlactones, on going from Z to E isomers, the CS of the C=O of the azlactone ring moves 2-3 ppm toward the strong field, while that of C^β moves ∿10 ppm toward the weak field (see Table 1). This change may be caused by an increase in the effective conjugation of the C=O group and the olefin bond in the E isomer [13]. It may also be assumed that more effective conjugation increases the

TABLE 5. Physical Properties of 2-Phenyl(methyl)-4-arylidene-Δ^2-oxazolin-5-ones

Compound	mp, °C	UV spectrum in dioxane λ_{max}, nm (ε)	IR spectrum in $CHCl_3$ ν, cm^{-1}
Z-(I)	150 (acetone)	330 (23 400)	1810, 1780, 1660, 900, 875
Z-(II)	135–137 (alcohol)	338 (27 700) *	1805, 1770, 1660, 900, 880
Z-(III)	110–111 (alcohol)	320 (13 700), 362 (23 300)	1790, 1770, 1660, 905, 880, 830
Z-(IV)	149–151 (benzene)	320 sh (17 750), 333 (21 000), 417 sh, (540) *	1800, 1765, 1660, 900, 810, 650, 630
Z-(V)	156–158 (benzene)	–	1805, 1770, 1665, 910, 880, 830, 630 sh
Z-(VI)	165–166 (alcohol)	242 (12 700), 250 (14 200), 260 (14 400), 350 (26 000), 365 (34 000), 386 (22 800)	1780, 1760, 1660, 980, 880, 860, 560
E-(VI)	146–147 (alcohol)	226 (15 300), 239 (15 300), 246 (13 500), 340 sh (40 300), 360 (47 500), 380 sh (33 500)	1780, 1760, 1650, 1000, 880, 640
Z-(VII)	174–176 (alcohol)	246 (19 200), 253 (20 100), 260 (19 200), 263 (18 200), 353 (42 000), 370 (55 000), 390 (37 000)	1790, 1760, 1655, 985, 915, 885, 860, 700, 690, 600, 560
Z-(VIII)	157–159 (alcohol)	251 (20 600), 261 (21 400), 278 sh (15 400), 365 sh (48 000), 402 sh (38 400)	1780, 1760, 1650, 980, 880, 860, 700, 560, 540, 520, 510
E-(VIII)	149–151 (benzene)	228 sh (14 500), 239 sh (15 400), 243 sh (16 500), 250 (17 100), 253 (16 100), 261 (13 900), 278 (7 300), 390 (38 800)	1780, 1760, 1640, 1000, 890, 700, 600
Z-(IX)	194–195 (alcohol)	223 (15 500), 263 (17 600), 361 (26 600), 380 (38 300), 395 (30 600)	1785, 1760, 1650, 990, 910, 890, 865, 700, 690, 625, 530
Z-(X)	154–155 (alcohol)	257 sh (13 700), 266 (15 300), 280 (9200), 400 (28 800), 417 sh (26 800)	1780, 1760, 1650, 980, 880, 860, 700, 630, 560
E-(X)	124–126 (alcohol)	240 (13 400), 263 (10 000), 280 (5800), 420 (34 000)	1780, 1755, 1645, 1010, 890, 700, 610, 570

*Spectrum obtained in $CHCl_3$.
†Spectrum obtained in KBr tablet

positive charge in C^{β}. This assumption agrees with the data of [14], which show that the Grignard reagent forms 1,2-adducts with Z-(VI), but 1,4-adducts with E-(VI) (the Z,E assignment given in [14] must be reversed).

EXPERIMENTAL

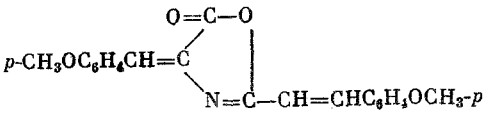
^{13}C spectra were obtained under impulse conditions on a Bruker WP-60 spectrometer with a working frequency of 15.08 MHz for ^{13}C nuclei. A ^{13}C spectrum with full quenching of spin–spin coupling with protons and a monoresonance spectrum were obtained for each compound. To increase sensitivity in the latter case we used the technique [15] of excluding and including the H_2 field before and after, respectively, obtaining the free induction signal (FIS) data. The impulse exciting FIS was 50 W. FIS accumulation under dual resonance conditions was carried out $(3\text{–}5)\cdot10^3$ times with 4-deg pulses of 0.5-μsec duration and pauses of 1 sec, while under monoresonance conditions it was $(10\text{–}13)\cdot10^3$ times with 45-deg pulses of 5.5-μsec duration and 5-sec pauses. The memory capacity of the computer recording FIS was 8K. The observable frequency range was 3750 Hz. Consequently, a resolution of ∿1 Hz per memory cell was obtained. The internal diameter of the ampuls was 10 mm.

PMR spectra were obtained on the same spectrometer with a 90-deg pulse of 3-μsec duration. The computer memory capacity was 8K, observed range was 750 Hz, resolution was 0.2 Hz per memory cell. In some cases additional PMR spectra were obtained on the Bruker WP-200 spectrometer (200 MHz). In both cases the internal diameter of the ampuls was 5 mm.

The concentration of the compounds was 0.45 mole/liter. To increase solubility the samples were thermostated at 35–45°C. Resonance conditions were stabilized by means of the ^2H signal of the solvent. TMS was the internal standard in all cases. The ^{13}C and ^1H chemical shifts are shown on a δ scale.

The Z-azlactones (I)-(IX) were prepared by Erlenmeyer condensation of the respective aldehydes with aceturic or hippuric acid in the presence of acetic anhydride and sodium acetate [16]. Azlactone Z-(X) was obtained by isomerization of E-(X). To a solution of E-(X) in $CHCl_3$ was added 1 drop of pyridine, the solution was evaporated for 1 h until crystallization began, and the precipitate was separated and crystallized from absolute alcohol. E-azlactones (VIII) and (X) were obtained according to [17] by condensation of anisaldehyde and vanillin with hippuric acid in the presence of polyphosphoric acid (PPA). E-(X) is completely converted to Z-(X) upon standing for several months. Azlactone E-(VI) was obtained according to [18] by isomerization of Z-(VI) with HBr. The melting point and UV and IR spectra of the azlactones are shown in Table 5. Attempts to obtain the pure E isomer of VI and the azlactone with $R^1 = OH$, $R^2 = H$, $R^3 = Ph$ according to [17] yielded a mixture of isomers which could not be separated by crystallization.

Condensation of benzaldehyde and anisaldehyde with aceturic acid in the presence of PPA according to [17], in order to obtain the E isomers of (I) and (III) yielded a resinous product that did not contain an azlactone ring. When the amount of PPA was cut in half, condensation of anisaldehyde yielded 2-p-methoxystyryl-4-p-methoxybenzylideneoxazolone-5:



mp 188-189°C (from benzene); UV spectrum [dioxane, λ_{max}, nm (ε)]: 248 (10,500), 320 (12,400), 410 (36,000). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1780 (stretch. CO), 1655 (stretch. C=N), 1600 (arom.). PMR spectrum ($CDCl_3$, δ, ppm): 3.74 singlet (CH_3O), 3.81 singlet (CH_3O), 6.65 doublet, 7.75 doublet (CH=CH) ($J_{H,H} = 15.8$ Hz); 6.97 singlet (CH=C); 6.80 doublet, 6.82 doublet (m-arom.), 7.3 doublet, 8.0 doublet (o-arom.) ($Z_{H,H}$ 8.6 Hz). Found: C 71.4; H 4.90; N 3.74%. $C_{20}H_{17}NO_4$. Calculated: C 71.63; H 5.10; N 4.17%. E- and Z-benzamidocinnamic acids were obtained by alkaline hydrolysis of E-(VI) and Z-(VI), respectively [18]; E-(XI), mp 187-189°C; Z-(XI), mp 224-226°C.

CONCLUSIONS

1. Z,E Configurations of unsaturated azlactones and their solvolysis products were established by means of the vicinal spin–spin coupling constant, $J_{^{13}C,H}$, determined in the ^{13}C NMR spectra. Previously published assumptions of a uniform olefin-bond configuration in unsaturated azlactones and their solvolysis products were confirmed.

2. Z and E isomers were identified by the number of signals in the 135-151 ppm region of the ^{13}C NMR spectrum.

3. The chemical shift values of the H^{β} proton are characteristic of Z,E isomers of unsaturated azlactones.

4. Conjugation of the olefin and carbonyl bonds is assumed to be more effective in the E isomers of azlactones than in the Z isomers.

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MECHANISM OF THE Z,E ISOMERIZATION OF α-NITRO-β-PHENYLAMINOACRYLATE

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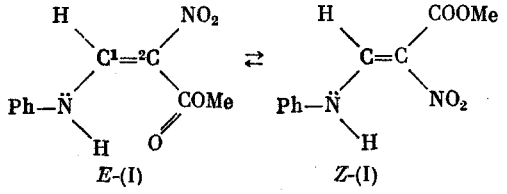
In the study of the kinetics of the Z,E isomerization of α-nitro-β-arylaminoacrylate esters it was shown that the Z,E conversion proceeds in inert solvents by a thermal rotation around the C=C bond [2], but in solvating media through a kinetically controlled ionization of the N—H bond [3]. The present work is a study of the Z,E isomerization of the nitroeneamine (I) in pyridine—CH_2Cl_2 mixtures, in order to determine whether the solvating medium participates in the isomerization.



In the PMR spectra of (I) in C_5D_5N:CH_2Cl_2, separate signals for all the groups of the Z and E isomers are observed [1, 3]. X-ray diffraction investigations [4] and ^{15}N NMR spectra of the related eneaminoketones [5] give evidence of a high degree of delocalization of the N electron pair, which ought to restrict rotation around the C^1—N bond [6]. However, spectral manifestation of such rotamers of (I) by splitting of the NH and CH signals has not been detected even when the sample is cooled to −85°C. There are three possible explanations: 1) there is little difference between the chemical shifts of the rotamers; 2) there is a high rate of rotation around the C^1—N bond on the PMR time scale; 3) one of the rotamers is thermodynamically more stable. To elucidate this problem we studied the PMR spectra in C_5D_5N of the α-nitro-β-aminoacrylate ester (II), which satisfied the requirements for Z,E isomers (Table 1).

TABLE 1. Parameters of Weak-Field Portion of PMR Spectra of Nitroeneamine (II) in C_5D_5N (δ, ppm relative to HMDS)

T., °C	δCH		δNH²		δNH¹	
	E	Z	E	Z	E*	Z
−30	8,96	8,33	9,49	10,44	10,5÷10,9	11,02
−40	8,99	8,35	9,56	10,51		11,10
−50	9,02	8,38	9,64	10,61		11,19
−60	9,07	8,39	9,74	10,74		11,24

*The NH^1 signal of the E isomer is close to the NH^2 signal of the Z isomer; this hinders the exact determination of its chemical shift due to the low E-isomer content; Z/E = 2 at −60°C.

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