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UV Spectra and Structure of 2-Diethylamino-3-phenylpropenal: Enamine or Enal?

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Abstract—According to the data of UV, IR, ^{1}H and ^{13}NMR spectra and also quantum-chemical calculations (B3LYP/631G*), *Z*- and *E*-isomers of 2-diethylamino-3-phenylpropenal in inert environment exist as antiperiplanar conformers. The energy of electron transitions therein depends on the orientation both f the benzene ring and the unshared electron pair of the nitrogen with respect to the C=C bond. 2-Diethylamino-3-phenylpropenal is an enamine, but the extent of the $p\pi^*$ interaction in its prevailing *Z*-isomer is small.

Capto-dative carbonyl-containing aminoalkenes attract attention because the chemical activity of this class compounds is nontypical both for common enamines and enals and reflects the specific features of the reciprocal location of electron-withdrawing and donor groups [1]. The specific structure of these molecules affects their reactions both with electrophilic and nucleophilic reagents. For instance, the presence of an electron-withdrawing group is one of the causes of the regiospecific N-protonation of *gem*-formyl(amino)alkenes and of the abnormal stability of their enammonium salts [2–4]. Unlike that, in reactions with nucleophilic reagents the main role in the transformations of the capto-dative aminoalkenes belongs to the electron-donor N,N-disubstituted amino group [5–8].

The specific features in reactivity of the compounds under consideration cannot be interpreted without a detailed analysis of their stereoelectronic structure for the unusual properties of the capto-dative carbonyl-containing aminoalkenes may depend on the special character of p,π and π,π-interactions of the substituents with the multiple carbon–carbon bond.

Investigations of a wide range of enamines with the use of photoelectron spectroscopy, X-ray structural analysis, and quantum-chemical calculations [9–11] revealed that the extent of overlapping of p and π orbitals of these compounds can be described by the angle (θ) between the bisector plane of the N,N-disubstituted amino group and a normal to the symmetry plane of the π-system. The magnitude of the angle significantly depends on steric factors from the substituents attached to nitrogen and double bond carbons. In this connection the study of the o,π-interaction in the capto-dative carbonyl-containing aminoalkenes, of relation between the efficiency of the interaction and the spatial structure of the molecule is necessary not only for interpretation of their specific reactivity, but also for solution of classification problems regarding these compounds.

In the present study the stereoelectronic structure of one representative of the mentioned compounds, 2-diethylamino-3-phenylpropenal, PhCH=C(NEt$_2$)CHO (**I**), was investigated with the help of UV, IR, ^{1}H and ^{13}NMR spectra and also quantum-chemical calculations. As model compound was chosen cinnamaldehyde PhCH=CHCHO (**II**). The analysis of enones UV spectra with the use of quantum-chemical calculations revealed the fairly high sensitivity of the energy of $\pi–\pi$-transitions to the spatial orientation of separate groups and to substitution effects [12]. The structure of aminoenal **I** containing simultaneously a heteroatom, a multiple bond, and a carbonyl group suggests that the characteristics of the electronic absorption bands in its UV spectrum would be affected by the same factors.

UV spectra of compound **I** in hexane and acetonitrile are similar to the spectra of cinnamaldehyde (**II**) recorded in the same solvents (Fig. 1). This similarity is very favorable for in analyzing the character of electronic transitions in the UV spectrum of compound **I** it will be possible to use as a model a simpler molecular system.

According to the data of NMR and IR spectra 3-phenylpropenal (**II**) exists in solutions as *E*-isomer
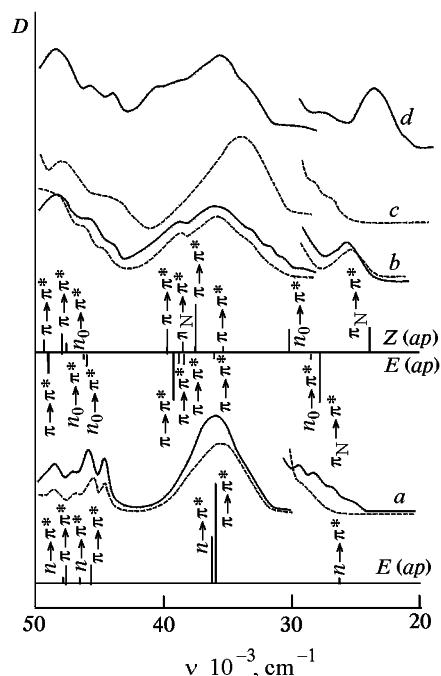
Fig. 1. UV spectra of cinnamaldehyde (**II**), (*a*) aminoenal **I**, (*b*) trifluoromethanesulfonate **IV**, (*c*) and aminoenal **III**, (*d*), solutions in hexane: continuous line, in CH$_3$CN: broken line. Calculated (B3LYP/6-31G*) spectra of *Z*-and *E*-isomers of compounds **I, II** are shown by vertical lines. Relative intensities of forbidden transitions are shown arbitrary.
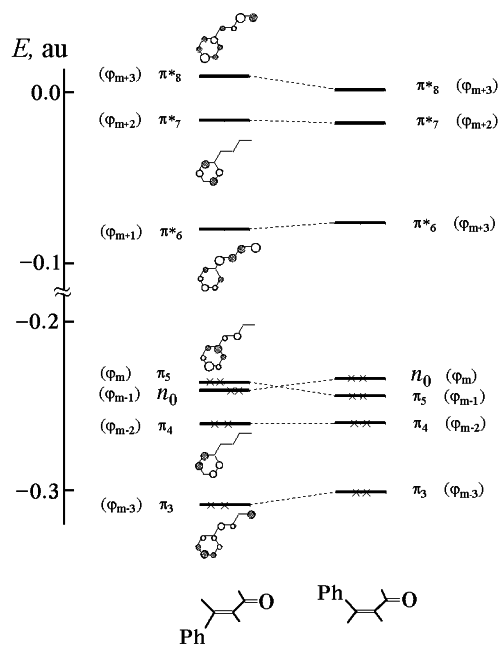

Fig. 2. Correlation of molecular orbitals in *E*- and *Z*-isomers of cinnamaldehyde **II**. The calculations were performed by the method B3LYP/6-31G*.

with antiperiplanar (*ap*) position of C=C and C=O bonds [13, 14]. Our nonempirical calculations (B3LYP/6-31G*) manifested that the residence of *E*-isomer of this compound in *ap*-form is energetically more favorable by 1.1 kcal mol^{-1} as compared to the corresponding *sp*-form. The *Z*-isomer is also more stable in *ap*-form. The energy gap between the states of *ap*-rotamers belonging to *E*- and *Z*-isomers amounts to 4.7 kcal mol^{-1}. This is in qualitative agreement with the experimental data and is apparently due to the noncoplanar structure of the *Z*-isomer molecule.
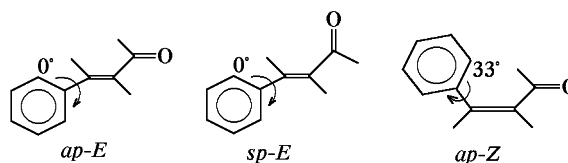
Characteristics of electronic transitions in the *E*- and *Z*-isomers of compounds **I, II** calculated by the method of density functional (B3LYP/6-31G*) within the framework of formalism of configurational interactions are presented in Tables 1, 2. The assignment of these transitions to the observed electronic absorption bands for the *E*-isomer of cinnamaldehyde (**II**) is shown on Fig. 1. The most long-wave weak absorption band in the UV spectrum of this compound is due to $n_0 \to \pi^*$ transition. The maximum of its $0 \to 0$ vibronic component in the spectrum taken in hexane is located at 25000 cm^{-1}. The fine structure of the band corresponds to vibrational interval of ~1400 cm^{-1} in keeping with the frequency of stretching vibrations of a carbonyl group weakened in the excited $n\pi^*$ state.

As an empirical confirmation of the above assignment serves the blue shift of the long-wave absorption band at recording the spectrum not in hexane but in more polar acetonitrile accompanied also with almost total smoothing of band's fine structure (Fig. 1). Alongside the low intensity the latter fact is the second indispensable indication of the $n_0 \to \pi^*$-transition [15]. The next transition with an oscillator of high force is associated with a $\pi \to \pi^*$-transition. According to calculations this transition is multielectronic and its wavenumber equals 35920 cm^{-1}. Its electronic nature is connected primarily with the presence of a configuration whose local excitation is accompanied by electron density transmission from the styrene fragment of the molecule to its carbonyl group (see Table 1 and the orbital diagram on Fig. 2). In the UV spectrum of aldehyde **II** in hexane to this transition corresponds the most strong absorption band with ν_{max} 36000 cm^{-1}. Fairly close on the energy scale to the transition with electron density

transfer ($\Delta\nu$ 280 cm^{-1}) is located the perturbed "benzene" transition forbidden due to overlap. Its elevated intensity in the spectrum of the E-isomer is caused by mixing of two locally excited configurations where one among these is a configuration with electron density transfer. In the observed UV spectrum of compound **II** the corresponding band is screened by a strong neighboring band. Further according to calculations follow two similar in energy forbidden $n_0 \to \pi^*$-transitions and two $\pi \to \pi^*$-transitions (Table 1). Only the latter two are worth consideration because of different probability of these transitions. In the third $\pi \to \pi^*$-transition an electron density transmission occurs from the double bond to the benzene ring (Table 1, Fig. 2). The fourth $\pi \to \pi^*$-transition results in an overall excitation of the molecule. These transitions in the E-isomer are divided by a considerable energy gap (~2100 cm^{-1}).

The sequence of the similar electronic transitions in E- and Z-isomers of compound **II** nearly coincides (Table 1). The only distinction of the Z-isomer is an inversion on the energy scale of the third and the fourth electronic $\pi \to \pi^*$-transitions and reduction of the gap between them to 200 cm^{-1}. Thus the E- and Z-isomers can be distinguished by the analysis of the short-wave group of absorption bands. The main indication that in solution of compound **II** is present predominantly ap-conformer of the E-isomer is the appearance of two absorption bands in the region 44000–49000 cm^{-1}. In the real spectrum the most long-wave of these bands has a fine structure with the distance between the vibronic components of ~1250 cm^{-1}. This vibrational interval corresponds to the stretching vibrations of the double carbon–carbon bond weakened in the excited $\pi\pi^*$ state due to transfer of its electron density to the benzene ring as was predicted by calculations for the third $\pi \to \pi^*$-transition in the E-isomer.

It was previously concluded from the ^{1}H and ^{13}C NMR data that the capto-dative formyl(amino)-alkenes (among them compound **I**) in CDCl$_3$ solution existed as a rule as mixtures of E- and Z-isomers [16]. Here prevails the Z-isomer (for aminoalkene **I** the ratio $Z:E = 85:15$). Like in the spectra of unsubstituted enamines [17] the olefin proton signal and the proton of formyl group in the E-isomer of capto-dative aminoalkenes always appears in a stronger field (6.61, 9.32 and 6.71, 9.48 ppm respectively). We demonstrated that in the ^{13}C NMR spectra the following pattern of signals appearance was observed: in E-isomer, =CH 131.05, =C–N 149.11, C=O 190.65 ppm; in Z-isomer, =CH 140.11, =C–N

146.58, C=O 194.74 ppm. The shielding of carbon atoms in the phenyl ring and in diethylamino group is rather sensitive to the reciprocal position of the substituents: in E-isomer, C$_1$ 135.80, C$_{2,6}$ 129.51, C$_{3,5}$ 128.34, C$_4$ 128.87, CH$_2$ 44.01 ppm; in Z-isomer, C$_1$ 135.20, C$_{2,6}$ 130.04, C$_{3,5}$ 128.42, C$_4$ 129.37, CH$_2$ 45.69, CH$_3$ 13.64 ppm.

ap-Z   *ap-E*
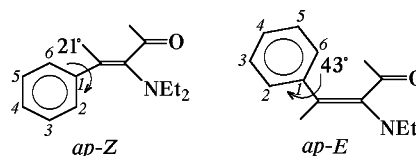
In the E-isomer of compound **I** all carbons save those in the =C–N group and in the ipso-position of the phenyl ring are more shielded than the corresponding carbons of the Z-isomer. Besides in the former the shielding of atoms C$_{2,6}$, C$_{3,5}$, and C$_4$ is close to that observed in unsubstituted benzene (128.5 ppm). This fact reveals unequal efficiency of the π-electron interactions in the styryl moieties of the E- and Z-isomers.

In the IR spectra of compound **I** recorded in mulls in mineral oil, KBr pellets, and solutions in CCl$_4$, CHCl$_3$ appeared a strong band of formyl group stretching vibrations at 1680–1690 cm^{-1}, and a weak band of the stretching vibrations in the olefin fragment (1605–1620 cm^{-1}). As in the case of aldehyde **II** [14] these data evidence the antiperiplanar position of the C=C and C=O bonds in the molecules of compound **I** both in solid state and in inert solvent.

Thus the spectral data obtained clearly show that both isomers of aminoenal **I** in the inert environment are present in the ap-form.

According to the ab initio calculations (B3LYP/6-31G*) the ap-conformer of the Z-isomer of compound **I** in the isolated state is more preferable by 1.8 kcal mol^{-1} than the respective conformer of the E-isomer. In both isomers the oxygen and nitrogen atoms and the C=C bond are located in almost the same plane. The angle (η) of benzene ring deviation from this plane in the E-isomer is equal to 43°. This value in agreement with the NMR data is significantly larger than that for the Z-isomer (21°). The carbon atoms of the methylene groups in both isomers of molecule **I** have essentially different orientation with respect to the plane where the multiple bonds are
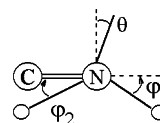
Table 1. Calculated and experimental UV spectrum of cinnamaldehyde (**II**)

Electronic transition	ν, cm⁻¹	f	Principal configuration	ν, cm⁻¹	f	Principal configuration	ν_{max}, cm⁻¹ in experiment[a]
			E-isomer			*Z*-isomer	
$n \to \pi^*$	26950	0.00	$0.67\Psi^{m+1}_{m-1}$	26500	0.01	$0.51\Psi^{m+1}_{m}$; $0.42\Psi^{m+1}_{m-1}$	25000 (ν^{0-0})
$\pi \to \pi^*$	35920	0.48	$0.53\Psi^{m+1}_{m}$; $0.33\Psi^{m+1}_{m-2}$	35860	0.35	$0.49\Psi^{m+1}_{m-1}$; $0.38\Psi^{m+1}_{m}$	36000
$\pi \to \pi^*$	36200	0.22	$0.55\Psi^{m+1}_{m-2}$; $0.30\Psi^{m+1}_{m}$	36400	0.02	$0.65\Psi^{m+1}_{m-2}$	
$\pi \to \pi^*$	45600	0.07	$0.58\Psi^{m+2}_{m}$	46740	0.05	$0.60\Psi^{m+2}_{m-1}$	44600
$n \to \pi^*$	46400	0.00	$0.56\Psi^{m+2}_{m-1}$; $0.38\Psi^{m+3}_{m-1}$	44610	0.00	$0.56\Psi^{m+3}_{m}$	
$\pi \to \pi^*$	47650	0.07	$0.54\Psi^{m+1}_{m-3}$; $0.42\Psi^{m+3}_{m}$	46520	0.10	$0.46\Psi^{m+1}_{m-3}$; $0.42\Psi^{m+3}_{m-1}$	48600
$n \to \pi^*$	47690	0.00	$0.42\Psi^{m+2}_{m-1}$; $0.39\Psi^{m+3}_{m-1}$	44120	0.02	$0.60\Psi^{m+2}_{m}$	

a Solution in hexane.

Table 2. Theoretical and Experimental UV spectrum of enaminoketone (**I**)

Electronic transition	ν, cm⁻¹	f	Principal configuration	ν, cm⁻¹	f	Principal configuration	ν_{max}, cm⁻¹ in experiment[a]
			E-isomer			*Z*-isomer	
$\pi_N \to \pi^*$	23920	0.15	$0.60\Psi^{m+1}_{m}$	27690	0.24	$0.63\Psi^{m+1}_{m}$	25600
$n_0 \to \pi^*$	30220	0.10	$0.50\Psi^{m+1}_{m-1}$; $0.39\Psi^{m+1}_{m-3}$	28750	0.00	$0.62\Psi^{m+1}_{m-1}$	29500 (ν^{0-0})
$\pi \to \pi^*$	34750	0.00	$0.55\Psi^{m+2}_{m}$; $0.44\Psi^{m+1}_{m-2}$	36220	0.00	$0.51\Psi^{m+2}_{m}$; $0.44\Psi^{m+1}_{m-2}$	
$\pi \to \pi^*$	37550	0.22	$0.49\Psi^{m+1}_{m-3}$; $0.35\Psi^{m+1}_{m-1}$	39240	0.20	$0.43\Psi^{m+3}_{m}$; $0.43\Psi^{m+1}_{m-3}$	35900
$\pi_N \to \pi^*$	37880	0.04	$0.49\Psi^{m+1}_{m-2}$; $0.41\Psi^{m+2}_{m}$	38720	0.02	$0.39\Psi^{m+1}_{m-2}$; $0.38\Psi^{m+2}_{m}$	
$\pi \to \pi^*$	39660	0.12	$0.62\Psi^{m+3}_{m}$	37830	0.02	$0.39\Psi^{m+3}_{m}$; $0.38\Psi^{m+1}_{m-3}$	38800
$n_0 \to \pi^*$	47430	0.02	$0.57\Psi^{m+2}_{m-1}$	45740	0.02	$0.43\Psi^{m+2}_{m-1}$; $0.38\Psi^{m+3}_{m-1}$	
$\pi \to \pi^*$	47810	0.06	$0.49\Psi^{m+1}_{m-4}$; $0.36\Psi^{m+3}_{m-1}$	49050	0.07	$0.54\Psi^{m+1}_{m-4}$	44300
$\pi \to \pi^*$	49490	0.04	$0.45\Psi^{m+3}_{m-1}$; $0.33\Psi^{m+1}_{m-4}$ $0.25\Psi^{m+3}_{m-3}$; $0.20\Psi^{m+1}_{m-2}$	46150[b]	0.00	$0.50\Psi^{m+3}_{m-1}$; $0.39\Psi^{m+2}_{m-1}$	48300

a Solution in hexane. b $n_0 \to \pi$-transition.

located. The torsion angles (φ) corresponding to this orientation are φ_1 8 and 55, φ_2 44 and 29 degrees for *E*- and *Z*-isomers respectively.

At the indicated position of the ethyl groups the angle θ characterizing the deviation of the bisector plane of the N,N-disubstituted amino group from the normal to the symmetry plane of the π-system equals for the *E*- and *Z*-isomers to 26 and 38 degrees respectively. The θ angle value obtained for the *Z*-isomer of compound **I** falls close to the upper limit of the range of the corresponding angle variation observed for a wide number of enamines (0–40°) [9]. This value is observed when the steric hindrances significantly reduce the overlap degree between the orbitals of unshared electron pairs and the double bond.

The involvement of NEt₂ group into conjugation with π-system of aminoenal **I** should have caused a strong blue shift of the electronic $\pi-\pi^*$-transition with electron density transfer as compared to that inherent to cinnamaldehyde (**II**), and a new absorption band would have appeared in the low energy region. For instance, in the spectra of *s-trans*-enones of general structure with R = NMe₂ the long-wave absorption band appears at ν_{max} 33500 cm⁻¹ whereas at R = H this band is observed at ν_{max} 44400 cm⁻¹ [12].

The calculations demonstrated that the transitions corresponding to the absorption bands in the UV spectrum of **I** are as a rule multielectronic. Their calculated energy and oscillator force are well consistent with the characteristics of the observed absorption bands (Table 2, Fig. 1).

The symmetry symbolism used in the treatment of cinnamaldehyde spectrum is a controversial procedure with respect to theoretical analysis of the UV spectra

of Z- and E-isomers of compound **I**. Their structure prevents a rigorous division of the molecular orbitals with respect to the symmetry into π-MO and σ-MO. Nonetheless we use this procedure for it provides clear understanding of the electronic nature of transitions under consideration. Therewith we imply that the molecular orbitals undergo transformations with respect to symmetry elements of a hypothetical form of the PhCH=CH–CH=O fragment where all heavy atoms are located in the same plane.

The first electronic transition in the spectrum of compound **I** corresponds formally to the $n_N \rightarrow \pi^*$ type. The calculated energy values thereof are essentially different for the geometrical isomers: 23920 and 27690 cm^{-1} for Z- and E-isomers respectively. The transition energy is affected by a number of factors. In particular, the difference in the angle θ values for isomers [38° (Z) and 26° (E)] that is a characteristics of overlap between unshared electron pairs orbitals and those of the double bond, suggests the opposite sequence of $n_N \rightarrow \pi^*$-transitions in the spectra of Z- and E-isomers. On the other hand, they should obviously be sensitive to the orientation of the aromatic substituent because in the excited $n\pi^*$ state the electron density redistribution occurs in the styrene moiety of the molecule. Actually, the energy of the transition in question varies in the order corresponding to the torsion angle ν. Consequently, according to this indication this may be classed as $\pi_N \rightarrow \pi^*$-transition. An additional proof of the above conclusion is the sufficiently high oscillator force (Table 2).

In the UV spectrum of enamine **I** taken in hexane to the $\pi_N \rightarrow \pi^*$-transition corresponds the absorption band with a maximum at 25600 cm^{-1}. Its distinctions from the long-wave absorption band in the spectrum of compound **II** ($n_N \rightarrow \pi^*$-transition) consist in higher relative intensity, lack of fine structure, and the presence of a little (but significant, $\Delta\nu$ 300 cm^{-1}) red (and not blue) shift in going from solution in hexane to that in acetonitrile (Fig. 1). This is an empirical evidence of the fact that the long-wave absorption band really belongs to the electronic $\pi_N \rightarrow \pi^*$-transition.

The second electronic transition in the spectrum of geometrical isomers of compound **I** corresponds to the $n_0 \rightarrow \pi^*$ type and is located according to calculations in the range 28000–31000 cm^{-1} (Table 2). We did not find in the experimental UV spectrum a separate absorption band corresponding to this transition. However on the long-wave side of a strong absorption band (ν_{max} 35900 cm^{-1}) whose nature will

be discussed further appears a fine structure with a 0–0 component at ~29500 cm^{-1}. The close energy value of the revealed $0 \rightarrow 0$ transition to the calculated one allows to attribute this weak absorption characterized by a fine structure as in the spectrum of compound **II** to the $n_0 \rightarrow \pi^*$-transitions in aminoenal **I**.

Then in the spectrum follows the forbidden with respect to overlap benzene transition in Z- and E-isomers of compound **I** with calculated energy values 34750 and 36220 cm^{-1} respectively.

The wavenumber calculated for the most intensive $\pi \rightarrow \pi^*$-transition in the spectrum of the Z-isomer of 2-diethylamino-3-phenylpropenal **I** equals 37550 cm$_{-1}$. This value is very close to the ν_{max} for the first $\pi \rightarrow \pi^*$-transition in the spectrum of Z- and E-isomers of cinnamaldehyde (**II**). The electronic nature of this transition as that in compound **II** is governed by the configuration whose local excitation occurs with transfer of the electron density to the carbonyl group. In the real spectrum this transition appears as an absorption band at 35900 cm^{-1} almost not displaced as compared to that in the spectrum of compound **II**. Taking into consideration the effect of amino group it may be concluded that also in solution the structure of the aminoenal **I** Z-isomer is not planar. The analogous transition in the E-isomer is shifted to the higher energy region (39240 cm^{-1}). The reason thereof as also for the long-wave absorption band of the $\pi \rightarrow \pi^*$ type lies in the stronger deviation of the π-system of the molecule from coplanarity. In the observed UV spectrum the corresponding band of this minor component is apparently screened by the bands of the Z-isomer.

The next $\pi \rightarrow \pi^*$-transition, more intensive in the Z-isomer (Z: ν_{max} 39660 cm^{-1}, f 0.12; E: ν_{max} 37830 cm^{-1}, f 0.02) causes the electron density redistribution mostly in the enamine moiety of the molecule. The corresponding absorption band has a maximum at 38800 cm^{-1}. This assignment is supported by the data on the UV spectrum of 2-[N-methyl(phenyl)-amino]-3-phenylpropenal PhCH=C(NMePh)CHO (**III**) (Fig 1). The registered absorption bands at 40500 and 38300 cm^{-1} in their energy correspond to the absorption bands in the UV spectra of aniline and styrene respectively [15] and appear due to electronic transitions occurring in the mentioned fragments of molecule **III**.

The calculations predict that alongside the $\pi \rightarrow \pi^*$-transitions in the same spectral region should be present a $\pi_N \rightarrow \pi^*$-transition of low intensity. The corresponding band is not observed experimentally since

it is concealed under the neighboring strong doublet absorption band. The next low-intensity $n_0 \rightarrow \pi^*$-transition also is not recorded.

High-energy electronic $\pi \rightarrow \pi^*$-transitions appear in the short-wave part of the spectrum as a system of two absorption bands (Fig. 1). Therewith the band with ν_{max} 48300 cm^{-1} is a single band, and the one located more to the long-wave region possesses a weakly resolved fine structure with $\nu_{0 \rightarrow 0}$ ~44300 cm^{-1}.

Thus the principal difference in the UV spectra of aminoenal **I** and cinnamaldehyde **II** is the presence in the former of an absorption band corresponding to the electronic $\pi_N \rightarrow \pi^*$-transition. This band is sensitive to the orientation of the aromatic substituent attached to the double bond, the feature characteristic of α,β-unsaturated carbonyl compounds [12]. A sufficiently high probability of this transition is possible only if an interaction exists of the unshared electron pair of the nitrogen and the π-system of the aminoenal **I** molecule. However this interaction is weak in both isomers. In case of $\pi_N \rightarrow \pi^*$-transitions the pπ^*-interaction does not compete with $\pi\pi^*$-interaction. As to the transitions with electron density transfer to the carbonyl group, this interaction compensates only the effects due to the noncoplanar structure of the π-system in the molecule. The pπ^*-interaction significantly affects only the electronic transition governing primarily the electron density redistribution in the enamine moiety of the molecule. For instance, the absorption band corresponding to this transition is observed in the UV spectra of compounds **I** and **III**, but lacks in the spectrum of the N-protonated form of **I** (Fig. 1). Overall pattern of the UV spectrum of enammonium salt **IV** prepared by reaction of **I** with trifluoromethanesulfonic acid is similar to the spectrum of the cinnamaldehyde. The above reasoning permits a conclusion, that 2-diethylamino-3-phenylpropenal **I** is still an enamine. But the extent of pπ^*-interaction in the prevailing *Z*-isomer of **I** is the smallest in the series of this type compounds. The variation of substituents at the double bond and nitrogen may result in situation when the compound would acquire qualities more characteristic of an enal.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra of compounds I–IV were registered on spectrometer Bruker DPX-400. IR spectra were recorded on spectrophotometer Specord 75IR, and UV spectra on Specord UV-Vis instrument.

Nonempirical calculations (B3LYP/6-31G*) of *Z*- and *E*-isomers of compounds **I** and **II** were carried out with full geometry optimization using software package GAUSSIAN-98 [20]. We are grateful to Professor V. A. Lopyrev who provided us a possibility to use the software.

Propenals **I** and **III** were prepared from chloro- or bromocinnamaldehyde and diethylamine or *N*-methylaniline respectively [18, 19].

2-Diethylamino-3-phenylpropenal trifluoromethylsulfonate (IV). To a solution of reagent **I** (0.47 g, 2 mmol) in anhydrous ether (30 ml) cooled to 0°C under conditions excluding moisture was added 0.3 g (2 mmol) of trifluoromethanesulfonic acid. The oily substance obtained crystallized at standing. The crystals formed were filtered off, rapidly washed on the filter with anhydrous ether, and dried in a vacuum desiccator over P$_2$O$_5$. ^{1}H NMR spectrum (CD$_3$CN): 1.22 t (6H, CH$_3$, *J* 7.1), 3.62 q (4H, NCH$_2$, *J* 7.1), 7.50–7.80 m (5H), 8.30 s (1H, CH=), 8.81 s (1H, NH), 9.86 s (1H, CHO). ^{13}C NMR spectrum (CD$_3$CN): 9.66 (CH$_3$), 54.24 (NCH$_2$), 129.40, 130.10, 131.11, 132.15 (Ph), 133.78 (=C–N), 145.95 (CH=), 186.18 (CH=O). IR spectrum (ν, cm^{-1}): 1632 (C=C), 1672 (C=O). Found, %: C 47.29; H 5.45; N 4.42; S 9.57. C$_{14}$H$_{18}$F$_3$NO$_4$S. Calculated, %: C 47.59; H 5.13; N 3.96; S 9.07.

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