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Electron transfer mediated geometrical photoisomerization of α,β-unsaturated ketones in the presence of electron donors in solution

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Abstract

The phototransformation of α,β-unsaturated ketones (**I**–**IV**) in the presence of electron donor triphenylamine in polar media has been investigated by using the chemically induced dynamic nuclear polarization (CIDNP) technique. For these compounds, it was demonstrated, that the electron transfer mechanism of isomerization results only in *cis*-isomers formation. Isomerization occurs in the triplet excited states of **I**–**IV** arising from back electron transfer in the triplet radical ion pairs of radical ions of ketone and triphenylamine. The set of isomers formed via this mechanism differs from phototransformation products observed after direct photolysis of these ketones in homogeneous and organized media.

Keywords: Unsaturated ketones; Isomerization; Electron transfer; CIDNP

1. Introduction

Phototransformations of α,β-unsaturated ketones, including geometrical photoisomerization, have been intensively studied during the last decade in both homogeneous solution and organized media [1–6]. It was demonstrated, in particular, that the set of isomers of ketones **I**–**IV** considerably differs for the cases of photolysis in homogeneous solution and in β-cyclodextrin (β-CD) inclusion complexes [1,2].

It was shown that the photolysis of ketones **I**–**IV** (see Scheme 1) in their *trans* configuration in homogeneous media mainly results in the formation of *cis*-isomers. On the other side, the photolysis of the inclusion complexes of ketones **I**–**IV** with β-cyclodextrin results in the formation of mono- and bi-cyclocompounds in addition to *cis*-isomers, as well as rearrangement products. The structures of these compounds depend on the structure of initial ketone [1,2]. Scheme 2 examplifies the structures of the phototransformation products of the β-CD inclusion complexes of ketone **I**.

The photolysis of the β-CD inclusion complexes of ketone **II** gives rise to a cyclocompound with a three-member ring, and that of ketone **IV** gives a bi-cyclocompound with four- and six-member rings. α-Ionone (**III**) does not form cyclocompounds. Its photolysis in homogeneous solution results in *cis*-isomer and retro-α-ionone. On the other hand, the photolysis of the β-CD inclusion complexes of ketone **III** provides only the rearrangement products of the 1,3 and 1,5 shifts of acyl group.

As the next step, it would be interesting to investigate the mechanism of phototransformation of α,β-unsaturated ketones in the presence of electron donors. The present work is devoted to the study of the role of the electron transfer (ET) mechanism of isomerization of ketones **I**–**IV**. For this purpose we have applied the chemically induced dynamic nuclear polarization (CIDNP) technique. Recently, the CIDNP method was used to study the role of paramagnetic species in the photoisomerization of some natural polyenes, namely, β-ionone [3–6] and all-*trans*-retinal [7] which have the structures close to those of the ketones under study.

2. Experimental

2.1. Chemicals

Ketones **I**–**IV** were a kind gift from the All-Unit R&D Institute of Synthetic and Natural Fragrances. Before usage, these ketones were purified by column chromatography. Triphenylamine (TPA) (Aldrich) was used as supplied. The commercial deuterated solvent, CD_3CN, (Isotop) was purified by distillation from P_2O_5. The solutions of ketones (10^{-2} to 10^{-1} M) in CD_3CN in the presence of the electron

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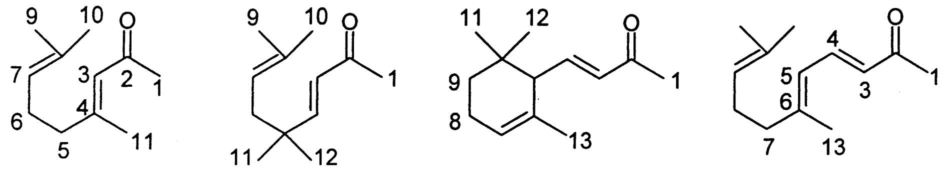
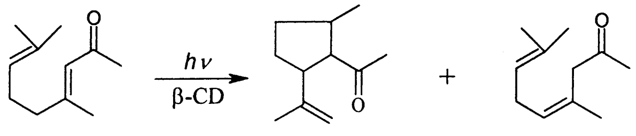


I II III IV

Scheme 1.



I V VI

Scheme 2.

donor (~10^{-2} M) were deaerated by Ar bubbling for 15 min.

2.2. NMR study

cis-Isomers were identified by analyzing their NMR spectra described in the previous studies [1,2].

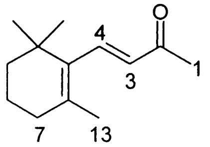
2.3. Photo-CIDNP

The samples in standard 5 mm pyrex NMR tubes were irradiated directly in the probe of NMR spectrometer at room temperature. An EMG 101 MSC Lambda Physik excimer laser was used as a light source ($\lambda = 308$ nm; 15 ns; 100 mJ). The photo-CIDNP spectra were detected using a DPX-200 Bruker NMR spectrometer (200 MHz ^{1}H operating frequency). Quasi steady state (QSS) CIDNP experiments were performed using the standard presaturation technique to suppress equilibrium signals: saturation—180° pulse—a number of laser pulses—evolution time—detection pulse—free induction decay. As the background NMR signals were suppressed in CIDNP spectrum, only signals of polarized products were detected.

The quantum chemical and ESR data from [8,9] were used to identify paramagnetic intermediates formed in these reactions.

3. Results and discussion

To investigate the ET mechanism of the *cis–trans* photoisomerization of α,β-unsaturated ketones, the appropriate electron donor was first chosen. As established in the previous study of ET processes involving β-ionone (**VII**), triphenylamine (TPA) is a convenient candidate for this role.



VII

Since β-ionone has the structure close to that of the ketones under study, we suggest that the E_{T}^{*} and $^{1/2}E_{\mathrm{red}}$ parameters are also similar for these compounds. The high extinction coefficient of TPA allows one to minimize the contribution of the direct isomerization of ketones. Besides, TPA, as an electron donor, satisfies the Weller-Zachariasse criterion for electron transfer [10]: ($\Delta G =^{1/2} E_{\mathrm{ox}}(\mathrm{donor}) -^{1/2} E_{\mathrm{red}}(\mathrm{acceptor}) - e^2/\varepsilon R - E_{\mathrm{S,T}}^{*}$). ET is possible if $\Delta G < 0$ ($^{1/2}E_{\mathrm{ox}}(\mathrm{TPA}) = 0.92$ V; E_T (TPA) $= 3.05$ eV [11,12]; $^{1/2}E_{\mathrm{red}}$(ketones) ~ -1.85 V*; and E_{T} (ketones) ~ 2.39 eV*, *—similarly to β-ionone [13,14]).

On the other hand, the back ET in the triplet radical ion pair (RIP) is possible if the energy of RIP, $\Delta H =^{1/2} E_{\mathrm{ox}}(\mathrm{donor}) -^{1/2} E_{\mathrm{red}}(\mathrm{acceptor})$, exceeds that of the excited triplet state of ketone: $\Delta H = 0.92 + 1.85 = 2.77\,\mathrm{eV} > 2.39$ eV. Electron transfer can occur only from the excited states of TPA to the ground state of ketone, because the energy of the ketone triplet excited state is insufficient for electron transfer in this system. The RIPs in the case of all ketones have enough energy for back ET in triplet state resulting in the triplet excited state of ketones.

The CIDNP effects detected during photolysis of ketones **I–IV** are presented in Table 1 and Figs. 1–3. As an example, Fig. 1 presents the CIDNP spectra observed upon the photolysis of ketone **II**.

Table 1
QSS ^{1}H CIDNP effects detected upon the photolysis of ketones **I–IV** in CD_3CN in the presence of TPA (A-absorption, E-emission)

	I	**II**	**III**	**IV**
trans	1,11-CH_3-E 5-CH_2-E	1-CH_3-E 4-CH-A	1-CH_3-E 4-CH-A 5-CH-E	1,13-CH_3-E 7-CH_2-E 4-CH-A
cis	1,11-CH_3-A 5-CH_2-A	1-CH_3-A 4-CH-E	1-CH_3-A 4-CH-E 5-CH-A	[a]1,13-CH_3-A 7-CH_2-A 4-CH-E

The starting isomer is *trans*.

[a] *cis–trans* and *cis–cis* isomers, see details in the text.

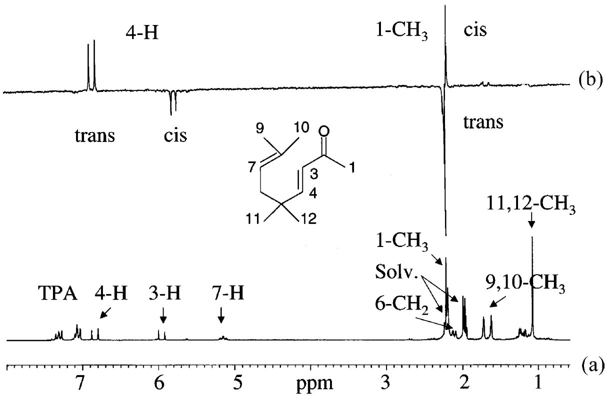


Fig. 1. (a) The ^{1}H NMR spectrum of ketone **II** in CD_3CN; (b) QSS ^{1}H CIDNP (200 MHz) spectrum observed during irradiation of **II** (20 mM) in the presence of TPA (20 mM) in CD_3CN.

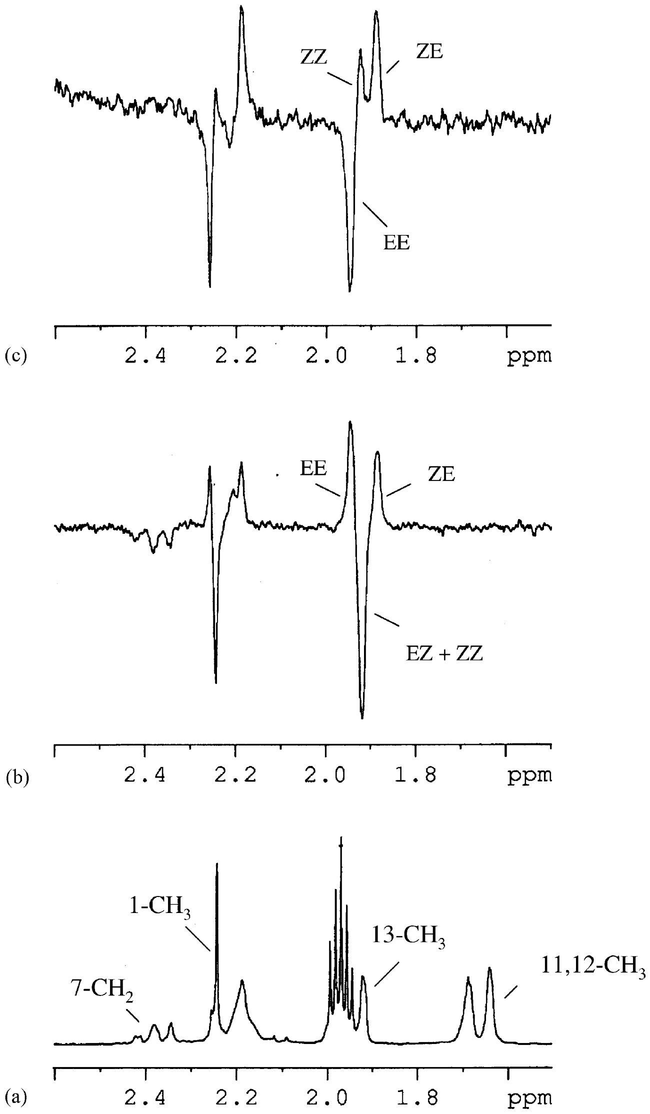


Fig. 2. (a) The fragment of the ^{1}H NMR spectrum (aliphatic part, EZ isomer) of ketone **IV** in CD_3CN; (b) and (c) QSS ^{1}H CIDNP spectra observed during irradiation of **IV** (20 mM) in the presence of TPA (20 mM) in CD_3CN. The starting isomers are EZ (b) and EE (c).

Note that the presence of CIDNP effects is a direct evidence for radical pair formation. Since the QSS CIDNP spectrum shows only polarized signals (see Section 2), this technique allows one to separately observe only the isomers formed via the ET mechanism. During the photolysis of **I**–**IV** in the presence of TPA, CIDNP effects of only *cis*- and *trans*-isomers have been detected. We failed to find any additional isomers, including cyclization and rearrangement products detected upon photolysis of **I**–**IV** in the β-cyclodextrin complex as well as upon direct photolysis in homogeneous media [1,2].

The analysis of CIDNP effects was based on the following. The intensities of polarized lines in CIDNP spectra are proportional to the hfi constants of the corresponding nuclei of the paramagnetic precursors of polarized products [15]. A number of experimental and calculation data indicates that the radical anions of α,β-unsaturated ketones have the maximum values of hfi constants of protons at C_1 and C_4 atoms (or CH_3, CH_2 or CH substitutents at the fourth position) for ketones **I**–**III**, and 1-CH_3, 4-CH, 7-CH_2 and 13-CH_3 for ketone **IV** [8,9]. We assumed that due to close structures, the hfi constant distribution in radical anion of ketone **IV** is similar to that of the previously well-studied β-ionone [4,8]. It has been shown that the CIDNP effects in the TPA-β-ionone system were formed in a corresponding radical ion pair. The main hfi constants of β-ionone radical anion are: $\mathbf{a}(1\text{-}CH_3) = 6.5\,G$, $\mathbf{a}(4\text{-}H) = -9.9\,G$, $\mathbf{a}(7\text{-}CH_2) = 12.5\,G$, $\mathbf{a}(13\text{-}CH_3) = 6.5\,G$, and the ratio of CIDNP intensities (per one proton) detected for these group was $I_1{:}I_4{:}I_7{:}I_{13} = 1{:}-1.8{:}2.4{:}1.2$. Indeed, the main polarized groups of protons for ketone **IV** are the same as for **VII**. The signs and relative intensities of CIDNP signals in this case are equal to $I_1{:}I_4{:}I_7{:}I_{13} = 1{:}-2.5{:}1.2{:}1.2$, which close to the assumed distribution of hfi constants.

The signs and intensities of CIDNP signals for other ketones (**I**–**III**) observed upon photolysis in the presence of TPA qualitatively correspond to the assumed hfi constants distribution of their radical anions (see Table 1 which demonstrates the signs of the main polarized lines of all isomers and also ref. [9]). Thus, we assume that the CIDNP effects for all ketones under study are formed in the corresponding RIPs. Since the *cis*-isomers have polarization signs opposite to that of the *trans*-isomers, it was suggested that the *trans*-isomers were formed via back ET in a singlet RIP, and *cis*-isomers are the products of back ET in the triplet radical ion pair (Scheme 3). The analysis of polarization signs by means of Kaptein's rule [16] leads to the conclusion about the triplet precursor for these RIPs. Note that the lifetime of the excited triplet state of TPA is longer ($\tau_T = 38\,ns$), than that of the singlet state ($\tau_S = 4.5\,ns$) [17].

Here, ↑ and ↓ mark the polarized products of opposite signs, and α is probability of *cis*-isomer formation from the excited triplet state of *trans*-isomer. Since the total of

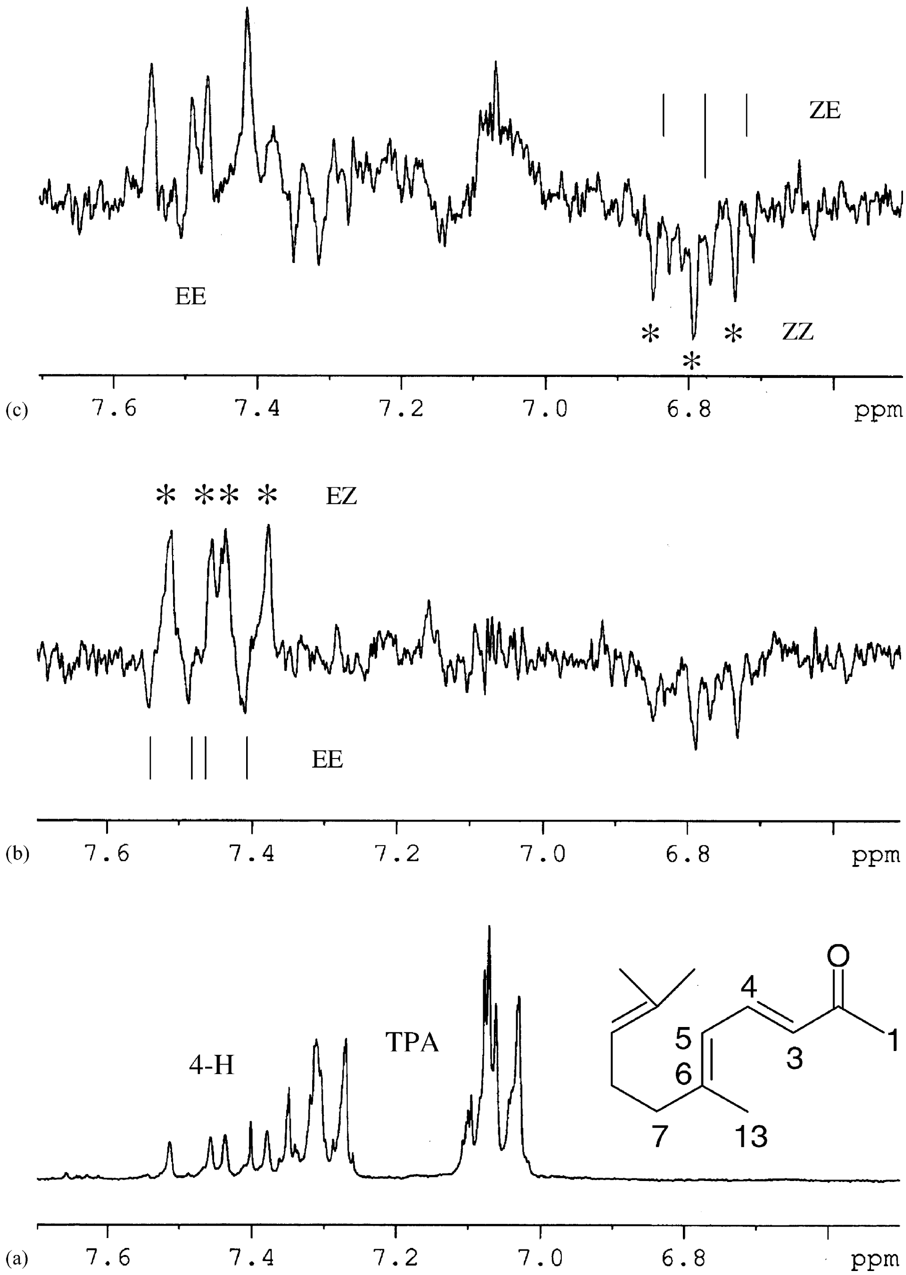
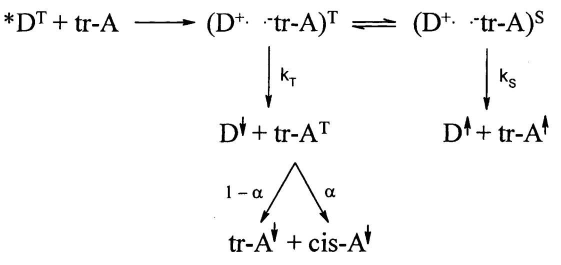


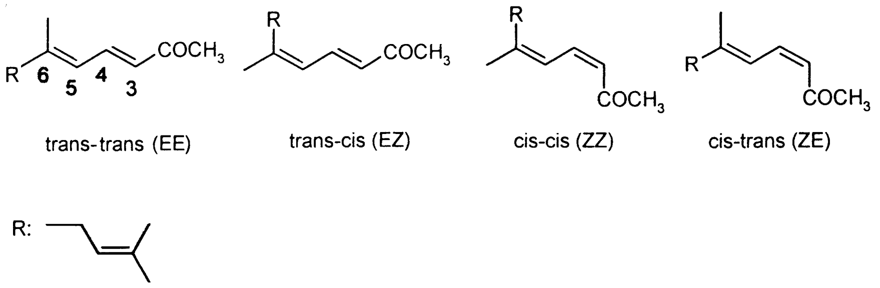
Fig. 3. (a) The fragment of ^{1}H NMR spectrum (4-CH group, EZ isomer) of ketone **IV** in CD_3CN; (b) and (c) the fragments of QSS ^{1}H CIDNP spectra (4-CH groups) observed during irradiation of **IV** (20 mM) in the presence of TPA (20 mM) in CD_3CN. The starting isomers are EZ (b) and EE (c).



Scheme 3.

integral polarization of all products is equal to zero in S–T_0 approximation, the *cis*-isomers should demonstrate the equal total polarization intensity, but opposite signs compared to starting *trans*-isomer. It is obviously, that for the simplest situation of two isomers, we can not determine isomerization probability α from the analysis of only the CIDNP spectrum.

More interesting is the photolysis of ketone **IV** (see Scheme 1). Due to the presence of two conjugated double bonds in this molecule, the formation of four *cis–trans* isomers could be expected: 3,4-*trans*–5,6-*trans* (EE), *cis–trans* (ZE), *trans–cis* (EZ) and *cis–cis* (ZZ), see Scheme 4. The



Scheme 4.

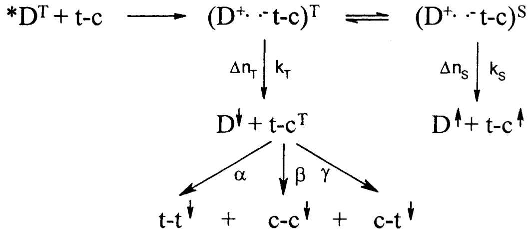
formation of these isomers has been already detected during direct isomerization in a homogeneous solution [2].

Indeed, the CIDNP spectrum demonstrates the presence of all these isomers (Fig. 2b and c). If the starting isomer is EZ, the three additional polarized isomers are observed in the NMR spectrum, namely EE, ZE and ZZ (Figs. 2b and 3b). The main polarized lines of all isomers are: 1,13-CH_3, 7-CH_2 and 4-H. The intensities of the polarized lines of all isomers are proportional to the expected values of hfi constants in the radical anion of **IV**, and they have the equal values and opposite signs for the initial EZ and products, EE, ZE and ZZ isomers. It allows one to conclude that all isomers were formed from a common precursor—the RIP of TPA radical cation and ketone radical anion. If the starting isomer is EE, the two polarized *cis*-isomers are observed, namely ZE and ZZ (Figs. 2c and 3c). The important point in these two experiments is the equal ratios of CIDNP intensities $I(\mathrm{ZE})/I\,(\mathrm{ZZ}) = 2$ if the starting isomer is EE or EZ (Fig. 3). For EE as a starting isomer the formation of ZE means the rotation around one double bond, and the formation of ZZ means the simultaneous rotation around two double bonds. For EZ as a starting isomer, the situation is opposite, and the formation of ZE isomer requires the simultaneous rotation around two double bonds. The question arises, if the equal ratios of CIDNP intensities of isomers ZE and ZZ mean their formation from the identical triplet excited state for isomers EE and EZ. Another question concerns the possibility of simultaneous isomerization around two double bonds.

To elucidate these questions the structure of the triplet excited state of **IV** was calculated by means of the AM1 method. The results of AM1 calculations demonstrate considerable changes in the bond length distribution of the triplet excited state compared with the ground state. The C_3–C_4 bond length increases from 1.34 to 1.39 Å, the C_4–C_5 bond length decreases from 1.45 to 1.37 Å, and the C_5–C_6 bond length increases from 1.34 to 1.45 Å. It means, that the second double bond becomes a single bond in the triplet state. Due to the free rotation around C_5–C_6 bond, one can conclude about the common triplet excited state for two isomers, EE and EZ. The same result was obtained for isomers ZE and ZZ. The calculations show, that the molecular fragment $-C_4H{=}C_3H{-}CO{-}C_1H_3$ remains flat in all cases, but the torsion angle $\varphi_{4\text{–}5\text{–}6\text{–}7}$ (rotation around C_5–C_6 bond) is close to 90° for optimal conformations. Thus, the calculation results and CIDNP observation point to the possibility of dual isomerisation around the two double bonds of ketone **IV** in triplet excited state.

Since the QSS CIDNP spectrum demonstrates only the polarized lines, and all isomers are formed from a common triplet, one can determine the probability of each isomer formation (excluding starting isomer) from this triplet excited state by measuring the ratio between the CIDNP intensities of different isomers. Scheme 5 illustrates this approach.

In this case, α, β and γ are the probabilities of corresponding isomer formation from the EZ (or EE) triplet excited state. We conclude that the EZ isomer is not formed from the excited triplet state, because this isomer is not polarized in the case where it is not the starting isomer (see Fig. 3c). Let us denote the non-stationary populations formed in the S and T pairs as Δn_S and Δn_T, respectively ($\Delta n_S = -\Delta n_T$). The polarization intensities of isomers are $I\,(\mathrm{EE}) = \alpha\,\Delta n_T$; $I\,(\mathrm{ZZ}) = \beta\,\Delta n_T$; $I\,(\mathrm{ZE}) = \gamma\,\Delta n_T$ and $I\,(\mathrm{EZ}) = \Delta n_S$. Since we did not observe any additional polarized products and the CIDNP spectra demonstrate good balance $I\,(\mathrm{EE}) + I\,(\mathrm{ZZ}) + I\,(\mathrm{ZE}) = -I\,(\mathrm{EZ}), \alpha+\beta+\gamma = 1$. Summarizing the experimental data for two starting isomers: EE and EZ, the following equations can be written: $I\,(\mathrm{EE})/I\,(\mathrm{ZE}) = \alpha/\gamma = 1.2$; $I\,(\mathrm{ZZ})/I\,(\mathrm{ZE}) = \beta/\gamma = 0.48$. These values were measured for 13-CH_3 groups because these polarized lines have the best signal-to-noise ratio. From simple calculations the following values have been obtained: $\alpha = 0.45$; $\beta = 0.18$; $\gamma = 0.37$ and the probability of EZ isomer formation from their triplet excited state is close to zero. As it was suggested earlier for 1-pyridyl,4-aryl-butadiene [18], an explanation of this behavior might be the H–bond-type interaction between the O atom and H atom of the diene chain, which stabilizes the molecule in a relatively rigid and planar ZE and ZZ configurations.



Scheme 5.

Finally, it will be interesting to point the difference in isomer distribution for various isomerization mechanisms. Earlier, we have already mentioned about the formation of presumable cyclic isomers upon the photolysis of inclusion complexes of these ketones with β-cyclodextrin. The present results indicate also a considerable difference in the probabilities of the isomers formation via ET mechanism compared with direct photolysis in homogeneous media. The ratio between isomers measured after UV irradiation of the methanol solution of **IV** was 32: 58: 10 for EE: EZ: ZE+ZZ. It is interesting, that the main isomer, EZ, is not formed via the ET mechanism of isomerization. In this case we assume the contribution of singlet excited state to the isomerization process.

In addition, some advantages of the CIDNP technique in studying the fine mechanisms of geometrical isomerization were demonstrated. Namely, the "visualization" of the isomerization process and the possibility of simple estimation of isomerization probability from one isomer to another. We have answered three important questions:

(1) Can various isomers have a common triplet excited state?
(2) Is the simultaneous isomerization around two double bonds possible?
(3) Can the CIDNP technique provide information about the probabilities of the isomers formation?

Our conclusions are in accordance with the results of the other groups (Sandros, Tokumaru, Mazzucato, and co-authors) which studied the *cis–trans* isomerization of diaryl substituted polyenes (see, for example [18–20]). By using fluorescence and laser flash photolysis techniques, the authors have shown that the extension of the unsaturated chain affects the excited state properties and opens alternative adiabatic and "one photon-two bonds" isomerization mechanisms. The insertion of second double bond can contribute in lowering the energy of the planar S_1 and T_1 states with respect to the perpendicular configuration, thus, favoring the adiabatic channel. For example, it was found that on excitation of the ZZ isomer both the isomers, ZE and EE, are produced initially, mainly by adiabatic processes on the singlet excited surface. On the other hand, *trans* isomers, EE and EZ, have very low photoisomerization quantum yields for these compounds. As it was said earlier, two-fold isomerization pathway from *trans* configuration observed in the present study was probably favored by an intramolecular H–bond.

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