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The role of radicals in the phototransformations of β-ionone in the presence of electron donors in solution

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Abstract

Formation of radical anions of *trans*-β-ionone (**I**) has been detected during its photolysis in acetonitrile in the presence of the electron donors triphenylphosphine (TPP) and triphenylamine (TPA) by using chemically induced dynamic nuclear polarization (CIDNP). Transformation of radical anions of (*E*)-β-ionone (**I**) to neutral radicals by protonation has also been observed, as has the participation of these paramagnetic particles: radical anions and neutral free radicals in the processes of geometrical isomerization of *trans*- to *cis*-(*Z*)-β-ionone (**III**) in the presence of TPA. The isomerization of **I** occurs in the triplet excited state (^{3}**I** → **I**+**III**), or in the free radical of **I** (**I**–H ↔ **III**–H). The triplet excited state of **I** results from back electron transfer in the triplet radical ion pair of radical ions of β-ionone and triphenylamine.

Keywords: β-Ionone; Radicals; CIDNP; Phototransformation; Triplet state; Isomerization

1. Introduction

The role of paramagnetic species in the photoprocesses of carotenoids has been of considerable interest in the last decade [1,2] due to their great fundamental and practical significance. Presently, the majority of the available data is related to photosynthetic processes [3]. Further, more recently carotenoids have been extensively used in medicine as antioxidants [4]. Understanding the nature of this antioxidant activity requires data on the structure and properties of carotenoid radical intermediates. However, information about the structure and reactivity of paramagnetic carotenoid species, i.e. radicals and radical ions, is scarce [5,6]. This is especially true for radical anions of carotenoids.

Recently chemically induced dynamic nuclear polarization (CIDNP) has been used for the investigation of the role of single electron transfer (SET) in the phototransformations of the simplest representatives of carotenoids, (*E*)-β-ionone (**I**) and its isomers in solution in the presence of electron acceptors [7], and all *trans*-retinal in the presence of electron donors and acceptors [8].

The present study is devoted to the investigation of the role of paramagnetic species in the phototransformation of **I** in the presence of electron donors. The detection of the radical anions of β-ionone was carried out by CIDNP.

2. Experimental

2.1. Chemicals

Triphenylamine (TPA) and triphenylphosphine (TPP) (Aldrich) and (*E*)-β-ionone (Sigma) were used as supplied. The commercial deuterated solvent, CD_3CN, ("Isotop") was purified by distillation with P_2O_5. Solutions of **I** (2×10^{-3} to 2×10^{-1} M) in CD_3CN in the presence of the electron donors (10^{-3} to 10^{-1} M) were deaerated by Ar bubbling for 15 min. Perdeutero acetic acid ("Isotop") was used as supplied.

2.2. CIDNP

Samples in standard 5 mm Pyrex NMR tubes were irradiated directly in the probe of the NMR spectrometer at room temperature. Lambda Physik EMG 101 MSC excimer laser was used as the light source (λ = 308 nm, 15 ns, 100 mJ at output window and 30 mJ per pulse in the sample). Time-resolved (TR) [9] and quasi steady state (QSS) [10] CIDNP experiments were carried out using an

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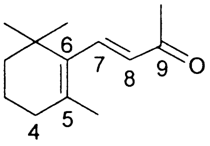
AM-250 Bruker NMR spectrometer (250 MHz ^{1}H operating frequency). QSS CIDNP experiments were performed using standard presaturation technique to suppress the equilibrium signals: saturation-delay (τ), 180° pulse, a number of laser pulses during time equals τ, detection pulse, free induction decay. As the background NMR signals in CIDNP spectrum were suppressed, only signals of polarized products were detected.

Quantum chemical and ESR data [11] were used for the identification of paramagnetic intermediates formed in these reactions. The quantum chemical calculation of hfc constants were performed as follows. Firstly, AM1 was used for geometry optimization of the paramagnetic species. The hfc values for these species were calculated by the INDO method parameterized for magnetic resonance [12]. The INDO method can eliminate the high spin states to give the average value for $\langle S^2 \rangle$ equal to 0.75 ± 0.01 which characterizes the free radical with spin 1/2. By this procedure more accurate data are obtained compared to the AM1 and PM3 [13] methods, especially for conjugated systems [8].

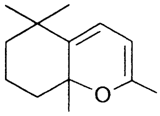
The integral intensities of polarized lines of the ^{1}H-NMR spectrum (per proton) were compared with hfc constants for the corresponding nuclei in the suggested radical-precursor of the polarized product.

3. Results

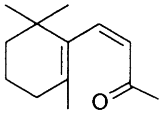
According to the literature [14,15] several isomers of ionone appear in solution during the direct photolysis of (*E*)-β-ionone (**I**). The two major resulting compounds as products of photolysis are α-pyran (**II**) and (*Z*)-β-ionone (**III**).



(E)-β-ionone (I)



α-pyran (II)



(Z)-β-ionone (III)

The radical anions of **I** and **III** can be generated by SET between corresponding isomers and TPA or TPP. Table 1 lists the characteristics of the electron donors and acceptors. It should be mentioned that in the systems under study light is absorbed by both partners, the donor and acceptor (see Table 1). In the case of photolysis with TPA, the ratio of optical densities of **I** and TPA change from 0.2 to 10. There are two types of processes that could occur simultaneously: direct isomerization and SET with subsequent isomerization. According to the Weller–Zachariasse criterion [16] ($\Delta G = {}^{1/2}E_{\mathrm{ox}}(\mathrm{donor}) - {}^{1/2}E_{\mathrm{red}}(\mathrm{acceptor}) - e^2/\varepsilon R - E^*_{\mathrm{S,T}}$) SET is possible if $\Delta G < 0$. Due to short lifetime of excited singlet state of **I** [28], in the systems under study electron transfer can occur only from excited states of the electron donors, TPA and TPP (see Table 1). In addition, all isomers formed via direct isomerization could participate in the reaction initiated by subsequent laser pulses.

Table 1
Excitation energies and polarographic half-wave potentials (eV)[a]

	ε (308 nm)	E^{S}	E^{T}	$^{1/2}E_{\mathrm{ox}}$	$^{1/2}E_{\mathrm{red}}$	Reference
I	9000	3.09	2.39	1.89	−1.85	[14,15]
II	2000		2.35	1.29		[7,14,15]
TPA	20000	3.61	3.05	0.92		[17,18]
TPP	1000			1.00	−2.02	[17,19]

[a] Data for isomer **III** are unknown due to its instability. The extinction coefficient is 4500 at 308 nm.

CIDNP effects of β-ionone isomers have only been observed in polar media and were absent in non-polar solvents. The experimental results are given in Table 2 and Figs. 1–3.

3.1. Reaction with triphenylphosphine

During irradiation of **I** in the presence of TPP the signs of ^{1}H CIDNP of β-ionone did not change as the concentration of **I** varied. The intensity of the polarization decreases with increasing concentration of **I**. Note, that the polarization decrease is stronger than it could be expected from only decreasing the light absorption by TPP. α-Pyran is not polarized in these experiments, and the *cis* isomer shows weak polarization of only 9-CH$_3$ and 7-H groups (Fig. 1). Note, that in the case of the photolysis of the mixture of isomers (the ratio of isomers: **I**:**II**:**III** ≈ 1:2:1) the same polarization pattern was observed as for pure **I**.

The polarization of TPP was not analyzed in this reaction, since it is known [20] that the photoexcitation of TPP results in its decay to yield phenyl radical. It has been shown in the present work that the photolysis of TPP in the absence of **I** also demonstrates CIDNP effect of TPP.

3.2. Reaction with triphenylamine

CIDNP effects of **I** and **III** are presented in Table 2 and Fig. 2. CIDNP of α-pyran was not detected in any experiments. Fig. 3 demonstrates the dependence of CIDNP effects of the various protons of **I** and **III** obtained during the photolysis of **I** in the presence of TPA on the concentration of **I**. Significant changes in the polarization pattern have been observed after addition of perdeutero acetic acid to the solution (see Table 2).

Table 2
QSS ^{1}H CIDNP effects detected upon (*E*)-β-ionone photolysis in CD_3CN in the presence of electron donors

I	**II**	**III**	Conditions
TPA			
$4\text{-}CH_2$, $5\text{-}CH_3$, 8-H, $9\text{-}CH_3$—A; 7-H—E	–	$4\text{-}CH_2$, $5\text{-}CH_3$, 7-H—A; 8-H, $9\text{-}CH_3$—E	0.004 M of **I**
$4\text{-}CH_2$, $5\text{-}CH_3$, $9\text{-}CH_3$—E; 7-H, 8-H—A	–	$4\text{-}CH_2$, $5\text{-}CH_3$, $9\text{-}CH_3$—A; 7-H, 8-H—E	0.1 M of **I**
$4\text{-}CH_2$, $5\text{-}CH_3$, $9\text{-}CH_3$—E; 7-H—A	–	$4\text{-}CH_2$, $5\text{-}CH_3$, 8-H, $9\text{-}CH_3$—E; 7-H—A	0.01 M of **I** + 0.1 M of acid
4, 5, 8, 9—A; 7—E	–	4, 5, 8, 9—E; 7—A	Photostat.[a]
TPP			
4, 5, 9—E; 7—A	–	9—E; 7—A	

[a] Photolysis of the mixture of isomers, **I**:**II**:**III** ≈ 1:2:1.
A: absorption; E: emission.

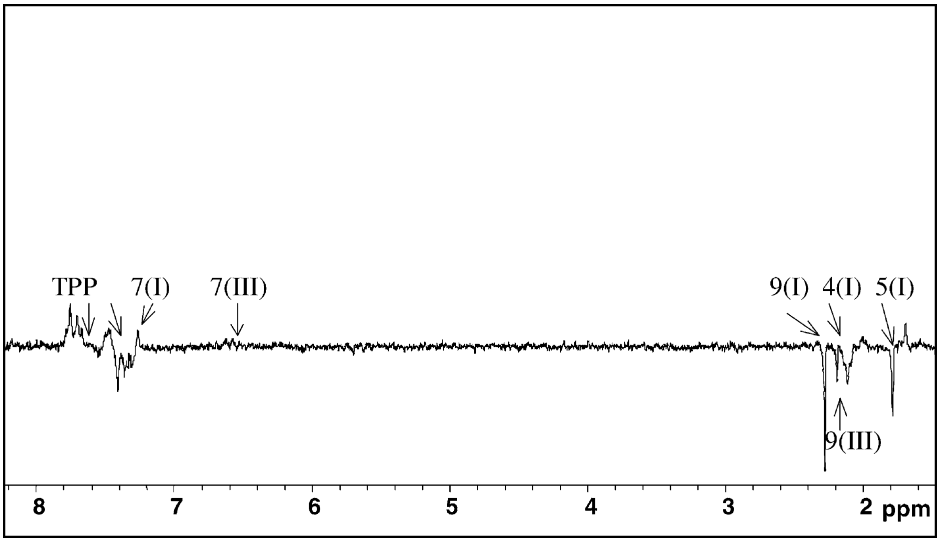


Fig. 1. QSS ^{1}H CIDNP spectrum observed during irradiation of **I** (5 mM) in the presence of TPP (10 mM) in CD_3CN, eight laser pulses per scan, 128 scans.

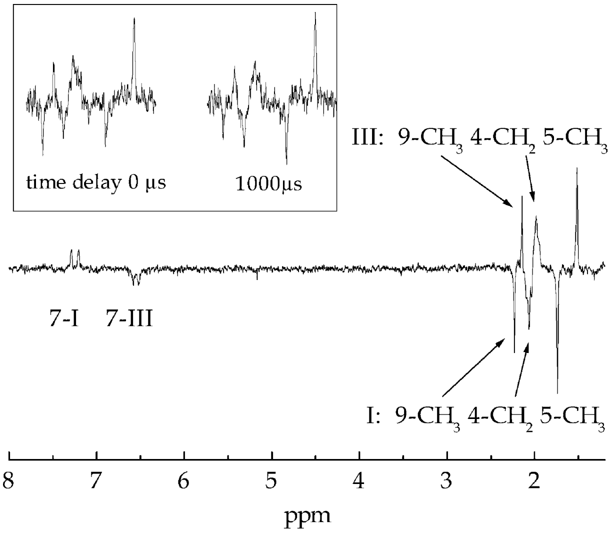


Fig. 2. QSS ^{1}H CIDNP spectrum observed during irradiation of **I** (100 mM) in the presence of TPA (30 mM) in CD_3CN, eight laser pulses per scan, 64 scans. Inset: time-resolved ^{1}H CIDNP spectra (right part) observed at different time delays during irradiation of **I** (20 mM) in the presence of TPA (20 mM) in CD_3CN, 128 scans, PW = 4 μs.

4. Discussion

The appearance of CIDNP effects on β-ionone in polar media, and the absence of polarization in non-polar solvents, are the typical situation for reversible electron transfer. The possibility of SET in the systems under study is indicated by the Weller–Zachariasse criterion [16] (see Table 1).

The analysis of CIDNP effects described earlier is based on the following. The intensities of the polarized lines in CIDNP spectra (TR and QSS experiments) are proportional to the values of the hfc constants of the corresponding nuclei of paramagnetic precursors of the polarized products [21]. The values of hfc constants are summarized in Table 3.

Table 3
The hfc constants (mT) of β-ionone radical anion and neutral radical

Compound	$4\text{-}CH_2$	$5\text{-}CH_3$	7-H	8-H	$9\text{-}CH_3$
Radical anion[a]	1.25[a]	0.65	−0.99	<0.5	0.65
Neutral radical[b]	0.17	0.16	−0.55	0.28	1.58, OH: −0.06

[a] ESR data from [11], the value for $4\text{-}CH_2$ is an average calculated for two non-equivalent protons.
[b] Calculated values, see details in text.

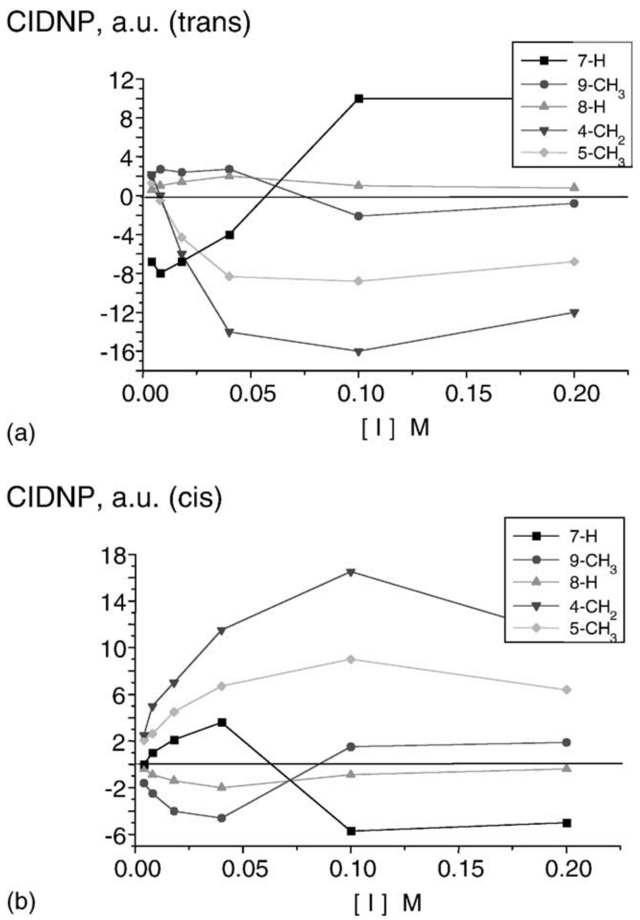


Fig. 3. The dependence of QSS ^{1}H CIDNP of the protons of (a) *trans* and (b) *cis* isomers on the concentration of **I** measured from integrated intensity (per one proton) of NMR lines during irradiation of **I** in the presence of TPA (10 mM) in CD_3CN.

The sign of polarization is determined by Kaptein's rule [22]: $\Gamma = \mu\varepsilon\,\Delta g\,a$. "Minus" corresponds emission, and "plus" enhanced absorption in CIDNP spectrum. Here, $\mu =$ (+) for triplet precursor of radical pair and (−) for singlet precursor; $\varepsilon =$ (+) for geminate polarization and (−) for escape products; Δg is the difference of g-factors of the radicals, and a hfi sign of corresponding proton.

4.1. Triphenylphosphine

The main polarized lines of **I** during the photolysis of β-ionone in the presence of TPP are 4-CH_2, 5-CH_3, 7-H and 9-CH_3 groups (Fig. 1). The ratios of the integral intensities of these polarized lines (per proton) equal, I_4:I_5:I_7:I_9 = 1:0.5:0.77:0.4. These ratios correspond to the distribution of the hfc constants in the radical anion of **I** (see Table 3). This leads us to the conclusion about formation the RIP: $I^{\bullet-}$ $TPP^{\bullet+}$. The analysis of CIDNP effects according to Kaptein's rule $g(I^{\bullet-}) < g(TPP^{\bullet+})$, **I** is polarized as the cage product of the RIP showing that **I** reacts with the excited triplet state of TPP.

CIDNP of the protons of α-pyran is absent, even under photolysis of the mixture of isomers (**II**/**I** = 2), which might be the result of a high reduction potential of **II**. Weak polarization of the *cis* isomer, even at equal concentrations of **I** and **III**, points to low reactivity of also isomer **III** in this system.

Thus, CIDNP effects detected during the photolysis of **I** in the presence of TPP reflect the only reversible SET between the radical anion of **I** and the radical cation of TPP.

4.2. Triphenylamine

During photolysis of **I** in the presence of triphenylamine, CIDNP of both isomers **I** and **III** has been detected (Table 2). The protons of α-pyran were not polarized in this case either. This fact confirms the suggestion that α-pyran is a weak electron acceptor.

As follows from comparison of the data of Table 3 and Fig. 2, the signs of ^{1}H CIDNP of **I** correspond to the signs of hfc constants of the radical anion of **I**, similar to the reaction with TPP. However, the ratios of intensities of the polarized protons differ significantly from the ratios of the hfc constants for the protons at the 9 position. The ratios of CIDNP intensities at the 4, 5, 7 and 9 positions of **I** are 1.0, 0.56, 0.8 and 0.06. These values for the *cis* isomer **III** have opposite signs and equal 1.0, 0.55, 0.64 and 0.18. The ratios of the corresponding hfc, obtained from the data of the Table 3, are 1, 0.52, 0.79 and 0.52. The deviations of CIDNP intensities observed for protons at the 9 position of *trans* and *cis* isomers from those expected for the radical ion precursor were the first indication of participation of other paramagnetic species in the phototransformation of **I** in the presence of TPA. The second reason for suggesting the existence of several contributors to observable CIDNP is the different dependence of CIDNP intensities of various protons of both isomers on the concentration of **I** (Fig. 3). Thus, the signs of CIDNP of the protons at the 7 and 9 positions of **I** and **III** change with increasing concentration of **I**, whereas CIDNP at the 4 and 5 positions is not changed (Fig. 3a,b). This means that there are at least two radical pairs of the paramagnetic species with the maximum difference of spin density distribution at the 7–9 positions.

It is expected that one of the paramagnetic species is the radical anion of **I**. And CIDNP detected at high concentrations of **I** results primarily from the RIP ($I^{\bullet-}$ $TPA^{\bullet+}$). In this case, the signs of CIDNP of all protons corresponds to the signs of hfc (Figs. 2 and 3, right part). We suggest that the opposite signs of the polarization of **I** and **III** are due to the cage product of the RIP for one isomer and another product in the bulk (all considerations relate to the protons at the 4 and 5 position of **I** and **III**). In the case of two possible recombinations, the products of singlet and triplet RIP also have opposite polarization signs. Note that the *trans* isomer could be formed as a cage product of both RIPs. The choice between the possibilities could be made by using time-resolved CIDNP measurements, but we have not observed remarkable changes of the CIDNP intensities (see inset in Fig. 2) of the protons of **I** and **III** in the time window of less than 1–2 ms. The absence of time dependence of CIDNP points to two possibilities: there are no processes in the bulk, or, if they take place (for example, ion-molecular recharging), these processes must be very fast.

In contrast to the *trans* isomer for which there could be three sources for polarization (the cage recombination of RIP in S and T spin states and bulk processes), the polarized *cis* isomer **III** in the case of photolysis of **I**, could be formed only as a cage recombination product of the triplet RIP ($I^{\bullet -}$ $TPA^{\bullet +}$). As is well known for olefins [23], when *cis–trans* isomerization occurs via the RIP, isomers of the initial olefin are formed via the excited triplet state resulting from back electron transfer of the triplet RIP.

Analysis of CIDNP of **III** by means of Kaptein's rule [22] leads to the conclusion about the triplet precursor for the RIP, ($I^{\bullet -}$ $TPA^{\bullet +}$), if $g(TPA^{\bullet +}) > g(I^{\bullet -})$. 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) [24].

The dependence of the CIDNP intensities of protons at the 4 and 5 positions of both isomers **I** and **III** on the concentration of **I** (Fig. 3) can be explained as follows. The increased CIDNP intensities of both isomers at higher concentrations are due to the faster quenching rate of the excited triplet state of the amine by ionone.

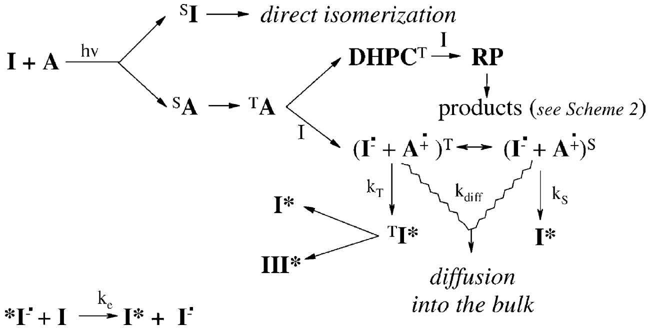
The weak decrease of the polarization of protons at the 4 and 5 positions of **I** and **III** at high concentration of **I** might result from absorption of light by the initial *trans*-ionone, which could lead to a decrease of the concentration of the RIP, since excited states of **I** would be isomerized without formation of the RIP (direct isomerization).

The different dependence of CIDNP of the 4, 5 and 7, 9 groups of protons on the concentration of **I** points to the contribution in CIDNP from other sources.

To discuss the source of the formation of other paramagnetic intermediates during the photoinitiated reaction of **I** with TPA, the following needs to be considered. It has been suggested [25,26] that the triplet excited state of TPA in solution might be the source of dihydrophenylcarbazole and radical cations of benzidine. On the other hand, an investigation of the photoinitiated interaction of TPA with quinones by CIDNP has shown the possibility of simultaneous formation of semiquinone anions and neutral radicals [25]. It has been suggested [25] that dihydrophenylcarbazole resulting from the triplet excited state of TPA might be the hydrogen donor that is necessary for the formation of RP of the semiquinone neutral radicals.

For the system under study, formation of a similar RP with the neutral radical of β-ionone as a second source of CIDNP (Scheme 1) is also possible.

Because data on the geometry and spin density distribution of this species are not known, quantum chemical modeling of the structure and calculations of hfc constants of the neutral radical of β-ionone were made. The results of the calculations are presented in Figs. 4–6 and Table 3.



Scheme 1.

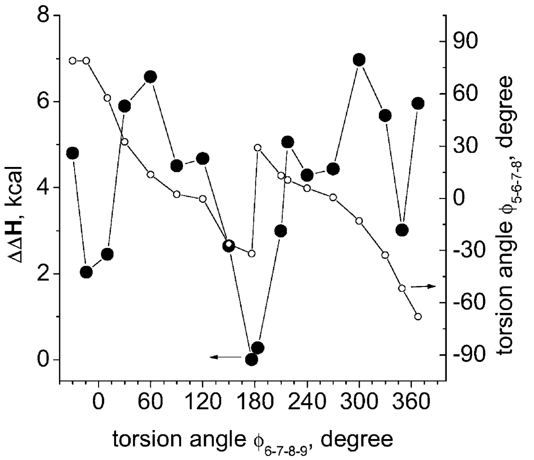


Fig. 4. AM1 calculated dependence of the heat of formation of β-ionone neutral radical (left axis) and of the optimal torsion $\varphi_{5\text{-}6\text{-}7\text{-}8}$ angles (right axis) on the torsion $\varphi_{6\text{-}7\text{-}8\text{-}9}$ angles (180° corresponds to *trans* isomer).

Analysis of the calculated dependence of the heat of formation of the neutral radical shows that the barrier of rotation around the C_7–C_8 bond in the neutral radical is about 7 kcal/mol (Fig. 4). At room temperature the estimated rate

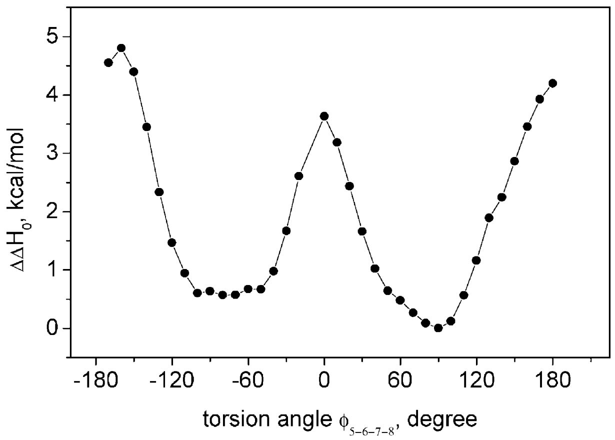


Fig. 5. AM1 calculated dependence of the heat of formation of *trans*-β-ionone neutral radical on the torsion angle $\varphi_{5\text{-}6\text{-}7\text{-}8}$.

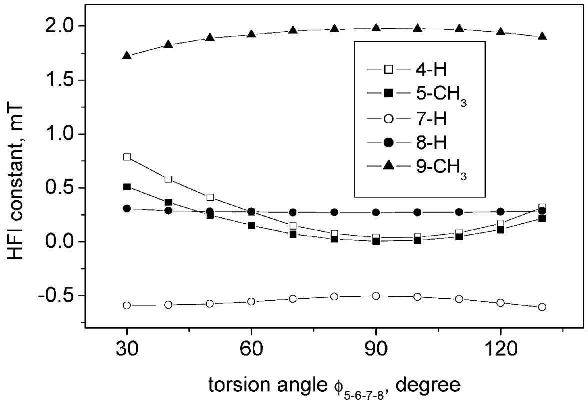


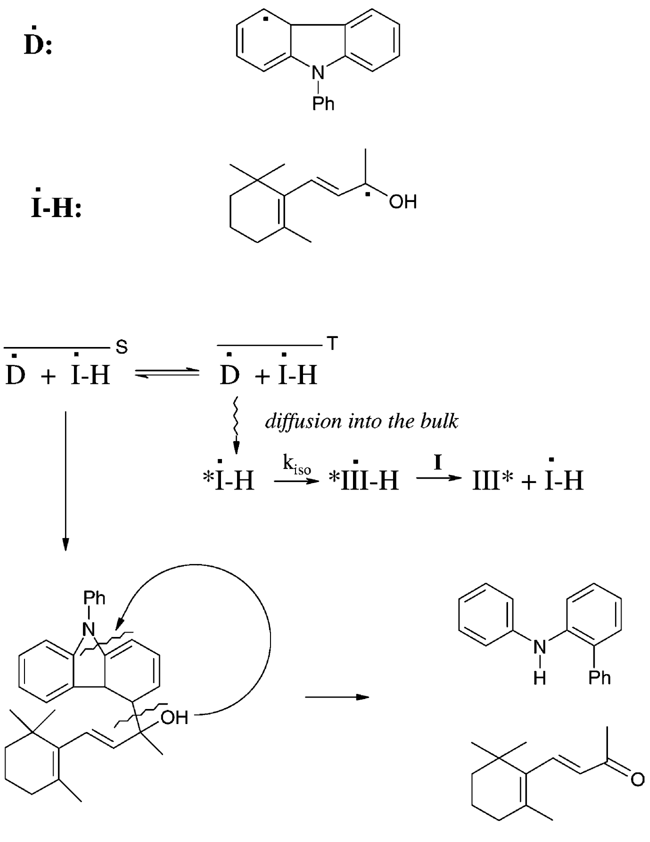
Fig. 6. Calculated dependencies of hfi values (in mT) of various groups of protons of *trans*-β-ionone neutral radical on the torsion angle $\varphi_{5\text{-}6\text{-}7\text{-}8}$.

of the radical *cis–trans* isomerization is about 10^{-6} s. This means that the neutral radical of **I** could not change its conformation within the CIDNP formation time (nanoseconds). However, for this time range, hfc values for individual (*cis* or *trans*) conformations of neutral radicals could be calculated. The results of AM1 calculations demonstrate that the deviation of the torsion angle $\varphi_{5\text{-}6\text{-}7\text{-}8}$ (rotation around C_6–C_7 bond) for the individual conformations from the optimal value within ±40° does not lead to significant energy changes (less than 1 kcal/mol, see Fig. 5). The dependence of the spin density distribution in the neutral radical of **I** on the change of this torsion angle (Fig. 6) was also calculated. The hfc constants of the neutral radical employed for CIDNP analysis (Table 3) were an average of the $\varphi_{5\text{-}6\text{-}7\text{-}8}$ torsion angle values.

Analysis of the hfc constants of possible radical-precursors of the isomers **I** and **III** (Table 3) shows that the considerable CIDNP effects on the 7 and 9 groups of protons together with small effects on the 4 and 5 groups is expected only in the case when the paramagnetic precursor is the neutral radical of β-ionone which has the largest hfc constants of the 7-H and 9-CH_3 groups.

Taking these facts into account, it is reasonable to attribute this contribution to the CIDNP effects of the 7-H and 9-CH_3 protons to the RP of the neutral radical of β-ionone and the radical of dihydrophenylcarbazole. The latter results from abstraction of a hydrogen atom from the excited triplet state of dihydrophenylcarbazole by β-ionone (Scheme 1). The presence of the keto group in β-ionone implies that the product of the recombination of this RP might be the aminoalcohol shown in Scheme 2. On the other hand, it is known [26], that aminoalcohols easily undergo C–C bond breaking yielding corresponding aldehydes or ketones. Therefore, we propose that the polarized *trans*-β-ionone is formed by decay of the short-lived aminoalcohols (Scheme 2).

The similarity of the concentration dependence of the CIDNP effects of all of the protons of **I** and **III** (cf. Fig. 3a,b) points to the same sources of the polarized isomers of **I** and **III**. The first source, the RIP, was described earlier (see Scheme 1). In addition, the *trans* and *cis* isomers might be the cage or escape products of the neutral RP (see Scheme 2). We suggest that the *trans* isomer formed through the decay of the aminoalcohol, according to Scheme 2, would be polarized as a cage product of the RP. Unfortunately, it is impossible to analyze CIDNP of the protons of TPA, since it has the same contribution effects as both the RIP and the RP.



Scheme 2.

The appearance of opposite signs of CIDNP of the 7-H and 9-CH_3 protons of *cis*-ionone means that it is polarized as an escape product. In this case the most reasonable way to form *cis*-β-ionone could be the isomerization of the neutral radical of **I** in the bulk. The polarization could be transferred from the isomerized radical to the diamagnetic molecule of *cis*-β-ionone via proton exchange of the radical with the *trans* isomer.

Several conditions are necessary for this path to be possible. First, the isomerization of the neutral radical should be faster than the spin-lattice relaxation in the radical ($T_{1R} \sim 5 \times 10^{-5}$ to 10^{-4} s). This is possible because, according to our molecular modeling calculations, the rate of the isomerization around C_7–C_8 bond is about $10^6\,s^{-1}$. Another condition that is necessary for the appearance of CIDNP of the *cis* isomer formed via neutral RP is fast transfer of polarization from the radical to a diamagnetic molecule. The rate of degenerate proton exchange ($k_H[\mathbf{I}] > T_{1R}^{-1}$) at the concentration of **I** in solution $\leq 7.5 \times 10^{-2}$ (the point of the change of signs of CIDNP of the protons at the 7 and 9 position of **I** and **III**, Fig. 3), should be about $10^5\ s^{-1}$. This value is known for ketones [27].

The analysis of CIDNP of the 7-H and 9-CH_3 protons with using Kaptein's rule is not in conflict with these suggestions, and leads to the conclusion regarding the triplet multiplicity of RP-precursor of isomers, if it is true that the *g* factor of dihydrophenylcarbazole is formed in the excited triplet state, it is reasonable to suggest that this state reacts with β-ionone.

The concentration dependence of CIDNP of the protons of **I** and **III** (Fig. 3) is also satisfactorily explained by the formation of a RP with the participation of dihydrophenylcarbazole in the reaction. The greater contribution from the RP is more evident at small concentration of β-ionone (less than 0.075 M, see Fig. 3). The increase of its concentration should lead to the decrease of the contribution of neutral RP due to an increase of the rate of SET between β-ionone and TPA in the triplet state. It leads to the growth of the concentration of RIP and decrease the yield of dihydrophenylcarbazole. At high concentration of β-ionone CIDNP signs of *trans* and *cis* isomers correspond to the predominant contribution from the RIP (Fig. 3 and Table 3).

One reliable way to confirm the formation of the neutral radical of β-ionone in the system under study could be the comparison of these results with the pattern of CIDNP detected upon the photolysis of **I** and TPA in the presence of acid. Protonation of the radical ion of **I** with formation of the neutral radical was proposed earlier [2]. However, this was found to be impossible, since photolysis of **I** in the presence of perdeuteroacetic acid and TPA leads to formation of a set of new products.

Thus, the formation of RIP of radical anion of **I** and radical cation of donors takes place during the photolysis of β-ionone in the presence of electron donors (TPP, TPA) in polar media. In addition to direct isomerization, *cis–trans* isomerization via the radical ion pair occurs, if back electron transfer in the RIP gives β-ionone in the excited triplet state. The *cis–trans* isomerization of neutral radical of β-ionone has been detected.

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