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Photoinitiated electron transfer interaction of all-trans retinal with electron donors and acceptors

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Abstract

Formation of radical ions of all-trans retinal (ATR) has been demonstrated using ^{1}H CIDNP on its photoinitiated interaction with electron donor (stilbene) and acceptors (2,5-dichlorobenzoquinone, chloranil). CIDNP data show qualitative agreement with calculations of spin density distribution in ATR radical ions conducted by means of the INDO/AM1 method. It has been found that CIDNP effects are formed in the reaction of reversible electron transfer between ATR and either electron donors or acceptors. Retinal isomers arising under irradiation also give rise to nonequilibrium population of spin states in NMR spectra. The correlation between CIDNP effects and the processes of cis–trans isomerization has been discussed. © 1997 Elsevier Science S.A.

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1. Introduction

During the past decade, the elementary stages of the photoinitiated transformations of carotenoids and retinoids have been extensively studied because of their biological, medical and technological importance [1,2]. For example, 11-*cis*-retinal is a chromophore of vision pigment rhodopsin. It is assumed [3,4] that its cis–trans isomerization process contributes to the formation of an image in the mammalian eye. The mechanisms of retinal isomerization, its all-trans, 11-cis, and 13-cis forms are the objects of continuous research [5–8]. However, the results obtained are rather contradictory owing to a substantial intricacy of isomerization, since the initial product gives a set of isomers. The composition of isomers is known to depend on irradiation wavelength [5,6], solvent [7,8], and sensitizer [5]. There is evidence in the literature for the participation of both S and T excited states of retinal in the act of isomerization [7]. The mechanisms of isomerization via energy transfer have been widely discussed [5,9,10], but little is known about the role of electron transfer processes [1]. Meanwhile, the radical ion stages play a key role in stilbene cis–trans photoisomerization [11]. The latter is often compared with the isomerization of retinoids [5].

At present, the radical ions of some carotenoids are obtained electrochemically [12], and they have been detected and characterized in pulsed radiolysis experiments [13]. Besides, the effects of chemically induced dynamic electron polarization [14] and external magnetic field effect on photoconductivity [15] have been detected in the systems involving carotenoids. Now, the role of charge transfer states in the phototransformation of carotenoids is investigated by different methods since these species are involved in the electron transfer chains in photosystem II [1,16–18].

The aim of the present work is to detect radical ion stages in photoinitiated interactions of all-trans retinal (ATR) with electron donors and acceptors in solution using the CIDNP technique. Since there is very little information available in the literature on the spin density distribution in retinoid radical ions, the INDO/AM1 method has been used in this work to calculate the geometry and electronic structures of radical anions and cations of ATR.

2. Experimental details

2.1. Chemicals

ATR (Sigma) was used as supplied. Quinones, 2,5-dichlorobenzoquinone (DBQ) and tetrachlorobenzoquinone (chloranil, CA) were purified by sublimation. CD_3CN and C_6D_6 (Isotop) were used as supplied.

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2.2. CIDNP

ATR solutions (0.001–0.03 M in CD_3CN and C_6D_6 in the presence of electron donors and acceptors (0.01–0.1 M) were deaerated by Ar bubbling. Samples in standard Pyrex NMR tubes were irradiated directly in the probe of the NMR spectrometer. Two NMR spectrometers with different magnetic fields were used in our experiments. The first was a JEOL FX 90Q NMR spectrometer (90 MHz ^1H operating frequency). The light source used in this case was a high-pressure mercury lamp (1 kW) with a thermal filter and a number of light filters: $280 < \lambda < 380$ nm (the transmission band covers: the absorption band of quinones, $\lambda_{1\ max} = 280$ nm, $\epsilon \approx 3000$; $\lambda_{2\ max} = 360$ nm, $\epsilon \approx 300$; the absorption band of *trans*-stilbene, $\lambda_{max} = 300$ nm, $\epsilon \approx 30\,000$; and the ATR band edge, $\lambda(300) \approx 10000$, $\lambda(360) \approx 20\,000$); and $\lambda > 380$ nm (the absorption band of ATR: $\lambda_{max} = 380$ nm, $\epsilon \approx 50\,000$ [10]). The second spectrometer used was a Bruker AM-250 NMR spectrometer (250 MHz for ^1H) with a Lambda Physik EMG101 MSC excimer laser as a light source ($\lambda = 308$ nm, 90 mJ).

2.3. Cis/trans isomerization

The retinal concentration in the samples was 0.01 M in CD_3CN. In the experiments with DBQ its concentration was 0.1 M. Prior to irradiation the samples were deaerated by Ar bubbling. Irradiation was performed in the probe of a JEOL NMR spectrometer at room temperature as long as photostationary conditions were attained: 10 min irradiation when using the filter with $\lambda > 380$ nm and 30 min for the filter with $\lambda < 380$ nm. The spectra of the products were recorded with a AM-250 NMR spectrometer just after irradiation and once again a day later. The cis/trans ratio was obtained from the intensities of the NMR signals of aldehyde protons of all-trans and different retinal cis isomers. To increase the signal-to-noise ratio the spectra were recorded by accumulating 64 scans with a delay between accumulations of 15 s $\gg T_1$(15-H) = 3.2 s. Chemical shifts of NMR spectral lines of the aldehyde proton (15-H, $\delta = 10.10$ ppm, doublet with $J = 7.8$ Hz) of ATR and its isomers allow the retinal isomers to be distinguished quite reliably (Fig. 1).

3. Results

3.1. CIDNP

During the irradiation of the ATR solutions in CD_3CN in the presence of electron donors and acceptors directly in the probe of the NMR spectrometer, we have observed the ^1H CIDNP effects of retinal and its isomers (see Fig. 2 and Table 1).

When the same reaction mixtures were irradiated in deuterobenzene, CIDNP was absent. Also, when benzoquinone and ubiquinone were used as electron acceptors no CIDNP effects were observed.

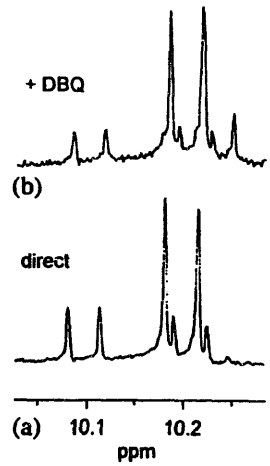


Fig. 1. NMR spectra (250 MHz) of ATR photolysis products with (b) and without (a) 0.1 M DBQ in CD_3CN. Irradiation with light of $280 < \lambda < 360$ nm for 15 min.

In the reaction of ATR with stilbene, the CIDNP effects were observed only in the case of laser irradiation ($\lambda = 308$ nm, the case when the light was absorbed by stilbene). For long wavelength irradiation ($\lambda > 380$ nm, absorption band of ATR) CIDNP effects have not been observed. In the former case, we detected a ^1H CIDNP effect of both stilbene forms and their isomerization. However, the formation of retinal cis isomers was not actually detected in the NMR spectra.

3.2. Cis/trans isomerization

The isomer composition was analyzed after the irradiation of both the reaction mixture and ATR in the absence of additives by means of comparison of the intensities of aldehyde protons (15-H) of ATR and its isomers in the NMR spectra. It should be mentioned that it is impossible to identify all retinal isomers formed under irradiation using the NMR method. As in the literature data [5,7,19], the basic isomers resulting from direct isomerization are 13-cis (δ(15-H) = 10.20 ppm), 11-cis ($\delta = 10.06$) and 9-cis ($\delta = 10.09$) (see Fig. 1). Experimental results are given in Table 2. As follows from the table, the ratio of isomers after photolysis with $\lambda > 380$ nm is slightly different when the reaction occurs in the presence of quinone. Note, however, that when the sample is kept for 24 h in the dark, the ratio of isomers changes. Similar effects have been described in the literature for sensitized ATR isomerization in nonpolar media [5]. The authors suggest that this is due to dark reactions involving unstable di-cis isomers.

When the samples are irradiated in the region $280 < \lambda < 380$ nm, the ratio of isomers substantially changes for both direct photolysis (compared to experiments with $\lambda > 380$ nm) and photolysis performed in the presence of electron acceptor–quinone (see Table 2). In the latter case, as well as for photolysis with $\lambda > 380$ nm, when the samples

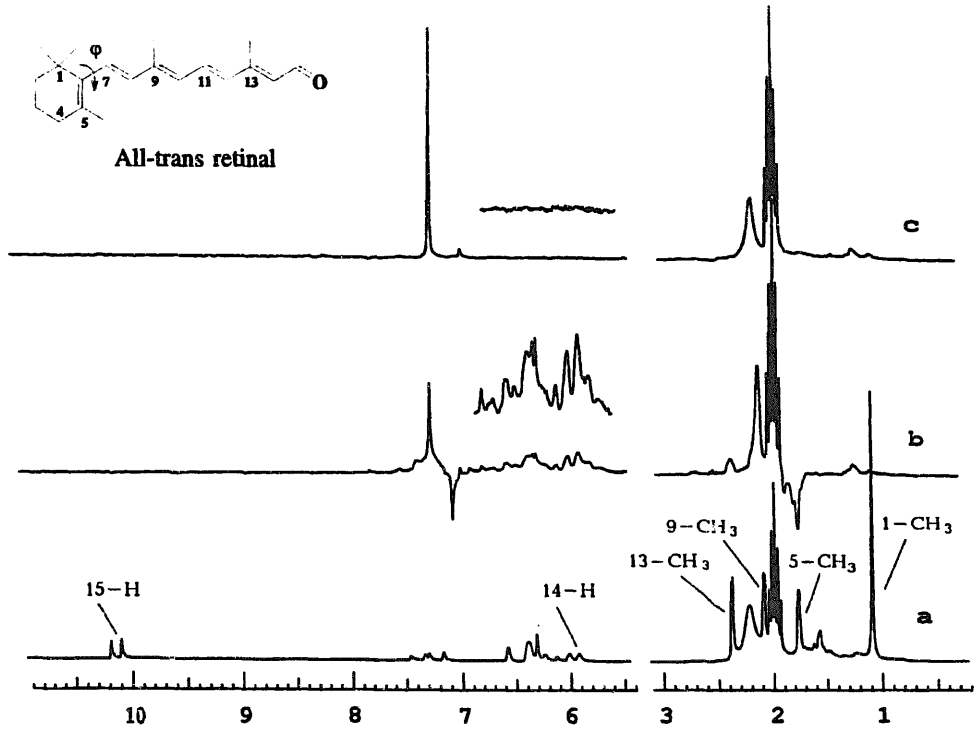


Fig. 2. (a) ATR NMR spectrum (90 MHz) in CD_3CN. (b) ^1H CIDNP spectrum on irradiation of 0.002 M ATR and 0.1 DBQ solution in CD_3CN. (c) The dark spectrum after photolysis. Retinal proton signals are actually unobservable owing to low concentration.

Table 1
^1H CIDNP effects detected upon ATR photolysis in CD_3CN in the presence of electron donors and acceptors

Partner	5-H tr (δ1.78)	14-H tr (δ5.94) [b]	15-H tr (δ10.11)	5-H cis (δ1.74–1.9)	4-H cis (δ5.83–6.07)	Other products
DBQ	E [a]	A	E	E	A	E(*Q*)
CA	E	A		E	A	
tr-stilbene	E		E			A(CH(*cis*-St)); E(*ortho*-, *para*-H (*tr*-St)) [c]

[a] E—emission, A—absorption.
[b] The adsorption has also been observed on other retinal =CH groups. However, only a minor difference in their chemical shifts prevents their separate observation.
[c] The CIDNP of =CH *trans*-stilbene is not given because its chemical shift coincides with that for the *cis*-stilbene phenyl group.

are kept for 24 h, the fraction of the initial all-trans isomer increases and that of the 11-cis isomer decreases.

3.3. Calculation results

According to CNDO/2 and INDO data [20–22] and X-ray crystallography [23], the ionone ring of retinal has a puckering structure: the $C_1C_6C_7C_5C_4$ fragment is almost flat, and C_2, C_3 atoms are located on both sides of the plane. The fragment of the conjugated chain C_7–$C_{15}O$ is almost flat and according to experimental data is swung through an angle (5–6–7–8) = −58.3° around the C_6–C_7 bond. This rotation is caused by the repulsion (greatest at $\varphi = 0$ and $\varphi = 180°$) of CH_3 groups of the ring from the C_7H and C_8H bonds [20]. The existence of similar minima separated by small (at $\varphi = 0°$) and large barriers was obtained from the calculations of $E(\varphi)$ energy by optimizing the remaining 139 geometrical parameters [20].

In the present work, a similar analysis of the geometry and energy of the molecule and its radical ions was performed using the AM1 method [24]. For the retinal molecule, this method gives significantly lower root-mean-square errors for bond lengths (0.0056 Å and 0.0079 Å) and valence angles (0.38° and 0.55°) as compared to the CNDO/2 method [20]. The spin density and isotropic hyperfine interaction (hfi) constants a_H were calculated for the configurations corresponding to given minimum energies by the INDO technique in the PUHF approximation using the SPIN-HAMILTONIAN program (by B.N. Plakhutin, Institute of Catalysis, Novosibirsk [25]).

Table 3 summarizes the values of angle φ and the relative energies for extreme points of retinal charge forms. The close

Table 2
The percentage of the distribution of retinal isomers under photostationary conditions in CD_3CN and on being kept in the dark for a day (in brackets). Experimental error is ±3%

Acceptor		all-trans	9-cis	11-cis	13-cis	Other
Direct	λ > 380 nm	35.5	20.5	18	17	9
		(38.5)	(22)	(14.5)	(17)	(8)
DBQ	λ > 380 nm	30	19	25	17	9
		(49)	(18)	(9)	(19)	(5)
Direct	λ < 360 nm	55	14.5	1	19.5	10
		(55)	(16)	(0)	(21)	(8)
DBQ	λ < 360 nm	40	11.5	21.5	16	11
		(54)	(13)	(4)	(20)	(9)
Direct [15]	λ > 380 nm	31	23	29	9.2	7.8

Table 3
The values of φ(grad) and ΔE (kcal mol^{-1}) for the minimum and maximum energy, calculated with geometrical optimization of retinal and its radical ions

Method		ATR		$ATR^{\bullet+}$		$ATR^{\bullet-}$
		CNDO/2		AM1		AM1
min 1	φ	−50	−54.8 [a]	−31.6	(−31.4) [b]	−45.0
	ΔE	0	0.25	0	(0.85) [b]	0.05
min 2	φ	90	57.3	30.0		50.1
	ΔE	0	0	0.06		0
max 1	φ	0	0	0		0
	ΔE	4.15	3.24	1.25		2.63
max 2	φ	−170	−170	−105		−160
	ΔE	6.46	3.91	3.95		3.68

[a] Experimental value is −58.3° [23].
[b] The values for terminal group C(O)H in the molecular plane.

values in energy minima correspond to approximately equal angles with opposite signs. These angles are slightly lower for retinal radical ions and the small barrier is noticeably lower than that in the neutral molecule. From the analysis of the calculated results, it is seen that the change in the charged state leads to comparatively insignificant changes in the majority of the geometrical parameters. In this case, the parameters of both minima (besides φ) are rather close. The most significant difference is in qualitative changes in the distribution of bond lengths in the conjugated chain where the charge and unpaired electron are located. In the neutral ATR molecule, the bond lengths alternate with alternating π-bond orders. The bonds are divided into double C_5–C_6, C_7–C_8, etc. bond length $l \approx 1.35$ Å, and single C_6–C_7, C_8–C_9, $l \approx 1.45$ Å. In radical ions, the alternation was observed in the starting and ending parts of the chain, whereas in the middle region of the radical cation the bond lengths C_8–C_9, C_9–C_{10}, C_{10}–C_{11} are about 1.41 Å, and in radical anions the bonds C_9–C_{10}, C_{10}–C_{11}, C_{11}–C_{12} are about 1.40 Å. Similar distributions of bond lengths are obtained by applying this theoretical approach to a flat model molecule $CH_2(CH)_{10}O$ and its radical ions. The redistribution of bond lengths was initiated by changes in the bond order when either the electron is removed from HOMO or the LUMO is populated, and is determined by the structure of these MOs.

For radical cations, the AM1 calculations demonstrate the rotation of the terminal group –C(O)H by an angle φ′(13–14–15–0) = −58.2°. A similar qualitative effect is also provided by the PM3 method [26]. The remaining part of the chain of radical cation is also flat, similar to that of the radical anion. The energy of the radical cation structure with a flat chain is higher by 0.85 kcal mol^{-1}.

Table 4 summarizes the INDO calculated spin densities of the carbon atoms of a conjugated chain. In this case, the spin populations of π-AO (orthogonal to the local plane σ-bonds) provide the major contribution to the calculated spin densities.

The spin density distributions for both energy minima are rather similar. However, the distributions in radical cations and anions are substantially different. In the radical anion the spin density is shifted towards the chain end, whereas in the radical cation it is localized on atoms 5, 7, 10, 12 and 14. At the beginning and at the end of the chain the signs of the spin densities alternate. In the middle part, however, where the alternation of bond lengths is disturbed, the spin densities of atoms 7–10 in the radical cation and atoms 9–14 in the radical anion have a positive sign. Table 5 shows the calculated hfi constants ($a_H > 0.1$ mT) of retinal radical ions. The ring protons (except for 4 − H and 5-CH_3) are γ-protons by their relation to the nearest 5,6 carbon atoms of the conjugated

Table 4
Spin density of carbon atoms of ATR radical ions, calculated for minimum energy configurations (see Table 2)

$N_{atom}\backslash\varphi$	$ATR^{\bullet+}$			$ATR^{\bullet-}$	
	−31.6	−31.4 [a]	30.0	−45.0	50.1
5	0.132	0.124	0.143	0.046	0.036
6	−0.012	−0.012	−0.010	−0.025	−0.020
7	0.127	0.112	0.127	0.138	0.131
8	0.049	0.047	0.052	−0.035	−0.034
9	0.068	0.054	0.064	0.176	0.176
10	0.217	0.209	0.214	0.013	0.010
11	−0.020	−0.031	−0.022	0.117	0.125
12	0.246	0.244	0.239	0.107	0.106
13	−0.047	−0.070	−0.047	0.041	0.046
14	0.178	0.205	0.170	0.190	0.191
15	−0.033	−0.087	−0.032	−0.031	−0.029
(O)	0.047	0.171	0.045	0.232	0.235

[a] The values for terminal group C(O)H in the molecular plane.

Table 5
Isotropic hfi constants a_H (mT) in ATR radical ions, calculated by the INDO method for energy minima from Table 3

$N_{atom}\backslash\varphi$	$ATR^{\bullet+}$			$ATR^{\bullet-}$	
	−31.6	−31.4 [a]	30.0	−45.0	50.1
4−H	0.48	0.45	0.88	0.12	0.21
4-H′	1.29	1.23	1.20	0.39	0.23
5-CH_3 [b]	0.59	0.56	0.66	0.17	0.13
7-H	−0.19	−0.18	−0.18	−0.27	−0.26
8-H	0.08	0.06	0.07	0.15	0.13
9-CH_3 [b]	0.33	0.27	0.29	0.67	0.68
10-H	−0.27	−0.27	−0.26	0.07	0.07
11-H	0.15	0.17	0.15	−0.12	−0.13
12-H	−0.34	−0.35	−0.33	−0.08	−0.08
13-CH_3 [b]	−0.21	−0.32	−0.20	0.12	0.15
14-H	−0.36	−0.35	−0.35	−0.23	−0.23
15-H	0.75	0.19	0.74	0.06	0.06

[a] The values for terminal group C(O)H in the molecular plane.
[b] Average value of a_H for CH_3 protons.

chain. For these, the a_H values do not exceed 0.1 mT. Other protons are either α- or β-protons with respect to carbon chain atoms. Using the well-known empirical expressions

$$a_H(\alpha) = Q_\alpha \rho_C \quad (1)$$

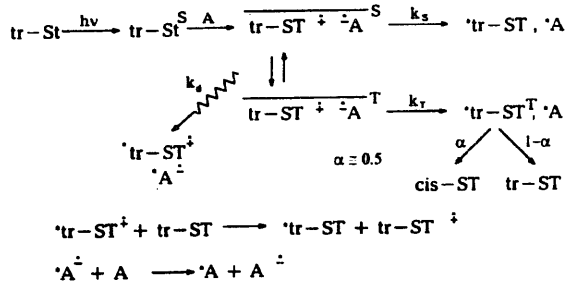
$$a_H(\beta) = Q_\beta \cos^2\chi\, \rho_C \quad (2)$$

we analyzed the correlation of calculated hfi constants with spin populations ρ_C of carbon atoms. For β-protons (4-H, protons of CH_3 groups bound to atoms C_5, C_9, C_{13}) the constants can be satisfactorily reproduced with $Q_\beta^+ = 9.0$ mT for the radical cation and with $Q_\beta^- = 7.2$ mT for the radical anion. The root-mean-square errors are 0.037 and 0.014 mT, respectively. A large constant a_H(15-H) ≈ 0.6 mT in the radical cation is determined by the rotation of the C(O)H group. As a result, the 15-H proton becomes a β-proton with respect to C_{14} with an angle $\chi = 33°$. When the groups are located in the chain plane, a_H(15-H) = 0.19 mT. A substantial mean constant has been predicted for 5-CH_3 protons.

For α-protons $Q_\alpha^+ = Q_\alpha^- = -1.5$ mT. Eq. (1) correctly predicts the signs of the a_H constant except for the minor constants 8-H of the retinal radical cation and 10-H for the anion. The a_H values in the radical anion are substantially lower because the spin density is localized on the carbon atoms possessing α-protons only, while $|Q_\alpha| \ll |Q_\beta|$. Besides, a substantial part (~0.23) of the spin density is located on the oxygen atom.

4. Discussion

Signs of net CIDNP effects of different protons (methyl and methine, see Table 1) correlate with the signs of the calculated hfi constants of these protons (Table 5). CIDNP effects were observed only for protons with maximum values of hfi constants. For example, photolysis in the presence of quinones shows polarization effects with opposite signs on the methyl (5, 13-CH_3) and methyne (12, 14-H) protons,



Scheme 1.

where the highest hfi values with different signs are assumed in the all-trans retinal radical cation (compare Tables 1 and 5). This is an argument in favour of single electron transfer (SET) between the ATR molecule in the excited state and quinone.

The absence of CIDNP effects in reactions in a nonpolar solvent is evidence of SET in the photoinduced interaction of all-trans retinal with electron acceptors. Indeed, there is a possibility of photoreduction of CA in the interaction with the double bonds of ATR [27] and the cyclohexene ring. However, no products of these reactions were observed in the NMR spectra. The absence of chemical polarization in benzene also testifies against the hypothesis of its appearance in the RIP of neutral radicals which are known [27] to be involved in the process of chloranil photoreduction. The polarization of DBQ protons (Fig. 2, Table 1) may result from both reversible electron phototransfer and reaction with a solvent [27,28].

A peculiar indicator of electron transfer is the CIDNP effect in the isomerization of *trans*-stilbene detected in the presence of all-trans retinal. It is known that the act of isomerization of *trans*-stilbene into the cis form is preceded by the transition of the initial stilbene molecule to the excited triplet state [29]. It has been found [11] that in the photoinduced interaction of stilbene with electron donors and acceptors, the stilbene excited triplet state results from the SET process according to Scheme 1 (asterisks indicate polarization).

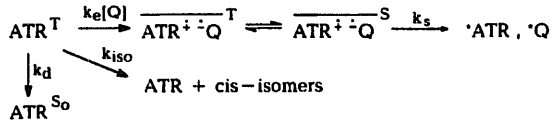
Indeed, the analysis of CIDNP effects detected in the reaction of *trans*-stilbene with ATR has shown *cis*-stilbene to be polarized as a cage product of a triplet radical ion pair (RIP) with singlet precursor. Thus, the *g*-factor of ATR is larger than that of stilbene, i.e. $g(\mathrm{ATR}) > 2.0028$ [30]. This agrees with the data given in Ref. [14].

As mentioned above, in the case of light absorption by ATR, CIDNP effects are absent, as they are in the photoinitiated interaction of ATR with benzoquinone and duroquinone. CIDNP effects were detected in the reactions of ATR with CA and DBQ only. In this case, the energy of RIP is lower than the ATR triplet energy (1.54 eV [15]). Thus, if we assume the reaction from the triplet state of ATR, only with these two quinones were the conditions for SET (Weller–Zachariasse criterion [31], see Table 6) satisfied. These facts and the value of the ATR fluorescence decay time, −47 ps, [33] point to the participation of the retinal triplet excited

Table 6
Excitation energy and polarographic half-wave potentials of the compounds studied (eV)

Substrate	$^1E^*$	$^3E^*$	E_+	E_-	ΔH [d]
ATR [a]	2.86	1.54	>1.2	−1.38	
DBQ				−0.18 [b]	1.2
CA		2.35		+0.01 [b]	1.0
tr-Stilbene [c]	3.8	2.12	1.51	−2.19	2.69

[a] The data are from Ref. [5].
[b] Redox potentials are from Ref. [32].
[c] The data are from Ref. [11].
[d] $\Delta H = E_+ - E_- - 0.2$ eV, the energy of RIP; $\Delta G = E_+ - E_- - {}^1E^* - 0.2$ eV [31].



Scheme 2.

state in the SET reaction. From the analysis of CIDNP effects in the reaction of ATR with quinones we have concluded that ATR was polarized as a cage product of reversible electron transfer in singlet RIP with a triplet precursor. The CIDNP effects of isomers will be discussed later.

The CIDNP intensities of ATR protons are sensitive to retinal concentration, but are independent of quinone concentration in the range from 10^{-1} to 10^{-3} M. Let us discuss all the possible reasons for the independence of the CIDNP effectiveness of quinone concentration. ATR phototransformation in the presence of quinone is presented in Scheme 2, where k_e is a rate constant of SET, and k_d and k_{iso} are the decay and isomerization rate constants. The lifetime of the ATR triplet in the absence of quinones is known to be 8 μs [33]. The CIDNP intensity should be proportional to the RIP formation probability (P):

$$P = k_e[Q]/(k_e[Q] + k_d + k_{iso}) \quad (3)$$

In this case, the CIDNP effectiveness will be constant with different quinone concentrations if the value of $k_e[Q]$ exceeds $k_d + k_{iso} \approx 10^5\ \mathrm{s}^{-1}$. In the range of quinone concentrations 10^{-1}–10^{-3} M, the value $k_e \approx 10^9\ \mathrm{M}^{-1}\mathrm{s}^{-1}$ ensures agreement with the experimental results. If $k_{iso} > 10^5\ \mathrm{s}^{-1}$ or k_e is lower than $10^9\ \mathrm{M}^{-1}\mathrm{s}^{-1}$, the dependence of CIDNP effectiveness on quinone concentration should be detected. Thus, we can conclude that the fastest process in the reaction under study is the electron transfer from the retinal excited triplet state to quinone.

Now, let us consider the CIDNP effects of retinal isomers. The isomer composition is presented in Table 2. The CIDNP effects of their methyl and methyn protons are summarized in Table 1. The phenomenon of isomer polarization itself and

the above-mentioned hypothesis on SET as the fastest process in this reaction indicate that isomerization can proceed via a radical ion pair. If these processes are independent, as shown in Scheme 2, the presence of quinone should decelerate isomerization to a great extent. Our investigation of the build-up rate of isomers by their NMR spectra does not show appreciable changes in the presence or absence of quinone.

As can be seen from Fig. 2 and Table 1, ATR and its isomers demonstrate the same polarization pattern. This suggests that isomer polarization results from either one or several similar RIPs, probably of the isomer radical cation and quinone radical anion.

Let us focus on the first suggestion, which actually means that isomerization occurs in the radical cation itself. There is a point of view widely discussed in the literature that the isomerization occurs in the so-called "twisted triplet" [5,34] (compare with "fantom triplet" taking place in stilbene isomerization [29]). If we assume formation from the "twisted triplet" radical cation with the same geometrical configuration, the isomer distributions should not differ significantly for direct isomerization and isomerization in the presence of an electron acceptor.

The most perceptible changes in isomer composition, however, are caused by variations in irradiation wavelength. This phenomenon has already been described in the literature [5,6] and is connected with the excitation of π–π^* or n–π^* transitions in the ATR absorption spectrum. In addition, the most striking difference was observed for 11-*cis*-retinal and di–cis isomers, their quantity depending on both the irradiation wavelength and the presence of acceptor (see Table 2). Thus, after irradiation with $\lambda < 360$ nm we observed a considerable decrease in the NMR signal in the area of the 11-cis aldehyde proton, compared with the results of irradiation with $\lambda > 380$ nm. This signal increases 20-fold in the presence of quinone, but decreases again after being kept in the dark for a day. We have assumed that these transformations are connected with the formation and decay of unstable di–cis isomers, whose aldehyde proton chemical shift coincides with those for 11-cis. Such reactions have already been described in the literature [5].

The changes in isomer composition in the presence and absence of acceptor can probably result from the difference in the electron structure of the ATR excited triplet state and its radical cation. It might be expected, however, that the role of quinone is not restricted to electron acceptance. We can assume that the different rates of back electron transfer to various isomers can also result in changes in isomer composition.

Also, we cannot exclude the possibility of formation of CIDNP in the SET reaction between quinone and a set of retinal isomers in the excited triplet states. We might imagine such a possibility if ATR and quinone form the triplet exciplex. The retinal cis isomers are then formed during the exciplex lifetime, after which the SET reaction with each isomer takes place. In this case, CIDNP efficiency will not depend on quinone concentration.

Thus, in the presented work, the formation of ATR cations and anion radicals in photoinduced interaction with electron acceptors (quinones) or donor (stilbene) was established. It was found that ATR reacts with quinones from the triplet excited state.

The influence of quinone on the cis/trans ratio of ATR isomers and CIDNP effects of isomers allows us to suggest the photoisomerization of ATR in the radical ion pair or exciplex. At present we are unable to make a choice between these two possibilities.

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