

## Excited state relaxation dynamics and electronic properties of a quinoid carotenoid

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### ARTICLE INFO

#### Article history:

Available online 6 May 2010

#### Keywords:

Carotenoid  
Femtosecond transient absorption  
Quantum chemical calculation  
Charge-transfer state

### ABSTRACT

A combined study of the quinoid carotenoid DHIRQ by femtosecond transient absorption spectroscopy and quantum chemical calculations revealed its very complex electronic structure and ultrafast relaxation dynamics. The two quinoid end rings are found to cause a strong bathochromic shift of the absorption spectrum and to decrease the main relaxation time of the  $S_1$  state to 400 fs. Transient absorption data of DHIRQ show a substantial difference of its spectroscopic features to other carbonyl carotenoids. Various alternative kinetic models including an intramolecular charge transfer (ICT) state are discussed in order to assign the electronic structure and the relaxation dynamics.

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### 1. Introduction

Despite intense research, the electronic excited-state level structure and the excited-state relaxation processes in carotenoids are not well understood (for a recent review see e.g. Polivka et al. [1]). While for all carotenoids the first excited state is characterized as the  $2A_g^-$  ( $S_1$ ) state, and the strongly absorbing state as the  $1B_u^+$  ( $S_2$ ) state, there exists a substantial controversy about the location of other states that should be present in carotenoids, e.g. the  $1B_u^-$  state and higher-lying  $A_g$  states. A particularly controversial point of fundamental relevance for the understanding of the excited state relaxation dynamics is the question whether additional electronic states are located between the  $2A_g^-$  state and the  $1B_u^+$  state [1]. We have recently shown that indeed the  $1B_u^+$  and the  $1B_u^-$  state are close to each other in carotenoids of conjugation lengths  $n = 10$  (lutein) and  $n = 11$  ( $\beta$ -carotene) [2] and that these states actually cross dynamically after electronic excitation upon conformational and electronic relaxation from the initially excited Franck–Condon (FC) region. Further poorly understood problems arise with carotenoids that contain hetero-atoms in the conjugated system. Here carotenoids carrying carbonyl groups are of special interest since they form intramolecular charge transfer (ICT) states. The spectroscopic features and relaxation dynamics of these carotenoids show

a strong dependence on the solvent polarity. In polar solvents their absorption spectra are essentially unstructured and the lifetime of the ICT state decreases by a factor of 3–10 in comparison to non-polar solvents [3–5]. These carotenoids play special roles in a number of photosynthetic antenna systems from marine organisms [6–9]. Among the carotenoids with a carbonyl group incorporated in the conjugated electronic system there are compounds which are substituted with a quinoid end groups. An example of such a carotenoid is 3,4-dihydro-4,3'-retro- $\Phi$ - $\Phi$ -carotene-3,3'-dione (DHIRQ) – a planar molecule with a system of fully conjugated double bonds [10] (Fig. 1). It is an oxidation product of the phenolic carotenoid 3,3'-dihydroxyisorenieratene (DHIR) which occurs in bacteria such as *Brevibacterium linens* and has been shown to be a very efficient multifunctional antioxidant [11]. In contrast to the yellow–red DHIR the oxidized molecule is a blue compound with an absorption maximum of ca. 580 nm in chloroform [12].

We present here the results of a spectroscopic and theoretical investigation of the excited-state energies and relaxation dynamics of the DHIRQ molecule. This molecule, in particular in more polar solvents, shows longer-wave absorption bands and lower excited-state energies than any naturally occurring carotenoid and belongs to a class of blue carotenoids which can be synthesized from natural starting compounds [13].

### 2. Experimental procedures and computational details

#### 2.1. Experimental

$\Phi$ , $\Phi$ -carotene-3,3'-dione (DHIRQ, isorenieratene-3,3'-dione) was synthesized and purified as described elsewhere [11].

Abbreviations: FC, Franck–Condon; ICT, intramolecular charge transfer state; LFD map, lifetime density map; DFT/MRCl, density functional theory/multireference configuration interaction method; ESA, excited-state absorption; SE, stimulated emission; GB, ground state bleaching; DHIR, dihydroxy-isorenieratene; DHIRQ, 3,4-dihydro-4,3'-retro- $\Phi$ - $\Phi$ -carotene-3,3'-dione.

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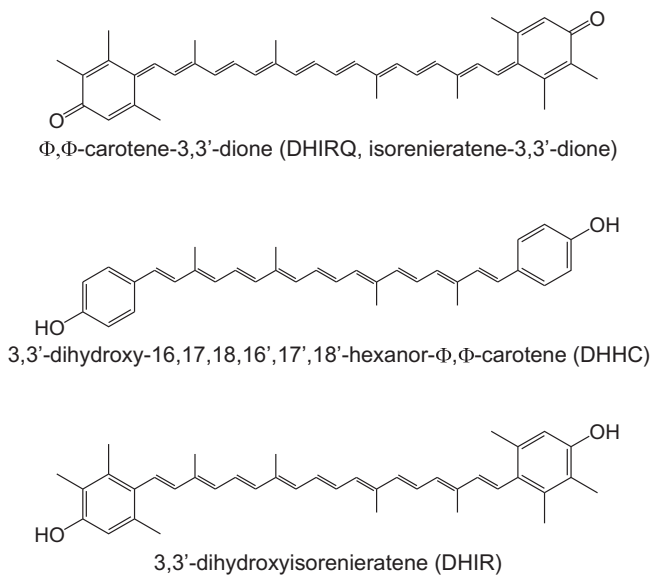


Fig. 1. Molecular structure of DHIRQ, DHIR and DHHC carotenoids.

Steady-state absorption spectra were measured on a Cary 100 (Varian) spectrometer in HPLC-quality dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), *n*-hexane (first dissolved in a very small amount of  $\text{CH}_2\text{Cl}_2$ ) and carbon disulfide ( $\text{CS}_2$ ). Before use solvents were dried on an aluminium oxide column and degassed and bubbled with argon.

Femtosecond transient absorption measurements were performed at room temperature in  $\text{CH}_2\text{Cl}_2$  and *n*-hexane as described earlier [14]. The excitation pulse width was  $\sim 80$  fs, FWHM of  $\sim 4$  nm, with low intensity excitation pulses of  $\sim 3 \times 10^{13}$  photons/( $\text{cm}^2$  pulse) in order to avoid saturation effects. Pump and probe pulses were polarized at magic angle to each other. All measurements were performed in a 1 mm cuvette (OD = 2–7/cm in the maximum of absorption) which was moved in a Lissajous scanner during experiments in order to keep the average irradiation per sample volume low. Sample stability was controlled by the absorption spectrum which was the same before and after the measurements.

Data were analyzed by lifetime distribution analysis and are shown as lifetime density maps (LFD maps) [14]. The LFD maps are calculated by an inverse Laplace transformation from the original transient absorption surfaces vs. time and wavelength and represent the amplitudes of the lifetime components in a quasi-continuous lifetime range (analogous to decay-associated difference spectra) [15]. Global target analysis testing various kinetic models was subsequently performed on the LFD maps. White–yellow regions correspond to positive amplitudes and reflect either absorption decay or rise of a bleaching signal. Blue–black regions correspond to negative amplitudes and reflect either absorption rise or decay of the bleaching [14].

## 2.2. Theoretical calculations

Equilibrium geometries of the  $1A_g^-(S_0)$  and  $1B_u^+$  states were taken from our previous work [10]. A linearly interpolated excited state relaxation pathway was constructed connecting the Franck–Condon region (reaction coordinate  $\text{RC} = 0$ ) and the  $1B_u^+$  potential minimum ( $\text{RC} = 10$ ). A parallelized version of the combined density functional theory/multireference configuration interaction (DFT/MRCI) method [16,17] was used for single-point energy calculations along this pathway. The performance of this method on linear conjugated  $\pi$ -systems (polyenes,  $\alpha, \omega$ -diphenylpolyenes, and  $\beta$ -carotenes) with experimentally known electronic excitation

energies has been carefully investigated [17–20]. As a general trend it is found that this method correctly describes the order of the low-lying  $2A_g^-$  and  $1B_u^+$  states, in contrast to most other quantum mechanical methods. Moreover, the experimental trends for the energy gap between these states are very well reproduced. Absolute excitation energies for extended  $\pi$ -systems with conjugation length  $n \geq 10$ , on the other hand, are typically underestimated by about 0.3 eV.

In all calculations the SV(P) basis set of the Turbomole library [21] was employed. The configuration state functions (CSFs) in the MRCI expansion are built up from Kohn–Sham (KS) orbitals using the BH-LYP [22] functional. A common set of reference CSFs was used for all spatial symmetries of the  $C_{2h}$  molecular point group. The 1s shells of the carbon atoms were kept frozen in the electron correlation treatment. The initial MRCI reference space was spanned by all single and double excitations from the five highest occupied molecular orbitals (MOs) to the five lowest unoccupied MOs of the ground state KS determinant. Wave functions and excitation energies were computed for six  $1A_g$ , two  $1A_u$ , two  $1B_g$ , and five  $1B_u$  states as well as five  $3A_g$ , two  $3A_u$ , two  $3B_g$ , and six  $3B_u$  states. In the second iteration, all configurations with a squared coefficient of at least 0.003 in one of the initial MRCI expansions were included in the final MRCI reference space from which all single and double excitations were allowed.

## 3. Results

### 3.1. Steady-state absorption spectra

Fig. 2 shows the steady-state absorption spectra of DHIRQ in  $\text{CH}_2\text{Cl}_2$ , *n*-hexane and  $\text{CS}_2$  (for solvent parameters see Table 1). Measurements in more polar or higher polarizable solvents were prevented on the one hand by the poor solubility of the compound and on the other hand by its chemical instability in more polar solvents. For this reason the femtosecond measurements were performed only in  $\text{CH}_2\text{Cl}_2$  and *n*-hexane. In all three solvents steady-state spectra are extremely red-shifted ( $\sim 100$  nm) in comparison to other carotenoids with  $n = 10$  double bonds in the polyene chain (formally, including the quinone rings, DHIRQ has  $n = 14$ ). DHIRQ shows stronger red-shift than even the homolog of  $\beta$ -carotene M19, which has the largest conjugation-dependent shift of the absorption maximum of carotenoids observed so far. M19 has  $n = 17\beta 2$  double bonds for the nomenclature see [23,24] and its

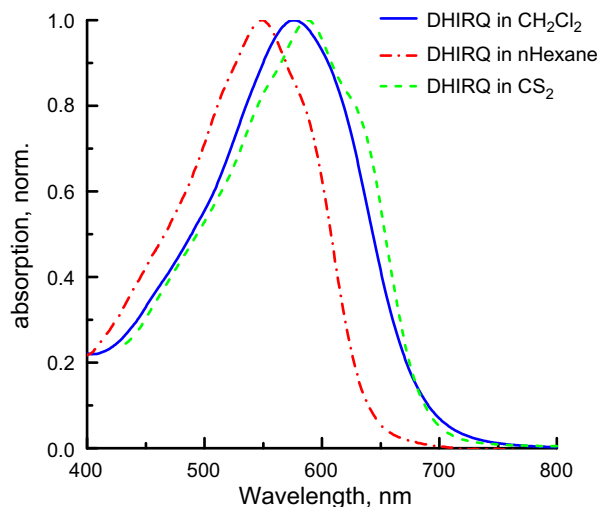


Fig. 2. Normalized steady-state absorption spectra of DHIRQ in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), *n*-hexane and carbon disulfide ( $\text{CS}_2$ ).

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