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Electrosynthesis of dixanthylene photochromic dye, characterization and ab initio calculations

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Abstract

The feasibility of electrosynthesis of dixanthylene photochromic dye by electrochemical reduction of xanthone in the presence of perchloric acid has been investigated in acetonitrile at glassy carbon electrode. The electrode shows a remarkable electrocatalytic effect for the reduction of xanthone. Reduction of xanthone at such an electrode occurs at potentials −0.8 V relative to the SCE. The electric charge passed corresponded to 1 electron/molecule relative to the amount of substrate in the electrolysis. In all cases fairly good yields of dixanthylinum perchlorate (95%) was obtained in acetonitrile. The products were analyzed by MS, IR and NMR spectroscopies. The mechanism of electro-reduction is discussed. The photochromic properties of dixanthylinum were studied by conductometric method, UV−vis, and NMR spectra. The optimized geometries were calculated by using restricted/unrestricted Hartree−Fock (RHF/UHF) with 6-31G basis set. Some molecular and spectroscopic properties have also been calculated at the same level of theory and the same basis set for the optimized structures.

Keywords: Electrosynthesis; Dixanthylene; Photochromic dye; Ab initio calculations

1. Introduction

A number of organic compounds undergo color changes with temperature and light which are so noticeable that special names, thermochromic and photochromic, respectively, have been given to the phenomena. The compounds showing them are some of the substituted ethylenes, with multiple or fused aromatic rings as substituents. The design of such molecular-level switching devices is directly linked to the chemistry of signal generation, transfer, conversion, storage, and detection (semiochemistry). Typical bistable species are the so-called photochromic compounds, molecules that can be interconverted between two forms (A and B) exhibiting different colors [1−7]. Most photochromic compounds change their color by photoexcitation and revert more or less slowly to their initial state when kept in the dark. Compounds exhibiting this behavior are useless for information storage (or switching purposes) since the written information (switching state) is spontaneously erased (back converted) after a relatively short time. The synthesis of bistricyclic aromatic enes such as dixanthylenes and its salts is of interest due to their photochromic and thermochromic properties as optical memory application [8]. This compound is the analogues of bianthron, and polycyclic quinones (periaryloxyquinones and perimidinespirocyclohexadienones) were used as variable transmission optical materials, optical information storage, cosmetics and, authentication systems [9−13]. The conventional synthesis of dixanthylene is based on Schonberg and Ault methods that suffers from several drawbacks such as the use of hazardous chemicals, the high temperatures required for the reactions and the long time period [14,15]. Schonberg et al. have tried to show how substitution affects the thermochromic properties of dixanthylenes [16].

Organic electrosynthesis is a powerful tool in organic synthesis. More than thirty years ago, Ahlberg and Parker [17]

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studied the electrosynthesis of several oxygenated polycyclic aromatic compounds by anodic oxidation of anthracene and related compounds and its derivatives [18–23]. The reactions were carried out at Pt anode in an undivided cell at constant potential and constant current densities in the presence of nucleophiles until 1 electron/molecule of anthracene was passed. In this study, we explore a new approach for the electrosynthesis of dixanthylinum and dixanthylene, based on the reduction of xanthone at GC cathode in acetonitrile solution. We also report here photoreductions accompanied by visible color developments (photochromism) and increasing of conductivity (photoionization), which have been observed for very low concentration of dye in dimethylsulfoxide solution.

Bianthrones and dixanthylenes are thermochromic and photochromic compounds suitable for use in optical data storage media [24,25] and as molecular functional units such as optical switches [26]. Both fields of application require optical bistability, which is provided by derivatization. Irradiation with visible light induces neutralization reaction (for dixanthylium) and change of conformation, leading to the production of A and B form isomers (see Scheme 3). The good photochromic performance of dixanthylene is based on a combination of the following properties: thermal stability of both isomers at room temperature, high conversion efficiencies due to both clearly separated absorption bands with high extinction coefficients in liquid solution. Different isomers can be distinguished by means of UV–vis absorption and NMR spectroscopies, which have been proved to be totally nondestructive methods for detecting the isomerization states. One of the prime reasons lacking industrial applications of the photochromic materials, particularly organic photochromic compounds, is their poor durability of colorization [27]. Although the extensive study on improving the durability for photochromic property was performed, the stable compound still remains rather limited in practical applications.

We report herein the electrosynthesis and absorption spectra of dixanthylinum and dixanthylene, which were prepared from xanthone (Scheme 1). Effects of solvent on the photochromic behavior of this compound, optimized geometries, and some molecular properties are also reported.

2. Experimental

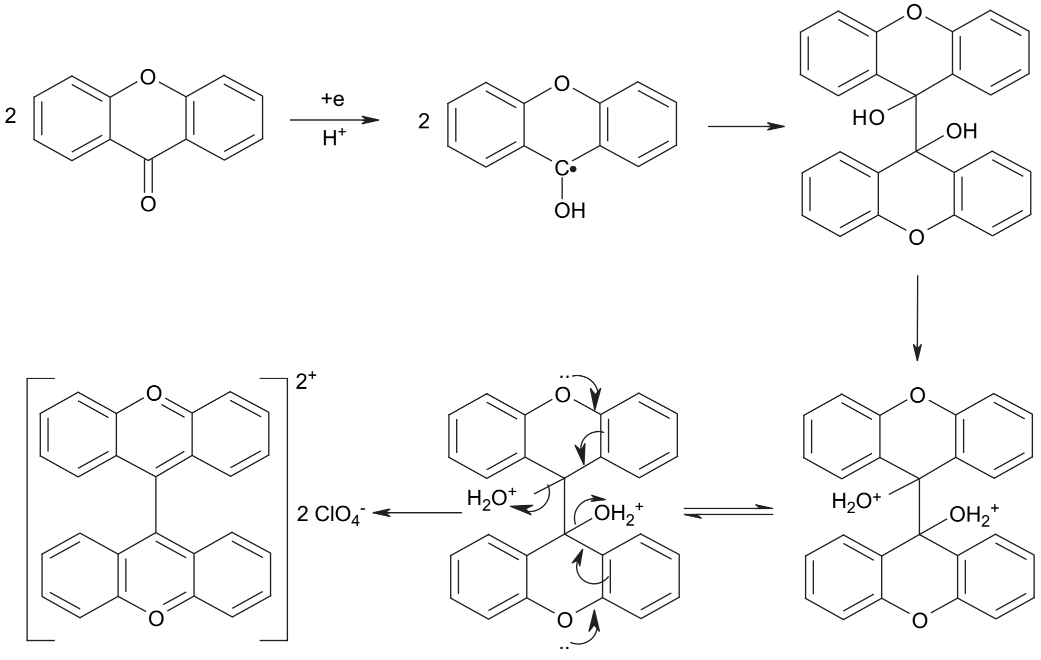
2.1. Chemicals

Xanthone and lithium perchlorate was purchased from Fluka and all other compounds used (all from Merck) were of the highest purity available and used without any further purification.

2.2. Instrumentation

Electrochemical reduction of xanthone was carried out by using Behpajuh (BHP 2061-C model, Isfahan, Iran) potentiostat/galvanostat. Cyclic voltammetry measurements were made at glassy carbon (GC) electrode. The counter-electrode electrode was a Pt (Pars Platin, Tehran, Iran) wire and all potentials are reported versus the KCl saturated calomel electrode (SCE, from Azar electrode, Tabriz, Iran).

Based on the potential observed voltammetrically, a controlled-potential bulk electrolysis experiment was conducted using two different cells: a two-compartment cell with a Pt anode and separated from the cathode (a graphite rod with a diameter of 8 mm and length 5 cm) compartment by salt bridge containing 0.1 M of lithium perchlorate. The graphite electrode was washed in acetone in order to reactivate it.



Scheme 1. Electrosynthesis reaction sequence of dixanthylinum.

The xanthone (0.50 g; 2.6 mmol) was electrolyzed at a graphite cathode in perchloric acid (2.3 mol l^{-1})–acetonitrile solution (20 ml), at −0.8 V (versus SCE) in a divided cell and a Pt anode. All solutions of the substrate were deoxygenated by purging them with nitrogen for 15 min, after which the gas stream through the cell was closed and a constant potential applied. All experiments were performed at 35 °C. The cathode compartment was continually stirred with a magnetic stirrer. A precipitate formed during electrolysis. After ca. 2.4 F mol^{-1} had passed, the cell current dropped close to the background value. In this mode of operation the product is continuously collected and the bulk electrolysis process is discontinued as soon as enough products for analysis has been obtained (typically 700 mg product). The precipitate was filtered and washed several times with acetonitrile and methanol to remove xanthone and perchloric acid, and dried in vacuo. The products were then dissolved in deuterated CH_3CN and DMSO and analyzed by ^1H NMR (Bruker DRX-500 MHz spectrometer) and MS (Finnigan–Matt MD 8430 with EI source). A photodiode array UV–vis spectrophotometer (Sinco 2100 series) was used for obtaining the absorption spectra. Infrared (IR) spectra of product were obtained using a Shimadzu IR-460 spectrometer using KBr tabulating. The product yield was determined by comparison of initial xanthone weight and integrals in ^1H NMR spectra. Melting point of the product was monitored on a Electrothermal Model 9100.

Yield and characterization of the product: m.p. > 320 °C. IR (KBr, cm^{-1}): 3050, 1618, 1568, 1563, 1518, 1518, 1114, 1005, 771; ^1H NMR (CD_3CN, d): 6.95 (t, 4H), 7.12 (d, 4H), 7.48 (d, 4H), 7.67 (dd, 4H); MS, *m/z* (%): 360 (M^+, 100), 329 (24), 178 (50), 149 (26), 111 (14), 95 (28), 69 (55), 43 (88).

Conductance measurements were carried out with a Metrohm 712 conductivity meter. A dip-type cell, made of platinum black, was used.

3. Results and discussion

3.1. Electrosynthesis

The electrochemical reduction of xanthone was investigated by cyclic voltammetry at GC electrode in acetonitrile containing lithium perchlorate as supporting electrolyte. Under all experimental conditions, xanthone give an irreversible reduction peak at quite negative potentials. Fig. 1 shows examples of the voltammetric response of xanthone at GC electrode in CH_3CN. The peak potentials (E_p) measured for the reduction of the compound at GC electrode is −0.8 V versus SCE.

The strong effects of the nature of the cathode material on E_p suggest that reduction of the xanthone at GC electrode proceeds with appreciable interaction between the electrode and the substrate and/or its reduction products and intermediates. The mechanism of the electrochemical reduction of aromatic ketones has been previously reported in the literature [28,29]. The overall process involves an e-reductive cleavage of the carbon–oxygen bond and is kinetically controlled by the electron transfer to carbonyl. According to the well-established reaction mechanism for the dissociative electron transfer to aromatic ketones [30] reduction of carbonyl at inert electrodes can be described by the reaction sequence shown in Scheme 1, where HA stands for any proton donor present in the reaction medium. The formed product dixanthylinum shows no reduction peaks up to the cathodic limiting discharge, so only the irreversible reduction peak of the starting carbonyl could be observed in cyclic voltammetry (Fig. 1a). The results reported in this work indicate that there is an electrocatalytic effect in the case of GC. There are no literature data for the reduction of xanthone at GC cathode. According to the reaction mechanism shown in Scheme 1, reduction of xanthone leads to a hydroxyl radical (pinacol) that readily reacts with a dimerization process in solution. Thus, pinacol is formed in the presence of proton (Scheme 1). The carbonyl of xanthone will be protonated by any acid ($HClO_4$, HCl and H_2SO_4) present in the reaction medium. The observed change of yield in favour of the protonation reaction on passage from H_2SO_4 and HCl to $HClO_4$ may be explained by the fact that perchlorate is a better anion in CH_3CN.

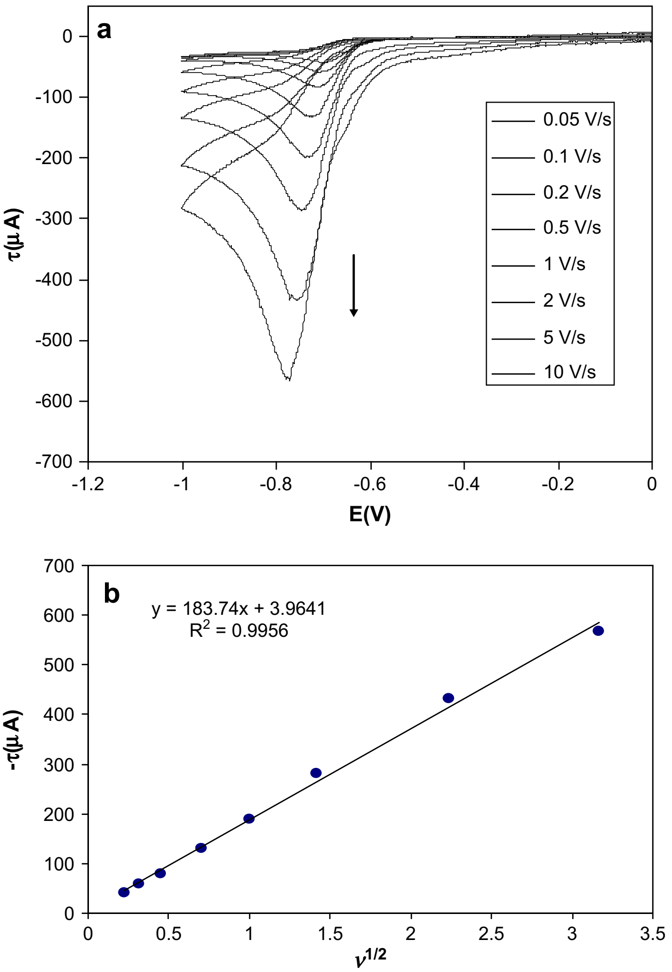


Fig. 1. (a) Cyclic voltammogram of 2×10^{-3} M xanthone in the presence of perchloric acid, at a glassy carbon electrode (1.8 mm diameter) and at various scan rates in acetonitrile. (b) Linear plot of the peak current (i_p) versus the square root of scan rate ($\nu^{1/2}$) at 25 °C.

Fig. 1 shows the voltammograms of xanthone at various scan rates and plot of the i_p of the xanthone (the reduction peak at −0.8 V) versus $\nu^{1/2}$ in acetonitrile. It is well known that the CV peak current (i_p) of electroactive molecules in solution is proportional to the square root of potential scan speed ($\nu^{1/2}$) at 35 °C (Fig. 1b). According to this plot, the i_p is varied linearly with the $\nu^{1/2}$ within the experimental region, indicating that the electrochemistry of xanthone product in acetonitrile was diffusion controlled and soluble product was directly formed during the experiment, and such behavior (appearing as an increase in the height of the cathodic peak at higher scan rates) is adopted as indicative of an EC mechanism (Fig. 1b).

The controlled-potential electrolyses, which were performed at a potential just E_p of the xanthone, require ca. 1 electron/molecule of xanthone. However, a gradual color change of the solutions in the bulk of the solution during electrosynthesis suggests that little solubility of product occurs. As a result, the product would be formed not only on the electrode but also in the solution. The red precipitate is not soluble in $CHCl_3$ due to dication formation (dixanthylinum).

3.2. Photoproperties

Photochemical reactions in organic materials can induce much change in physical properties such as solubility, optical transparency, dielectric constant, and refractive index and conductivity. Among many kinds of photoreactive materials, photochromic compounds have attracted much attention because of their potential ability for various photoactive devices, such as optical memory system, display device, optic, and electro-optic component [9–13]. The photoproperties of the resulting product were studied by conductometric method and UV–vis, NMR spectra in CH_3CN and DMSO.

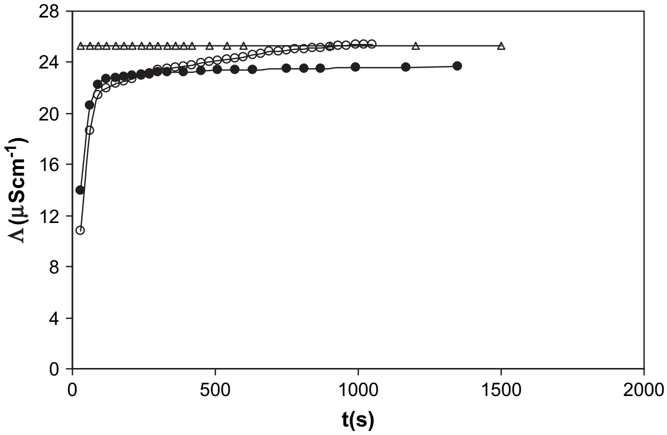
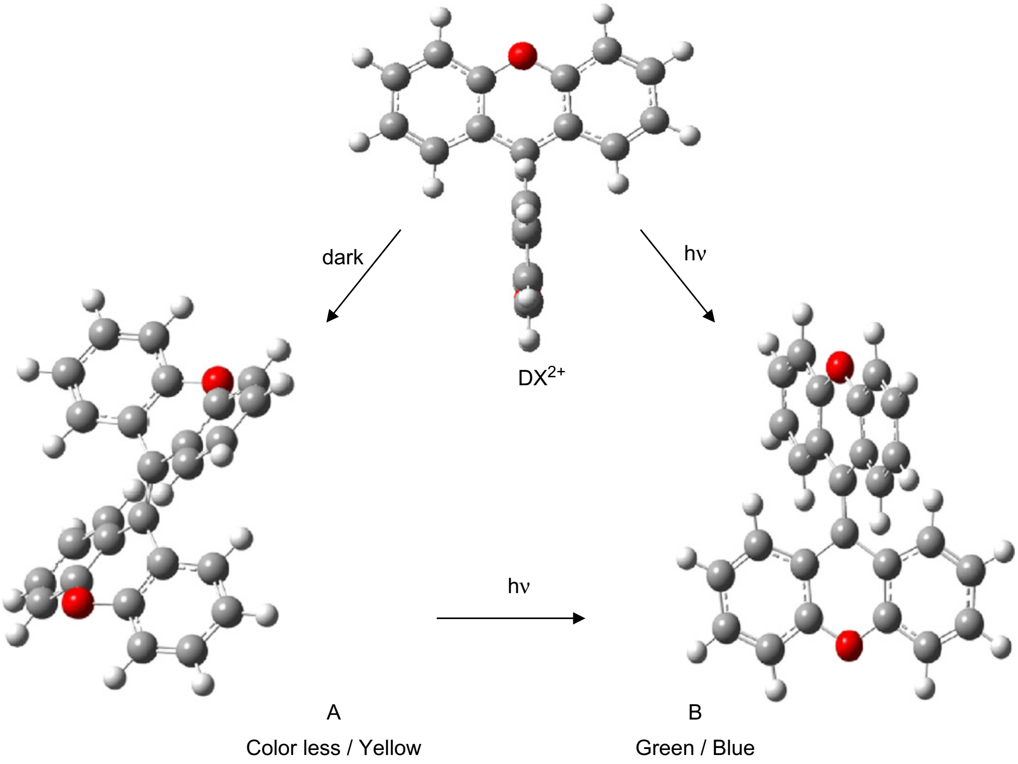


Fig. 2. Electrical conductivity of dixanthylenium perchlorate, 2×10^{-4} M in DMSO in the presence (○) and absence of light (●) and compared with conductivity of 4×10^{-4} M $HClO_4$ in DMSO at room temperature (△).

3.2.1. Conductivity and spectroscopy

The conductivity of dixanthylinum is measured in the order of 11 μS cm^{-1} (2.0×10^{-4} M of dixanthylinum); after irradiation with sunlight, its conductivity markedly increased up to the order of 25 μS cm^{-1} which is closer to that of traditional free perchlorate and proton ions (Fig. 2). In the absence of light and same conditions the conductivity of dixanthylinum solution is measured in the order of 11–24 μS cm^{-1}. The



Scheme 2. The mechanism of thermochromism of BAEs using 3D structures of dixanthylene calculated with HF/6-31G.

irradiated products become soluble in $CHCl_3$ and many other organic solvents. These phenomena indicated the neutralized dixanthylene formation during the irradiation of dixanthylinum in DMSO solution and formation of green form of dixanthylene. In the absence of light colorless form of dixanthylene is the predominant isomer and on irradiation with sunlight, A (colorless) form of dixanthylene was converted to the B (green) isomer, the isomer which exhibited photochromic properties. The synthesized dixanthylinum perchlorate readily dissolved in DMSO, sparingly soluble in CH_3CN and insoluble in less polar solvents, such as $CHCl_3$. Photochromism of this compound was observed in DMSO, which can be attributed to the photoinduced isomerization of the red dixanthylinum form to the green-colored form (Scheme 2). Fig. 3a shows the isomerization spectral changes of dixanthylinum perchlorate in a DMSO solution and in dark conditions. The dication form has two absorption peaks at 265 and 390 nm, while the A (neutral) form displayed typical double peaks at 295 and 350 nm. The fact that photoreaction involves only the conversion of A to B form in the presence of sunlight was proven by the isosbestic points observed at 310, 405 and 460 nm (Fig. 3b). The B form has triple absorption peaks at 295, 350 and 425 nm. Compared with the absorption spectrum of isomer A, the corresponding peak of isomer B was shifted 75 nm to longer wavelengths. As it is seen, sunlight irradiation of A form results in the appearance of a new absorption maximum at 425 nm in the expenses of the gradual disappearance of the A isomer absorption maxima at 350 nm through a well-defined isosbestic point at 405 nm, presumably due to the formation of a B form isomer in solution. Spectrophotometric experiments of dixanthylene (A form irradiated by sunlight) at DMSO solution indicate that during the decay of the absorption at 350 nm there is a parallel build-up of the B isomer (425 nm, Fig. 4). The photoisomerization of dixanthylinum was not observed after 4 h sunlight irradiation, under the same experimental conditions in CH_3CN solution (results were not shown). This finding indicates that the donocity (basicity) of the solvent has a strong effect on the stability and photochromic behavior of dixanthylinum.

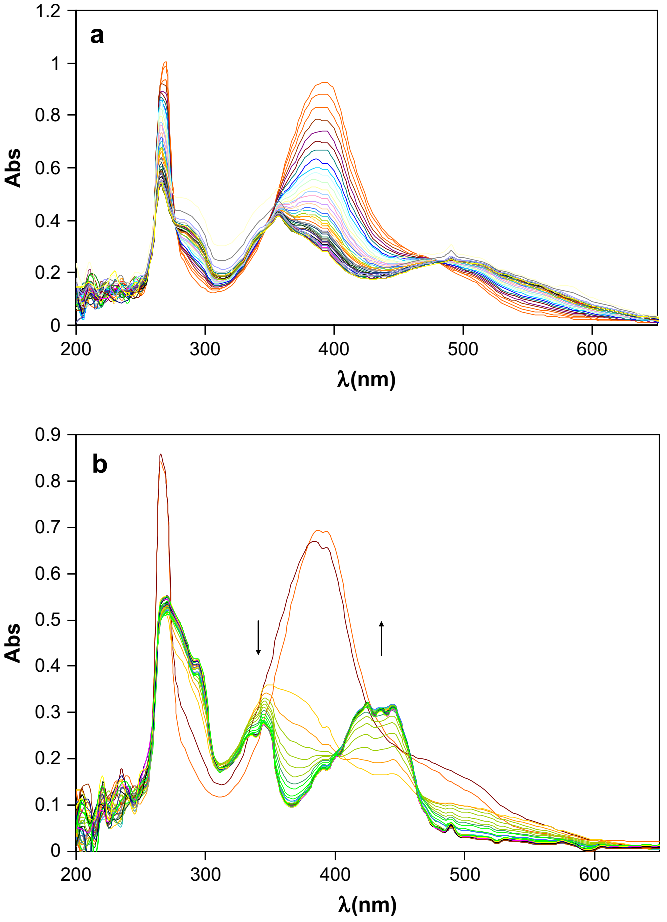


Fig. 3. (a) Spectral changes of dixanthylenium (DX^{2+}), 2.8×10^{-5} M in DMSO in the absence of sunlight after every minute and formation of dixanthylene A form, DX(A). (b) Spectral changes of the above solution, dixanthylene DX(A), due to sunlight irradiation with time interval of 3 min and formation of dixanthylene B form, DX(B); the spectra of DX^{2+} in dark conditions. Abs ≈ 0.7 was also included for comparison.

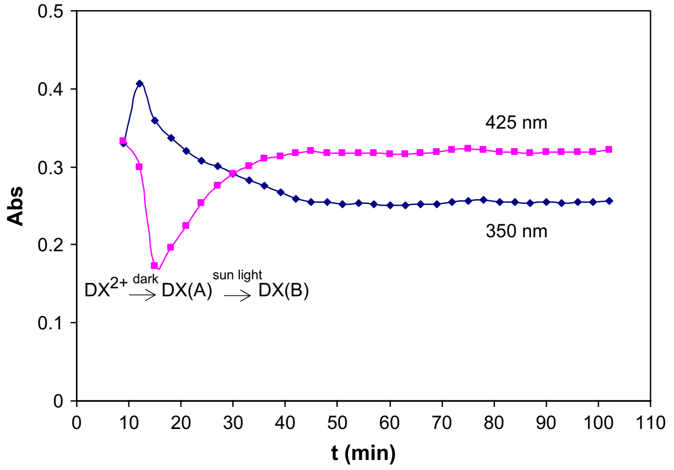


Fig. 4. Variation of the absorbance of compounds DX^{2+}, DX(A), and DX(B) in DMSO with time at different wavelengths: DX^{2+}, until 15 min in dark conditions, DX(A) at 350 nm; DX(B) at 425 nm was achieved using 35 min of sunlight irradiation.

3.3. Ab initio calculations

Sterically overcrowded alkenes have attracted considerable interest in view of their unique photochromic and thermodynamic

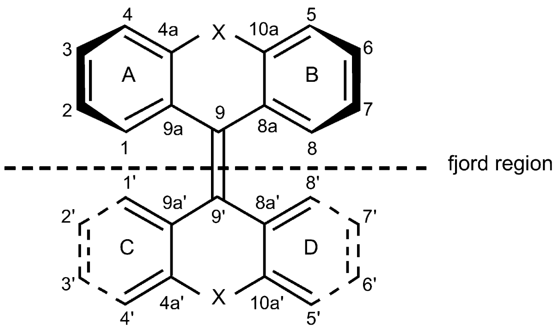
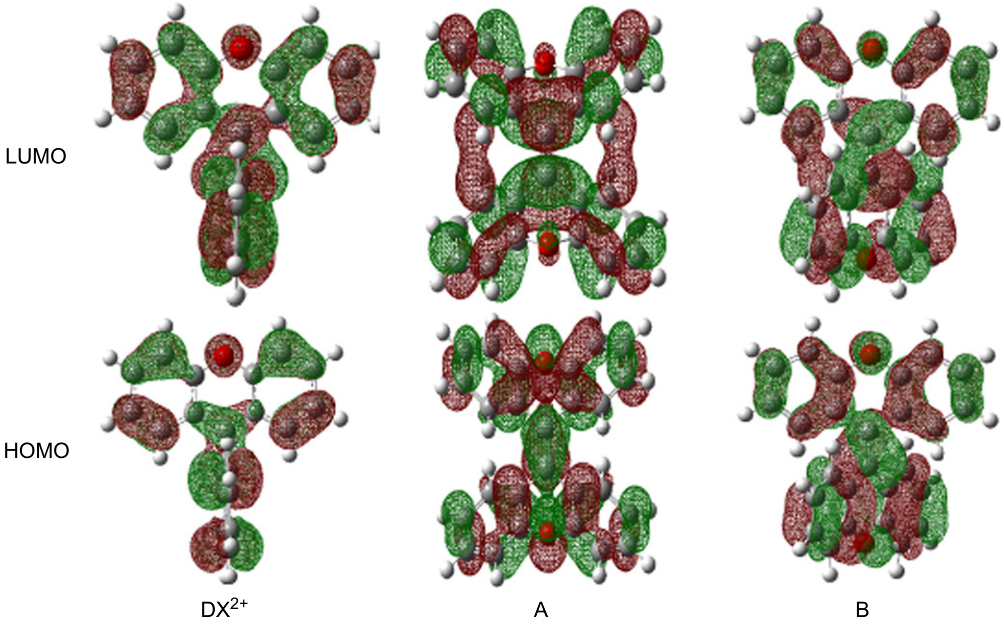


Fig. 5. Dixanthylidene structure.



Scheme 3. The HOMO–LUMO molecular orbital diagrams of DX^{2+}, DX(A), and DX(B).

properties. Planarity in the ground state conformations of overcrowded alkenes is prevented by the very strong non-bonded carbon–carbon and hydrogen–hydrogen interactions in the fjord region of the molecule (Fig. 5). Usually two mechanisms, generally known as twisting and folding, are responsible for the release of strain in overcrowded alkenes. The bistricyclic aromatic enes (BAEs) such as dixanthylene were found to have a folded ground state conformation. In the schematic drawings, depicted in the lower portion of Fig. 5, the structures are viewed along the central C9=C9′ bond. The lines represent the peripheral benzene rings of the tricyclic moieties. These schematic projections should not be confused with Newman projections of the double bond. In a folded structure the substituents at the central double bond are folded away from the plane defined by the double bond in a point-symmetric manner. This results in boat conformations in the central rings of the tricyclic moieties. Thus induced nonplanarity of the individual tricyclic moieties of folded structures is expressed quantitatively by the folding angles A–B and C–D (Fig. 5) of the least-squares-planes defined by the carbon atoms of the peripheral benzene rings. Twisted structures are usually found when both halves of the overcrowded alkenes are either sterically very demanding or planar and rigid.

The nonplanarity at the central carbon atoms (C9 and C9′, Fig. 5) of the double bond of both, twisted and folded, structures is quantified by the pure twist (ω) of the central double bond (C9=C9′) and the pyramidalization (χ) of the individual atoms C9 and C9′ of the double bond. The pure twist is defined [31] as the average of the torsion angles τ(C9a–C9–C9′–C9a′) and τ(C8a–C9–C9′–C8a′):

$$\omega = 1/2[\tau(\mathrm{C9a{-}C9{-}C9'{-}C9a'}) + \tau(\mathrm{C8a{-}C9{-}C9'{-}C8a'})]$$

Through the years several measures for pyramidalization have been applied in the literature [32,33]. The pyramidalization angle (C9) is defined as the improper torsion angle τ(C9a–C9–C9′–C8a) minus 180° [34].

Structures of dixanthylene were initially optimized at PM3 level of theory. The PM3 optimized structures were then optimized without symmetry constraints using restricted/unrestricted Hartree–Fock (RHF/UHF) with 6-31G basis set. Molecular properties, such as molecular volume, atomic charges, electronic spatial extent, electric dipole moment and polarizability tensor elements, corresponding to the optimized geometries have also been calculated and analyzed. A spectroscopic property has been calculated at the same level of theory

Table 1
Results of molecular properties are shown for dixanthylinum and dixanthylene

Parameter	A form	B form	Dixanthylinum
C9=C9′	1.33521	1.37034	1.52666
Pure twist (ω)	0.00	−43.9	−90.0572
⟨C2C9C7	128.63488	148.36659	154.16511
⟨C2′C9′C7′	128.60537	148.36942	154.16512
Pyramidalization angle χ (C9)	4.1927	0.02397	0.00
HOMO	−5.66001	−4.24501	−9.52406
LUMO	5.142992	4.027317	-6.83011
Dipole moment	0.0012	0.0807	0.0001
Quadrupole moment (Debye-Ang)	−143.62	−144.632	−89.5172
Electronic spatial extent	9106.6777	9194.7641	8862.4702
Volume	983.50	977.96	995.93
Hydration energy (kcal/mol)	−7.33	−7.59	−7.46
Log P	5.77	5.77	6.55
Polarizability	42.62	42.62	44.79
NICS (ring between A and B or ring between C and D)	1.3	2.9	−4.53
NICS (A,B,C,D)	−9.3	−8.5	−6.7

Table 2
Results (absorption maxima λ/nm and oscillator strengths *f*) for dixanthylene conforms (the *f* values are given in parentheses)

Excitation energies	λ_1 (nm) Oscillator strengths	λ_2 (nm) Oscillator strengths	λ_3 (nm) Oscillator strengths	λ_4 (nm) Oscillator strengths	λ_5 (nm) Oscillator strengths	λ_6 (nm) Oscillator strengths
A form	467.01(0.0)	371.36(0.0)	364.32(0.0)	325.34(0.0)	246.34(0.75)	244.87(0.0)
B form	1321.33(0.0)	401.65(0.50)	392.98(0.0)	382.58(0.0)	334.80(0.0)	269.17(0.0)

and the same basis set for the optimized structures. The ab initio molecular orbital calculations were carried out using the Gaussian 98 program [35]. The HOMO–LUMO molecular orbital diagrams for dixanthylinum, A, and B forms are presented in Scheme 3. The corresponding HOMO and LUMO orbitals of DX^{2+}, A and B forms are different. It can be clearly seen that both HOMO and LUMO orbitals of the A form as well as B and DX^{2+} conformations are fully delocalized. With the exception of A form (node of LUMO is located at C9═C9′), the higher coefficients of both orbitals are on the central carbon atoms (C9 and C9′, Fig. 5). Comparing, molecule DX^{2+} with A and B forms, spreading of the HOMO for B form is more compared to that of LUMO of DX^{2+} and can be explained because of the greater twisting in the C9═C9′ double bond for B relative to the A conformation.

The NMR was calculated using a ghost atom in the center of each ring, with the purpose of analyzing the aromaticity of dixanthylene, by using the NICS (nuclear independent chemical shift) aromaticity criterion based on the value of the shielding of that ghost atom. That is to say, if the value of the shielding is negative, the molecule is aromatic, while if it is positive, the molecule is non-aromatic. The screening values for this calculation done with the basis set 6-31G are shown in Table 1. The higher difference between the level of HOMO and LUMO energies leads to higher transition energy, consequently the color change observed in photochromic structures can be explained. The A conformation is considerably higher in HOMO–LUMO gaps, therefore causing a substantial blue shift and it is colorless, while the B conformation is smaller in HOMO–LUMO gaps, causing a substantial red shift and it is colored. The results are summarized in Table 1.

The nucleus-independent chemical shifts (NICS) were calculated at the geometrical center of the ring. NICS is the negative of the absolute magnetic shielding constant computed at the ring center. Negative NICS denote aromaticity and positive NICS antiaromaticity; non-aromatic molecules show negligible NICS. This parameter was obtained for A, B and DX^{2+} conformations as −9.3, −8.5 and −6.7, respectively. These numbers suggest that A has more aromaticity than B and DX^{2+}.

Electronic excitation energies (wavelengths λ/nm), oscillator strengths *f*, and nature of the respective excited state (principal CI-coefficients) of dixanthylene calculated by the TDHF method are summarized in Table 2.

4. Conclusions

The electrochemical reduction of xanthone in the presence of perchloric acid is an interesting method for the synthesis dixanthylinum salt. We found that GC and graphite have an electrocatalytic effect on the reduction of xanthone in CH_3CN. The E_p of xanthone at GC is −0.8 V relative to SCE, which makes possible the selective reduction and, hence, hydroxylation of the compound in the presence of acid. The process in CH_3CN consumes 1 electron/molecule of xanthone, 95% in the presence of acid leads mainly to pinacol, protonation of the carbonyl and dimerization reaction. Dixanthylinum salt is stable in the presence and absence of sunlight at CH_3CN but neutralization (reduction) and change in conformation occurred in DMSO solution. The colorless isomer A form is the predominant isomer in dark condition and is converted to green isomer (B form) in the presence of sunlight.

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References

[1] Emmelius M, Pawlovski G, Vollman HW. Angew Chem Int Ed Engl 1989;28:1445.
[2] Ball P, Garwin L. Nature 1992;355:761.
[3] Eigler DM, Lutz CP, Rudge WE. Nature 1991;352:600.
[4] Tapuhi Y, Kalisky O, Agranat I. J Org Chem 1979;44:1949.
[5] Feringa BL, Jager WF, de Lange B. Tetrahedron 1993;49:8267.
[6] Feringa BL, Huck NPM, Schoevaars AM. Adv Mater 1996;8:681.
[7] Jager WF, de Jong JC, de Lange B, Huck NPM, Meetsma A, Feringa BL. Angew Chem Int Ed Engl 1995;34:348.
[8] Agranat I, Tapuhi Y. J Am Chem Soc 1979;101:665.
[9] Issue on photochromism: memories and switches. Chem Rev 2000;100.
[10] Willner I, Willner B. Bioelectrochem Bioenerg 1997;42:43.
[11] Willner I. Acc Chem Res 1997;30:347.
[12] Feringa BL, editor. Molecular switches. Darmstadt: Wiley-VCH; 2001.
[13] Willner I, Rubin S. Angew Chem Int Ed Engl 1996;35:367.
[14] Ault A, Kopet R, Serianz A. J Chem Educ 1971;48:410.
[15] Schonberg A, Kickel S. Ber 1931;64:2323.
[16] Schonberg A, Mustafa A, Sobhy MEE. J Am Chem Soc 1953;75:3377.
[17] Ahlberg E, Parker VD. Acta Chem Scand 1980;34:97.
[18] Wang HJ, Zheng G, Parker VD. Acta Chem Scand 1995;49:311.
[19] Parker Vd, Pedersen M, Reitstoen B. Acta Chem Scand 1993;47:560.
[20] Hammerich O, Parker VD. Acta Chem Scand 1982;36:519.
[21] Hammerich O, Parker VD. Acta Chem Scand 1981;35:341.
[22] Nielsen MF, Hammerich O, Parker VD. Acta Chem Scand 1984;38:809.
[23] Hammerich O, Parker VD. Acta Chem Scand 1983;37:379.
[24] Abdou WM, Elkhoshnieh YO, Sidky MM. J Chem Res 1994;5:184.
[25] Matsue T, Williams DG, Evans DH. J Electroanal Chem 1987;233:63.
[26] Evans DH, Busch RW. J Am Chem Soc 1982;104:5057.

[27] Kawata S, Kawata Y. Chem Rev 2000;100:1777.

[28] Cognet P, Ghanem-Lakhal A, Berlan J, Wilhelm A-M, Delmas H, Fabre PL. Chem Eng Sci 2000;55:2571.

[29] Baizer MM, editor. Organic electrochemistry. 3rd ed. New York: Marcel Dekker; 1991. p. 433.

[30] Elving PJ, Leone JT. J Am Chem Soc 1958;80:1021.

[31] Shoham G, Cohen S, Suissa RM, Agranat I. Molecular structure: chemical reactivity and biological activity. In: Stezowsky JJ, Huang J-L, Shao M-C, editors. IUCR crystallographic symposia 2. Oxford: Oxford University Press; 1988. p. 290.

[32] Haddon RC. J Am Chem Soc 1990;112:3385.

[33] Radhakrishnan TP, Agranat I. Struct Chem 1991;2:107.

[34] Biedermann PU, Stezowsky JJ, Agranat I. Eur J Org Chem 2001;15.

[35] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 98, revision A.6. Pittsburg, PA: Gaussian Inc.; 1998.