

Article

The Photochemical Reaction of 1,1-dicyano-3-phenylbut-1-ene. Simultaneous Occurrence of π -methane and di- π -methane Rearrangements

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A fotólise direta de 1,1-diciano-3-fenilbutene-1 (**3-MDCN**) foi pesquisada a temperatura ambiente em solventes de diferentes polaridades (hexano, diclorometano e acetonitrilo). Foram obtidos fotoprodutos originários dos processos di- π -metano e π -metano (migração de hidrogênio 1,2). As estruturas dos produtos foram determinadas por ¹H-NMR, GC/MS, IV e cromatografia. Os resultados das determinações dos rendimentos quânticos relativos e as análises cromatográficas de irradiações sequenciais evidenciaram que i) não ocorrem reações secundárias, até a altas conversões; ii) o rearranjo di- π -metano é mais afetado pelas variações de solvente que o rearranjo π -metano. Não foram observados produtos por fotossensitização com acetofenona ou acetona. A presença de mecanismo simultâneos e os efeitos de solvente foram considerados como evidência de excitações localizadas e deslocalizadas sobre a superfície de energia potencial.

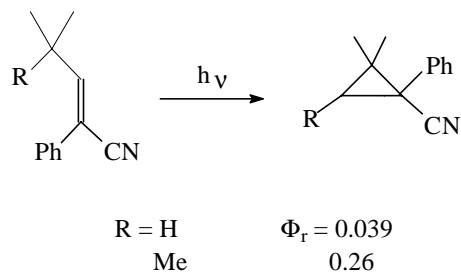
The direct photolysis of 1,1-dicyano-3-phenylbut-1-ene (**3-MDCN**) was investigated at room temperature in solvents of different polarities (hexane, dichloromethane and acetonitrile). Cyclopropanes arising from both the di- π -methane and π -methane (1,2-H migration) processes were obtained as photoproducts. The structures of the products were elucidated by ¹H-NMR, GC/MS, IR and chromatography. Relative quantum yield determination and GC analysis of sequential irradiations gave evidence that: i) no secondary reactions occur, even at high conversions; ii) the di- π -methane rearrangement is significantly more affected by the solvent variation than the π -methane reaction. Photosensitization with acetophenone or acetone did not yield any observable products. The existence of the simultaneous mechanisms and the observed effects were considered as evidence of a possible differentiation between localized and delocalized excitation on the excited state surface.

Keywords: organic photochemistry, di- π -methane rearrangement, π -methane rearrangement, 1,2-hydrogen-photomigration

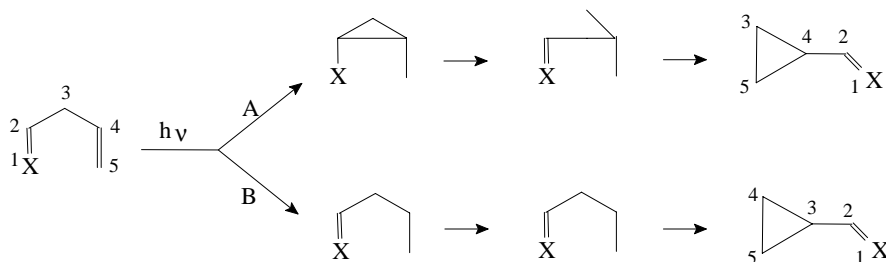
Introduction

The photochemical formation of cyclopropanes from π -methane systems (Scheme 1) is a well known and quite general reaction¹⁻⁴.

A special case that has been widely studied⁵⁻⁹ arises for compounds with an sp³-carbon supporting two π -bonds. The accepted mechanism for these reactions is a di- π -methane rearrangement that involves both π -bonds and can be formulated as a $\pi^2 + \sigma^2 + \pi^2$ concerted process¹⁰ or as the sequential formation of 1,4- and 1,3-diradicals¹¹ (Scheme



Scheme 1.



Scheme 2.

2A). An alternative mechanism proposed earlier¹² (Scheme 2B), involves only one of the π -bonds, with the cyclopropane being formed in a $\pi^2 + \sigma^2$ concerted process,¹³ or by cyclization of a 1,3-diradical formed after a 1,2-migration.

In the presence of a second homoconjugated π -bond the di- π -methane rearrangement usually predominates, as proved by Hixson¹⁴ and Zimmerman and Little¹⁵ (Scheme 3).

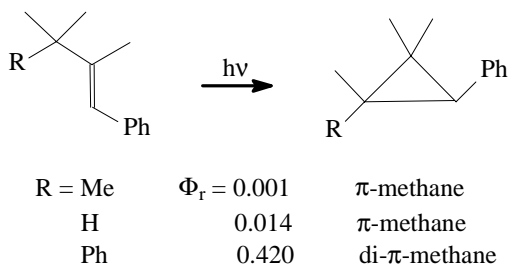
The formation of different cyclopropanes from the same starting compound by both mechanisms should provide a good opportunity for comparative studies, since the reactivity ratios could be obtained directly from the quantum yields or from the chemical yields at low conversions.

Therefore, we report here the results of the photolysis of 1,1-dicyano-3-phenylbut-1-ene, **3-MDCN**, and 1,1-dicyano-3-methyl-3-phenylbut-1-ene, **3-DMDCN**. The former is, to our knowledge, the first example of a compound whose photoreaction proceeds simultaneously by both pathways with comparative rates. **2-MDCN** and its single di- π -methane product¹⁶ were used for chromatographic and spectroscopic comparisons, and as actinometer with an already determined quantum yield.

Experimental

General methods

Irradiations at 254 nm were performed in a Rayonet photoreactor (The Southern New England Ultraviolet Co.) with low-pressure mercury arc lamps (RPR2537). In general, 3 or 4 mL of the solution of **3-MDCN** with concentrations between 4.25 and 11.8 mM were placed in quartz tubes and deoxygenated by flushing thoroughly with nitrogen. After irradiation for the required time, 1 mL of the



Scheme 3.

solution of the chromatographic standard was added and the reaction mixture was analyzed by gas chromatography.

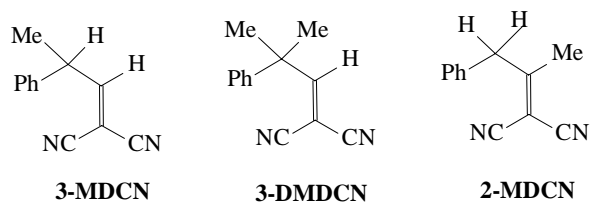
All chemicals and solvents (spectrophotometric or HPLC grade) were from Aldrich or Merck and used without further purification.

The reaction mixtures were analyzed by: Gas chromatography (Shimadzu GC-14B and Varian 3300) using 25 m OV-1 or PONA capillary columns and 1-dodecene as internal standard; UV-VIS spectroscopy (Hitachi U2000); FTIR spectroscopy (Bomem MB 102); GC/MS (HP5890 / HP5970) and ¹H-NMR (Bruker AC200, shifts in ppm from TMS).

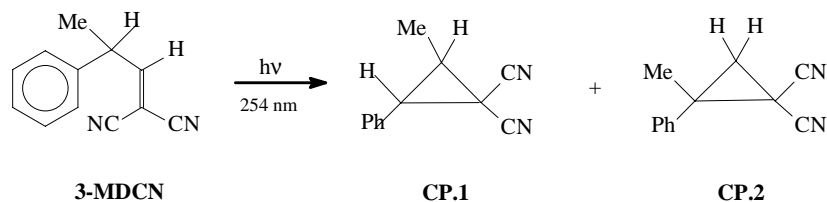
Syntheses

3-MDCN was synthesized by a Knoevenagel condensation¹⁷. A mixture of 4 mmoles of 2-phenylpropanal (hydropaldehyde), 5 mmoles of malononitrile, 3 mmoles of ammonium acetate, and 40 drops of glacial acetic acid were dissolved in 40 mL of benzene and refluxed for 4 h. In order to increase the amount of recovered products, a Dean-Stark-type distillation head was used to separate, by azeotropy, the produced water. The final yield after extraction and distillation of the reaction mass was 67% (colourless oil, 146 °C/0.75 torr). $\nu_{\max}/\text{cm}^{-1}$ 3090m, 2990m, 2240s, 1600s, 1500s, 1450s and 700s; δ_{H} (200 MHz, Me₄Si) 7.35 (6 H, m, H_{vinyl} + 5 H_{arom}), 4.13 (1 H, dq, *J* 11.6 and 7.0, H_{benzyl}) and 1.54 (3 H, d, *J* 7.0, CH₃); *m/z* 183 (*M*⁺+1, 10%), 182 (*M*⁺, 83), 181 (100), 167 (55), 154 (30) and 140 (88). The NMR data is similar to that found by Kruger *et al.* for the same compound¹⁸.

2-Methyl-2-phenylpropanal used as a precursor in the synthesis of **3-DMDCN** was obtained by a Grignard reaction between methyl mandelate and CH₃I with pinacol formation (78%), followed by H₂SO₄/AcOH/I₂ treatment (yield ~60%), as described by Wolfe *et al.*¹⁹ The aldehyde was converted to **3-DMDCN** with 61% yield by a



Scheme 4.



Scheme 5.

Knovenagel procedure, as described above. (Colourless oil, 138-142 °C/0.6 torr). $\nu_{\max}/\text{cm}^{-1}$ 3050m, 2980m, 2250s, 1600s, 1500s, 1450s and 750s; δ_{H} (200 MHz, Me_4Si) 7.30 (6 H, m, $\text{H}_{\text{vinyl}} + 5 \text{H}_{\text{arom}}$) and 1.70 (6 H, s); m/z 197 ($\text{M}^{*+}+1$, 9%), 196 (M^{*+} , 62), 195 (47), 181 (95), 154 (100) and 127 (40).

2-MDCN, was synthesized using similar conditions²⁰. This compound was used as actinometer and for chromatographic and spectroscopic comparisons, as its photolysis rendered a single product. The quantum yield, previously determined¹⁶, using both *trans-cis* isomerization of *trans*-1-phenylbut-2-ene and potassium ferrioxalate, is 0.018.

The cyclopropane **CP.1** (see Scheme 5) was synthesized thermally²¹. In a flask with an outer jacket with boiling toluene, 7.5 mmoles of β -methylstyrene and 15 mmoles of malononitrile were mixed under agitation with the catalyst [CuCl_2 (8 mmoles) / $\text{Cu}(\text{AcO})_2$ (8 mmoles) / LiCl (12 mmoles)] in 20 mL of *N,N*-dimethylformamide. After refluxing for 5 h with stirring the mixture was concentrated and extracted with petroleum ether. The final yield after drying and distillation was 31% of a yellow oil. $\nu_{\max}/\text{cm}^{-1}$ 3090m, 2940m, 2240s, 1500m, 1450m, 790m, 740s and 650m. *E*-CP.1 m/z 183 ($\text{M}^{*+}+1$, 10%), 182 (M^{*+} , 70), 181 (100), 167 (26), 154 (30) and 140 (55). *Z*-CP.1 m/z 183 ($\text{M}^{*+}+1$, 12%), 182 (M^{*+} , 70), 181 (100), 167 (30), 154 (30) and 140 (53). *E*-CP.1 δ_{H} (200 MHz, Me_4Si) 7.35 (5 H, m, H_{arom}), 2.75 (1 H, d, J 8.4, $\text{CH}_{\text{benzyl}}$), 2.25 (1 H, dq, J 8.4 and 6.2, CH), 1.30 (3 H, d, J 6.2, CH_3). *Z*-CP.1 δ_{H} (200 MHz, Me_4Si) 7.35 (5 H, m, H_{arom}), 3.05 (1 H, d, J 5.4, $\text{CH}_{\text{benzyl}}$), 2.25 (1 H, dq, J 5.4 and 6.4, CH) and 1.20 (3 H, d, J 6.4, CH_3). The geometric isomers were identified taking into account the anisotropy effect of the phenyl group, the coupling constants and the similarity of the cleavage patterns in MS.

Results

Photolysis of 3-MDCN

In order to identify the reaction products a preparative photolysis was carried out. Thus, 1.6 mmoles of the dicyanoolefin **3-MDCN** in hexane (100 mL) were degassed and irradiated for 5 h. A yellow oil was obtained after concentration of the reaction mixture in vacuum. The fraction recovered by bulb-to-bulb distillation showed three products by GC analysis (areas corresponding to 66, 10 and 19%, approximately), as well as the substrate (3%). Chro-

matographic and spectroscopic comparisons with **CP.1** obtained by catalytic thermal synthesis²¹ and **CP.2**, obtained by the of photolysis **2-MDCN**¹⁶, allowed their identification as *E*- and *Z*-**CP.1** and **CP.2**. The spectroscopic data for **CP.2** was $\nu_{\max}/\text{cm}^{-1}$ 3084m, 2935m, 2250s, 1228m, 772s, 710s and 650m; m/z 183 ($\text{M}^{*+}+1$, 11%), 182 (M^{*+} , 76), 181 (100), 167 (72), 154 (30) and 140 (63); δ_{H} (200 MHz, Me_4Si) 7.35 (5 H, m, H_{arom}), 2.20 (1 H, d, J 6.0, H of CH_2), 1.80 (1 H, d, J 6.0, H of CH_2) and 1.65 (3 H, s, CH_3). Double irradiation experiments on the reaction mixture confirmed coupling between the ring protons in each cyclopropane (*e.g.*, for **CP.2**, upon irradiation at 2.20 δ the doublet at 1.80 δ collapsed and *vice-versa*). The analysis of the products confirms the photoreaction reaction scheme (Scheme 5) leading to two cyclopropanes arising from the di- π -methane (**CP.1**) and π -methane (**CP.2**) rearrangements, respectively.

The absorption spectrum of **3-MDCN** and its time evolution during photolysis are shown in Fig. 1. A blue-shift of the band around 230-220 nm during the photolysis, as well as the general decrease of the absorbance at wavelengths below 280 nm, suggests a bichromophoric interaction between the phenyl group and the double bond, which will be destroyed during the reaction.

It can be seen from Fig. 2, that the sum of the amounts of both cyclopropanes obtained during the photolysis is always equal to the consumption of **3-MDCN**. This indicates a competition between the mechanisms leading to

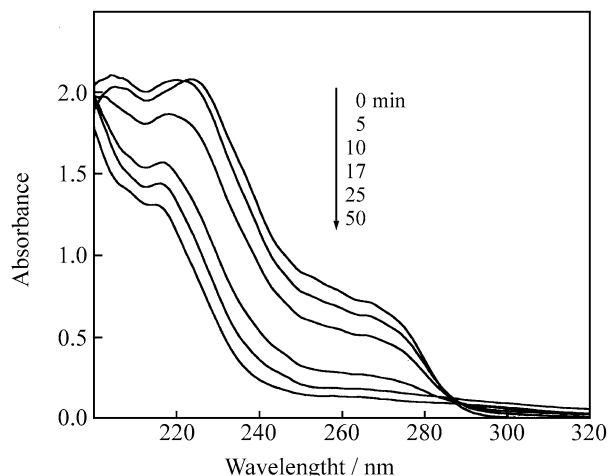


Figure 1. Spectral changes of **3-MDCN** in hexane (1.86×10^{-4} M) when irradiated at 254 nm.

both photoproducts. Similar behavior can also be observed when the reaction is carried out in acetonitrile or dichloromethane. In addition, the ratio between both cyclopropanes also remains constant throughout the reaction, up to high conversions. This proves that there is no photochemical interconversion between the products **CP.1** and **CP.2**, as expected from the low extinction coefficients of the cyclopropanes at the irradiation wavelength (*i.e.*, at 254 nm, $\epsilon_{3\text{-MDCN}} \cong 5000$, $\epsilon_{\text{CP.1}} \cong \epsilon_{\text{CP.2}} \cong 200 \text{ M}^{-1} \text{ cm}^{-1}$).

Solvent effect

The photolysis of **3-MDCN** was performed in three solvents with different polarity. The quantum yields for both cyclopropanes (*i.e.* both types of rearrangements) are shown in Table 1. The overall conversion is influenced by the solvent polarity due to the effect on the di- π -methane rearrangement. The formation of **CP.1** always prevails over that of **CP.2** (π -methane rearrangement), the latter practically not being affected by the change of solvent.

Photolysis of 3-DMDCN

To compare with the results obtained for **3-MDCN**, a hexane solution of **3-DMDCN** (2.57 mmol/100mL) was photolyzed for 6 h. Only one product was observed, corresponding to the di- π -methane rearrangement. It crystallized in the reaction solvent (white crystals, m.p. = 62-65 °C) with a yield of 41% and was identified as **CP.3**. The corresponding spectroscopic data are: $\nu_{\text{max}}/\text{cm}^{-1}$ 3040m, 2960m, 2240s, 1400s, 760s and 700s; m/z 197 ($\text{M}^{+}+1$, 10%), 196 (M^{+} , 60), 195 (44), 181 (90), 154 (100) and 127 (33); δ_{H} (200 MHz, Me_4Si), 7.3 (5 H, m, H_{arom}), 3.0 (1 H, s, $\text{CH}_{\text{benzyl}}$), 1.73 (3 H, s, CH_3) and 1.32 (3 H, s, CH_3).

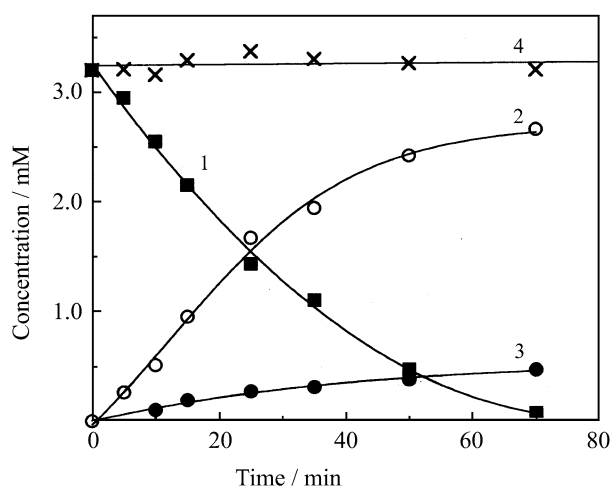


Figure 2. Time evolution of the concentrations of the dicyanoolefin **3-MDCN** (1), and its photoproducts cyclopropane **CP.1** (2) and cyclopropane **CP.2** (3), during photolysis in hexane at 254 nm. Line (4) corresponds to the sum of the concentrations of substrate and photoproducts at any time.

Table 1. Solvent effect on the quantum yields for the photoreaction of **3-MDCN**^a.

Solvent	Dielectric Const.	$A_{\text{CP.1}}/A_{\text{CP.2}}$ ^b	$\Phi_{\text{CP.1}}$	$\Phi_{\text{CP.2}}$
Hexane	1.88	5.6 ± 0.1	0.054	0.0095
CH_2Cl_2	8.93	3.1 ± 0.1	0.030	0.0094
CH_3CN	35.94	2.2 ± 0.2	0.022	0.0091

^ausing the reaction of **2-MDCN** as actinometer ($\Phi = 0.018$).

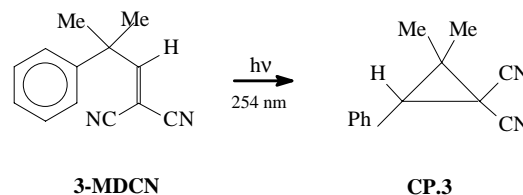
^bratio between the areas of the peaks of chromatographic analysis.

No products were observed when attempting to sensitize the reaction of **3-MDCN** and **3-DMDCN** in hexane with acetophenone ($E_{\text{T}} = 74 \text{ kcal/mol}$) or acetone ($E_{\text{T}} = 78 \text{ kcal/mol}$).

Discussion

The absorption spectrum of **3-MDCN** suggests a bichromophoric interaction as the extinction coefficients in the 230 and 270 nm regions ($\epsilon_{270} = 3610$ and $\epsilon_{230} = 10000 \text{ M}^{-1} \text{ cm}^{-1}$) are larger than those corresponding to the separate chromophores ($\epsilon_{261}^{\text{max}} = 295 \text{ M}^{-1} \text{ cm}^{-1}$ for toluene). The same behaviour has been observed also for **2-MDCN**^{16,20}. The increase of the extinction coefficient for similar compounds was assumed to be due to the excitation to a delocalized state (aromatic $\pi +$ double bond π^*)²²⁻²⁴. In this interaction the phenyl group acts as the donor and the double bond as the acceptor, giving rise to a charge transfer complex in the vertical excited state. Assuming that the 1,2-migration of H results from electronic excitation on the double bond, the observation of products resulting from both mechanisms from the same compound, suggests the excitation to a delocalized orbital.

The absorption peaks in the short wavelength region of the spectrum of **3-MDCN** can be ascribed to the transitions to localized and delocalized states, both having singlet character. Those states correspond to potential energy surfaces that lead to different photoproducts. On the lower energy surface, corresponding to the delocalized excited state, excitation leads to a charge-transfer complex (CTC), which will take to the di- π -methane rearrangement. The increase of solvent polarity will stabilize this complex, decreasing the quantum yield of **CP.1**, $\Phi_{\text{CP.1}}$. The 1-2 H photomigration (or π -methane rearrangement) originates from the localized excited surface. A possible potential



Scheme 6.

energy scheme is shown in Fig. 3. The small effect of the solvent polarity on $\Phi_{CP,2}$ seems to indicate that the excited state surface leading to the 1,2-photomigration of H has a more accentuated radical character. The pathway on this surface should not be affected by the motions leading to the surface corresponding to the di- π -methane rearrangement (“touching” motion between both π moieties²⁵).

On the surface leading to the **CP.1** formation, the charge transfer complex in the excited state is stabilized by polar solvents, decreasing the formation rate of this cyclopropane. This decrease in the efficiency of di- π -methane rearrangement ($\Phi_{CP,1}$) with increasing solvent polarity has already been observed before^{16,20}. It was considered an evidence for the competition between the deactivation of the excited singlet state by reversible electron transfer from the phenyl group to the dicyanovinyl moiety, and the formation of a 1,4-diradical leading to homolytic ring-opening and reclosure on the di- π -methane pathway. Both processes originate from the same intramolecular motion from the

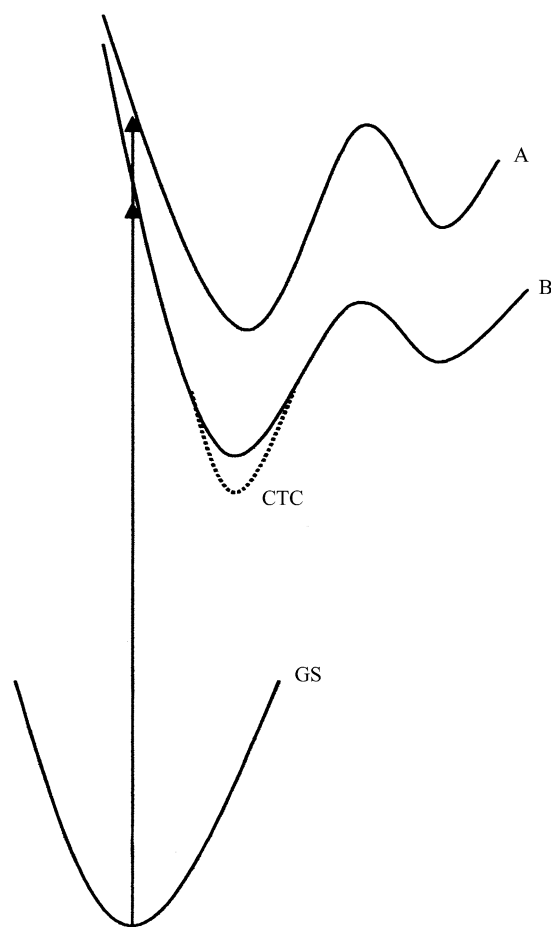


Figure 3. Potential energy surface diagram for the photoreactions leading to di- π -methane (B) and π -methane reactions (C). GS corresponds to the ground state.

vertical excited state (“touching”). This deactivation process by electron transfer between two chromophores was also proposed for di- π -methane rearrangements in the triplet state²⁶.

Previous studies on similar systems proved that both mechanisms (π -methane^{4,14} and di- π -methane^{22,24}) originate from singlet excited states. For the structurally related compound in which one of the CN groups is replaced by an ester, the sensitization with acetophenone leads to isomerization around the double bond, with no formation of cyclopropanes. The latter were only observed upon direct photolysis with 254 nm light. From these results it can be assumed that triplet states are not involved in the photoreactions of **3-MDCN** and **3-DMDCN**, which should proceed via a singlet excited state.

In general, from data found in the literature (Scheme 3) it can be seen that the di- π -methane rearrangement is much more efficient than the π -methane reaction. As expected, the photomigration is easier for hydrogen than for methyl group, as found when comparing the photochemistry of **3-MDCN** with that of **3-DMDCN**, where only the di- π -methane process occurs, with the same efficiency as for **3-MDCN** ($\Phi_{CP,3} = 0.054$). The photochemistry of **2-MDCN** should show the same products as **3-MDCN**, wouldn't it be by the inhibition of the 1,2 photomigration by substitution on the end carbon of the migration, due probably to steric and electronic effects⁴. Thus, **3-MDCN** seems to be the only compound for which both mechanisms occur simultaneously with comparable efficiency.

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