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Spectrokinetic study of 2,2-diphenyl-5,6-benzo(2H)chromene: a thermoreversible and photoreversible photochromic system

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Abstract

In this paper the photochromic reaction of the 2,2-diphenyl-5,6-benzo(2H)chromene is investigated by spectrophotometric methods using monochromatic irradiation wavelengths in the UV and visible ranges. Two coloured species are produced upon irradiation, one is thermoreversible, the other is photoreversible. The colour-forming kinetics were followed under steady irradiation using UV light (357 nm). The kinetic parameters (rate coefficient and activation energy) of the thermal ring-closure reaction were determined. The photochemical bleaching was induced by exciting with visible light (422 nm). To determine reaction quantum yields and molar absorption coefficients of the metastable species, both photostationary and photokinetic methods were employed. Based on the results obtained, a plausible reaction mechanism is proposed

Keywords: Photochromism; Chromene

1. Introduction

The photochromic behaviour of chromenes was first established and extensively studied by Becker and coworkers [1–8]. These molecules, upon UV irradiation, yield open coloured forms, the structure of which was shown to be an *o*-quinone-allide [2]. Generally, these species are thermally unstable; their stability is increased by benzo-annelation in position 5,6 or 7,8 and conjugative substituents in position 2 and decreased by benzo-annelation in position 6,7 and bulky substituents in position 4 [1]. The photochemistry and photophysics of these compounds were first studied in a rigid matrix at 77 K [1,3–6]. More recently they were investigated at room temperature, using microsecond and nanosecond flash photolysis techniques [8], as well as steady irradiation [9]. Semiempirical theoretical calculations of the electronic transitions of the photocoloured forms [7] and of the potential energy curves in the ground and lowest excited states, along the C–O bond-cleavage coordinate, were carried out [10]. Ab initio calculations of the ring opening reaction in the ground state were recently performed [11]. The synthesis of new chromenes and study of their photocolourability has also received great attention [12,13].

In this paper, a spectrokinetic investigation of the photochromic reaction of the 2,2-diphenyl-5,6-benzo(2H)-chromene (**Ch**, see Scheme 1) is described. Existing information on this molecule concerns the determination of the spectral absorption range of the coloured form [8,14], the rate coefficient of the thermal bleaching [14,15] and calculation of optimised structures of the coloured species [16]. No photokinetic data on colour-forming and colour-bleaching reactions have ever been reported.

The photocolouration of this molecule upon UV irradiation, which was first investigated in a rigid matrix at 77 K under steady irradiation [1] and in a fluid solution by nanosecond flash photolysis [8], is here examined under continuous monochromatic irradiation in a fluid solution and in a temperature range (285–325 K) which includes room temperature. Colour-forming kinetics and thermal- and photobleaching kinetics indicated that two coloured forms are involved in the photochromic reaction, one thermoreversible and the other principally photoreversible.

Using photostationary and photokinetic methods permitted determination of (1) the molar extinction coefficients of the two coloured forms, (2) the quantum yield of the colour-forming reaction, (3) the quantum yield of the photochemical bleaching, and (4) the kinetic parameters—rate coefficient and activation energy—of the thermal bleaching.

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Evaluating molar absorption coefficients (ε) of the metastable photoproducts and photoreaction quantum yield (Φ) of photochromic materials is not easy to achieve because the coloured species, produced under UV irradiation, reconvert to the colourless molecule within a few seconds [17–26]. Several methods have been employed to determine the ε and Φ values. To avoid the thermal back-reaction, the most frequently employed methods have been (1) the saturation method, using an exciting flash and times of analysis much shorter than the metastable-form lifetime, and (2) the low temperature method, producing the coloured species at 77 K with steady irradiation and assuming a complete photoconversion. Both of these procedures have some disadvantages; because the first one uses very intense pulsed irradiating light, there is the possibility of side photoreactions, local heating and inhomogeneity; while the second one is applied at low temperature which is far from the conditions of operational interest. As an alternative, photokinetic and photostationary methods have been used at room temperature under steady irradiation [21–26].

2. Experimental details

The photochromic molecule studied, 2,2-diphenyl-5,6-benzo(2H)chromene, was supplied by Great Lakes Chemical Italia. The solvent was reagent grade Carlo Erba methylcyclohexane (MCH).

Absorption spectra were recorded on a Beckman diode array DU 7500 or a Perkin–Elmer Lambda 16 spectrophotometer. The photometric accuracy of the latter is better than 10^{-3} absorbance units.

For the temperature control in the range 285–325 K, a cryostat (Oxford Instruments) was used. The temperature precision was within ± 1°C; the accuracy in the temperature control was of the order of ± 0.2°C.

The irradiation wavelengths ($\lambda_{exc} = 357$ and 422 nm) were selected from the emission of a 150 W Xe lamp filtered by a monochromator (Jobin-Yvon H10 UV). The light intensity, which was constant during each run, was determined using potassium ferrioxalate actinometry. The **Ch** concentration was 6.6×10^{-5} mol dm^{-3}. The light exposure of the sample (1-cm path cell, 1 cm^3 of solution) was carried out in the spectrophotometer holder at right angle to the analysis light. The photoreaction was followed, under stationary irradiation, at 422 nm (the photoproduct absorption maximum wavelength) up to photostationary state attainment. The spectral changes were recorded at constant temperature; recording was repeated on the same solution at temperature intervals of 5 K in the 285–325 K range. To assure the attainment of thermal equilibrium, about 30 min elapsed after resetting the temperature control.

The kinetics of the ring-closure back reaction were recorded at each temperature, following the colour-bleaching of the irradiated solution at constant wavelength, immediately after having removed the irradiating source. Then, the photochemical decolouration was carried out by exciting with visible light (422 nm). Nonlinear fit procedures were run on the Mathematica for Windows Program (nonlinear fit package).

3. Results and discussion

3.1. General photochemical feature and thermal bleaching

The **Ch** is colourless since its absorption spectrum, which exhibits peaks in the UV region at 290, 302, 315, 346 and 360 nm, drops down at 370 nm. Upon steady irradiation with UV light (357 nm, corresponding to an isosbestic point between coloured and colourless forms), a broad absorption appears in the visible region (400–500 nm), the intensity of which, at the photostationary state, markedly increases with decreasing temperature. The band maximum of the coloured form (422 nm) corresponds to that determined by Becker on flashing this molecule [8]. A typical time-course of the colour-forming reaction of **Ch** in MCH is illustrated in Fig. 1; at longer irradiation time, a slight modification of the colour band (blue-shift of the maximum) was observed. Three isosbestic points (262, 332 and 357 nm) were maintained during the irradiation.

The colour-forming kinetics were formally described by monoexponential ($T > 300$ K) and biexponential ($T < 300$ K) functions (Eqs. (1) and (2)). In these equations A represents the absorbance at the colour maximum wavelength (422 nm) and a, α, b and β are parameters determined by the fit procedure. Despite the low absorbance values monitored at the higher temperatures (Fig. 2a) the fitting was statistically satisfactory due to the large number of experimental points considered (200).

$$A = a(1 - e^{-\alpha t}) \quad (1)$$

$$A = a(1 - e^{-\alpha t}) + b(1 - e^{-\beta t}) \quad (2)$$

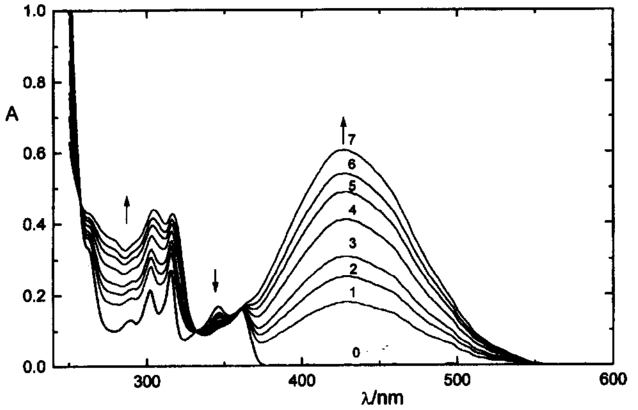


Fig. 1. Time course of the spectral changes during the colour-forming reaction of **Ch** in MCH at 280 K: 0, before irradiation: 1–7, irradiation times: 60″, 90″, 120″, 180″, 240″, 300″, 420″.

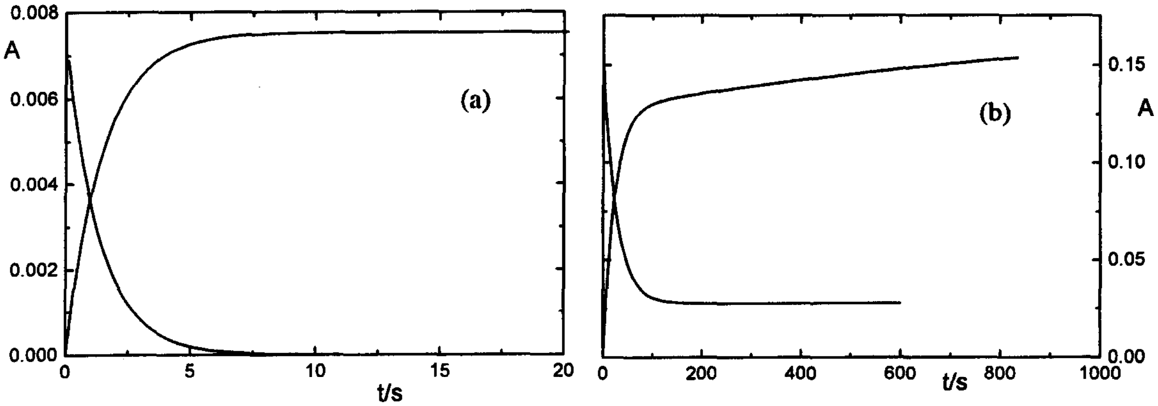


Fig. 2. Colour-forming and colour-bleaching kinetics of **Ch** under steady irradiation (λ_{exc} = 357 nm) at two temperatures: (a) 325 K; (b) 285 K.

The kinetics of the thermal ring-closure reaction were recorded following the colour-bleaching of the irradiated solution immediately after having removed the irradiating source; under certain conditions the decolouration observed was partial. Complete decolouration was achieved by irradiating with visible light (422 nm). The behaviour of the thermal bleaching kinetics were also temperature-dependent. At relatively high temperatures ($T > 300$ K) the bleaching curves tended monoexponentially to zero, while at lower temperatures ($T < 300$ K) a residual absorption remained unchanged in the dark over about 500 s but bleached over longer times. The residual colour faded upon irradiation with visible light at a much faster rate than thermal bleaching and was approximately independent of temperature.

Colour-forming and thermal-bleaching kinetics at two different temperatures are compared in Fig. 2.

The bleaching rate constants were determined by first-order kinetic treatment of the experimental points (correlation coefficient ≥ 0.99). However, while the faster kinetics were well reproducible in different runs, the slower ones were scarcely reproducible and, under certain experimental conditions, they were unmeasurable. The difference between the two bleaching rates was about two orders of magnitude. The temperature-dependence of the fast decay allowed the activation energy of thermal bleaching to be determined (60 ± 4 kJ mol^{-1}) from Arrhenius plot (correlation coefficient ≥ 0.98). Determination of the slower rate was made possible at relatively high temperatures, by irradiating at a wavelength (366 nm) where the photoproduct strongly absorbs (see later); the corresponding activation energy (very uncertain) was smaller (20 ± 10 kJ mol^{-1}). Arrhenius plots of the two bleaching processes are shown in Fig. 3.

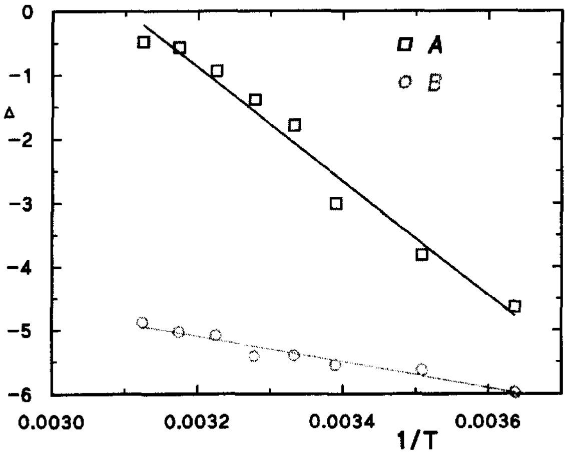


Fig. 3. Arrhenius plots for the thermal bleaching of *A* and *B*.

3.2. Photostationary and photokinetic methods

In previous papers [25,26], we described two methods, one photostationary and the other photokinetic, for treating spectroscopic data on thermo-reversible photochromic systems in order to obtain the molar absorption coefficient of the metastable form and the quantum yield of the colour-forming reaction. These methods were applied to spirooxazine ⇄ photomerocyanine systems, using different types of data sets.

By the first method (photostationary method), limiting absorbances of the coloured form at the photostationary state (A^∞) and bleaching rate parameters (k_Δ) were recorded at different temperatures [25]. A relationship was developed, relating A^∞ with k_Δ, which allowed the quantum yield of the photoreaction (Φ) and the molar absorption coefficient at the colour maximum (ϵ) to be obtained (Eq. (3)):

$$\frac{1}{A^\infty} = \frac{1}{\varepsilon c_0} + \frac{k_\Delta}{\Phi I^0 \varepsilon' F^\infty} \times \frac{1}{\varepsilon c_0} \qquad (3)$$

In Eq. (3), c_0 is the initial concentration of the photochromic compound; $F(F = [1 - \exp(-2.3A')]/A')$ represents the photokinetic factor [27–29]; A' and ϵ' refer to the absorbance and molar absorption coefficient of the colourless form at the irradiation wavelength and I^0 is the intensity of the incident light.

By the second method (spectrokinetic method), the differential equation describing the kinetics of the colour-forming reaction was integrated by introducing some reasonable approximations [26]. Then, the experimental points (absorbance/time data) were entered into the integrated function; the unknown parameters (molar absorption coefficient and quantum yield) were optimised so as to minimise the interpolation errors.

In the case of **Ch**, the kinetics are more complicated since the experimental data indicate that two coloured species are produced upon irradiation. Therefore, more than two parameters have to be determined in order to fully describe the photochromic behaviour of this system.

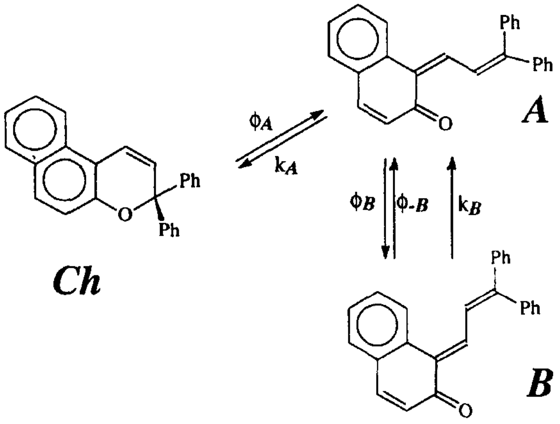
In order to write the kinetic equation, a plausible reaction mechanism, yielding two coloured species (***A*** and ***B***) and accounting for the experimental features, is assumed which involves the following steps:

Since both ***A*** and ***B*** absorb in the visible region and their spectra approximately overlap,the total absorbsance, A, in the visible is given by the contribution of ***A*** and ***B*** absorptions (A_A and A_B). Therefore, the colour-forming rate follows Eq. (4):

$$\begin{aligned} \mathrm{d}A/\mathrm{d}t &= \mathrm{d}A_A/\mathrm{d}t+\mathrm{d}A_B/\mathrm{d}t \\ &= \varepsilon_A(I_{\mathrm{Ch.}}\Phi_A+I_B\Phi_{-B}-I_A\Phi_B-k_A[A]+k_B[B]) \\ &\quad +\varepsilon_B(I_{A.}\Phi_B-I_B\Phi_{-B}-k_B[B]) \end{aligned} \tag{4}$$

In Eq. (4), ϵ_A and ϵ_B are the molar absorption coefficients of ***A*** and ***B*** at the analysis wavelength (maximum of the colour band at 422 nm); I_{Ch}, I_A and I_B refer to the irradiating light (357 nm) absorbed by the three species; the thermal (k) and photochemical (Φ) coefficients are indicated in the reaction Scheme 1. The intensity of light absorbed by a single species can be expressed as the product of its absorbance at the irradiating light, the total incident light and the photokinetic factor $F=[1-\exp(-2.3A')]/A'$ (A' is the total absorbance at the excitation wavelength). Moreover, the instantaneous **Ch** concentration is related to ***A*** and ***B*** concentrations and the initial **Ch** concentration (c_0),

$$[\mathbf{Ch}]=c_0-[A]-[B]=c_0-A_A/\varepsilon_A-A_B/\varepsilon_B$$



Scheme 1.

thus, Eq. (4) can be rearranged to Eq. (5):

$$\begin{aligned} \mathrm{d}A/\mathrm{d}t &= I^\circ F\varepsilon_{\mathrm{Ch}}c_0\varepsilon_A\Phi_A \\ &\quad -\{I^\circ F\varepsilon_{\mathrm{Ch}}(\Phi_A+\Phi_B-\varepsilon_B/\varepsilon_A\Phi_B)+k_A\}A_A \\ &\quad -\{I^\circ F\varepsilon_{\mathrm{Ch}}(\Phi_{-B}+\varepsilon_A/\varepsilon_B\Phi_A-\varepsilon_A/\varepsilon_B\Phi_{-B}) \\ &\quad +k_B(1-\varepsilon_A/\varepsilon_B)\}A_B \\ &= C-DA_A-EA_B \end{aligned} \tag{5}$$

where $\varepsilon_{\mathbf{Ch}}$ represents the absorption coefficient of **Ch** at the irradiating wavelength. As can be seen, the colour-forming rate, $\mathrm{d}A/\mathrm{d}t$, consists of two time-dependent terms, since the absorbances of ***A*** and ***B*** increase with the irradiation time, and a term which is constant, if the photokinetic factor F is constant. Since the irradiation wavelength (357 nm) corresponded to an isosbestic point, the condition $F=$ constant was wholly accomplished. Thus, C, D and E are constant parameters. If the hypotheses assumed were correct, integration of the differential Eq. (5) should give a time-function of A describing the experimental absorption/time trends as Eqs. (1) and (2) formally do. If the instantaneous A_A and A_B absorbances in Eq. (5) are replaced by the experimental time-dependent terms of Eq. (2), integration yields Eq. (6):

$$\begin{aligned} A &= Da/\alpha+Eb/\beta+(C-Da-Eb)t-Da/\alpha e^{-\alpha t} \\ &\quad -Eb/\beta e^{-\beta t}=a(1-e^{-\alpha t})+b(1-e^{-\beta t}) \end{aligned} \tag{6}$$

from the condition $A=0$ at $t=0$:

$$C=a\alpha+b\beta;\ D=\alpha;\ E=\beta \tag{7}$$

where: $C=I^\circ F\varepsilon_{\mathbf{Ch}}c_0\varepsilon_A\Phi_A$;
$D=I^\circ F\varepsilon_{\mathbf{Ch}}(\Phi_A+\Phi_B-\varepsilon_B/\varepsilon_A\Phi_B)+k_A$;
$E=I^\circ F\varepsilon_{\mathbf{Ch}}(\Phi_{-B}+\varepsilon_A/\varepsilon_B\Phi_A-\varepsilon_A/\varepsilon_B\Phi_{-B})$
$+k_B(1-\varepsilon_A/\varepsilon_B)\}A_B$

Determining the unknown parameters (ε_A,ε_B, Φ_A, Φ_B, Φ_{-B}) by using the integrated Eq. (6) as interpolating curve for the experimental absorbance-time data sets and optimising their values so as to minimise the interpolation errors (χ^2), did not give reliable results. This was probably due to both the large number of parameters to be determined and the numerical sensitivity of the equation. To obtain at least an approximate evaluation of these numbers, we took advantage of the monoexponential kinetics of this system at relatively high temperatures ($T>300$ K). Under this condition the photochromic behaviour was principally governed by the fast thermal decay of the primarily formed isomer ***A*** ($k_A>10^{-1}$ s^{-1}), while ***B*** was undetectable and did not contribute to the overall absorption. Thus, the photostationary method (Eq. (3)), developed for thermoreversible systems, could be applied. From the linearity (correlation coefficient >0.99, over six points) of the $1/A_\infty$ vs. k_A plot in the temperature range 300–325 K, Φ_A resulted approximately unitary and $\varepsilon_A=15\,100$ dm^3 mol^{-1} cm^{-1}.

When temperature decreased below 300 K, the $A\rightarrow B$ photoconversion competed efficiently with the thermal decay of ***A***; therefore, ***B***, which is more thermally stable than ***A***, cumulated. By irradiating with visible monochromatic light

Table 1
Spectrokinetic parameters of the **Ch** photochromic system

Thermal parameters				Photochemical parameters		
300 K						
k_A (s^{-1})	k_B (s^{-1})	E_A (kJ mol^{-1})	E_B (kJ mol^{-1})	Φ_A	Φ_B	Φ_{-B}
150 ± 10	4 ± 2	60 ± 4	20 ± 10	0.9 ± 0.1	0.3 ± 0.1	0.2 ± 0.1
				$\varepsilon_A = 16000 \pm 1000$ dm^3 mol^{-1} cm^{-1}		
				$\varepsilon_B = 8000 \pm 3000$ dm^3 mol^{-1} cm^{-1}		

(422 nm, $I^\circ = 8.1 \times 10^{-7}$ Einstein dm^{-3} s^{-1}) the thermally equilibrated solution ($T = 285$ K), the product $\varepsilon_B \Phi_{-B}$ was determined by using the following equations:

$$-\mathrm{d}A_B/\mathrm{d}t = \varepsilon_B \Phi_{-B} I^\circ (1 - e^{-2.303 A_B}) \\ = \varepsilon_B \Phi_{-B} I^\circ 2.303 A_B \tag{8}$$

The approximation in Eq. (8) held under the experimental conditions (very dilute solution, $A_B < 0.02$). By integration, Eq. (9) is obtained:

$$A_{B(t)} = A_{B(t=0)} \, e^{-2.303 A_B \varepsilon_B \Phi_{-B} I^\circ t} \tag{9}$$

which represents an interpolating function for the experimental points. The result obtained was: $\varepsilon_B \Phi_{-B} = 1400$ dm^3 mol^{-1} cm^{-1}.

Eq. (7) and the photostationary state conditions were applied to experiments at relatively low temperatures (285–295 K) to obtain the remaining unknown parameters. In order to adjust the values in different experiments, the uncertainties reported on the numbers in Table 1 are very large.

3.3. Concluding remarks

The results obtained give an idea of the dynamic behaviour of this photochromic system. Two species are produced upon irradiation in consecutive steps, which have similar absorption spectra but different absorption coefficients and thermal stabilities. The energy barrier to closure is relatively high for ***A*** (60 kJ mol^{-1}) and this makes its bleaching rate very sensitive to temperature. Consequently, the amount of ***A*** produced at relatively high temperatures is very small. For the other isomer (***B***), the energy barrier is much lower (20 kJ mol^{-1}). The low value of k_B is due to negative activation entropy, as can be inferred from the small frequency factor (4 s^{-1}) extrapolated from the Arrhenius plot (Fig. 3). The number obtained is unreliable as an absolute value, because of the uncertainty in the extrapolation, but it is meaningful as an order of magnitude.

For ***A*** a *cis–trans* and for ***B*** a *trans–trans* structure are proposed in Scheme 1; other quasi-planar structures are not conceivable because of steric hindrance. In both structures, the terminal phenyls are twisted and out of plane due to steric interaction between the ortho hydrogens [16]. The primarily formed metastable photoproduct, ***A***, involves a torsion around a single bond following the bond rupture. The thermal back-reaction, to which the barrier is of the same order of magnitude as that found for another chromene derivative [30], consists in a torsion around a single bond. For the other isomer, ***B***, where a torsion around a double bond is required, the main back-way is photochemical as is its formation from ***A***.

The kinetic analysis described is useful, but not exhaustive to fully understand the photochromic behaviour of systems which give rise to two coloured species, as often occurs with chromenes. In order to determine the unknown parameters, additional, independent information is needed. In the present case this information was extracted by isolating the photoprocess yielding one of the isomers, ***A***, by enhancing temperature, and by investigating the photochemical bleaching of ***B***, by decreasing temperature. From a quantitative point of view, the uncertainties on some parameters are not within a desirable limit. However, the proposed reaction Scheme 1 is the most plausible based on qualitative observation; other conceivable mechanisms do not account for the experimental findings as well as this one does.

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