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Pyranyl Radicals and Their Dimers

Hiroki KAWATA and Shigeya NIIZUMA*
College of Humanities and Social Sciences, Iwate University, Ueda, Morioka 020
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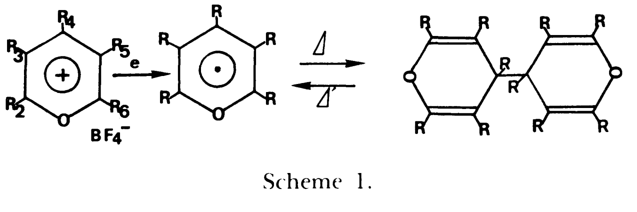
Photochemical and chemical reduction of pyrylium salts in THF solution gave their corresponding radicals which were in equilibrium with dimers. The quantum yields for raidcal formation and the standard enthalpy change ΔH_0 for dimerization decrease with increasing the electron-donating character of the substituting groups in the pyrylium ring. Specially, ΔH_0 for pentaphenylpyranyl and pentaphenylthiopyranyl radicals, in which all carbons in the ring are substituted by phenyl groups, become possitive. The absorption maxima and their molar extinction coefficients of pyranyl radicals, and concurrently the equilibrium constants for the dimerization were determined spectrophotometrically.

Pyranyl radicals are formed by one-electron reduction of the parent pyrylium salts with chemical (organic reducing agent,1) zinc or other metals,2) and Grignard reagent3)), electrochemical4) and photochemical5) reactions in the degassed aprotic solvents. They are in equilibrium with their diamagnetic dimers (Scheme 1). This equilibrium lies in favor of the radical at room temperature except the compounds which have a methyl group1) or a hydrogen atom2f,6a,c) at 4-position carbon in the pyrylium ring. In such compounds, no equilibrium is observed and the dimer is formed directly at room temperature, so that no ESR signal can be detected. The NMR spectra of the dimers obtained by zinc metal reduction or the reduction with disodiocyclooctatetraene reflected the configuration of the σ bonding between the 4-position carbons of each pyranyl moiety.1,6c) The equilibrium between pyranyl radicals and their dimers is similar to the case of the dimerization of pyridinyl radicals,7) where the dimeric intermediate, radical pair, was involved in the dimerization of the radical.

Photoirradiation of 2,4,6-triphenyl-, 2-*t*-butyl-4,6-diphenylpyrylium and 2,4,6-triphenylthiopyrylium tetrafluoroborates in degassed tetrahydrofuran (THF) gave the corresponding radicals by electron transfer from the solvent, THF, itself with relatively high quantum yields.5) 2,4,6-Triphenylpyranyl radical has a light red color in THF solution and shows the ESR signal with well-resolved hyperfine structure (hfs) at room temperature. With decreasing the temperature, the color fades and at the same time the intensity of the ESR signal decreases because of its dimer formation. In this paper, the investigation of the chemical properties of various kinds of pyranyl radicals formed by the photoreduction or by the zinc metal reduction of pyrylium salts is reported. The dimerization of 2,3,4,5,6-pentaphenylpyranyl and 2,3,4,5,6-pentaphenylthiopyranyl radicals was found to be an endothermic reaction, it being remarkable in comparison with that of other pyranyl radicals.



Scheme 1.

Experimental

The pyrylium salts used are all tetrafluoroborates and were supplied by Prof. Suzuki in this University. They decompose gradually in solution if the solvent contains a small amount of water. The solvents THF and 2-methyl-THF (G.R. of Wako Junyaku) were distilled over calcium hydride and stocked on a sodium–potassium alloy in an ampoule connected to a vacuum line. Triphenylphosphine (G.R. of Kanto Kagaku) was recrystallized twice from ethanol. The degassed sample solution was exposed to a continuous irradiation in a 1×1×4 cm quartz cell. The light source was a Toshiba SHL-100 UV mercury lamp with Toshiba filter system (UVD-35 and L-1A for the 365 nm, P-39B and L-39 for the 406 nm, and V-40 and Y-43 for the 436 nm irradiation). The quantum yield of the photoreaction was determined at 25 °C using potassium tris-oxalatoferrate(III) as an actinometer. The absorption and the ESR spectra were measured with a Hitachi ERI-G3 spectrophotometer and a JEOL PE-1 or RE-2 ESR spectrometer, respectively. The ESR intensity was calculated by a double integration of the first derivative curve with a Graphtec KD-4030 degitizer on-line with a NEC PC-9801 personal computer. The absorption spectra at low tem-

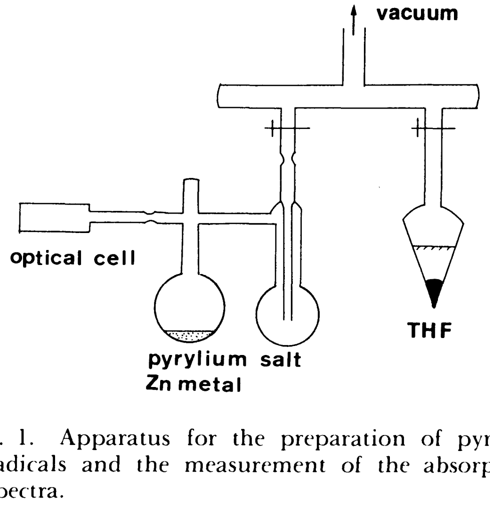


Fig. 1. Apparatus for the preparation of pyranyl radicals and the measurement of the absorption spectra.

perature were measured using a quartz Dewar vessel. The temperature was controlled with Dry Ice–methanol and liquid nitrogen.

The procedure of the preparation of the radical with zinc metal is as follows: Known amounts of pyrylium salt and an excess mole of zinc granular were put together into the reaction vessel connected to the vacuum line (see Fig. 1). After degassing the system, we introduced known amounts of solvent THF to it by distillation. The system was sealed and disconnected from the vacuum line. The solution was stirred with a Teflon-coated magnetic bar until the absorption of the starting material disappeared completely. All the sample solutions were degassed by means of the distillation method. The method of least squares was applied when a straight line was drawn in the analysis of the data.

Results and Discussion

Steady Light Irradiation. Photoirradiation of the degassed THF solution of 3-methyl-2,4,6-triphenyl-, (**1**), 2,3,4,6-tetraphenyl-, (**2**), 2,3,4,5,6-pentaphenyl-, (**3**), 2,4,6-tris(*p*-methoxyphenyl)pyrylium tetrafluoroborate (**4**), and 2,3,4,5,6-pentaphenylthiopyrylium tetrafluoroborate (**5**) gives the corresponding radicals when a reducing agent is added to the solution such as triphenylphosphine or hexamethylbenzene. Without these reductants, the radicals are not formed by the irradiation. Even with the reductants, they are not formed by dark reaction (i.e. by thermal reaction). The photoproducts for **2**, **3**, **4**, and **5** exhibited the strong but broad structureless ESR signals, while that for **1** had a well-resolved hfs. All of those photoproducts are considered to be neutral radicals produced by one-electron reduction. In the case of the photoreduction of 2,4,6-triphenylpyrylium salt, the solvent (THF) itself behaves as a reducing agent.

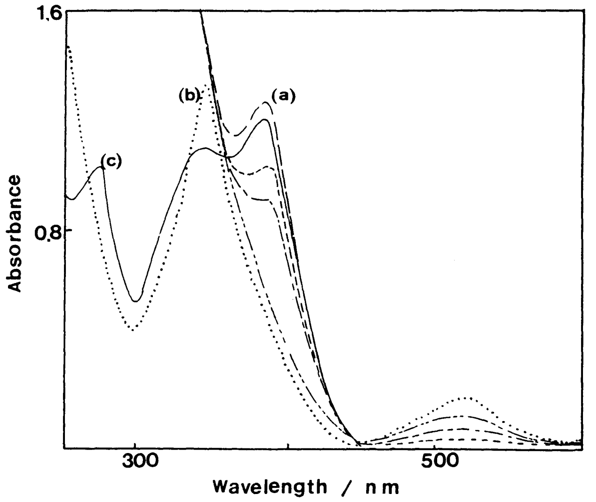


Fig. 2. (a) Spectral change of a solution of **1** containing 1.5×10^{-2} mol dm^{-3} triphenylphosphine on irradiation of 365 nm light with time: ——, 0 min; ----, 15 min; —-—, 45 min. (b) ------, Absorption spectrum of the radical for **1** (ca. 1.4×10^{-4} mol dm^{-3}) produced by the zinc metal reduction. (c) ——, Absorption spectrum of **1** (1.4×10^{-4} mol dm^{-3}). All the spectra for (a), (b), and (c) were measured using the degassed THF solution and at 25 °C.

On the photoirradiation, the concentration of pyrylium salts and triphenylphosphine were fixed to be 1.2×10^{-4} and 1.5×10^{-2} mol dm^{-3}, respectively. The irradiation wavelength was chosen to be 365 nm for **1** and **2**, 406 nm for **3** and **5**, and 436 nm for **4**. The spectral change observed on irradiating of **1** at 365 nm is shown in Fig. 2(a). The absorption of the product at 520 nm increases with the irradiation time at the expense of that of **1** at 385 nm. An isosbestic point appeares at 448 nm. The absorption band shorter than 330 nm could not be measured due to that of triphenylphosphine overlapping there. All the photoproducts have a very weak absorption extending beyond 900 nm. Molar extinction coefficient, ε, is 50—200 dm^3 mol^{-1} cm^{-1} at the wavelength region 600—900 nm. Since both pyrylium salts and the corresponding dimers have no absorption band at the wavelength 480—570 nm, the quantum yields for the formation of radical can be determined photometrically using the second main peak of radicals located in this region (discussed later) if only the extinction coefficient of the radical and the equilibrium constant K_d for the dimer formation are known. On the other hand, the same radicals as those produced by photoreaction were obtained chemically by the reduction with granules of zinc metal in degassed THF solution. The absorption spectrum of the radical produced from **1** obtained in this way is shown in Fig. 2(b). It has the absorption maxima at 342 and 520 nm. Making a comparison between the absorption spectrum of **1** (Fig. 2(c)) and that of the zinc reduction product, we found that **1** was quantitatively converted into the radical by zinc metal reduction. Other pyrylium salts are also reduced completely to the corresponding radicals by zinc metal. The radicals obtained in this way are stable in the degassed THF solution. But they all decompose on introducing air to the solution except for the radical from **4**, which reverts to the starting substance.

In order to know the exact molar extinction coefficients of these radicals, we must refer to the reaction the radical is concerned with. Consider the equilibrium between the radical and its dimer as

$$2\ \text{Radical} \rightleftarrows \text{Dimer}. \qquad (1)$$

The equilibrium constant K_d for the dimer formation is

$$K_d = [\mathrm{D}]/[\mathrm{R}]^2 = \{C_0 - [\mathrm{R}]\}/2[\mathrm{R}]^2, \qquad (2)$$

where [D] and [R] are the concentration of the dimer and the radical, respectively, and C_0 is the initial concentration of the pyrylium salt and equals [R]+2[D]. If α is the ratio of [R] to C_0,[8] then K_d is

$$K_d = (1-\alpha)/2C_0\alpha^2. \qquad (3)$$

Table 1. Absorption Maxima of Radicals, Quantum Yield of Radical Formation, Standard Enthalpy Variation for Dimer Formation, and Equilibrium Constant of Dimer Formation

Compound	Absorption maxima (nm) and ε of radicals[a)]	Quantum yield of radicals[b)]	ΔH_0/kcal mol^{-1} for $2R \longrightarrow D$	K_d (25 °C)
1	342(10800), 520(1780)	0.022	−14.5[c)], −14.2[d)]	1690
2	345(13800), 515(3180)	0.029	−12.3[c)]	875
3	355(11200), 376(11000) 490(3760)	0.017	+2.36[d)]	18700
4	358(34600), 562(3770)	0.014	−15.4[c)]	505
5	363(10900), 470(1690)	—	+3.72[d)]	1770

a) Obtained by the use of the Eq. 5 in degassed THF solution and ε is in 10^{-3} mol^{-1} cm^2. b) Quantum yield for the radical formation irradiated with the 365 nm for **1** and **2**, the 405 nm for **3** and the 436 nm for **4** at 25 °C. The value for **5** could not be determined since the absorption of the starting **5** was overlapping to that of the radical around 470 nm because of the conjugation of *p*-methoxyphenyl group with pyrylium ring. c) Determined photometrically. d) Determined by the ESR method.

We define the apparent molar extinction coefficient ε at a given wavelength by the following equation.

$$\varepsilon = \alpha\varepsilon_R + (1-\alpha)\,\varepsilon_D/2. \qquad (4)$$

Here, ε_R and ε_D are the molar extinction coefficients for the radical and its dimer. As the dimer has no absorption at an observing wavelength, we put ε_D as zero. Then, Eq. 3 becomes Eq. 5.

$$\varepsilon = \varepsilon_R - (2K_d/\varepsilon_R)\,C_0\varepsilon^2. \qquad (5)$$

We derive respectively ε_R and K_d from the intercept and the slope of the straight line obtained by plotting ε vs. $C_0\varepsilon^2$. The absorption maxima and their molar extinction coefficients for the several kinds of radicals generated by the reduction with the zinc metal are summarized in Table 1 together with the equilibrium constants for the dimerization. The K_d value for **2** was determined to be 875 (at 515 nm) and 915 dm^3 mol^{-1} (at 345 nm) by the method mentioned above. The former is more reliable than the latter in view of the absorption band purity.

The quantum yields listed in Table 1 were calculated as follows: the initial concentration of the radical, $[R]_0$, formed by the irradiation is expressed as $[R]_0=[R]+2[D]$. $[R]$ can be obtained directly from the absorption of the radical and $[D]$ can be calculated from the relation $[D]=K_d[R]^2$. Thus, we can know the true concentration of the radical immediately after irradiation. The quantum yields listed in Table 1 indicate that the compound containing the pyrylium ring substituted by the stronger electron-donating groups has a lower quantum yield. The quantum yields of 2,4,6-triphenylpyranyl and 2,4,6-tris(*p*-methoxyphenyl)pyranyl radical formation are respectively 0.21[5)] and 0.014, the latter containing three additional methoxyl groups to the former. The same tendency is seen in the data for **1**, **2**, and **3**. This is explained by the fact that the electron-donating group destabilizes the lowest unoccupied molecular orbital (LUMO) of the pyrylium cation and, as a consequence, destabilizes the highest occupied molecular orbital (HOMO) of the radical. The pyrylium salt substituted by electron-donating group has a higher absolute value of the reduction potential,[2f,9)] which is related to the LUMO with the equation of $E_{red}^{1/2}=E(\text{LUMO})+C$.[10)] Here $E_{red}^{1/2}$ is the reversible polarographic half-wave reduction potential and C is a constant including the potential of the reference electrode. All the pyranyl and thiopyranyl radicals prepared so far have the absorption maxima at the wavelength region from 340 to 360 nm, 470 to 560 nm and near IR (weaker compared with the other two bands). These characteristic absorption bands are very useful in identifying the pyranyl or thiopyranyl radicals.

Dimerization of Pyranyl Radicals. Generally the pyranyl radicals are in equilibrium with their corresponding dimers as described above. It is confirmed by measuring the change of the intensity of the ESR signals and/or of the absorbance of the pyranyl radicals with various temperature range. Figure 3 depicts the temperature dependence of the absorption spectra of the radical for **1** in THF. The 520 nm band decreases in intensity with lowering the temperature and almost disappears at −50 °C. It recovers, however, the original intensity through warming back to the room temperature. The equilibrium is favorable for dimer at low temperature. While 2,2′,4,4′,6,6′-hexamethyl-4,4′-bi-4*H*-pyran has a tail of the absorption band at 220 nm in ethanol,[1)] 2,2′,3,3′,5,5′,6,6′-octaphenyl-4,4′-bi-4*H*-pyran shows the absorption maxima at 248 nm and the shoulder at 290 nm in degassed THF solution.[6c)] 2,2′,4,4′,6,6′-Hexaphenyl-4,4′-bi-4*H*-pyran has an absorption band at 248 nm in degassed cyclohexane.[2a)] Thus, we can infer from their structure that the σ-bonding dimers of other radicals may have no absorption band at longer wavelength region.

We can know the concentration of the radicals which come to equilibrium with their dimers by observing the absorbance at 520 nm for the radical from **1**, 515 nm for that from **2**, 490 nm for that from **3**, 562 nm for that from **4**, and 470 nm for that from **5** at a

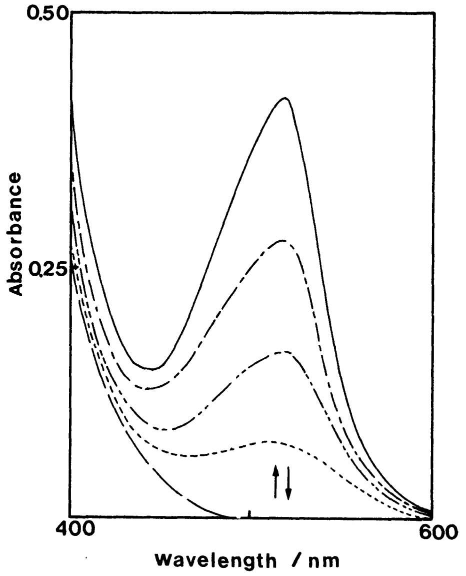


Fig. 3. Temperature effect on the absorption spectrum of the radical for **1**. The concentration of the radical is 2.4×10^{-4} mol dm^{-3}. (a) —, 25 °C; (b) ---, 10 °C; (c) ----, −5 °C; (d) ------, −20 °C; (e) —, −50 °C. These changes are reversible.

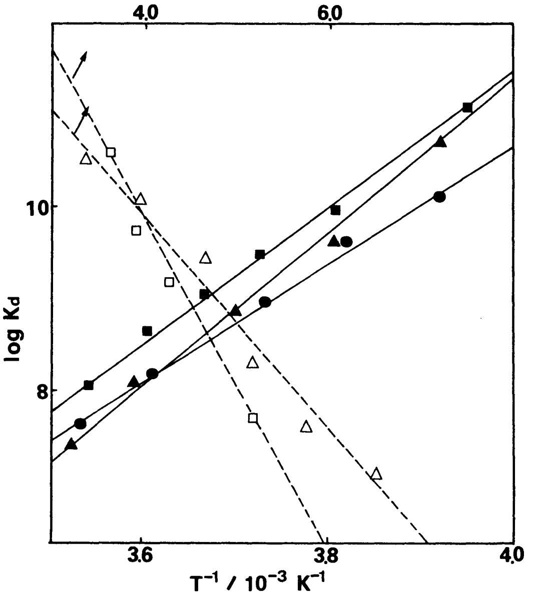


Fig. 4. The plot of log K_d for the various dimer formations vs. T^{-1}; (■) for **1**, (●) for **2**, (▲) for **4**, (△) for **3**, and (□) for **5**.

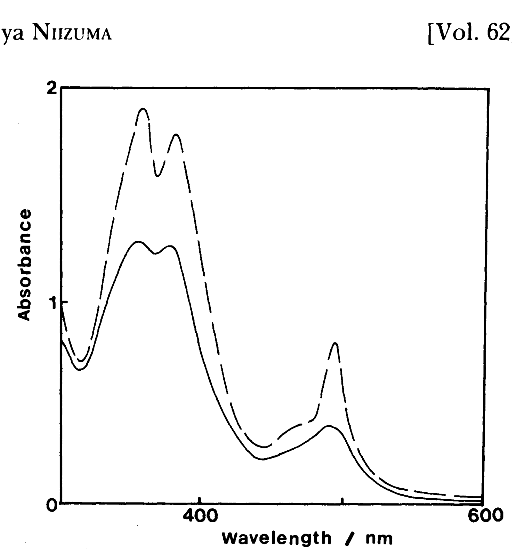


Fig. 5. The absorption spectra of the radical for **3** in the degassed 2-methyl-THF solution: (a) —, 25 °C; (b) —, 77 K. The concentration of the radical is 1.0×10^{-4} mol dm^{-3}.

given temperature. The plot of log K_d (from Eq. 2) against T^{-1} gave a good linear correlation for various radicals as shown in Fig. 4. From the possitive slope of these lines, the standard enthalpy change ΔH_0 involved in the dimer formation are calculated to be −14.5, −12.3, and −15.4 kcal mol^{-1} for **1**, **2**, and **4**, respectively, as listed in Table 1. On the contrary to the above cases, the intensity of the absorbance of the radical from **3** at 490 nm increases with lowering the temperature and vice versa. Similarly the absorption of the radical from **5** behaves the same temperature dependence as that from **3**.

Figure 5 shows the absorption spectra of the 2-methyl-THF solution of the radical from **3** at room temperature and 77 K, respectively. Indeed the 355, 376 and 490 nm absorbances for the radical increase at 77 K.

The amount of the absorbance change within the temperature range of −40—+30 °C is so small and not enough to determine ΔH_0 for the radicals from **3** and **5**. We took advantage of their ESR signals, which were easily measurable over a wide range of temperature. The equilibrium constant K_d can be calculated by Eq. 6, provided we estimate the signal intensity at an infinite (either plus or minus) temperature, I_∞, by the extraporation.

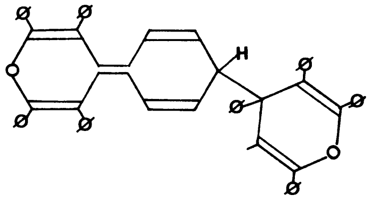
$$K_d = (I_\infty - I)/I^2. \tag{6}$$

The standard enthalpy change for the dimerization of the radical for **1** obtained by the ESR method is −14.2 kcal mol^{-1}, which is in good agreement with that determined photometrically, −14.5 kcal mol^{-1}. ΔH_0 for **3** and **5** determined by the ESR method are possitive, being 2.36 and 3.72 kcal mol^{-1}, respectively. ΔH_0 of the latter is larger than that of the former. This should be attributed to the difference in the electronegativities between oxygen and sulfur atom in the heterocycles: the oxygen atom enhances the electron-donating charactor of the phenyl groups more than the sulfur atom does. Consequently, the oxygen destabilizes the radical more than the sulfur does. This argument is applicable for the difference in K_d between **3** and **5**. The K_d for the former is larger about one order of magnitude than that for the latter, as similar to the results for 2,4,6-triphenylpyranyl radical and

2,4,6-triphenylthiopyranyl radical.[2f] The order of the electron-donating power of the substituents is *p*-methoxyphenyl>methyl>phenyl group. ΔH_0 values for the compounds containing these three groups increases in this order (see Table 1). This may be due to the radical destabilizing character of the electron-donating groups. On the other hand, as the number of phenyl group increases, the values of ΔH_0 of the radicals for **3** and **5** become large, and turn to positive, the equilibrium between radical and its dimer being favorable for radical at low temperature. This abnormality can be explained by the steric hindrance of the phenyl groups with respect to the dimerization (see below).

Configuration of Dimer. All dimers mentioned above may be expected to be formed through the σ bonding between the carbons at 4-position of each radical in the light of the configuration of the dimers of 2,4,6-trimethyl- and 2,3,5,6-tetraphenylpyranyl radicals. In practice, it is possible to assemble the dimers of σ-bonding configuration for **1**, **2**, and **4** with a Corey–Pauling–Kolton (CPK) space filling molecular models, though the dimer for **1** or **2** which has a substituent larger than a hydrogen atom at 3-position carbon is highly strained. As to the dimer for **3** and **5**, however, it is absolutely impossible to construct them with the CPK molecular model because of the large steric hindrance of phenyl groups both 3- and 5-position in the pyrylium or thiopyrylium ring. The apparent temperature effects on the intensity of the radical absorbances at 490 (for **3**) and 470 nm (for **5**) are similar to that for 1-alkyl-4-carbomethoxy pyridinyl radical,[11] where the intensity of the absorbance at ca. 640 nm increases with decreasing the temperature, due to a charge-transfer complex formation between two pyridinyl radicals.

In our case, however, the amounts of these pyranyl and thiopyranyl radicals are confirmed to increase with lowering the temperature by the ESR measurement. The absorption in visible region is not the charge-transfer band but the monomer radical band in comparison with those of radicals for **1**, **2**, **4**, and other pyrylium salts.[5] Thus, a potential energy of a radical and a dimer vs. the reaction coordinate diagram is considered to be different between the equilibrium for ordinary pyrylium salts and that for **3** and **5**. Taking into account the large steric hindrance of phenyl groups, it is reasonable that the potential energies of the radicals of **3** and **5** are lower than that of the dimers. Moreover, the dimers for **3** and **5** may not have the tight σ bonding at 4-position carbon of the radical. Then, two possible structures of the dimer are considered. One is **6** in which one radical attacks a benzene ring of another radical in 4-position carbon, analogous to the case of the dimerization of triphenylmethyl radical.[12] It is possible to make the molecule of **6** with CPK model. The other is the ordinary dimer configuration with a σ bonding at 4-position carbon, not tight but very loose bonding taking into account the flexibility of the pyrylium or thiopyrylium ring.



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