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Super-strong bathochromic and hyperchromic effects of methoxy-substituted aromatic bis(1,3-diketones)

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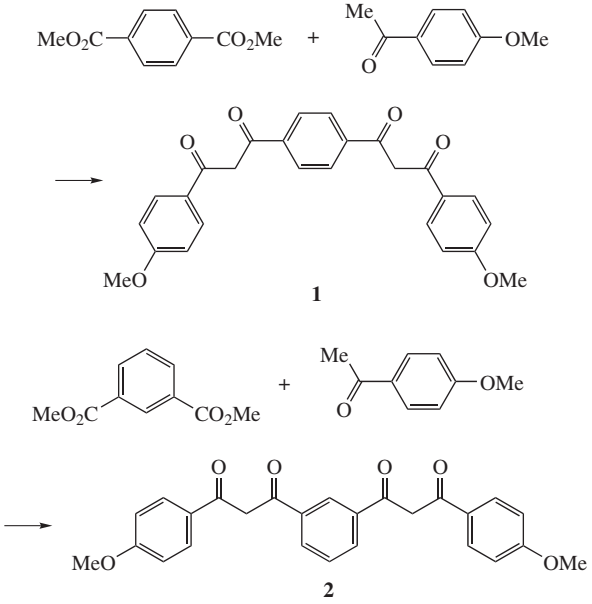
1,3(4)-Bis[3-(4-methoxyphenyl)-1,3-dioxopropyl]benzenes show super-strong bathochromic and hyperchromic effects in relation to dibenzoylmethane and Avobenzone, a common UV-A sunscreen agent.

Recently[1] we described spectral properties of aromatic bis(1,3-diketones) obtained from acetophenone and methyl terephthalate and isophthalate. These compounds showed strong hyperchromic effects in comparison with the simplest aromatic 1,3-diketone – dibenzoylmethane (DBM), which arise from existence of two 1,3-dicarbonyl moieties. Similar effects were observed for *p*-methoxy-substituted DBM derivatives.[2] Therefore, it seemed reasonable to study spectral properties of *p*-methoxy-substituted aromatic bis(1,3-diketones). There are few articles concerning phenyl-substituted aromatic bis(1,3-diketones)[3–7] and only one reports on *p*-methoxyphenyl-substituted aromatic bis(1,3-diketone).[6] However, the latter described mainly the synthesis lacking the UV spectral data.

Aromatic bis(1,3-diketones) **1** and **2** (Scheme 1) with methoxy group in *para* position were synthesized from *p*-methoxyacetophenone and dimethyl benzenedicarboxylates according to the published procedure.[1,†] Their UV spectra (Figure 1) were compared with those of standard DBM (**3**) and 1-(4-*tert*-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione **4** (Avobenzone). Molar absorption coefficients and absorption maxima are given in Table 1.

Compounds **1** and **2** revealed strong hyperchromic effects which exceed the expected from spectra of aromatic 1,3-diketones with methoxy groups in *para* position[2] and bis(1,3-diketones) without methoxy groups.



Scheme 1

In the case of compound **1** with dicarbonyl moieties in *para* position, the molar absorption coefficient was >109 000 dm^3 mol^{-1} cm^{-1} which is >4.3 and >3.2 times higher than those of DBM **3** and Avobenzone **4**, respectively. Moreover, **1** also exhibited very strong bathochromic shift relative to DBM: $\Delta\lambda_1 = 45.2$ nm. Such strong red shift consequently results in absorption of visible radiation and is responsible for a yellow colour of this compound. Bathochromic and hyperchromic effects result from conjugation of 1,3-dicarbonyl moieties which are in *para* position in relation

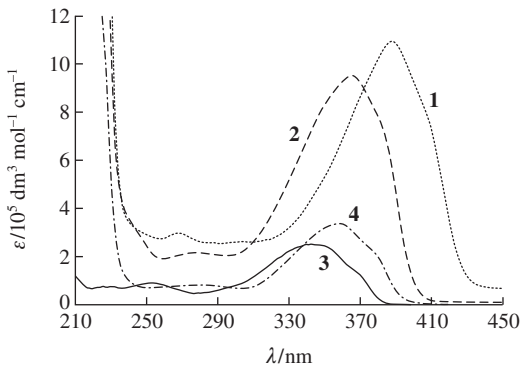


Figure 1 Absorption spectra of compounds **1**–**4** in ethanol.

† Bis(1,3-diketones) **1** and **2** were synthesized by condensation between the corresponding dimethyl benzenedicarboxylates and 4-methoxyacetophenone by the described method.[1] Compounds **3** and **4** were prepared according to the reported procedure.[2]

UV-VIS spectra were collected on a Shimadzu UV-2101 PC double beam spectrophotometer. The melting points were determined on a Stanford Research Systems EZ-Melt MPA120 automated melting point apparatus. NMR spectra were recorded on NMR Varian Inova 300 MHz.

1,4-Bis[3-(4-methoxyphenyl)-1,3-dioxopropyl]benzene **1**: yield 46%, mp 239–240 °C (lit.,[6] 233–234 °C). ^{1}H NMR (DMSO-d_6) δ: 3.88 (s, 6H, OMe), 7.12 (d, 4H, H$_{Ar}$, *J* 8.7 Hz), 7.40 [s, 2H, C(OH)=C*H*–CO], 8.21 (d, 4H, H$_{Ar}$, *J* 8.7 Hz), 8.29 (s, 4H, H$_{Ar}$), 17.31 [br. s, 2H, C(O*H*)=CH–CO]. ^{13}C NMR (DMSO-d_6) δ: 60.7 (OMe), 99.5, 123.4, 133.2, 136.7, 138.8, 146.5, 157.3 [C(OH)=*C*H–CO, C$_{Ar}$], 180.2, 181.6 (CO). UV [EtOH, λ_{max}/nm (logε)]: 387.6 (5.04). Found (%): C, 72.50; H, 5.08. Calc. for $C_{26}H_{22}O_6$ (%): C, 72.55; H, 5.15.

1,3-Bis[3-(4-methoxyphenyl)-1,3-dioxopropyl]benzene **2**: yield 72%, mp 238–239 °C. ^{1}H NMR (DMSO-d_6) δ: 3.87 (s, 6H, OMe), 7.12 (d, 4H, H$_{Ar}$, *J* 9.0 Hz), 7.40 [s, 2H, C(OH)=C*H*–CO], 7.74 (t, 1H, H$_{Ar}$, *J* 7.8 Hz), 8.21 (d, 4H, H$_{Ar}$, *J* 8.7 Hz), 8.38 (d, 2H, H$_{Ar}$, *J* 7.5 Hz), 8.71 (s, 1H, H$_{Ar}$), 17.39 [br. s, 2H, C(O*H*)=CH–CO]. ^{13}C NMR (DMSO-d_6) δ: 55.6 (OMe), 91.0 [C(OH)=*C*H–CO], 114.3, 122.6, 129.9, 138.9, 149.9, 154.4, 157.2, 163.4 (C$_{Ar}$), 185.5, 186.2 (CO). UV [EtOH, λ_{max}/nm (logε)]: 365.8 (4.98). Found (%): C, 72.61; H, 5.06. Calc. for $C_{26}H_{22}O_6$ (%): C, 72.55; H, 5.15.

Table 1 Molar absorption coefficients and absorption maxima of obtained 1,3-diketones.

Diketone	λ_1 = 280–400 nm			λ_2 = 235–280 nm		λ_3 = 210–235 nm	
	λ_{max}/nm	$\Delta\lambda$[a]/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}
1	387.6	45.2	109.5×10^3	267.2	29.6×10^3	217.8	446.4×10^3
2	365.8	23.4	95.4×10^3	276.6	21.4×10^3	218.2	304.3×10^3
3	342.4	0.0	25.0×10^3	253.0	9.0×10^3	<210.0	—
4	359.8	17.4	33.8×10^3	<235.0	—	218.0	169.8×10^3

[a] Difference between absorption maxima of the test diketone and DBM.

to each other, and are additionally conjugated with methoxy group in benzene rings. Enol content of **1** calculated from ^{1}H NMR (DMSO-d_6) data was 96.4%.

UV spectrum of bis(1,3-diketone) **2** with dicarbonyl moieties in *meta* position is rather different. In this molecule, dicarbonyl moieties are not conjugated, however, each dicarbonyl system is conjugated with methoxy group. Enol content of **2** calculated from ^{1}H NMR (DMSO-d_6) data was 85.4%. Molar absorption coefficient of this compound is >95 000 dm^3 mol^{-1} cm^{-1}, that is >3.8 times and > 2.8 times greater than those of DBM **3** and Avobenzone **4**, respectively. Red shift of compound **2** is strong ($\Delta\lambda_2$ = 23.4 nm relative to DBM) but significantly smaller than that for *para* isomer **1**. Due to this, the absorption band ends at about 400 nm and the compound does not absorb visible light. Taking into consideration its strong hyperchromic effects being insignificantly weaker than those of **1**, compound **2** is superior to commonly used Avobenzone **4**. Moreover, compound **2** is readily accessible from cheap and available reactants. These qualities make it a prospective high-efficient UV-A sunscreen.

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