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UV absorption and keto–enol tautomerism equilibrium of methoxy and dimethoxy 1,3-diphenylpropane-1,3-diones

Jan Zawadiak, Marek Mrzyczek*

Silesian University of Technology, Department of Chemical Organic Technology and Petrochemistry, Krzywoustego 4, 44-100 Gliwice, Poland

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ABSTRACT

UV absorption spectra of 1,3-diphenylpropane-1,3-dione (**1**), its three methoxy derivatives (**2**–**4**) and its six dimethoxy derivatives (**5**–**10**) in various solvents dissolved were collected. The keto–enol tautomerism equilibrium constant was calculated with ^{1}H NMR. The position of the methoxy group in 1,3-diphenylpropane-1,3-dione was shown to have an influence on the molecule's UV absorption spectrum and the keto–enol tautomerism equilibrium constant. The methoxy group in the *para* position increases the absorption of radiation in the UV-A range. A shift to the keto form in the keto–enol tautomerism equilibrium is experienced by compounds with methoxy groups in *ortho* position. When two methoxy groups are present, the influence of their position is cumulative.

1. Introduction

1,3-Diphenylpropane-1,3-dione is a representative example of aromatic 1,3-diketones. The presence of two carbonyl groups separated by a methylene group causes occurrence of keto–enol tautomerism. In the cis-enol form, an intra-molecular hydrogen bond can be formed (Scheme 1).

The ratio of the keto to enol forms is given by the keto–enol tautomerism equilibrium constant:

$$K_T = \frac{c(\text{enol})}{c(\text{diketo})}$$

The equilibrium constant of the tautomerism is affected by the solvent and the substituents R and R′ [1]. In the case of aromatic 1,3-diketones, R and R′ are aryl groups and the equilibrium favors the enol form. Because of their strong UV absorption in the wavelength of range 320–400 nm and their photostability, these compounds are commonly found in UV-A sunscreens [2]. Currently, one of the few UV-A sunscreens approved both in the USA and in Europe is 1-(4′-*tert*-butylphenyl)-3-(4″-methoxyphenyl)-propane-1,3-dione (Scheme 2), which is known under the trade names Avobenzone® and Parsol 1789® (λ_{max} = 357 nm) [3].

Radiation in the UV-A range causes $\pi \rightarrow \pi^*$ transitions in the enol form, which has a longer conjugated chain than the keto form. Due to resonance, groups such as OCH_3 in the *para* position of the aryl groups increase the extent of conjugation and cause a bathochromic band shift and a strong hyperchromic effect [4]. The presence of electron-donating groups in the *meta* position has no effect. In the *ortho* position, however, methoxy groups cause steric hindrance, inducing rotation of the planar molecule about the Ph–CO bond with a subsequent decrease in the molecular coplanarity, which gives rise to a strong hypochromic effect. Absorption in the UV-A range leads also to $\pi \rightarrow \pi^*$ transitions in the keto form as well as $n \rightarrow \pi^*$ transitions in the enol and keto forms.

There are only a few articles on the rotational isomers of **1** that arise from introduction of methoxy groups in the *ortho* and *meta* positions. Usually these compounds are used as starting material, for example in the chromenone synthesis [5]. There are studies on their inhibition of 2-nitrofluorene mutagenicity in *Salmonella typhimurium* [6] and on their hydrolysis to proper acids and ketones [7]. However, the electronic structure of rotational isomers with the methoxy group in the *ortho* position has not been carefully studied up to now; there is a scarcity of UV spectroscopic work on these isomers.

Our goal was to determine how aromatic 1,3-diketones with the methoxy group at various positions on one and/or two phenyl rings absorb UV radiation and how the presence of the methoxy group affects the keto–enol tautomerism equilibrium in various solvents.

2. Results

1 and its nine derivatives (**2**–**10**) were synthesized by condensation of the appropriate ketone and ester. Yields are between 61 and 80% (Scheme 3).

* Corresponding author at: Silesian University of Technology, Department of Chemical Organic Technology and Petrochemistry, Krzywoustego 4, 44-100 Gliwice, Poland. Tel.: +48 322372971; fax: +48 322371032.
E-mail address: marek.mrzyczek@polsl.pl (M. Mrzyczek).

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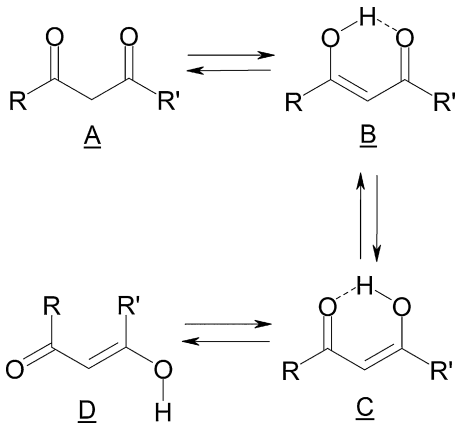
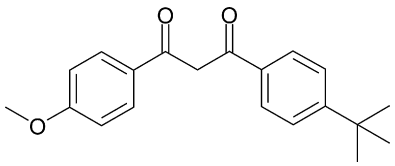


Scheme 1. Keto–enol tautomerism and intra molecular hydrogen bonding in the enol forms.



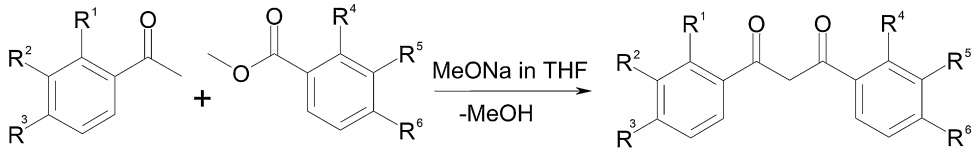
Scheme 2. Molecular structure of the UV-A blocker Parsol 1789 and Avobenzone.

The enol percentage of each 1,3-diketone **1**–**10** was determined by measuring their ^{1}H NMR spectra at 20 °C in four solvents of increasing polarity, i.e. benzene-d_6, $CDCl_3$, acetone-d_6, and DMSO-d_6; the results are given in Table 1. The sample concentrations were always 100 ± 10 mmol/dm^3. The keto–enol tautomerism equilibrium constants are also shown in Table 1. The ^{1}H NMR chemical shifts for each 1,3-diketone are listed in Table 2.

The equilibrium of all the investigated 1,3-diketones was found to favor the enol form. Moreover, as the solvent polarity decreases, the keto content decreases too; in benzene, the 1,3-diketones are almost completely in the enol form. The enol percentage of **1** change from 94 to 99% with decreasing solvent polarity. With a methoxy group in the *ortho* position (**2**) the equilibrium shifts to the keto form; this effect was stronger in polar solvents. In the case of (**5**) derivative with two methoxy groups in *ortho* positions, the enol percentage varied from 70% (in DMSO) to 96% (in benzene). With methoxy groups in the *meta* (**3**) and *para* (**4**) positions no significant influence on the keto–enol equilibrium was observed except for **7**, where the presence of a methoxy group in the *para* position shifts the equilibrium to the keto form, but not as large as the shift resulting from the methoxy group in the *ortho* position.

UV absorption spectra of the compounds **1**–**10** in various solvents were collected. The solvents used were ethanol (λ = 210–400 nm), 1,4-dioxane (λ = 215–400 nm), trichloromethane (λ = 240–400 nm) and n-heptane (λ = 200–400 nm). The concentrations of the samples were $c = 50 \pm 0.5$ μmol/dm^3 and the UV spectra were obtained at ambient temperature. Some typical UV spectra in the range of λ = 240–400 nm are shown in Figs. 1–4. The molar extinction coefficients and the absorption maxima for the UV spectra of **1**–**10** are given in Tables 3–5.

In the UV spectra of the aromatic 1,3-diketones, three characteristic absorption bands can be distinguished: λ_1 = 280–400 nm, λ_2 = 230–280 nm and λ_3 = 200–230 nm. As first band, all of the investigated diketones have a broad absorbance peak over λ = 335–362 nm. The absorption maxima of the other two bands are shifted or overlapped and difficult to interpret. Only the methoxy



Formula number	R^1	R^2	R^3	R^4	R^5	R^6	Yield
1	H	H	H	H	H	H	80%
2	OMe	H	H	H	H	H	66%
3	H	OMe	H	H	H	H	69%
4	H	H	OMe	H	H	H	75%
5	OMe	H	H	OMe	H	H	61%
6	H	OMe	H	OMe	H	H	66%
7	OMe	H	H	H	H	OMe	70%
8	H	OMe	H	H	OMe	H	66%
9	H	OMe	H	H	H	OMe	70%
10	H	H	OMe	H	H	OMe	73%

Scheme 3. Yields of synthesized 1,3—diketones.

Table 1
The enol percentage of synthesized 1,3—diketones.

1,3-Diketone	c (enol) in Mol-%				K_T			
	DMSO	Acetone	$CDCl_3$	C_6D_6	DMSO	Acetone	$CDCl_3$	C_6D_6
1	94.0	97.7	97.8	99.9	15.7	42.2	44.6	1536.0
2	90.2	93.6	91.6	99.4	9.2	14.5	10.9	163.3
3	94.6	99.3	97.3	99.3	17.4	141.7	36.0	148.4
4	93.7	97.3	95.7	99.7	14.8	35.8	22.3	370.1
5	70.1	87.1	86.6	95.7	5.2	6.8	6.5	22.5
6	90.7	95.3	95.2	96.7	9.7	20.1	19.8	29.0
7	82.5	92.0	88.2	96.7	4.7	11.6	7.9	29.5
8	94.6	97.8	97.2	98.8	17.4	43.7	34.4	88.6
9	94.0	96.4	96.1	99.7	15.7	26.9	24.8	376.9
10	95.0	96.7	97.9	99.8	19.2	29.7	47.0	506.3

Table 2
The ^{1}H NMR chemical shifts of synthesized 1,3—diketones.

1,3-Diketone	^{1}H NMR shifts referenced against TMS in ppm											
	(C=O)CH_2(C=O)				(C=O)CH=C-OH				(C=O)CH=C-OH			
	DMSO	Acetone	$CDCl_3$	C_6D_6	DMSO	Acetone	$CDCl_3$	C_6D_6	DMSO	Acetone	$CDCl_3$	C_6D_6
1	4.89	4.84	4.63	4.10	7.36	7.27	6.86	6.61	17.21	17.27	16.90	17.74
2	4.64	4.66	4.60	4.34	7.24	7.35	7.15	7.31	17.08	17.19	16.88	17.84
3	4.88	4.83	4.62	4.13	7.34	7.26	6.84	6.67	17.20	17.26	16.85	17.77
4	4.80	4.75	4.59	4.16	7.28	7.20	6.81	6.65	17.37	17.42	17.01	18.00
5	4.50	4.55	4.60	4.70	7.16	7.59	7.32	7.73	17.10	17.24	16.89	17.95
6	4.63	4.64	4.59	4.37	7.21	7.32	7.13	7.37	17.00	17.14	16.83	17.84
7	4.57	4.59	4.57	4.40	7.18	7.29	7.02	7.33	17.19	17.32	16.99	18.07
8	4.87	4.80	4.61	4.16	7.32	7.23	6.82	6.73	17.21	17.25	16.85	17.79
9	4.79	4.74	4.57	4.19	7.26	7.16	6.78	6.71	17.36	17.41	16.99	18.04
10	4.72	4.67	4.53	4.22	7.20	7.12	6.74	6.68	17.52	17.58	17.14	18.24

group in the *para* position (**4**) increases the absorption in the range $\lambda = 280–400$ nm. Methoxy groups in the *ortho* (**2**) and *meta* (**3**) positions caused a hypochromic effect in this range, with an *ortho*-methoxy group giving a stronger effect than a *meta*-methoxy group. The effect of two methoxy groups is an aggregate of the effects of the individual methoxy groups and thus, over the range $\lambda = 280–400$ nm, the strongest hyperchromic effect was achieved for the derivative with two methoxy groups in *para* positions (**10**) and the strongest hypochromic effect was achieved for the derivative with two methoxy groups in *ortho* position (**5**). Having methoxy groups in all the positions causes a bathochromic shift, and for groups in *ortho* and *para* positions, the shift is much higher ($\Delta\lambda \approx 10–17$ nm) than that for groups in *meta* positions ($\Delta\lambda \approx 7–10$ nm), due to resonance. For the wavelength range $\lambda = 200–280$ nm, it is difficult to examine the changes effected by the position of the methoxy group because the absorption maxima is hard to distinguish.

Increasing the solvent polarity shifts the absorption maxima (and hence the $\pi \rightarrow \pi^*$ transitions) in the ranges $\lambda = 280–400$ nm and $\lambda = 230–280$ nm to the red, as expected [8]. The absorption intensity, however, was solvent independent. Some compounds have the highest absorbance in the range $\lambda = 280–400$ nm in ethanol (**1**, **3**, **4**, **9** and **10**) and the rest has the highest absorption in n-heptane. This shows that the solvent has only a small influence on the keto–enol equilibrium of these compounds, since the $\pi \rightarrow \pi^*$

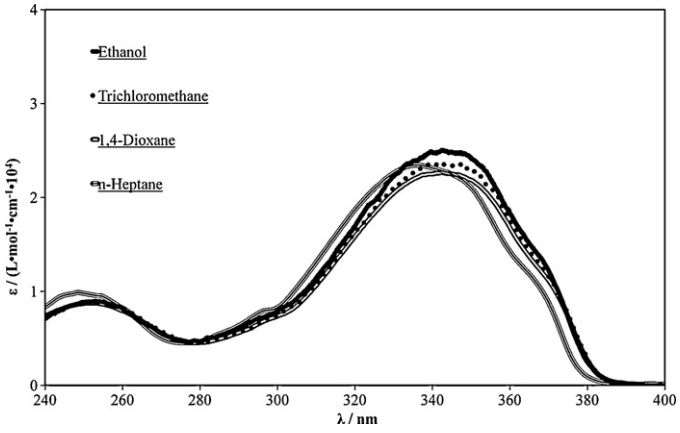


Fig. 1. UV absorption spectra of **1** in ethanol, 1,4-dioxane, trichloromethane and n-heptane.

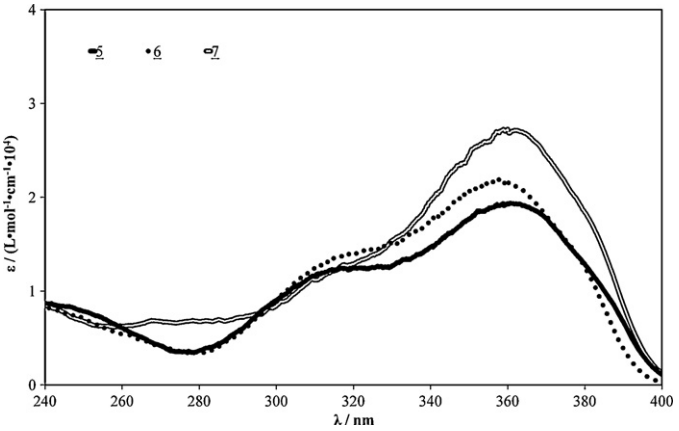


Fig. 3. UV absorption spectrum of **5**, **6**, and **7** in ethanol.

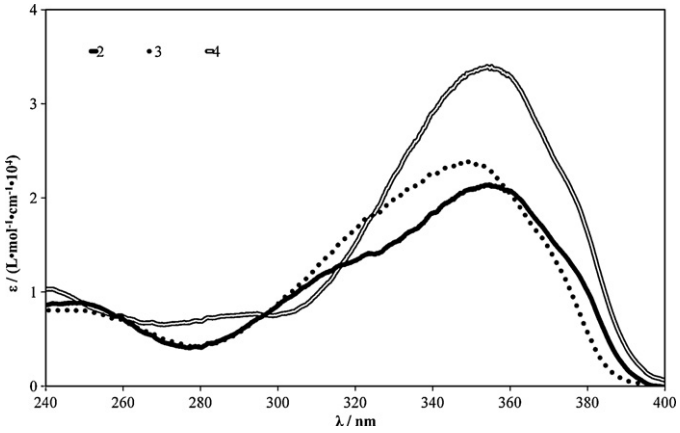


Fig. 2. UV absorption spectra of **2**, **3**, and **4** in ethanol.

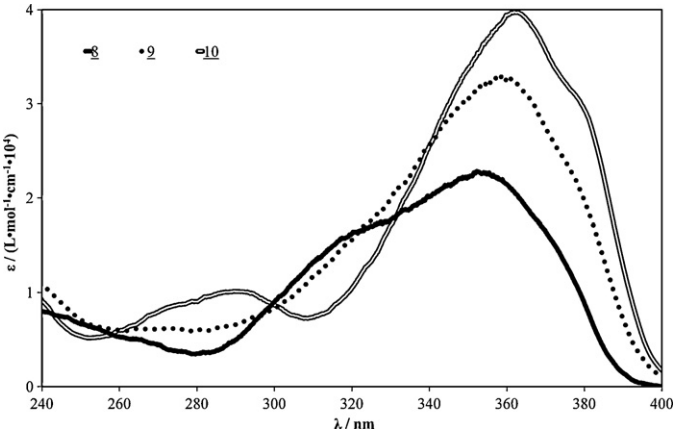


Fig. 4. UV absorption spectrum of **8**, **9**, and **10** in ethanol.

Table 3
The molar extinction coefficients (L mol^{-1} cm^{-1}) of the 1,3-diketones in the range of λ = 280–400 nm.

1,3-Diketone	Ethanol		Trichloromethane		1,4-Dioxane		n-Heptane	
	λ_{max}/nm	ε	λ_{max}/nm	ε	λ_{max}/nm	ε	λ_{max}/nm	ε
1	342.4	25,037	339.6	23,622	342.6	22,822	335.6	23,629
2	354.6	21,413	356.2	21,571	352.4	21,330	349.6	22,621
3	349.2	23,839	347.6	22,851	350.0	23,306	346.0	22,298
4	354.0	33,973	355.8	31,711	353.6	29,395	346.2	28,750
5	360.6	19,383	357.2	20,403	357.2	16,704	354.0	22,268
6	357.8	21,879	358.8	20,717	356.6	19,286	353.0	23,518
7	360.0	27,261	361.8	27,004	359.0	26,411	353.0	29,073
8	352.2	22,827	354.4	23,533	353.8	20,219	349.6	23,769
9	358.6	32,974	357.6	30,471	356.6	29,637	352.2	29,194
10	361.8	39,761	363.4	36,170	361.0	37,701	356.0	37,097

Table 4
The molar extinction coefficients (L mol^{-1} cm^{-1}) of the 1,3-diketones in the range of λ = 230–280 nm.

1,3-Diketone	Ethanol		Trichloromethane		1,4-Dioxane		n-Heptane	
	λ_{max}/nm	ε	λ_{max}/nm	ε	λ_{max}/nm	ε	λ_{max}/nm	ε
1	253.0	8979	251.6	8929	252.8	8748	248.6	9884
2	249.4	8898	246.6	9291	<230	–	248.0	8332
3	<230	–	<240	–	<230	>9376	<230	–
4	<230	–	<240	–	235.8	9024	230.4	10680
5	238.2	8854	<240	–	236.8	6202	<230	–
6	<230	–	<240	–	236.4	8763	<230	–
7	<230	–	<240	–	<230	–	265.8	5824
8	<230	–	<240	–	235.8	8238	<230	–
9	273.6	6192	270.2	5636	268.6	5096	262.2	5724
10	<230	–	<240	–	<230	–	<230	–

Table 5
The molar extinction coefficients (L mol^{-1} cm^{-1}) of the 1,3-diketones in the range of λ = 200–230 nm.

1,3-Diketone	Ethanol		1,4-Dioxane		n-Heptane	
	λ_{max}/nm	ε	λ_{max}/nm	ε	λ_{max}/nm	ε
1	<210.0	–	–	–	213.4	9,036
2	<210.0	–	216.6	16,340	214.8	13,604
3	217.4	16,268	222.2	13,728	219.0	16,020
4	<210	–	–	–	–	–
5	<210	–	–	–	214.6	21,171
6	216.2	22,397	–	–	217.4	22,450
7	<210	–	218.4	12,396	214.8	14,548
8	219.6	22,518	–	–	219.6	24,768
9	<210	–	220.2	13,988	218.6	17,100
10	<210	–	226.4	11,112	227.8	13,632

transitions exist only in the enol form, and this form is favored by less polar solvents [1]. In summary, solvent effects on the UV absorption behavior of the studied 1,3-diketones **1**–**10** are educed mainly by changes in solvent polarity and not by the negligible influence the solvent has on the keto–enol tautomerism equilibrium ratio of the diketones.

3. Conclusions

Due to the limited access to deuterated solvents, the solvents used to investigate the keto–enol equilibrium dynamics of ten 1,3-diketones **1**–**10** synthesized in this study were not the same as the ones used to prepare the samples for which the UV absorption spectra were collected. We found that having the methoxy group in the *para* position increases the absorption of radiation in the UV-A range, due to an increase in conjugation length. Having the methoxy group in the *meta* position has no significant effect on the 1,3-diketones' UV spectra. However, having the methoxy group in the *ortho* position, due to steric effects, causes the aromatic ring to rotate and the molecular coplanarity decreases. Disruption of the conjugation by steric hindrance causes the keto–enol tautomerism equilibrium to shift to the keto form. Therefore, UV absorption of compounds with an *ortho*-methoxy group is worse than that of **1**. When two methoxy groups are present, the effects of their position are cumulative. The strongest increase in UV absorption is obtained when there are two methoxy groups in *para* positions. The strongest shift to the keto form in the keto–enol tautomerism equilibrium is experienced by compounds with two methoxy groups in *ortho* positions. Increasing solvent polarity causes an insignificant change in the percentage of 1,3-diketones that are in enol form; the equilibrium of all the investigated compounds is shifted to the enol form regardless of the solvent polarity. The change in intensity of UV absorption is insensitive to the solvent used.

4. Experimental

General method for the synthesis of the 1,3-diketones **1**–**10**:

A freshly prepared 30% solution of sodium methoxide (0.06 mole) in water-free methanol was added to 100 cm^3 of "THF". Next, the ester (0.06 mole) was added, the mixture was warmed up to the boiling temperature, and the ketone (0.05 mole) was added dropwise for 30 min. After addition of the ketone, the reaction mixture was refluxed for 4 h, monitored by TLC (CH_2Cl_2:acetone = 40:1). The mixture was then cooled in an ice bath, 10% aqueous hydrochloric

acid was added until pH = 7, and the mixture was extracted twice with CH_2Cl_2. The organic fractions were combined, washed with 5% aqueous $NaHCO_3$, and dried with $MgSO_4$. After the solvent was evaporated, the crude solid was purified by two crystallizations from water-free ethanol; yields 61–80% (see Scheme 3).

Obtained compounds:

1,3-Diphenylpropane-1,3-dione (1): m.p. 77–78 °C. ^{1}H NMR ($CDCl_3$): δ 6.86 (s, 1H, C*H*=C–OH), 7.44–7.58 (m, 6H, Ar–H), 7.97–8.01 (m, 4H, Ar–H), 16.90 (s, 1H, CH=C–O*H*). ^{13}C NMR ($CDCl_3$): δ 93.3, 127.4, 128.9, 132.7, 135.7, 185.9. $C_{15}H_{12}O_2$: Calcd. C 80.34; H 5.39. Found: C 80.39; H 5.42.

1-(2′-Methoxyphenyl)-3-phenylpropane-1,3-dione (2): m.p. 65–66 °C (lit. [7] 65 °C). ^{1}H NMR ($CDCl_3$): δ 3.96 (s, 3H, OCH_3), 6.99–7.09 (m, 2H, Ar–H), 7.15 (s, 1H, C*H*=C–OH), 7.45–7.59 (m, 4H, Ar–H), 7.93–7.99 (m, 3H, Ar–H), 16.88 (s, 1H, CH=C–O*H*). ^{13}C NMR ($CDCl_3$): δ 56.0, 98.7, 111.8, 121.0, 125.1, 127.4, 128.8, 130.5, 132.4, 133.3, 136.1, 158.6, 184.4, 186.0. $C_{16}H_{14}O_3$: Calcd. C 75.58; H 5.55. Found: C 75.42; H 5.45.

1-(3′-Methoxyphenyl)-3-phenylpropane-1,3-dione (3): m.p. 59–60 °C (lit. [7] 59.5 °C). ^{1}H NMR ($CDCl_3$): δ 3.89 (s, 3H, OCH_3), 6.84 (s, 1H, C*H*=C–OH), 7.08–7.12 (m, 1H, Ar–H), 7.40 (t, 1H, J = 7.5 Hz, Ar–H), 7.47–7.59 (m, 5H, Ar–H), 7.97–8.01 (m, 2H, Ar–H), 16.85 (s, 1H, CH=C–O*H*). ^{13}C NMR ($CDCl_3$): δ 55.7, 93.6, 112.2, 118.8, 119.8, 127.4, 128.9, 129.9, 132.7, 135.7, 137.3, 160.1, 185.6, 186.1. $C_{16}H_{14}O_3$: Calcd. C 75.58; H 5.55. Found: C 75.53; H 5.37.

1-(4′-Methoxyphenyl)-3-phenylpropane-1,3-dione (4): m.p. 130–131 °C (lit. [7] 132 °C). ^{1}H NMR ($CDCl_3$): δ 3.89 (s, 3H, OCH_3), 6.81 (s, 1H, C*H*=C–OH), 6.99 (d, 2H, J = 9.0 Hz, Ar–H), 7.46–7.57 (m, 3H, Ar–H), 7.96–8.01 (m, 4H, Ar–H), 17.01 (s, 1H, CH=C–O*H*). ^{13}C NMR ($CDCl_3$): δ 55.7, 92.6, 114.2, 127.2, 128.4, 128.9, 129.5, 132.4, 135.7, 163.4, 184.2, 186.4. $C_{16}H_{14}O_3$: Calcd. C 75.58; H 5.55. Found: C 75.69; H 5.52.

1,3-Bis-(2′-methoxyphenyl)propane-1,3-dione (5): m.p. 66–67 °C (lit. [6] 63–65 °C). ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 6H, OCH_3), 6.97–7.08 (m, 4H, Ar–H), 7.32 (s, 1H, C*H*=C–OH), 7.43–7.48 (m, 2H, Ar–H), 7.89–7.93 (m, 2H, Ar–H), 16.89 (s, 1H, CH=C–O*H*). ^{13}C NMR ($CDCl_3$): δ 55.9, 103.7, 111.8, 120.9, 125.6, 130.5, 133.0, 158.6, 184.7. $C_{17}H_{16}O_4$: Calcd. C 71.82; H 5.67. Found: C 72.04; H 5.53.

1-(2′-Methoxyphenyl)-3-(3″-methoxyphenyl)propane-1,3-dione (6): m.p. 54–55 °C. ^{1}H NMR ($CDCl_3$): δ 3.86 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 7.01 (d, 1H, J = 8.4 Hz, Ar–H), 7.05–7.10 (m, 2H, Ar–H), 7.13 (s, 1H, C*H*=C–OH), 7.38 (t, 1H, J = 8.1 Hz, Ar–H), 7.45–7.55 (m, 3H, Ar–H), 7.94 (dd, 1H, J = 7.8, 1.8 Hz, Ar–H), 16.83 (s, 1H, CH=C–O*H*). ^{13}C NMR ($CDCl_3$): δ 55.6, 56.0, 98.9, 111.8, 112.2, 118.6, 119.9, 121.0, 125.0, 129.8, 130.5, 133.3, 137.7, 158.6, 160.0, 184.0, 186.1. $C_{17}H_{16}O_4$: Calcd. C 71.82; H 5.67. Found: C 72.05; H 5.54.

1-(2′-Methoxyphenyl)-3-(4″-methoxyphenyl)propane-1,3-dione (7): m.p. 75–76 °C (lit. [5] 71 °C). ^{1}H NMR ($CDCl_3$): δ 3.88 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 6.95–7.07 (m, 4H, Ar–H), 7.09 (s, 1H, C*H*=C–OH), 7.43–7.51 (m, 1H, Ar–H), 7.91–7.98 (m, 3H, Ar–H), 16.99 (s, 1H, CH=C–O*H*). ^{13}C NMR ($CDCl_3$): δ 55.7, 56.0, 97.9, 111.8, 114.1, 121.0, 125.1, 128.9, 129.6, 130.4, 133.0, 158.5, 163.2, 182.4, 186.6. $C_{17}H_{16}O_4$: Calcd. C 71.82; H 5.67. Found: C 71.92; H 5.64.

1,3-Bis-(3′-methoxyphenyl)propane-1,3-dione (8): m.p. 70–71 °C (lit. [6] 68.5–69 °C). ^{1}H NMR ($CDCl_3$): δ 3.89 (s, 6H, OCH_3), 6.82 (s, 1H, C*H*=C–OH), 7.08–7.12 (m, 2H, Ar–H), 7.40 (t, 2H, J = 7.8 Hz, Ar–H), 7.52–7.58 (m, 4H, Ar–H), 16.85 (s, 1H, CH=C–O*H*). ^{13}C NMR ($CDCl_3$): δ 55.7, 93.7, 112.1, 118.8, 119.8, 129.9, 137.1, 160.1, 185.7. $C_{17}H_{16}O_4$: Calcd. C 71.82; H 5.67. Found: C 72.41; H 5.50.

1-(3′-Methoxyphenyl)-3-(4″-methoxyphenyl)propane-1,3-dione (9): m.p. 88–89 °C (lit. [7] 91 °C). ^{1}H NMR ($CDCl_3$): δ 3.89 (s, 6H, OCH_3), 6.78 (s, 1H, C*H*=C–OH), 6.96–7.01 (m, 2H, Ar–H), 7.06–7.10 (m, 1H, Ar–H), 7.39 (t, 1H, J = 8.1 Hz, Ar–H), 7.51–7.56 (m, 2H, Ar–H), 7.95–8.00 (m, 2H, Ar–H), 16.99 (s, 1H, CH=C–O*H*). ^{13}C NMR ($CDCl_3$): δ 55.6, 55.7, 92.8, 112.1, 114.2, 118.5, 119.6, 128.3, 129.5, 129.8, 137.3, 160.1, 163.5, 184.3, 186.1. $C_{17}H_{16}O_4$: Calcd. C 71.82; H 5.67. Found: C 72.07; H 5.55.

1,3-Bis-(4′-methoxyphenyl)propane-1,3-dione (1): m.p. 118–119 °C (lit. [6] 114–116 °C). ^{1}H NMR ($CDCl_3$): δ 3.89 (s, 6H, OCH_3), 6.74 (s, 1H, C*H*=C–OH), 6.98 (d, 4H, J = 9.0 Hz, Ar–H), 7.96 (d, 4H, J = 9.0 Hz, Ar–H), 17.14 (s, 1H, CH=C–O*H*). ^{13}C NMR ($CDCl_3$): δ 55.7, 91.7, 114.2, 128.4, 129.3, 163.2, 184.8. $C_{17}H_{16}O_4$: Calcd. C 71.82; H 5.67. Found: C 71.97; H 5.76.

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