

# **<sup>13</sup>C- and <sup>1</sup>H-NMR chemical shifts of substituted 2-benzylidene-1,3-cycloheptanediones**

**<sup>a</sup>E. SOLČÁNIOVÁ, <sup>b</sup>P. HRNČIAR, and <sup>b</sup>J. ŠRAGA**

*<sup>a</sup>Institute of Chemistry, Komenský University,  
CS-842 15 Bratislava*

*<sup>b</sup>Department of Organic Chemistry, Faculty of Natural Sciences,  
Komenský University, CS-842 15 Bratislava*

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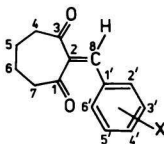
The <sup>13</sup>C- and <sup>1</sup>H-n.m.r. chemical shifts of substituted 2-benzylidene-1,3-cycloheptanediones have been assigned. Correlations of <sup>13</sup>C-n.m.r. substituent chemical shifts of both carbonyl carbons as well as ethylenic carbons with the Hammett substituent constants have been found. The transmission of electronic substituent effects on the chemical shifts of these carbon atoms is discussed.

Соотнесены химические сдвиги <sup>13</sup>C- и <sup>1</sup>H-ЯМР спектров замещенных 2-бензилиден-1,3-циклогептандионов. Найдены корреляции <sup>13</sup>C-ЯМР химических сдвигов в заместителях как обоих карбонильных атомов, так и этиленовых углеродов с константами Гамметта. Обсуждается воздействие электронных эффектов заместителей на химические сдвиги этих углеродных атомов.

Good single parameters correlations of the carbonyl carbon chemical shifts with the Hammett or  $\sigma^+$  (Brown—Okamoto) constants have been found only in such cases [1—4], where two carbonyl groups are bonded to the  $\beta$ -carbon of the styryl group. In the case of monocarbonyl derivatives, with the carbonyl group bonded directly to the aromatic ring [5] or bonded to the  $\beta$ -carbon of the styryl group [6, 7], the carbonyl chemical shifts are less sensitive to the substituent effects and therefore poor correlations with the Hammett constants were usually found.

## **Results and discussion**

The 2-benzylidene derivatives of 1,3-cycloheptanedione were prepared by standard synthetic method [8, 9] (Scheme 1).



Scheme 1

The  $^{13}\text{C}$ -n.m.r. data for the substituted 2-benzylidene-1,3-cycloheptanediones are shown in Table 1. The assignment of the chemical shifts for the *E* and *Z* carbonyl groups can be unambiguously made on the basis of the vicinal coupling constants between the carbonyl carbon and the ethylenic proton. The value of  $^3J(\text{CO}, \text{H}) = 9.4$  Hz was found for the carbonyl signal in the lower field. It means that this signal belongs to the *Z* carbonyl group and vice versa, the signal in the higher field with  $^3J(\text{CO}, \text{H}) = 6.6$  Hz corresponds to the *E* carbonyl group. The substituent chemical shifts (SCS) of the *Z* carbonyl groups are quite susceptible to the substituent effects ( $\Delta\delta_r = \delta_r(\text{NMe}_2) - \delta_r(\text{NO}_2) = 2.4$  ppm), while the SCS of the *E* carbonyl group are less affected by substituent effects ( $\Delta\delta_r = 0.8$  ppm). Very similar effect can be seen in 3-benzylidene derivatives of 2,4-pentanedione [2]. The chemical shifts of the *E* carbonyl group in these open chain derivatives do not correlate with the substituent constants because of the small SCS effect. This can be explained by deviation of the *E* carbonyl group from the planarity of the styrene moiety, or by its rotation around the single bond at ambient temperature. The structure of the studied compounds is also not rigid and therefore at least one carbonyl group can twist as a consequence of diminution of ring strain in the seven-member ring.

The SCS of the ethylenic carbons are similar to those observed previously in other comparable styrene derivatives [1–7]. Chemical shifts of the aromatic carbons were assigned using the additive substituent constants of monosubstituted benzenes [10]. The chemical shifts of the C-4 and C-7 were assigned on the basis of the larger substituent effects on the C-7 and the assignment of the C-5 and C-6 may be reversed.

The  $^1\text{H}$ -n.m.r. chemical shifts are shown in Table 2. The aromatic protons were assigned using the additive increments of monosubstituted benzenes [11]. The triplet signal at  $\delta_r \approx 2.8$  ppm was assigned to the H-4 protons and the triplet signal at  $\delta_r \approx 2.6$  ppm to the H-7 protons. Four-proton triplet at  $\delta_r \approx 2.0$  ppm belongs to the H-5 and H-6 positions.

Results of correlations, given in Table 3, reveal similarities with other dicarbonyl derivatives bearing two carbonyl groups bonded to the  $\beta$ -carbon atom of the styryl group. Excellent correlations were found for the chemical shifts of both carbonyl groups finding the *E* carbonyl group less sensitive to the substituent effects.

Table 1  
 $^{13}\text{C}$ -N.m.r. chemical shifts<sup>a</sup> ( $\delta$ ,/ppm) of 2-benzylidene-1,3-cycloheptanediones in  $\text{CDCl}_3$

X	C-1 <sup>b</sup>	C-2	C-3 <sup>c</sup>	C-4	C-5 <sup>d</sup>	C-6 <sup>d</sup>	C-7	C-8	C-1'	C-2',6'	C-3',5'	C-4'	Others
4'-N(CH <sub>3</sub> ) <sub>2</sub>	210.3	134.2	196.5	43.5	24.0	24.2	41.0	142.8	120.2	133.7	111.5	152.3	40.0
4'-OH	210.9	137.3	196.3	43.8	24.3	24.3	41.2	141.6	125.2	133.2	113.1	158.7	—
4'-OCH <sub>3</sub>	209.8	137.7	196.1	43.8	24.3	24.5	41.3	140.7	125.4	132.9	114.3	161.9	55.4
4'-CH <sub>3</sub>	209.6	139.4	195.9	43.9	24.4	24.8	41.7	140.6	130.1	130.7	129.5	141.5	21.5
H	209.5	140.3	196.0	43.9	24.4	24.8	41.5	140.5	132.9	130.5	128.8	130.8	—
4'-F <sup>e</sup>	209.1	139.9	195.9	43.9	24.4	24.7	41.4	139.4	129.2	132.8	116.0	164.0	—
4'-Cl	208.9	140.7	195.9	43.9	24.4	24.8	41.5	139.1	131.4	131.8	129.0	139.1	—
4'-Br	208.9	140.8	195.9	43.9	24.4	24.8	41.5	139.2	132.0	131.9	132.0	125.3	—
4'-CN	208.1	142.9	195.8	43.9	24.5	24.8	41.7	138.1	137.5	130.6	132.3	116.7	118.2
3'-NO <sub>2</sub>	207.8	142.8	195.8	43.9	24.5	24.7	41.7	137.9	134.8	124.7	148.3	124.9	—
4'-NO <sub>2</sub>	207.9	143.5	195.7	43.9	24.5	24.9	41.7	137.6	139.5	135.7 130.9	129.8 123.8	148.4	—

a) Chemical shifts are relative to TMS. b)  $^3J(\text{CO}, \text{H}) = 9.4 \text{ Hz}$ ; c)  $^3J(\text{CO}, \text{H}) = 6.6 \text{ Hz}$ ; d) assignments may be reversed; e)  $^1J(\text{C}, \text{F}) = 252.0 \text{ Hz}$ ,  $^2J(\text{C}, \text{F}) = 20.5 \text{ Hz}$ ,  $^3J(\text{C}, \text{F}) = 8.8 \text{ Hz}$ ,  $^4J(\text{C}, \text{F}) = 4.4 \text{ Hz}$ ,  $^6J(\text{C}, \text{F}) = 3.0 \text{ Hz}$ .

Table 2

<sup>1</sup>H-N.m.r. chemical shifts<sup>a</sup> ( $\delta_i$ /ppm) and coupling constants<sup>b</sup> of 2-benzylidene-1,3-cycloheptanediones in CDCl<sub>3</sub>

X	H-4	H-5,6	H-7	H-8	H-2',6'	H-3',5'	Others	J/Hz
4'-N(CH <sub>3</sub> ) <sub>2</sub>	2.784	1.970	2.593	7.593	7.471	6.605	3.029	9.05
4'-OH	2.824	2.010	2.618	7.609	7.389	6.789	6.5	8.65
4'-OCH <sub>3</sub>	2.789	1.990	2.608	7.584	7.475	6.867	3.823	9.03
4'-CH <sub>3</sub>	2.794	1.990	2.603	7.593	7.367	7.157	2.348	8.30
H	2.815	2.009	2.622	7.623	7.5 — 7.3	—	—	—
4'-F	2.789	2.005	2.627	7.579	7.503	7.039	—	8.55
4'-Cl	2.784	2.005	2.627	7.559	7.324	7.410	—	9.05
4'-Br	2.784	2.005	2.627	7.539	7.343	7.489	—	8.55
4'-CN	2.802	2.010	2.660	7.581	7.551	7.639	—	8.54
3'-NO <sub>2</sub>	2.828	2.049	2.676	7.637	8.3 — 7.4	—	—	—
4'-NO <sub>2</sub>	2.813	2.044	2.676	7.633	7.614	8.194	—	8.55

a) Chemical shifts are relative to TMS. b)  $J = J_{ortho} + J_{para}$  determined from the spectra.

Table 3

Correlations of <sup>13</sup>C-n.m.r. chemical shifts against  $\sigma$  Hammett constants

Parameter	$a$ /ppm	$b$ /ppm	$r$	$d$ /ppm
C-1	209.3	-1.85	0.935	0.987
C-2	139.5	5.45	0.984	2.762
C-3	196.0	-0.43	0.916	0.236
C-4	43.8	0.18	0.750	0.121
C-5	24.4	0.26	0.900	0.142
C-6	24.6	0.37	0.798	0.229
C-7	41.4	0.43	0.976	0.221
C-8	140.1	-3.22	0.985	1.628
C-1'	129.8	10.80	0.954	5.645

Number of data points in all correlations is 11.

 $a$ ,  $b$  are regression coefficients of the equation  $\delta_i = a + b\sigma$ . $r$  — correlation coefficient. $d$  — standard deviation of  $\delta$ .

Excellent correlations were found also for both carbon atoms of the ethylenic group which are in accord with the results of our previous studies on similar styryl derivatives.

## Experimental

A Jeol FX-100 FT spectrometer was used for measuring  $^{13}\text{C}$ -n.m.r. spectra. The samples were run as 10 % or saturated solutions in deuteriochloroform. TMS was used as an internal standard.

A Tesla 487 BS spectrometer operating at 80 MHz was used for measuring  $^1\text{H}$ -n.m.r. spectra. The samples were run as 5 % solutions in  $\text{CDCl}_3$ . TMS was used as an internal standard.

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