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Excellent correlations have been observed between σ^+ constants and the ^{13}C nmr chemical shifts of several of the carbon atoms of 5-arylidenebarbituric acids and of 2-arylidene-1,3-indanediones.

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Introduction.

Several workers have found very good linear free energy relationships between Hammett σ constants (1) or more commonly between Brown and Okamoto σ^+ constants (2-4) and the ^{13}C nmr chemical shifts of the β -carbon of styrene derivatives; however, none of these workers has reported correlations with functional group carbons further removed from the benzene nucleus. In this work we report that excellent correlations have also been observed between σ^+ and the ^{13}C nmr chemical shifts of the carbonyl groups attached to the β -carbon of the styrene moiety in arylidene derivatives of barbituric acids and 1,3-indanediones.

Results and Discussion.

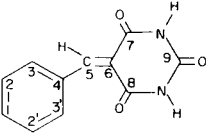
The benzylidene derivatives of barbituric acid were prepared by standard synthetic methods previously reported by Vvedenskii (5) and the indanedione derivatives were prepared by the method of Agranat, *et*.

al., (6). In addition to the indanediones listed in Table II, 2-*p*-nitrobenzylidene-1,3-indanedione was also prepared; however, its solubility in the solvents being used in this study was so low that the nmr peaks of interest here were not observed.

The ^{13}C nmr data for the 5-arylidenebarbituric acids are reported in Table I. Several observations can be made concerning these data. First excellent correlations are apparent from Figure I between the Brown and Okamoto σ^+ values and the chemical shifts of the number 6 carbon atom ($r = 0.994$; see Table III) (we have chosen this numbering system starting with the carbon atom to which the substituent group is attached for convenience in making peak assignments according to the table of Levy and Nelson (7) and for consistency throughout the two series of compounds). The above correlation was to be expected from similar correlations on other styrene derivatives;

Table I

Carbon-13 Shieldings of 5-Arylidenebarbituric Acids (a)



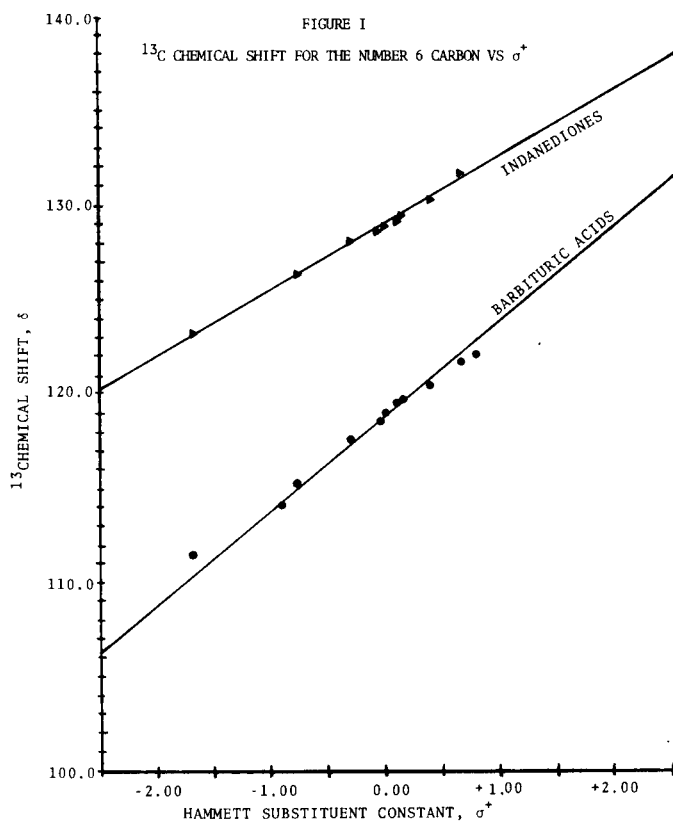
	<i>p</i> -NMe ₂	<i>p</i> -OH	<i>p</i> -OMe	<i>p</i> -Me	<i>p</i> -F	H	<i>p</i> -Cl	<i>p</i> -Br	<i>m</i> -Cl	<i>p</i> -CN	<i>p</i> -NO ₂
C-1	155.4	163.0	163.4	143.4	164.2 (b)	132.6	136.8	125.7	132.5	112.6	148.0
C-2	111.1	115.5	113.9	128.8	115.2 (c)	128.0	128.0	131.0	134.8	131.9	122.6
C-2'	—	—	—	—	—	—	—	—	129.7	—	—
C-3	138.9	138.2	137.4	133.9	136.3 (d)	133.0	134.6	134.6	131.2	131.4	132.2
C-3'	—	—	—	—	—	—	—	—	131.2	—	—
C-4	120.0	123.8	125.1	129.8	129.2 (e)	132.1	131.5	131.9	131.2	137.8	139.9
C-5	154.1	155.7	154.9	155.1	153.6	154.8	153.1	153.1	152.5	151.7	151.1
C-6	109.6	114.1	115.5	117.7	118.6 (f)	119.0	119.6	119.7	120.5	121.8	122.3
C-7	164.6	164.1	163.8	163.5 (g)	163.3	163.3	163.1	163.1	163.0	162.6	162.5
C-8	162.6	162.2	162.1	161.7 (h)	161.7	161.5	161.5	161.4	161.4	161.1	161.1
C-9	150.2	150.2	150.1	150.1	150.1	150.1	150.1	150.0	150.1	150.1	150.1
R	39.6	—	55.6	21.3	—	—	—	—	—	118.4	—

(a) In ppm, downfield from TMS; solvent DMSO-*d*₆. (b) $J_{\text{F-C}} = 253.0$ Hz. (c) $J_{\text{F-C}} = 21.7$ Hz. (d) $J_{\text{F-C}} = 9.1$ Hz. (e) $J_{\text{F-C}} = 2.9$ Hz. (f) $J_{\text{F-C}} = 1.4$ Hz. (g) $J_{\text{cis}^{\text{HC}=\text{C-C}_7}} = 7.6$ Hz. (h) $J_{\text{trans}^{\text{HC}=\text{C-C}_8}} = 11.3$ Hz.

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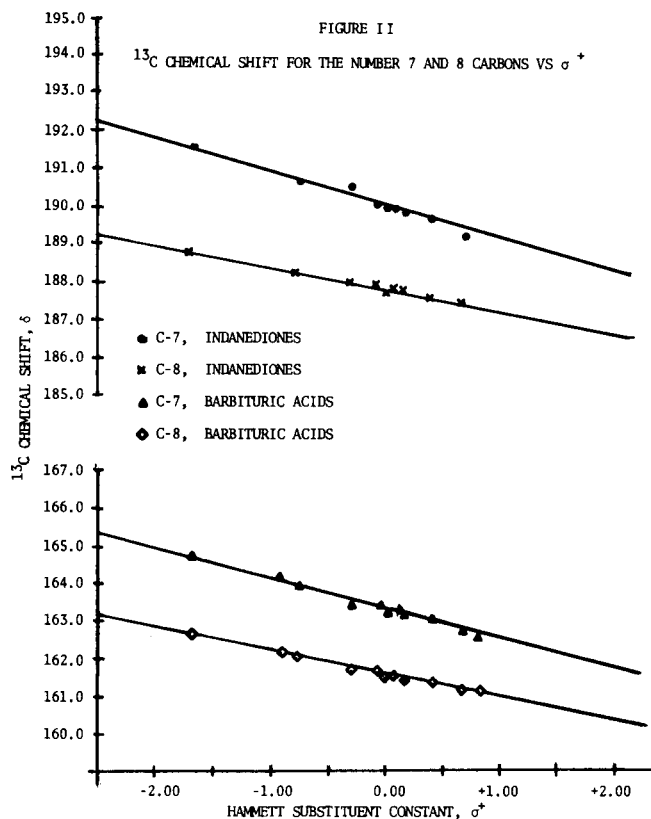
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however, the excellent correlations observed for the chemical shifts of the number 7 and 8 carbonyl groups ($r = -0.994$ and -0.991 , respectively) in the barbituric acid moiety were unexpected. These are especially good correlations in view of the low slopes of the lines indicating that the carbonyl carbons are not very susceptible to



substituent effects. It should also be noted that the substituent effect is completely attenuated before reaching the number 9 carbonyl carbon.

It had previously been observed (unpublished results) that ketonic groups attached to the β -carbon of the styrene moiety do not always give good correlations with σ^+ (for example, the arylidene derivatives of acetone, 1-indanone, and α -tetralone give poor correlations); however, in the case of the 2-arylidene-1,3-indanediones the correlations at these two positions (number 7 and 8 in our numbering system) are again quite good ($r = -0.990$ and -0.985 , respectively; see Tables II and III and Figure II). While it has yet to be shown that there is a structural requirement for obtaining good correlations with carbonyl compounds (*i.e.*, only cyclic dicarbonyls), these two series are presented together in order to point up the possibility of a connection between the similarities in their structures and the excellent correlations obtained.



The correlation at the number 6 carbon of the indanediones has a correlation coefficient of 0.996 (see Figure I) which is in line with the excellent coefficients normally observed at this position. It might also be observed that the number 4 carbons of the barbituric acid derivatives and the indanediones give correlation coefficients of 0.960 and 0.977, respectively, which are better than is usually observed for this position in styrene derivatives.

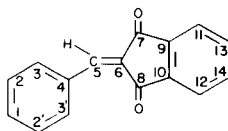
EXPERIMENTAL

A Varian CFT-20 spectrometer was used for determining ^{13}C nmr spectra. The indanediones were run as saturated solutions in deuteriochloroform; the barbituric acids were too insoluble in deuteriochloroform and were run as saturated solutions in $\text{DMSO-}d_6$. TMS was added as an internal standard in both cases and chemical shifts are reported as ppm downfield from TMS.

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Table II
Carbon-13 Shieldings of 2-Arylidene-1,3-indanediones (a)



	<i>p</i> -NMe ₂	<i>p</i> -OMe	<i>p</i> -Me	<i>p</i> -F	H	<i>p</i> -Cl	<i>p</i> -Br	<i>m</i> -Cl	<i>p</i> -CN
C-1	153.9	164.0	144.6	165.6 (b)	(c)	139.5	128.3	132.8	115.5
C-2	111.4	114.4	129.6	116.1 (d)	128.7	129.1	132.1	134.6	132.3
C-2'	—	—	—	—	—	—	—	129.9	—
C-3	138.0	137.2	134.5	136.9 (e)	133.1	135.3	135.4	133.3	133.7
C-3'	—	—	—	—	—	—	—	132.1	—
C-4	122.1	126.6	130.7	129.7 (f)	134.1	131.6	131.9	134.8	136.8
C-5	147.4	146.7	147.1	145.4	146.7	145.0	145.7	144.8	143.3
C-6	123.0	126.5	128.3	128.7 (g)	129.1	129.5	129.7	130.3	131.9
C-7	191.6	190.7 (h)	190.5	190.1	190.0	189.8	189.8	189.6	189.2
C-8	189.9	189.4 (i)	189.1	189.1	188.8	188.9	188.9	188.7	188.5
C-9	142.3	142.4	142.5	142.5	142.4	142.5	142.5	142.6	142.7
&/or									
C-10	139.9	140.0	140.1	140.1	140.0	140.1	140.1	140.1	140.3
C-11	122.4	123.0	123.3	123.4	123.2	123.4	123.4	123.5	123.7
&/or									
C-12	122.4	123.0	123.3	123.4	123.2	123.4	123.4	123.5	123.7
C-13	134.3	135.0	135.2	135.9	135.3	135.5	135.4	135.6	135.9
&/or									
C-14	134.0	134.8	135.0	135.9	135.1	135.3	135.4	135.4	135.8
R	40.0	55.6	22.0	—	—	—	—	—	118.2

(a) In ppm, downfield from TMS; solvent deuteriochloroform. (b) $J_{F,C_1} = 257.6$ Hz. (c) Peak unobserved. (d) $J_{F,C_2} = 21.6$ Hz. (e) $J_{F,C_3} = 9.4$ Hz. (f) $J_{F,C_4} = 3.1$ Hz. (g) $J_{F,C_6} = 2.0$ Hz. (h) $J_{cis-HC=C-C_7} = 3.7$ Hz. (i) $J_{trans-HC=C-C_8} = 13.0$ Hz.

Table III
Correlation Coefficients, Slopes, and Intercepts of ¹³C Shifts vs σ^+ Data

	C-4	C-6	C-7	C-8
Barbituric Acids	$r = 0.960$ $m = 7.51$ $y = 131.4$ $n = 11$ pts	$r = 0.994$ $m = 5.01$ $y = 118.8$ $n = 11$ pts	$r = -0.994$ $m = -0.840$ $y = 163.3$ $n = 11$ pts	$r = -0.991$ $m = -0.628$ $y = 161.5$ $n = 11$ pts
Indanediones	$r = 0.977$ $m = 5.99$ $y = 131.7$ $n = 9$ pts	$r = 0.996$ $m = 3.60$ $y = 129.2$ $n = 9$ pts	$r = -0.990$ $m = -0.995$ $y = 190.0$ $n = 9$ pts	$r = -0.985$ $m = -0.581$ $y = 188.9$ $n = 9$ pts

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