

¹³C-NMR STUDY OF SUBSTITUTED QUINONE METHIDES.
2- AND 2,6-SUBSTITUTED FUCHSONES*

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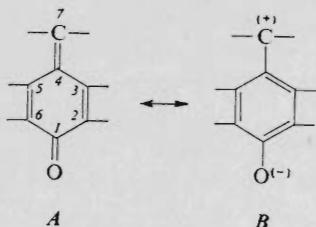
Carbon-13 chemical shifts and ¹J(CH) coupling constants for 11 fuchsones of the types I and II in deuteriochloroform are reported. The assignments are based on an analysis of proton coupled and proton decoupled spectra and on the analogy to chemical shifts of some structurally related compounds. Satisfactory Swain-Lupton *F* and *R* correlations which were found for most of ¹³C chemical shifts afforded values for percent resonance contributions to transmission of substituent effects as follows, C₍₁₎, 19%; C₍₃₎, 71%; C₍₇₎, 43%. Some alternative correlations for other similar systems *e.g.* quinones and tropones are also given.

p-Quinone methide derivatives constitute a class of unsaturated cyclic cross-conjugated carbonyl compounds, several of which occur in nature as fungal metabolites and wood pigments^{1,2}. Others are proposed as intermediates in many chemical³⁻⁵ and biochemical⁶ reactions. In recent years, much attention has been paid to this type of compounds^{7,8}. More than one hundred of substituted quinone methides are now known and many of them are designed for use in the industry of dyes (*e.g.* Mordant Blue, C.I. 43825), medicine⁹, as well as antioxidants in the polymer industry¹⁰.

Structurally, the *p*-quinone methide moiety is characterized by a high degree of conjugation, which has been mostly described by the canonical structures *A*–*B*. Evidence for the reality of this kind of electron delocalization seems to be given by several facts. For example, the ground state dipole moment studies^{11,12} suggest a contribution of approximately 10–20% of the dipolar mesomeric structure *B* which is increased up to 40% for strongly polar 2,6-ditert-butyl-7,7-bis(dimethylamino)quinone methide ($\mu = 25.99 \cdot 10^{-30}$ Cm) (ref.¹³). Moreover, all other available data, including the carbonyl frequencies^{14,15}, carbonyl stretching intensities¹⁶, electronic spectra¹⁷ and results of quantum chemical calculations^{7,18-20} also

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confirm a strong conjugation within the quinone methide system. It appears that the electron-donating ability of the substituents adjacent to the $C_{(2)}$, $C_{(6)}$ and $C_{(7)}$ carbons and the release of the steric compression which may exist between substituents and nonbonding electrons of the carbonyl group in 2,6-substituted derivatives constitute



the two major factors responsible for a significant weight of the form *B*.

Since ^{13}C chemical shifts are known to depend on charge distribution and steric effects, they could be reasonably expected to yield further information on both of these factors. However, very few reports are available on NMR spectra of quinone methides including several ^1H -NMR studies²¹⁻²⁵ mostly directed²²⁻²⁴ to rotation barriers around the exocyclic double bond, and ^{13}C chemical shift assignment for 2,6-ditert-butyl-4-[(dimethylamino)(methylthio)methylene]-2,5-cyclohexadien-1-one and 3-methoxy-4[bis(methylthio)methylene]-2,5-cyclohexadien-1-one²³. Up to now no information seems to be available concerning ^{13}C -NMR spectra of quinone methides of the fuchsone type.

Our attention in the present investigation has been focused on the ^{13}C -NMR spectra of compounds represented by structures *I* and *II*. The choice of the quinone methides used was influenced by the low stability of the simplest derivatives. Introduction of two phenyl groups on the $C_{(7)}$ carbon atom brings a considerable decrease in the reactivity of quinone methide system and makes the isolation of these compounds possible.

The purpose of this paper is *a*) to report assignments of ^{13}C chemical shifts of the compounds examined and define the scope and limitation of ^{13}C -NMR spectroscopy as a characterization technique in this area, *b*) to seek the possible relation between the polar character of substituents and the extent of conjugation as measured by the ^{13}C chemical shifts of the $C_{(1)}$ to $C_{(7)}$ atoms, and *c*) to compare the substituent effect in the quinone methides with respect to other structurally related compounds such as quinones and tropones.

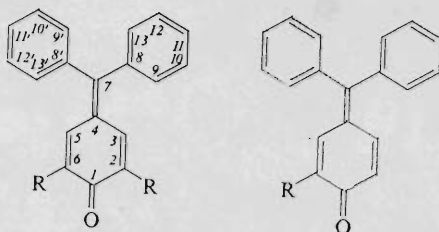
EXPERIMENTAL

The fuchsones *I* and *II* were prepared by the known methods^{8,12,16} and their physicochemical constants agreed with those reported in the literature. The ^{13}C -NMR spectra were obtained on a JNM-FX 100 (JEOL) spectrometer operating at 25.047 MHz in the Fourier transform mode.

Spectra were measured in a 10 mm o.d. NMR tubes as approximately 0.4 mol solutions in CDCl_3 at 25°C and the solvent provided the internal deuterium lock. Typical settings for the FT parameters were: spectral width 5 000 Hz (for compounds *II* 2 000 Hz additionally); pulse width $7\ \mu\text{s}$ (flip angle *c.* 30°); 8 K data points and pulse repetition time 3 s. The ^{13}C chemical shifts were determined under proton-noise decoupled conditions and reported relative to internal tetramethylsilane. The $^1J(\text{CH})$ coupling constants were measured with the gated decoupling technique using digital resolution 0.244 Hz/point. Standard measurements errors were ± 0.05 ppm for the chemical shifts and ± 0.5 Hz for the $^1J(\text{CH})$ coupling constants. The linear free energy statistical treatment of the data was carried out using the program for multiple regression analysis (Hewlett-Packard Standard Statistic Pac No 2) on a Hewlett-Packard 9830A Calculator.

RESULTS AND DISCUSSION

The ^{13}C -NMR chemical shifts and carbon-hydrogen coupling constants, $^1J(\text{CH})$, for fuchsones *I* and *II* are listed in Tables I and II. The assignment of the carbonyl carbon $\text{C}_{(1)}$ was unambiguous in all cases since it appears as a single band at the lowest field. Assignment of carbons $\text{C}_{(2)}$ and $\text{C}_{(6)}$ was made possible by comparison



Ia; R = H

Ib; R = CH_3

Ic; R = C_2H_5

Id; R = $i\text{-C}_3\text{H}_7$

Ie; R = $t\text{-C}_4\text{H}_9$

If; R = OCH_3

Ig; R = Br

IIa; R = CH_3

IIb; R = $i\text{-C}_3\text{H}_7$

IIc; R = Br

IId; R = OCH_3

of chemical shifts of *Ib*–*Ig* with those of *Ia*, considering multiplicity of signals in the coupled spectra. Carbons $\text{C}_{(3)}$ and $\text{C}_{(5)}$ display doublets of doublets (one-bond and three-bond coupling) which are in some cases more complex due to the long-range coupling with alkyl groups. Unfortunately it was impossible to make full use of substituent chemical shift²⁶ (SCS) additivity because of uneven transmission of substituent effects from $\text{C}_{(2)}$ into the positions $\text{C}_{(1)}$ and $\text{C}_{(3)}$ (the similar substituent effect was observed with substituted 1,4-benzoquinones)²⁷. The resonance of carbon $\text{C}_{(4)}$ in coupled spectrum of *Ia* appears as a broadened triplet $^3J(\text{C}_4, \text{H}_2) = ^3J(\text{C}_4, \text{H}_6) \approx 9$ Hz, in compounds *Ib*–*Ig* as a unresolved broad signal (two-bond and four-bond coupling). This assignment is supported by coupled spectra of *IIa*–*IId*, where $\text{C}_{(4)}$ appeared as a broadened doublet. Carbons $\text{C}_{(8)}$ to $\text{C}_{(11)}$ of the geminal phenyl

TABLE I
 ^{13}C Chemical shift values and $^1J(\text{CH})$ coupling constants for 2,6-disubstituted fuchsones

Compound	$C_{(1)}$	$C_{(2,6)}$	$C_{(3,5)}$	$C_{(4)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(11)}$	Other
<i>Ia</i>	186.8	128.4 (160.9) ^a	139.3 (159.9)	129.3	160.1	139.7	131.9 (161.9)	128.0 (161.6)	129.9 (161.4)	—
<i>Ib</i>	186.8	135.5	135.3 (158.7)	129.6	156.4	140.4	131.8 (161.8)	127.9 (161.1)	129.1 (161.1)	16.6 (CH ₃) (128.2)
<i>Ic</i>	186.0	141.1	133.7 (158.7)	129.9	156.4	140.6	131.9 (161.1)	127.9 (161.1)	129.2 (161.1)	23.1 (CH ₂) (129.6) 12.9 (CH ₃) (126.2)
<i>Id</i>	184.9	145.5	131.7 (158.0)	130.0	156.5	140.7	132.1 (161.4)	128.0 (161.0)	129.3 (161.0)	26.8 (CH) (130.4) ^b 22.0 (CH ₃) (126.2)
<i>Ie</i>	185.1	147.5	131.9 (159.0) ^b	129.7	155.9	140.8	131.9 (161.1) ^b	128.0 (161.1)	129.1 (161.1)	35.3 (C _q) (125.7)
<i>If</i>	174.6	152.2	109.9 (159.6)	127.8	154.2	140.7	131.6 (161.0)	127.9 (161.1)	129.0 (161.4)	55.2 (OCH ₃) (144.5)
<i>Ig</i>	172.6	124.1	140.5 (167.2)	129.5	163.6	139.4	132.4 (162.8)	128.6 (162.4)	131.1 (161.9)	—

^a Coupling constants in parentheses; ^b ±1 Hz.

TABLE II
Experimental and calculated ^{13}C shifts for fuchsones II

Compound	$\text{C}_{(1)}$	$\text{C}_{(2)}$	$\text{C}_{(3)}$	$\text{C}_{(4)}$	$\text{C}_{(5)}$	$\text{C}_{(6)}$	$\text{C}_{(7)}$	$\text{C}_{(8)}$ or $\text{C}_{(8')}$	$\text{C}_{(9)}$ or $\text{C}_{(9')}$	$\text{C}_{(10)}$ or $\text{C}_{(10')}$	$\text{C}_{(11)}$ or $\text{C}_{(11')}$	
<i>IId^a</i>	exp.	186.9	136.1	138.8	129.6	135.9	128.0	140.1	—	131.9; 131.8	128.1; 128.0	129.6
	calc.	186.8	135.4	139.3	129.5	136.3	128.5	—	—	—	—	—
<i>IIf^b</i>	exp.	186.9	145.4	137.9	129.7	132.5	128.5	140.1; 140.0	131.8; 131.7	127.9; 127.9	129.6; 129.4	
	calc.	185.9	145.2	138.3	129.7	132.6	128.7	—	—	—	—	
<i>IIf^c</i>	exp.	179.0	125.9	140.5	129.4	139.0	127.1	139.3	—	128.2; 128.1	130.5; 130.4	
	calc.	179.7	124.1	132.2	129.4	147.6	128.4	—	—	—	—	
<i>IId^c</i>	exp.	180.1	152.5	110.2	129.4	138.0	127.3	139.9; 139.8	131.6; 131.3	127.8; 127.6	129.3; 129.2	
	calc.	180.7	151.4	133.2	128.6	115.9	127.6	—	—	—	—	

^a $\delta(\text{CH}_3) = 16.4$; ^b $\delta(\text{CH}) = 26.4$, $\delta(\text{CH}_3) = 21.5$; ^c $\delta(\text{OCH}_3) = 46.1$.

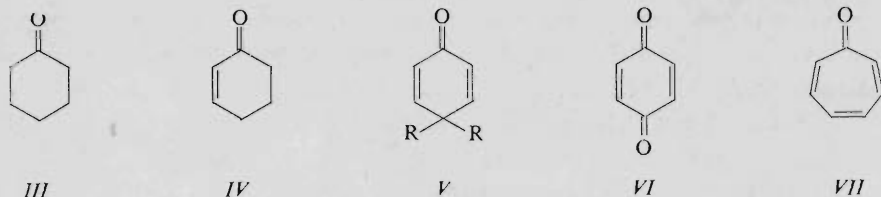
groups exhibit signal patterns similar to monosubstituted benzene (relative signal intensity 1 : 2 : 2 : 1, characteristic number and value of $^1J(\text{CH})$ and $^3J(\text{CH})$ couplings) in coupled as well as decoupled spectra. In comparison with equivalent carbons of benzophenone²⁸ the resonances of $\text{C}_{(8)}$ and $\text{C}_{(9)}$ were shifted to lower field and that of $\text{C}_{(11)}$ to higher field.

The assignment of various carbon signals of monosubstituted fuchsones *II* required a combination of two different arguments: (i) ^1H selective decoupling experiments and (ii) analysis of substituent effects by comparing the mono (*II*) and disubstituted (*I*) derivatives. Selective proton decoupling experiments provided evidence for the unambiguous assignment of the $\text{C}_{(3)}$ and $\text{C}_{(6)}$ carbon signals of the methoxy- and bromo-fuchsones *Iic* and *Iid* (*Iic* (2-Br) = $\delta(\text{C}_3\text{H}) = 7.80$, doublet, $J = 2.4$ Hz, $\delta(\text{C}_6\text{H}) = 6.58$, doublet, $J = 10.0$ Hz; *Iid* (2-OCH₃) = $\delta(\text{C}_3\text{H}) = 6.61$, doublet, $J = 2.2$ Hz, $\delta(\text{C}_6\text{H}) = 6.50$, doublet, $J = 9.80$ Hz). On the other hand, this technique cannot be used for alkyl derivatives *Iia* and *Iib*, because the splitting of carbon signals of the 2,5-cyclohexadien-1-one moiety in their ^1H coupled spectra is rather complex²⁹⁻³¹. Moreover, the olefinic and aromatic phenyl carbon signals in some cases partly coincide. The examination of the data shown in Table II reveals that the empirical correlations based on SCS values have proven to be useful for these compounds. Related calculations for *Iic* and *Iid* agreed only with experimental chemical shift values of $\text{C}_{(1)}$, $\text{C}_{(2)}$, $\text{C}_{(4)}$, $\text{C}_{(6)}$ and $\text{C}_{(7)}$ carbons. On the contrary, large differences between the calculated and experimental shifts for $\text{C}_{(3)}$ and $\text{C}_{(5)}$ are observed. It is obvious, that an unambiguous chemical shift assignment for all quinonoid ring carbons from SCS values alone is impossible.

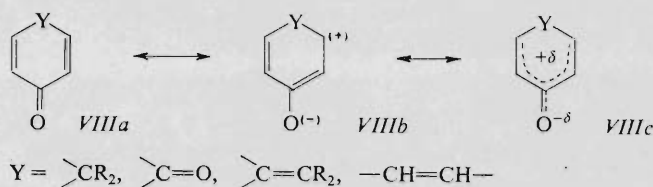
Let us now compare the carbonyl carbon chemical shift of parent fuchsones *Ia* with those of some other cyclic systems. As a first approximation we assume that the substitution of the quinone methide moiety by two phenyl groups on the $\text{C}_{(7)}$ carbon represents only a small perturbation* at the other side of the conjugated system (*i.e.* in the vicinity of the carbonyl group); thus the $\text{C}_{(1)}$ chemical shifts of fuchsones *Ia* and structures such as *III-VII* may be compared (Table III). It appears that upfield shifts for the carbonyl carbon resonances as large as 14 ppm are obtained as a result of conjugation of the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ π -electrons, and that cross-conjugation is approximately twice more effective in depolarizing the carbonyl double bond. Conversely, the carbonyl carbon resonances of different cyclic cross-conjugated systems (*Ia, V-VII*) remain quite unaffected by the character of unsaturation of the rest of the system ($\Delta\delta = 2.7$ ppm at most).

It is tempting to seek an explanation of this phenomenon in terms of almost total absence of structure such as *VIIIc* in a general system *VIII*, because the weight of the charge separated form would have to be considerably different for tropones

* A similar assumption was recently used in discussion of the ^{13}C -NMR spectra of substituted fulvenes³².



and quinones, respectively. Such explanation seems to be consistent with both the current opinion regarding nonaromaticity of 4-pyrone and tropone³⁷ and a small but distinct interaction occurring between the butadiene and CO₂ portions of the 2-pyrone system (based upon long range H,H couplings)³⁸.



On closer examination this model must be regarded as unlikely for two reasons. Firstly, it appears unreasonable from IR results to assume the same polarization of C=O bond in all cross-conjugated systems because of the large differences in carbonyl stretching frequencies $\tilde{\nu}(C=O)$ on going from *p*-benzoquinone (1 671, 1 657 cm⁻¹) (ref.³⁹) to fuchsones *Ia* (1 627 cm⁻¹ (ref.¹⁶) and tropone (1 590 cm⁻¹, ref.⁴⁰). Secondly, the equilibrium geometries calculated by MINDO/3 after complete optimization of geometry²⁰ also indicate an important lengthening of the C=O bond in tropone 0.1220 nm as compared with the unsubstituted quinone methide (0.1209 nm).

Two tentative explanations of the data are presented below; the experimental data does not permit a choice between them in absence of more detailed information from electronic and ¹⁷O-NMR spectra. In the first model the slight variation of $\delta(C=O)$ is explained by the fact that in the canonical formulae *VIIIa*–*VIIIc* the carbonyl carbon does not change its *sp*² character. The paramagnetic contributions σ_p to the screening constants of *VIIIa*–*VIIIc* are then nearly equal and the electron density released to C₍₁₎ by the conjugated system is almost completely removed to the oxygen end of the C=O dipole. Another explanation could arise from the inverse dependence of the paramagnetic term on the charge density Q_{AB} and the energy of excitation ΔE (Eq. (1)). As a consequence, the observed insensitivity of

$$\sigma_p = C \cdot \Delta E^{-1}(r^{-3})_{2p} \sum Q_{AB} \quad (1)$$

¹³(C=O) shifts to some kind of structural changes may be caused by a fortuitous cancellation of two roughly equal effects.

In view of the foregoing arguments, our further discussion will deal in part with an analysis of *ortho*-substituent effects on the carbonyl carbon chemical shifts in systems *I*, *II*, *IV*, *VI* and *VII*.

For fuchsones *I* and *II* the carbonyl carbon signals appear over the range 186.8 to 172.6 ppm. A comparison of the values for substituted fuchsones relative to fuchsones *Ia* itself shows that the symmetrical 2,6-disubstitution by alkyl groups (CH_3 , C_2H_5 , $i\text{-C}_3\text{H}_7$ and $t\text{-C}_4\text{H}_9$) affects the $\text{C}_{(1)}$ chemical shift only slightly. However, this effect seems not to be linearly dependent on the magnitude of inductive substituent constants, but shows a maximum for the isopropyl group. Marked down field shifts of the carbonyl absorption are found for *If* and *Ig* derivatives.

TABLE III

The ^{13}C carbonyl chemical shifts of some unsaturated systems

Compound	$\delta(\text{C}=\text{O})$ ppm	References
<i>III</i>	211.6	33
<i>IV</i>	199.2	33, 34
<i>V</i>	185.0 ± 1.1	33, 34
<i>VI</i>	187.0	27, 29
<i>Ia</i>	186.8	this work
<i>VII</i>	187.7	35, 36

TABLE IV

Substituent chemical shifts for 2-substituted fuchsones

Substituent ^a	$\text{C}_{(1)}$	$\text{C}_{(2)}$	$\text{C}_{(3)}$	$\text{C}_{(4)}$	$\text{C}_{(5)}$	$\text{C}_{(6)}$	$\text{C}_{(7)}$
CH_3	0.1	7.7 (9.3) ^b	-0.5 (0.8)	0.2 (0.0)	-3.4 (-2.9)	-0.4	-1.4
$i\text{-C}_3\text{H}_7$	0.1	17.0 (20.2)	-1.3 (-2.5)	0.3 (0.1)	-6.7 (-2.4)	0.1	-1.6
Br	-7.8	-2.5 (-5.5)	1.2 (3.4)	0.0 (1.7)	-0.3 (-1.6)	-1.3	-2.3
OCH_3	-6.7	24.1 (31.4)	-29.0 (-14.4)	0.1 (1.0)	-1.2 (-7.7)	-1.1	-2.9

^a Substituent effects are relative to fuchsones *Ia*; positive values indicate a downfield shift; ^b the values given in parentheses are the known SCS of monosubstituted benzenes²⁶.

Some substituent parameters were derived from the data in Table II using the fuchsones *Ia* carbon chemical shifts as reference (Table IV). It is instructive to compare these effects with those known for the same substituents on benzene; for this purpose the C—X, C-*o*, C-*m* and C-*p* values are also listed in Table IV. It may be observed, that significant differences exist in the substituent parameters of the fuchsones compared to analogously substituted benzenes, notably for methoxy and bromo substituents.

Attempts to derive linear correlations of the ^{13}C shift data (given in Table I) for each quinone methide ring carbon with a broad variety of Hammett-like electronic substituent constants produce successful results only for $\text{C}_{(7)}$ carbon ($r = 0.991$ for σ_p set). In order to study directly the competition between polar and resonance contributions to total substituent effect, the shifts were analyzed against Swain-Lupton *F* and *R* values using the two-parameter equation (2). Table V contains the results of the correlations for all quinonoid ring carbons, including data for $^{13}\text{C}(\text{C}=\text{O})$ shifts

$$\delta(\text{C}_i) = A \cdot F + B \cdot R + C \quad (2)$$

from series of 2,6-substituted quinones, 2,7-substituted tropones and 2-substituted 2-cyclohexenones. According to the multiple correlation coefficient the fit is satisfactory in all but two cases ($\text{C}_{(2)}$ and $\text{C}_{(4)}$ carbons, respectively). For the $\text{C}_{(4)}$ carbon the chemical shifts differ by at the most 2.19 ppm and no satisfactory relationship can be obtained between this shift and any type of substituent constants. This result was anticipated since also in the benzene ring the variation of charge densities induced by substituents in the *meta* positions are about ten times lower than those induced by the *ortho* substituents³⁴. In consequence other contributions to the shift such as anisotropic or solvent effects, or even experimental errors, become relatively important, and prevent the achievement of satisfactory correlations. The chemical shift variation of the carbon directly bonded to the substituent ($\text{C}_{(2)}$) must be theoretically dominated by the inductive effect of the substituent. However, no satisfactory linear correlation can be established between these two quantities. On the other hand, some linear relationships between shifts of the carbon adjacent to the substituent have already been given in the literature: C_{ipso} chemical shifts of substituted methanes *versus* those of substituted ethylenes⁴¹, C_{ipso} chemical shifts of monosubstituted benzenes *versus* those of monosubstituted ethylenes, butadienes and α -enones^{42,43}. The slopes near to unity in equations (3)–(6) (where the $\Delta\delta\text{C}_{\text{ipso}}^{\text{B}}$ denotes the SCS increments from the benzene series²⁶) indicate, that as a first approximation, such relationships may be extended to some other systems, such as quinones, tropones and fuchsones.

$$\Delta\delta\text{C}_{\text{ipso}} = 0.94\Delta\delta\text{C}_{\text{ipso}}^{\text{B}} - 7.13 \quad (\text{enones}, \quad n = 4, \quad r = 0.947) \quad (3)$$

$$\Delta\delta C_{\text{ipso}} = 0.62\Delta\delta C_{\text{ipso}}^{\text{B}} + 4.26 \text{ (quinones, } n = 4, r = 0.978) \quad (4)$$

$$\Delta\delta C_{\text{ipso}} = 0.73\Delta\delta C_{\text{ipso}}^{\text{B}} + 1.62 \text{ (tropones, } n = 4, r = 0.999) \quad (5)$$

$$\Delta\delta C_{\text{ipso}} = 0.76\Delta\delta C_{\text{ipso}}^{\text{B}} + 0.91 \text{ (fuchsones, } n = 4, r = 0.982) \quad (6)$$

These results confirm the suggestion of the authors^{4,2} that the shifts of carbons directly bonded to the substituent essentially depend only on the variation of the σ electron density q^σ , and are independent of the number of π -bonds in the structure under study.

In all other cases ($C_{(1)}$, $C_{(3)}$, $C_{(7)}$ carbons) the good quality of the results of the multiple correlations permit evaluation of the direction and magnitude of the influence of field and resonance characteristics of substituents on the ^{13}C chemical

TABLE V

Statistics of Eq. (2) for 2,6-substituted fuchsones, 2,6-substituted quinones, 2,7-substituted tropones and 2-substituted 2-enones

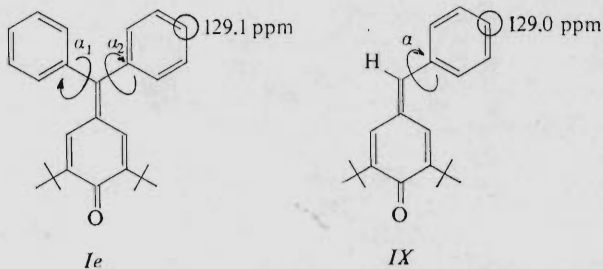
Compound series	Parameter correlated	A ^a	B ^a	C ^a	R ^b	n ^c	% Resonance
Fuchsones	$\delta C_{(1)}$	-13.26 (1.04)	4.58 (1.25)	185.98	0.988	11	18.9
	$\delta C_{(2)}$	-42.45 (13.34)	-61.49 (16.20)	132.85	0.895	7	—
	$\delta C_{(3)}$	19.18	71.35 (9.54)	143.04 (11.58)	0.954	7	71.5
	$\delta C_{(4)}$	-18.65 (0.38)	1.68 (0.45)	129.95	0.860	11	—
	$\delta C_{(7)}$	8.95 (0.54)	10.14 (0.65)	159.74	0.988	11	43.3
Quinones ^d	$\delta C_{(1)}$	-15.68 (1.09)	1.67 (0.60)	186.29	0.987	9	14.1
Tropones ^e	$\delta C_{(1)}$	-13.51 (1.30)	6.45 (0.93)	186.98	0.995	8	42.3
Enones ^f	$\delta C_{(1)}$	-18.69 (1.99)	1.15 (0.82)	198.59	0.984	6	13.9

^a Coefficients of the equation (2) with their standard deviations in parentheses; ^b multiple correlation coefficient; ^c number of data points; ^d data taken from refs^{26,29}; ^e data taken from refs^{35,36} (only substituents without any ability to form H-bondings considered); ^f data taken from refs^{29,30}.

shifts. The relative importance of field and resonance effects on the NMR parameters was examined using the Swain–Lupton expression⁴⁴, which takes into account both A and B and also the range in the *F* and *R* substituent constants employed in the multiple correlations.

Inspection of the results given in Table V shows that the transmission of the electronic influence of *ortho*-substituents to the carbonyl carbon is additive and heavily dominated not by the resonance but by the field effects in all series of considered compounds. It is further concluded that the resonance contributions to transmission of substituent effect on the $C_{(1)}$ carbons decrease in the order: tropones (42.3%) > fuchsones (18.9%) > quinones and 2-cyclohexenones (14.1 and 13.9%, respectively). Considering the Y group in VIII to be a perturbation inserted into the cyclic dienone ring, both the C=O and C=CR₂ groups seem to be almost equivalent insulators^{28,45} of resonance effects. Much greater dependence of $C_{(1)}$ chemical shift on substituent resonance effects is evident when data on tropone derivatives are considered. Additional information which may be derived from the data are as follows: a) in the fuchsones series the magnitude of resonance effect is much larger for $C_{(3)}$ and $C_{(7)}$ carbons than for $C_{(1)}$, but only in the case of $C_{(3)}$ carbon the resonance predominates; b) the slopes *A* (Eq. (1) for carbons $C_{(2)}$ and $C_{(4)}$) have opposite signs than those for $C_{(3)}$ and $C_{(7)}$ carbons.

Because of the sensitivity of ¹³C chemical shifts to the geometrical changes, ¹³C-NMR spectra seem to provide a convenient method for studying the ground state geometry in the vicinity of the exocyclic double bond, too. Especially, a twisting of the $C_{(7)}$ bonded phenyl groups from the molecular plane would be reflected by ¹³C chemical shifts of aromatic carbons⁴⁶. It is interesting to note in this connection that the aromatic $C_{(11)}$ carbon chemical shifts of both the fuchsones *Ia* and monophenyl derivative IX are almost identical (129.1 ± 0.05 and 129.0 ± 0.05 ppm, respectively). Thus, one may conclude that torsion angles α are also equal in both the systems considered. As the twisting angles α_1 and α_2 were found⁴⁷ to be 38° and 43° in a recent X-ray study of *Ib* we assume that the α angle in compound IX may not be zero. Further support for a nonplanarity of derivative IX comes from a molecular model. Hence it follows that the planarity of the system IX proposed²⁴ from ¹H-NMR spectra is not correct.



The following conclusions can be drawn from this study. First, additivity of the well known increments²⁶ for the carbon-13 NMR chemical shifts does not generally hold for quinone methide ring system. Second, the carbonyl carbon chemical shifts cannot be used as a diagnostic tool for substituted cyclohexadienones. Third, similar to the *p*-benzoquinone system the effect of C₍₂₎ bonded substituents on $\delta(\text{C}=\text{O})$ involves about 80% of inductive contribution; only in the case of C₍₃₎ quinone methide ring carbon the transmission of substituent effect is predominantly directed by resonance mechanism.

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