

$^{13}\text{C}$ -NMR STUDY OF 7,7-DISUBSTITUTED QUINONE METHIDES\*

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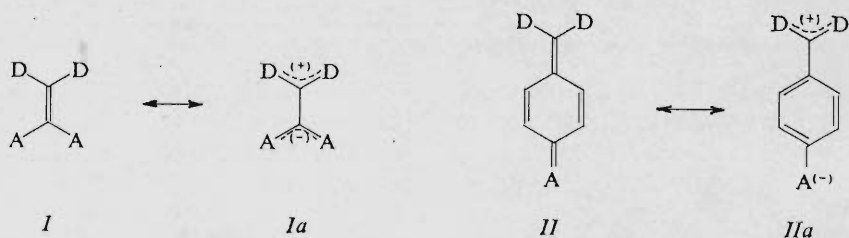
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Carbon-13 chemical shift assignments for nine 7,7-disubstituted 2,6-ditert-butylquinone methides of the types III–VI are reported. The  $^{13}\text{C}$  shifts of the exocyclic double bond carbon atoms are extraordinarily sensitive to  $\text{C}_{(7)}$  substitution, viz.  $\Delta\delta\text{C}_{(7)} = 82.4$  ppm and  $\Delta\delta\text{C}_{(4)} = 56.7$  ppm on going from the dimethylamino to the cyano substituent. In contrast, electronic properties of the substituents are only weakly expressed on the carbonyl carbon atom. Satisfactory Swain–Lupton correlations were found for  $\text{C}_{(1)}$ ,  $\text{C}_{(2)}$  and  $\text{C}_{(4)}$  chemical shifts yielding more than 50% of resonance contribution to the total transmission of substituent effects. Intercorrelations between the exocyclic double bond carbon chemical shifts of quinone methides and of identically substituted fulvenes as well as styrenes are also presented.

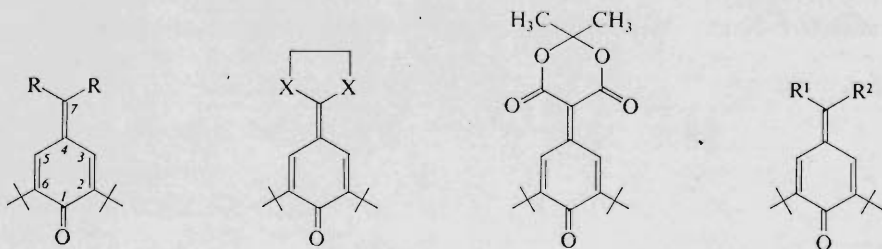
The interaction between electron-donating (D) and electron-withdrawing (A) groups across a conjugated system has been studied<sup>1–6</sup>. In contrast to the simple polarized ethylenes I, only little attention has been paid to cyclic conjugated systems II. Among the few known representatives of this class of conjugated compounds, quinone methides (II, A = O) seem to be the most important members. In these molecules the interaction occurring between the D and C=O groups results in creation of an aromatic phenolate system. Experimental evidence for this type of dipolar stabilization



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comes from dipole moment measurements<sup>7,8</sup> as well as from electronic<sup>9</sup> and infrared<sup>10</sup> spectra. The low barriers to rotation around the exocyclic double bond found for some 7-dimethylamino derivatives ( $\Delta G^\ddagger$  35–60 kJ mol<sup>-1</sup>)<sup>11,12</sup> also support the ease of polarization of these compounds. There remains the need to determine the degree of  $\pi$ -electron delocalization more quantitatively and explain it within the context of plausible D–A interaction mechanism. Carbon-13 magnetic resonance has proven to be especially relevant to the detailed study of such problems. However, values of the <sup>13</sup>C chemical shifts for only 2,6-ditert-butyl-4-(dimethylamino) (methylthio)methylene-2,5-cyclohexadien-1-one and 3-methoxy-4-bis(methylthio)methylene-2,5-cyclohexadien-1-one have been given<sup>12</sup>. To our knowledge no systematic <sup>13</sup>C-NMR study of 7,7-disubstituted derivatives has been reported.

We have previously studied<sup>13</sup> the <sup>13</sup>C-NMR spectra of 2,6-disubstituted fuchsones (7,7-diphenylquinone methides). In that work polarization of exomethylene double bond was demonstrated to be a function of the inductive and resonance effects of ring substituents in approximately equal manner. Moreover the strong electron deficit at C<sub>(7)</sub> was found. On the other hand, the C<sub>(4)</sub> chemical shifts exhibited a relatively narrow range (130.0–127.8 ppm) and were almost unaffected by electronegativities of substituents. The question of whether or not the  $\pi$ -electron delocalization in quinone methide system would be affected by C<sub>(7)</sub> bonded substituent in a related way remained to be solved. Accordingly we prepared series of 7,7-substituted quinone methides *III*–*VI* and measured their <sup>13</sup>C-NMR spectra. The C<sub>(7)</sub> substituents in given systems differ in both their electronic character and availability of the electrons which can conjugate. In this way, regarding the cross-conjugated hexatriene linkage to be a transmission moiety between the substituent and C=O group, electron delocalization not only in the “push-pull” but also in “pull-pull” polarized quinone methides may be discussed.



*IIIa*; R = CH<sub>3</sub>

*IIIb*; R = CN

*IIIc*; R = N(CH<sub>3</sub>)<sub>2</sub>

*III d*; R = C<sub>6</sub>H<sub>5</sub>

*III e*; R = Cl

*IVa*; X = S

*IVb*; X = SO<sub>2</sub>

*V*

*VIa*; R<sup>1</sup> = H, R<sup>2</sup> = C<sub>6</sub>H<sub>5</sub>

*VIb*; R<sup>1</sup> = N(CH<sub>3</sub>)<sub>2</sub>,  
R<sup>2</sup> = SCH<sub>3</sub>

## EXPERIMENTAL

The quinone methides *IIIa–IIIc*, *IV–VIa* were prepared by the known methods<sup>14</sup> and their physical constants agreed with those reported in the literature.

*2,6-Ditert-butyl-7,7-dichloroquinone methide (IIIe)*. Chloroform (2.4 g; 0.02 mol) in heptane (40 ml) was added over 30 min to a stirred, ice cooled mixture of triphenylphosphine (5.24 g; 0.02 mol) and potassium tert-butoxide (2.24 g; 0.02 mol) in heptane (50 ml). The suspension was concentrated to *c.* 50 ml *in vacuo* at 15–20°C. 2,6-Diter-butylbenzoquinone (4.40 g; 0.02 mol) in heptane (20 ml) was added, and the mixture was heated at 40–50°C for 30 min. After filtration the solvent was removed *in vacuo*, and the residue chromatographed on silica gel (250 g; ether–light petroleum 1 : 20–1 : 1) affording *IIIe* (65%), m.p. 91–93°C (ethanol). UV spectrum (CH<sub>2</sub>Cl<sub>2</sub>): 323 nm (log  $\epsilon$  = 4.14); IR spectrum (CCl<sub>4</sub>): 1 631.5 cm<sup>-1</sup> (C=O); Mass spectrum: 286 (M<sup>+</sup>). The physical constants are in agreement with those obtained for a photochemically prepared<sup>15</sup> sample.

The <sup>13</sup>C-NMR spectra were obtained at 25.047 MHz in 10 mm tubes using a JNM-FX 100 (JEOL) spectrometer. All spectra were recorded at 25°C for approximately 0.4 mol l<sup>-1</sup> solutions in deuteriochloroform using tetramethylsilane as internal standard. Field frequency lock was established on the deuterium resonance of the solvent. Typical FT parameters were: spectral width 5 000 Hz, pulse width 7  $\mu$ s (flip angle *c.* 30°); 8 K data points and pulse repetition time 3 s. The <sup>1</sup>J(CH) coupling constants were measured with the gated decoupling technique using digital resolution 0.244 Hz/point and the <sup>13</sup>C chemical shifts were determined under proton-noise decoupling conditions. Standard measurements errors were  $\pm$ 0.05 ppm for the chemical shifts and  $\pm$ 0.5 Hz for the <sup>1</sup>J(CH) coupling constants.

The linear free energy statistical treatment of the data was carried out using program for multiple regression (Hewlett–Packard Standard Statistics Pac No 2) on a Hewlett–Packard 9830 Calculator.

## RESULTS AND DISCUSSION

The <sup>13</sup>C-NMR chemical shifts and <sup>1</sup>J(CH) coupling constants for the compounds in this study together with the <sup>13</sup>C shifts of *VIb* taken from the literature<sup>12</sup> are listed in Table I. The assignment of the carbon signals were made using the following criteria: (i) analyses of the <sup>13</sup>C spectra without proton noise-decoupling; (ii) consideration of the molecular symmetry (all compounds except *VI* have the C<sub>2v</sub> symmetry); (iii) consideration of earlier reports<sup>12</sup> on <sup>13</sup>C-NMR spectra of *VIb*, differently substituted fuchsones<sup>13</sup> and fulvenes<sup>16,22</sup>.

It follows from Table I that the <sup>13</sup>C chemical shifts of the C<sub>(2)</sub>, C<sub>(4)</sub> and C<sub>(7)</sub> atoms are very sensitive to substitution. The most interesting information can be gained by the comparison of the C<sub>(7)</sub> and C<sub>(4)</sub> atoms chemical shifts among each other, since they are mostly influenced by the nature of the C<sub>(7)</sub> substituent. The C<sub>(7)</sub> shieldings span a range of about 80 ppm (170.6 ppm for *VIb* to 87.0 ppm for *IIIb*), while the C<sub>(4)</sub> atoms absorb over 55 ppm (154.7 ppm for *IIIb* to 98.0 ppm for *IIIc*). On the contrary, electronic properties of the substituents are only weakly expressed on the carbonyl carbon atom (compare the shifts of C<sub>(1)</sub> in *IIIa–IIIe*).

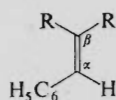
Before proceeding with any analysis of substituent effects on the  $^{13}\text{C}$  chemical shifts it is necessary to characterize the parent 2,6-ditert-butylquinone methide itself. Because of its low stability<sup>14</sup> we have not included the parent compound to our series *III–VI*, but we attempted to approximate  $C_{(7)}$  and  $C_{(4)}$  chemical shifts of parent compound from an examination of the data for systems such as *VII* and *VIII*, having geminal substituents related to our series. Although the electron system in the

TABLE I  
 $^{13}\text{C}$  Chemical shift values and  $^1J(\text{CH})$  coupling constants for quinone methides *III–VI*

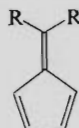
Compound <sup>a</sup>	$C_{(1)}$	$C_{(2,6)}$	$C_{(3,5)}$	$C_{(4)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	Other
<i>IIIa</i>	186.3	145.9	127.9 (154.5)	127.5	152.5	35.1	29.4 (126.0)	22.2 ( $\text{CH}_3$ ) (127.2)
<i>IIIb</i>	185.4	155.9	126.1 (164.2)	154.7	87.0	36.4	29.4 (126.7)	111.8 (CN)
<i>IIIc</i>	180.4	140.2	129.0 (151.4)	98.0	169.4	35.0	29.7 (125.7)	42.5 ( $\text{CH}_3$ ) (138.9)
<i>III d</i>	186.1	147.5	131.9 (159.0)	129.7	155.9	35.3	29.5 (125.7)	<sup>b</sup>
<i>III e</i>	186.1	148.7	126.7 (161.8)	129.7	132.8	35.5	29.4 (126.3)	—
<i>IVa</i>	185.5	144.4	128.3 (155.3)	121.0	163.1	35.0	29.3 (126.0)	38.4 ( $\text{CH}_2$ ) (146.0)
<i>IVb</i>	185.3	155.9	124.1 (165.3)	136.0	140.0	36.5	29.4 (127.0)	49.8 ( $\text{CH}_2$ ) (146.2)
<i>V</i>	186.6	154.7	128.1 (167.2)	149.2	118.1	36.2	29.5 (127.0)	160.5 (C=O) 104.3 ( $C_{\text{quart}}$ ) 27.3 ( $\text{CH}_3$ ) (129.4)
<i>VIa<sup>c</sup></i>	186.5	<sup>d</sup>	<sup>e</sup>	131.9	142.5	35.4 35.0	29.5	135.9 130.3 128.7 129.0 ( $\text{CH}$ ) <sub>ar</sub>
<i>VIb<sup>f</sup></i>	182.8	141.7	129.7	109.7	170.6	35.1	29.7	45.1 ( $\text{CH}_3\text{N}$ ) 19.0 ( $\text{CH}_3\text{S}$ )

<sup>a</sup> Coupling constants in parentheses; <sup>b</sup> see ref.<sup>13</sup>; <sup>c</sup> the  $C_{(2)}$ ,  $C_{(3)}$  and  $C_{(4)}$  were assigned by consideration of  $^{13}\text{C}$ -NMR spectra of 6-phenylfulvenes<sup>16</sup>; <sup>d</sup>  $\delta C_{(2)} = 149.3$  ppm,  $\delta C_{(6)} = 147.7$  ppm; <sup>e</sup>  $\delta C_{(3)} = 127.7$  ppm,  $\delta C_{(5)} = 135.1$  ppm; <sup>f</sup> taken from ref.<sup>12</sup>.

quinone methides is necessarily more complicated than in ethylenes because of multiple possibilities of cross and linear conjugation, the  $^{13}\text{C}$  chemical shifts of the  $\text{C}_{(4)}$  and  $\text{C}_{(7)}$  atoms closely follow chemical shifts of the corresponding carbons in the above mentioned models.



VII



VIII

This type of correspondence, although not exact, suggests that substituent effects derived for  $\beta,\beta$ -substituted styrenes<sup>4,18-21</sup> and 6,6-disubstituted fulvenes<sup>16,22</sup> should correctly predict the trends in the chemical shifts for 7,7-disubstituted quinone methides. We have therefore correlated the exocyclic double bond  $^{13}\text{C}$  shifts of the quinone methides under study (QM) with equivalent shifts of both model ethylenes (*E*) and fulvenes (*F*) according to Eqs (1) and (2)

$$\delta\text{C}_{(i)}^{\text{QM}} = A \cdot \delta\text{C}_{(i)}^{\text{E}} + C, \quad (1)$$

$$\delta\text{C}_{(i)}^{\text{QM}} = B \cdot \delta\text{C}_{(i)}^{\text{F}} + C', \quad (2)$$

TABLE II

Observed and predicted exocyclic double bond  $^{13}\text{C}$  chemical shifts of some quinone methides

Quinone Methide	$\delta\text{C}_{(7)}$			$\delta\text{C}_{(4)}$		
	obs.	calc. <sup>a</sup>	calc. <sup>b</sup>	obs.	calc. <sup>a</sup>	calc. <sup>b</sup>
<i>IIIa</i>	152.5	153.3	148.7	127.5	128.1	—
<i>IIIb</i>	87.0	87.2	84.6	154.7	154.7	152.8
<i>IIIc</i>	155.9	156.0	—	129.7	129.4	129.6
<i>IIIe</i>	132.8	—	132.2	129.7	—	—
<i>V</i>	118.1	—	124.8	149.2	—	151.2
<i>VIa</i>	142.5	142.0	—	131.9	131.5	—
Parent	—	125.6	122.6	—	138.3	135.8

<sup>a</sup> According to Eq. (2) in the forms  $\delta\text{C}_{(7)}^{\text{QM}} = 1.05 \delta\text{C}_{(6)}^{\text{F}} - 4.01$  ( $r = 0.999$ ),  $\delta\text{C}_{(4)}^{\text{QM}} = 1.04 \delta\text{C}_{(5)}^{\text{F}} - 20.92$  ( $r = 0.999$ ); <sup>b</sup> according to Eq. (1) in the forms  $\delta\text{C}_{(7)}^{\text{QM}} = 1.25 \delta\text{C}_{(\beta)}^{\text{E}} - 18.76$  ( $r = 0.985$ ),  $\delta\text{C}_{(4)}^{\text{QM}} = 0.73 \delta\text{C}_{(\alpha)}^{\text{E}} + 35.19$  ( $r = 0.989$ ).

where the  $C_{(i)}$  denotes the  $C_{(7)}$  and  $C_{(4)}$  atoms of quinone methides and equivalent carbons of the model systems *VII* and *VIII*.

Adopting the conventional confidence limit criterion ( $\alpha = 0.025$ ) it seems reasonable to conclude that the correlations according to Eqs (1) and (2) are statistically significant. As demonstrated by the data in Table II where the observed and calculated chemical shifts for some quinone methides are compared, the observed shifts are correctly predicted by Eq. (2). In some cases the magnitude of the predicted shifts matches the observed shifts within experimental error ( $\pm 0.1$  ppm). The average difference in magnitude of observed and calculated values is lower than 0.4 ppm. As shown at the bottom of Table II this permits a reasonably accurate prediction of shifts expected in the previously unobserved  $^{13}\text{C}$  spectrum of parent quinone methide.

In order to obtain more detailed information about the substituent effects on the  $^{13}\text{C}$  chemical shifts it is instructive to analyse the experimental data *via* the dual substituent parameter treatment shown in Eq. (3).

$$\delta C_{(i)} = AF + BR + C \quad (3)$$

All ten derivatives were used in the calculations, assuming the additivity of the substituent effects. As a first approximation the substituent constants of  $\text{SCH}_3$ ,  $\text{SO}_2\text{CH}_3$  and  $\text{COOCH}_3$  groups were used for the derivatives *IV* and *V*. The statistics of Eq. (3) is summarized in Table III. According to the correlation coefficient ( $R$ ) or the standard deviation of the least squares fit the correlations are satisfactory in all but two cases ( $C_{(3)}$  and  $C_{(7)}$  atoms). These atoms gave poor results as they may be subject to additional interactions.

Based on results of recently available CNDO calculations for monosubstituted ethylenes<sup>2,3</sup>, it is tempting to suggest that the observed shifts for directly bonded carbon atoms reflect the degree of inductive electron donation by substituents. But it is clear from Table I that inductive effects do not dominate since the  $C_{(7)}$  atoms are shielded in the cyano (*IIIb*) and oxo (*V*) derivatives relative to parent quinone methide and deshielded by all other substituents with the most pronounced down field shift found for dimethylamino derivatives *IIIc* and *VIb*. An explanation of this unexpected phenomenon may be that the electric field effect is linear only for compounds whose dipole-creating substituents are separated from the double bond by a large distance, since the contribution of high order electric field terms is then considered negligible in view of their strong decrease with distance<sup>17</sup>. The proximity of the two 7,7-substituents in the quinone methides prevents an assessment of the importance of the linear electric field effect for these substances. Additionally, the anisotropy and steric effects may be also of great importance. The details are not entirely clear and further investigations of these effects in related systems will doubtless prove of interest.



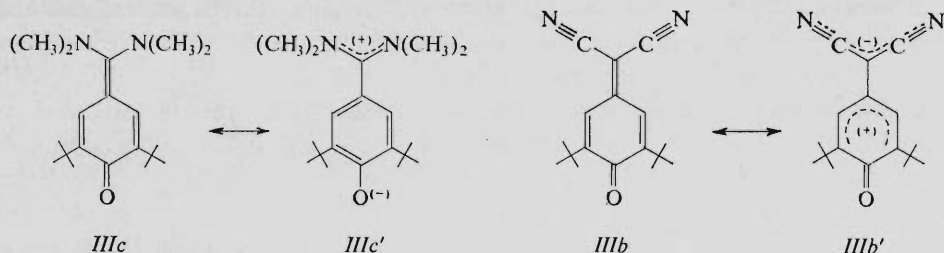
The behaviour of  $C_{(1)}$ ,  $C_{(2)}$  and  $C_{(4)}$  atoms is unexceptional. The percent resonance contribution to the substituent induced chemical shifts as defined<sup>23</sup> by Swain and Lupton (Table III) is of interest in that it shows that the  $C_{(1)}$ ,  $C_{(2)}$  and  $C_{(4)}$  shifts are directed predominantly by resonance interactions. Apart from the carbonyl carbon atom chemical shift (which is relatively little affected by  $C_{(7)}$  substitution), the alternating sign of the substituent shift (*vs*  $C_{(7)}$ ) is consistent with the  $\pi$ -bond polarization mechanism. The intercept value for  $C_{(4)}$  atom (Table III) provided an additional verification of prediction made for parent quinone methide (Table II). However, it is difficult to discuss the deviations from the straight-line dependence because of rather high uncertainty in the used substituent constants for *IV* and *V*.

From the data presented in this paper it can be concluded that the total polarization in the quinone methides depends on the electron-withdrawing effects of the carbonyl part of the molecule as well as on the electronic properties of the geminal substituents. Qualitatively, it may be assumed that  $C_{(7)}$  substituents can direct the redistribution of the  $\pi$ -electrons *via* resonance in either of two ways: (i) the substituents can donate the electrons to the electronegative carbonyl end such that the  $C_{(7)}$  atom assumes partial positive charge or (ii) the substituents can accept electrons from the ethylenic bonds with the effect that the  $C_{(7)}$  atom acquires enhanced electron density.

TABLE III  
Statistics of Eq. (3) for 7,7-disubstituted quinone methides *III*–*VI*

Parameter correlated	$A^a$	$B^a$	$C^a$	$R^{b,c}$	% Resonance
$\delta C_{(1)}$	– 2.02 (0.78)	3.05 (0.45)	186.94 (0.51)	0.933	68.3
$\delta C_{(2)}$	4.75 (1.82)	5.92 (1.05)	148.00 (1.20)	0.956	62.7
$\delta C_{(3)}$	– 3.24 (1.55)	– 0.50 (0.89)	129.30 (1.02)	0.732	–
$\delta C_{(4)}$	9.98 (4.82)	22.04 (2.50)	132.36 (3.77)	0.975 <sup>d</sup>	78.8
$\delta C_{(7)}$	–25.75 (17.16)	–18.63 (10.10)	149.77 (11.31)	0.792	–

<sup>a</sup> Coefficients of the equation (3) with their standard deviations in parentheses; <sup>b</sup> multiple correlation coefficient; <sup>c</sup>  $n = 10$ ; <sup>d</sup>  $n = 9$ , with exclusion of derivative *IVb*.



The dimethylamino and cyano methides may be regarded as typical examples. Whereas the two dimethylamino groups in *IIIc* serve to stabilize the positive charge on the C<sub>(7)</sub> atom (formally represented by canonical forms *IIIc* or *IIIc'*), the cyano groups in *IIIb* severely polarize the  $\pi$ -bond system in opposite direction and the importance of resonance hybrids such as *IIIb'* is increased. The observation that the C<sub>(7)</sub> chemical shift of *IIIb* is considerably upfield as compared to olefinic carbons<sup>20</sup> (*i.e.* is closer to the carbanion shift region) provides an evidence in support of this suggestion.

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