IR SPECTRA OF SOME QUINONE METHIDES.
A STUDY OF THE *ortho*-EFFECT*

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Experimental values of frequencies and integrated intensities of carbonyl stretching vibrations in sixteen 2- and 2,6-substituted fuchsones were correlated with electronic substituent constants σ and steric parameters ϑ. For disubstituted fuchsone derivatives the *ortho*-effect is additive and is adequately described by the relationship $\tilde{\nu}(C{=}O) = 35.6\,\Sigma\sigma_1 - 9.1\,\Sigma\vartheta + 1625.5$ ($r = 0.982$) and $A(C{=}O)^{1/2} = -33.2\,\Sigma\sigma_1 - 1281\,\Sigma\vartheta + 141.1$ ($r = 0.942$). Wavenumber und integrated intensity of the carbonyl band decrease with increasing van der Waals volume of substituents. Contribution of the steric effect to the total transmission is substantially higher (about 30%) for 2,6-disubstituted than for 2-monosubstituted fuchsones.

It is well known[1,2] that the unsubstituted quinone methide *I* is an unstable compound characterized so far only by UV spectrum of its dilute solution (10^{-5} mol . . dm^{-3}) in dichloromethane[3] ($\tilde{\nu}_{max} = 35460$ cm^{-1}) and by its basicity, measured by ion cyclotron resonance[4] (PA = 915 kJ mol^{-1}). In general, the cross-conjugated system of quinone methide *I* can be stabilized in various ways, such as by substitution with two phenyl groups[5] at the $C_{(7)}$ carbon, annelation of an aromatic ring[6] in positions 2,3 or 5,6, substitution with groups forming stable intramolecular hydrogen bonds with the carbonyl oxygen[7], or introduction of tert-butyl groups[8] to $C_{(2)}$ and $C_{(6)}$. Whereas in the first three cases reasons of stabilisation of the quinone methide skeleton are understandable, the origin of the effect of tert-butyl groups is not quite clear; usually it is ascribed[9,10] intuitively to a steric effect of the bulky tert-butyl group. However, the effect of substituents in positions 2 and 6 on the reactivity and physicochemical properties of quinone methides is more complex and an investigation of its nature requires separation of the steric and proximity electronic component.

General approach to a quantitative evaluation of the *ortho*-effect is based[11] on the multiparameter correlation (*1*)

$$P - P_0 = L\sigma_1 + D\sigma_R + S\vartheta, \tag{1}$$
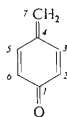
I

where P is the studied property in energy units, P_0 corresponds to the reference state, σ_1 and σ_R represent localized (field and/or inductive) and delocalized (resonance) effects of substituents bonded to the carbon atom. The parameter ϑ is a measure of steric effect and L, D, and S are susceptibility constants.

In order to investigate the *ortho*-effect in the fuchsone series in more detail, we analyzed IR spectra of sixteen compounds of this type. The substituents were chosen so that the scope of numerical values of steric and polar effects was in the given series as wide as possible; our set contains even substituents which are often omitted in order to improve the statistical significance of the correlation (*e.g.* H, tert-C_4H_9, NO_2). Using models of the type *II* and *III* we try to evaluate factors affecting decisively frequency and intensity of the carbonyl stretching vibration and particularly to study operation of steric effects of the groups R^1 and R^2.
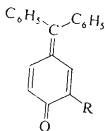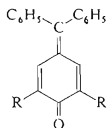
II	*III*
IIa; R = H	*IIIa*; $R^1 = R^2 = CH_3$
IIb; R = CH_3	*IIIb*; $R^1 = R^2 = C_2H_5$
IIc; R = C_2H_5	*IIIc*; $R^1 = R^2 = $ i-C_3H_7
IId; R = i-C_3H_7	*IIId*; $R^1 = R^2 = $ t-C_4H_9
IIe; R = t-C_4H_9	*IIIe*; $R^1 = CH_3$; $R^2 = $ t-C_4H_9
IIf; R = OCH_3	*IIIf*; $R^1 = R^2 = OCH_3$
IIg; R = Br	*IIIg*; $R^1 = R^2 = Br$
IIh; R = NO_2	
IIi; R = OH	

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Analytical samples were dried at room temperature and 13·3 Pa for 7 h. Mass spectra were measured on an AEI 902 mass spectrometer (70 eV, source temperature 110—230°C; accuracy of high resolution measurements 2 ppm).

The fuchsones *II* and *III* were prepared from the corresponding phenols and diphenyldichloro-methane by the described procedure[10,12]. The yields, physical constants and analyses of the new compounds are summarized in Table I.

The IR spectra were taken on a Perkin–Elmer 621 spectrophotometer; separation of absorption bands and calculation of the integrated intensities were performed using the recommended procedure[13] on a Hewlett–Packard 9839A calculator.

Results of the measurements were treated according to the multiple linear regression program (Hewlett–Packard Standard Statistic Pac No 2). Substituent constants used were taken from the reviews[14–17].

RESULTS AND DISCUSSION

Spectra of many carbonyl group containing compounds exhibit a complex absorption in the C=O stretching vibration region. The occurrence of a carbonyl multiplet can be ascribed to intermolecular associations, intramolecular effects or Fermi resonance between the carbonyl fundamental vibration and the first overtone or combination band near the carbonyl bands[18]. Also the spectra of quinone methides *II* and *III* display several absorption maxima of various intensity in the region $1600 - 1660$ cm^{-1}. Assigning the bands we assumed that absorption in this region

TABLE I

Yields and Properties of the New Quinone Methides

Compound	Yield[a], % m.p., °C	Formula[b] (mol.w.)	Calculated/Found	
			% C	% H
IIc	40 103—104	$C_{21}H_{18}O$ (286·4)	88·15 87·91	6·32 6·14
IId	32 122—123	$C_{22}H_{20}O$ (300·4)	88·06 88·31	6·72 7·52
IIe	25 127—129	$C_{23}H_{22}O$ (314·4)	87·91 88·36	7·14 7·54
IIh	45 163—165	$C_{19}H_{13}O_3N$ (303·3)	75·26 74·82	4·32 4·82
IIi	65 133—135	$C_{19}H_{14}O_2$ (274·3)	83·21 82·81	5·16 5·44
IIIe	27 150—152	$C_{24}H_{24}O$ (328·4)	87·85 87·62	7·43 7·19

[a] The yields were not optimized; [b] agrees with the mass spectral data.

is affected both by the Fermi resonance and the double bond stretching vibration. The $\tilde{v}(C=O)$ and $\tilde{v}(C=C)$ bands were separated by the usual method[19] based on different sensitivity of these bands towards change in solvent polarity. The fundamental carbonyl frequencies, not perturbed by Fermi resonance, were obtained[20] by weighing according to intensities and the thus-obtained values (Table II) were used in further considerations.

We tested first the simplest non-additive relationship between carbonyl characteristics and substituent constants according to the graphic procedure described by Exner[21]. Since the results of this test were negative, we evaluated the relative contributions of inductive, resonance and steric effects to the total effect of *ortho* substituents, using the additive form of the three-parameter equation (2), recommended by Charton[11].

$$P - P_0 = \varrho_I \sum \sigma_I + \varrho_R \sum \sigma_R + \varrho_S \vartheta \,. \tag{2}$$

Using the steric parameter $\vartheta (\vartheta = r_v^X - r_v^H$, where r_v is the van der Waals volume) we assume that r_v can be taken as a measure of the intramolecular steric effect.

TABLE II
Experimental and Calculated Wavenumbers, Normalized and Integrated Intensities of Bands in the $v(C=O)$ Region (in tetrachloromethane)

Compound	Fundamental transitions			Normalized transitions			$\tilde{v}(CO)^a$	$A^b \cdot 10^{-4}$
	1	2	3	A_1	A_2	A_3		
IIa	1 627	—	—	1·00	—	—	1 627	1·92
IIb	1 625	1 606	—	0·65	0·35	—	1 621	1·96
IIc	1 623	1 613	—	0·54	0·46	—	1 618	2·25
IId	1 621	1 611	—	0·47	0·32	—	1 616	2·22
IIe	1 620	1 610	1 594	0·64	0·23	0·13	1 614	1·97
IIf	1 640	1 631	1 608	0·25	0·68	0·07	1 632	1·75
IIg	1 635	1 626	—	0·54	0·46	—	1 631	1·77
IIh	1 653	—	—	1·00	—	—	1 653	1·16
IIi	1 620	1 625	—	0·89	0·11	—	1 621	1·98
IIIa	1 615	—	—	1·00	—	—	1 615	1·95
IIIb	1 608	1 601	—	0·81	0·48	—	1 607	1·58
IIIc	1 609	1 599	—	0·42	0·58	—	1 603	1·76
IIId	1 607	1 599	—	0·10	0·89	—	1 606	1·34
IIIe	1 612	1 598	—	0·73	0·27	—	1 608	1·55
IIIf	1 645	—	—	1·00	—	—	1 645	1·20
IIIg	1 652	1 646	1 637	0·02	0·76	0·21	1 644	0·96

^{a} Calculated according to the procedure[20]; ^{b} integrated intensities (l mol^{-1} cm^{-2}).

Statistical significance of the third term of equation (2) was tested by comparison of this equation with its two-parameter analogues (3) and (4).

$$P - P_0 = \varrho_I \sum \sigma_I + \varrho_R \sum \sigma_R , \qquad (3)$$

$$P - P_0 = \varrho_I \sum \sigma_I + \varrho_S \sum \vartheta . \qquad (4)$$

Statistical analysis of the equations (2)–(4) ($P = \tilde{\nu}(C{=}O)$) for all studied compounds (excluding IIi) and for the separately correlated mono and disubstituted fuchsones (II and III, respectively) is summarized in Table III. Statistical significance of the single regression coefficients was tested at a significance level given by $\alpha = 0.05$ for $N - q - 1$ degrees of freedom (where N is the number of data and q is the number of regressors). It follows from the F as well as t-tests (Table III) that the resonance term $\varrho_R \sum \sigma_R$ is invariably statistically insignificant. On the contrary, the polar contribution $\varrho_I \sum \sigma_I$ has always the highest statistical weight (in majority

TABLE III
Statistics of Equations (2)—(4) for Carbonyl Frequencies of Compounds II and III

System	ϱ_I ϱ_R	ϱ_S	ν_0	R^a $\hat{F}^b$	$\hat{F}(\varrho_I)$ $\hat{t}(\varrho_I)$	$\hat{F}(\varrho_R)$ $\hat{t}(\varrho_R)$	$\hat{F}(\varrho_S)$ $\hat{t}(\varrho_S)$
$II + III^c$	39·77 3·61	—8·37	1 625·7	0·979 86·8	237·5 13·5	1·36* 1·1*	21·6 4·6
$II + III^c$	38·41 —	—8·39	1 624·9	0·977 127·1	232·9 14·2	— —	21·3 4·6
$II + III^c$	41·99 3·78	—	1 617·5	0·938 44·1	87·7 8·8	0·4* 0·7*	— —
II^d	41·28 —	—6·18	1 624·0	0·975 48·7	94·8 9·8	— —	2·6* 1·6*
II^d	40·23 8·25	—	1 621·7	0·972 42·4	83·25 9·2	1·5* 1·2*	— —
III^d	35·64 —	—9·11	1 625·5	0·982 67·9	120·8 9·7	— —	15·1 3·8
III^d	37·85 —1·83	—	1 614·0	0·926 15·1	30·2 4·1	0·0* 0·1	— —

^{a} Multiple correlation coefficient; ^{b} total F-test (the asterisk denotes factors with significance level $<95\%$); ^{c} $N = 15$; ^{d} $N = 8$.

of cases even higher than 99·9%, according to the t-test) and plays therefore a domi-
nant role in transmission of the effect of substituent from the *ortho*-position.

The exclusive position of the hydroxy derivative *IIi* in the whole series is illustrated
by Fig. 1. The marked deviation of the point corresponding to this compound
from the regression line is not unexpected and it can be ascribed to participation
of hydrogen bond (*IV*) of the OH group. This type of *ortho*-effect cannot, of course,
be described by the steric parameter of the OH substituent; moreover, we cannot
exclude even the tautomeric equilibrium $IV \rightleftharpoons V$.

*IV*   *V*
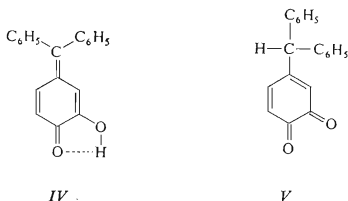
The steric effect contribution is to be discussed separately for monosubstituted
and disubstituted derivatives. For disubstituted fuchsones all the statistical para-
meters show that the steric effect is important and its contribution to the total trans-
mission is 28·4% (according to the Swain–Lupton procedure[22] which takes into
account the difference in variance of σ_I and ϑ). For monosubstituted fuchsones *II*
the steric effect is much less pronounced but it has still the reverse direction than the
inductive effect, *i.e.* with increasing van der Waals volume the wavenumber of the
carbonyl band decreases.

Integrated intensities $A(C=O)$ of the fuchsones *II* and *III* range from 9 560 l .
. mol^{-1} cm^{-2} (*IIIg*) to 22 500 l mol^{-1} cm^{-2} (*IIb*) (Table II). We tried also to cor-
relate $A(C=O)^{1/2}$ according to equations (2)–(4). The results, summarized in Ta-
ble IV, indicate that about 82—88% of variability in $A(C=O)^{1/2}$ can be ascribed
to σ_I and ϑ. The lower correlation coefficients are probably caused by greater rela-
tive error in $A(C=O)$ than in $\tilde{v}(C=O)$ measurements. The conclusions following
from Table IV are identical with those derived from Table III. The steric effect
contribution to total transmission in 2,6-disubstituted fuchsones, as calculated
from the intensities, is somewhat higher (about 36%).

Since both the experimental quantities apparently exhibit similar dependence
on substituent constants, it was interesting to know the direct relation between
$A(C=O)$ and $\tilde{v}(C=O)$ in all the studied fuchsones. This relation is of course only
of an approximate character because the frequency $\tilde{v}$ is determined preponderantly
by the force constant of the C=O bond whereas the intensity A by electro-optical

parameters of the molecule; thus, in principle, there cannot exist any direct connection between $\tilde{v}$ and A. In spite of this, the relationship mentioned has been used several times in order to classify some compounds, such as unsaturated ketones[23] or nitriles[24], into groups.

In Fig. 2, the plot of $A(C=O)$ against $\tilde{v}(C=O)$ for fuchsones II and III is compared with an equivalent relationship for some carbonyl compounds of the type VI and VII (X is OCH_3 (ref.[25]), H (ref.[26,27]) and CH_3 (ref.[26,28]; R are alkyl groups[29,30]).
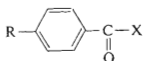
VI   VII

Although we consider Fig. 2 to be only a qualitative scheme (in which, moreover, some of the series contain insufficient number of data), it shows some trends (in Fig. 2 denoted ----) which are probably of a more general validity. Thus, an increased
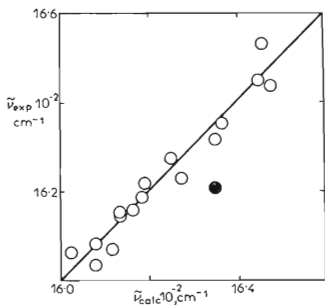

FIG. 1

Graphical Representation (left side *vs* right side) of Equation (4) for All Derivatives; ● 2-Hydroxyfuchsone (*IIi*)
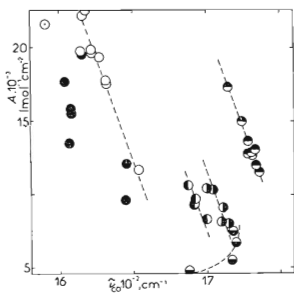
FIG. 2

Diagram of Relation between Frequency and Band Intensity of Fundamental Carbonyl Group Vibrations

○ 2-Substituted fuchsones, ● 2,6-disubstituted fuchsones, ◐ 4-substituted methylbenzoate, ◒ 4-substituted benzaldehydes, ◑ 4-substituted acetophenones, ◓ symmetrical dialkyl ketones, ⊙ tropone.

conjugation in the molecule is accompanied by an increased intensity and a lower frequency of the carbonyl group. Also the trend to exhibit higher intensity and lower frequency with increasing electron donor ability of the substituent R is apparent. The model *VII* shows also that an increasing alkyl size is accompanied by a non-linear shift towards lower values of $\bar{\nu}$ and A. From this point of view it is not surprising that the studied compounds form two series according to the number of *ortho*-substituents. For disubstituted derivatives with a substantial contribution of the steric effect one can expect a deviation towards lower intensities and frequencies, qualitatively similar to that for the model *VII*. Further, it is obvious that the integrated intensity of the unsubstituted fuchsone (19 300 l mol^{-1} cm^{-2}) is comparable with that of tropone[31] (21 600 l mol^{-1} cm^{-2}); this is an indication of a high degree of conjugation.

Contrary to the saturated ketones *VII* in which substituents are bonded directly to the carbonyl carbon and their steric effect is directly related to the magnitude of the C—C(O)—C angle[29], an interpretation of the steric effect in fuchsones is substantially more difficult. Steric strain in 2- and 2,6-substituted fuchsones can be alleviated by one of the three following mechanisms (Scheme 1): *a*) by distorsion

TABLE IV
Statistics of Equations (2)—(4) for Squared Integrated Intensities of Compounds *II* and *III*

System	ϱ_I ϱ_R	ϱ_S	$A_0^{1/2}$	R^a $\hat{F}^b$	$\hat{F}(\varrho_I)$ $\hat{t}(\varrho_I)$	$\hat{F}(\varrho_R)$ $\hat{t}(\varrho_R)$	$\hat{F}(\varrho_S)$ $\hat{t}(\varrho_S)$
II + III^c	−32·80 6·24	−16·35	151·2	0·916 19·3	35·5 5·6	1·0* 0·9*	21·3 4·6
II + III^c	−35·14 —	−16·40	149·9	0·909 28·6	35·7 6·7	— —	21·5 4·6
II^d	−38·59 —	− 2·05	144·0	0·919 16·4	27·4 5·0	— —	0·0* 0·3*
II^d	−39·79 − 9·84	—	141·3	0·931 18·2	31·7 5·7	0·8* 0·9*	— —
III^d	−33·16 —	−12·05	141·1	0·941 19·6	27·9 5·9	— —	11·1 3·3

^{a} Multiple correlation coefficient; ^{b} total F-test (the asterisk denotes factors with significance level <95%); ^{c} $N = 15$; ^{d} $N = 8$.
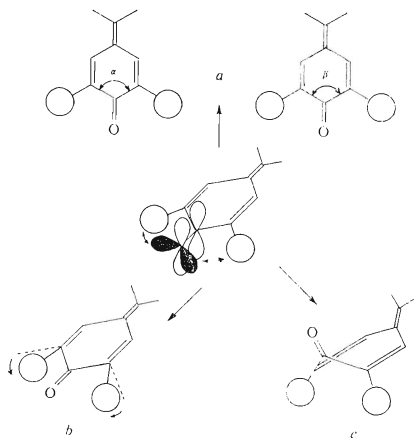
SCHEME 1

of angles in the quinonoid ring without affecting the planarity of the system ($\alpha <$ $< 115\cdot2°$ (ref.[4]) $< \beta$); b) by bringing the substituent out of the ring plane with retention of the planarity of the cycle, and c) by distortion of the quinonoid ring under formation of a boat form. The first of these mechanisms obviously operates in the case of monosubstituted fuchsones. On the other hand, for disubstituted fuchsones we consider the mechanisms (b) an (c) as probable; however, we are not able to decide between them on the basis of IR spectra only. It is worth mentioning that the X-ray analysis of 2,6-dibromofuchsone[32] agrees with the latter mechanism.

We can thus summarize that our statistical approach is satisfactory for interpretation of the *ortho*-effect in 2-substituted and 2,6-disubstituted fuchsones using carbonyl frequencies and integrated intensities. With 2,6-disubstituted fuchsones the effect of substituents on frequency and intensity of the carbonyl band is additive and involves about 70% of inductive and 30% of steric contribution. The contribution of steric effect in monosubstituted derivatives is much less pronounced.

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Translated by M. Tichý.