π-ELECTRON STRUCTURE AND UV SPECTRA OF 4-ALKYLIDENE-2,5-CYCLOHEXADIEN-1-ONES*

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The MO LCAO SCF method was used to examine the π-electron structure of compounds *I—XX* and the absorption bands in UV spectra of these compounds were characterised by means of the LCI procedure. A discussion is presented on the effect of substituents on position of the dominant absorption band of the π–π* type, the effect of position isomerism and parametrisation of theoretical and experimental characteristics as well as the electron polarisation of transition from the ground into the excited state

Compounds with the quinone methide framework represent a class of substances asserting themselves particularly in the chemistry of phenolic resins[1–3] or biosynthesis and degradation of lignin[4]. From the chemical standpoint, quinone methides are structurally related to quinones. Whereas the physicochemical characteristics of quinones have been widely examined (for an exhaustive treatise see ref.[5]), much less attention has been paid to quinone methides[6]. The quinone methides are usually identified by means of their UV absorption spectra using a separate, very intensive absorption band in the $26\,300 - 35\,700 \text{ cm}^{-1}$ region. Dependence of the position of this band on substitution has been examined in this Laboratory in connection with the empirical additive method[7]. In the present paper, attention has been focussed on rationalisation of these spectral features by means of semiempirical π-electron calculations of quinone methides *I—XIX*, on classification of the particular transitions, and on determination of relations between the quinonoid and the quinone methide system on the basis of a comparison of the electron structures and calculated transitions in the simplest members of the two classes of compounds.

Quantum-chemical calculations of quinone methides have been reported in several papers. Thus, the reactivity and stability of *p*-quinone methide (*I*), *p*-benzoquinone (*XX*), and the imino as well as thio analogues has been interpreted on the HMO level by Coppinger and Bauer[8]. The same method was used by Wagner and Gompper[6] to analyze the relation between quinone methides and the more stable benzhydry-

lidene-2,5-cyclohexadien-1-ones (fuchsones); furthermore, the calculated HMO characteristics of p-benzoquinone (XX), p-quinone methide (I), and p-quinone dimethide (XXI) were compared by the same authors[6]. The HMO approximation was also used to evaluate the spectral behaviour of eriochromcyanin[9] which, however, is structurally more related to triphenylmethane derivatives than to quinone methides.

EXPERIMENTAL

Compounds I—$XVIII$ were prepared by reported procedures[7]. The UV spectra were taken on a UV-VIS-Specord apparatus (Carl Zeiss, Jena) in dichloromethane, unless stated otherwise.

Calculations

Calculations of spectral characteristics and electron structures were performed by means of the standard PPP version of the SCF MO LCI procedure[10,11] on a NE Elliott 503 computer. In all cases, 16 monoexcited configurations were included with the use of fixed values of α_μ^c integrals or their variations according to equation (1):

$$\alpha_\mu^c = \alpha_\mu^0[1 + 0.4(q_\mu - Q_\mu)] . \qquad (1)$$

In the case of p-benzoquinone (XX), an additional calculation was performed with an increased value[12] of the $\beta_{\mu\nu}^c$ integral for the C=O bond. One-center repulsion integrals $\gamma_{\mu\mu}$ were calculated according to the Pariser approximation[13] and the two-center repulsion integrals $\gamma_{\mu\nu}$ were obtained according to Nishimoto and Mataga[14]. The geometry of the quinone methide framework was inferred from the X-ray analysis of p-benzoquinone[15] (XX); the value 1.354 Å was used for the length of the exocyclic C=C bond. For the other parameters see Table I. For numbering of the quinonoid and quinone methide framework and their location in the coordinate system see Fig. 1.

TABLE I

Parameters in SCF MO LCAO Calculations

Atom	IP, eV	EA, eV	Ref.	Bond	k^a	r, nm	Ref.
$C(sp^2)$	11.22	0.69	16	$C(sp^2)$—$C(sp^2)$	0.9	0.148	15
				$C(sp^2)$=$C(sp^2)$	1.1	0.132	15
$C(H_3)$	11.42	0.58	16	$C(sp^2)$—CH_3	0.51^d	0.152	19
				C=H_3	1.25	0.11	16
Br	24.60	11.72^b	17	C—Br	0.70	0.186	17
$O(sp^3)$	33.90	12.8	c	C—O	0.95	0.140	17
				O—CH_3	0.51	0.142	17
$O(sp^2)$	16.00	2.0	18	C=O	1.25	0.122	15

^{a} In β units ($\beta = -2.318$ eV); ^{b} the EA value decreased with respect to the original one by 2 eV; ^{c} this paper; ^{d} for the CH_3 group attached to the ring, $k = 0.45$.

RESULTS AND DISCUSSION

In the UV spectral region of 4-methylene-2,5-cyclohexadien-1-one (I), the existence of three $\pi - \pi^*$ transitions was inferred by means of PPP calculations. The longest wavelength transition at $34\,900 \text{ cm}^{-1}$ with intensity corresponding to log ε 4·05 (calculated from the oscillator strength on the basis of the relation $\log \varepsilon = \log f + 4$) is of the $1-1'$ type with 96% weight. It is a symmetrically allowed $^1A_1 - ^1A_1$ transition with the polarisation vector identical with the rotational axis of symmetry C_{2v} (Fig. 1). Position of the transition corresponds to the experimentally observed absorption band at $35\,460 \text{ cm}^{-1}$. The two remaining transitions $(36\,560$ and $43\,650 \text{ cm}^{-1})$ exhibit the $^1A_1 - ^1B_1$ symmetry and are polarised parallel to axis x. These almost pure transitions of the $2-1'$ and $1-2'$ type are of low intensity (log ε 1·5 to 2·5) and were not confirmed experimentally. In the vacuum UV region $(58\,600 \text{ cm}^{-1})$, the existence of a symmetrically allowed $^1A_1 - ^1A_1$ transition is worth of mention, with intensity corresponding to log $\varepsilon \sim 4$ and polarised in direction of the longitudinal axis of the molecule (direction of the C=O bond).

The calculated spectral characteristics of the parent compound I and the corresponding data of compounds $II-XIX$ exhibit numerous common features. In the region of the experimentally measured absorption curve, the presence of three $\pi - \pi^*$ transitions was always established by calculation; these transitions are exclusively of the $1-1'$, $2-1'$, and $1-2'$ type. This order (starting with the longest wavelengths) is observed with most compounds tested except for the methylene derivatives
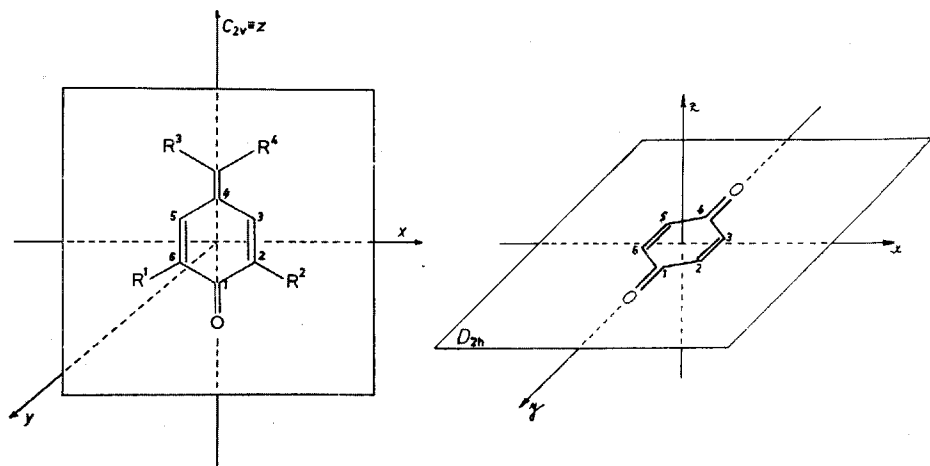

FIG. 1

Numbering of the Quinonoid and Quinone Methide System and Location in Cartesian Coordinates

IV, VII, X, and *XIII* that exhibit an interchanged order of the first two transitions. A further analogy to the theoretically calculated spectrum of compound *I* is shown in the case of the symmetrically disubstituted derivatives *II — XII* (with respect to the substitution on the ring). Their transitions are almost pure, with weights higher than 90%. The *1 — 1'* transitions are always dominant, are polarised in direction of the longitudinal axis of the molecule only, and correspond in all cases to the experimentally determined maxima on absorption curves. The two remaining transitions are less intensive and the corresponding vectors of polarisation are perpendicular to the longitudinal axis of the molecule. The two latter transitions have not been confirmed experimentally in any of these compounds.
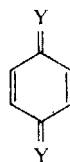
The spectral characteristics of the unsymmetrically substituted compounds *XIII* to *XVIII* belonging to the point group of symmetry C_s, are somewhat different from those of the preceding group of substances.* It is characteristic of the whole series
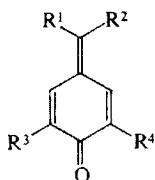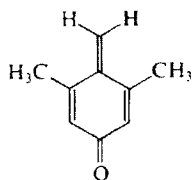
$I—XVIII$ XIX XX Y $=$ O
                                                    XXI Y $=$ CH$_2$

	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
I	H	H	H	H	*XI*	CH$_3$	H	OCH$_3$	OCH$_3$
II	CH$_3$	H	H	H	*XII*	CH$_3$	CH$_3$	OCH$_3$	OCH$_3$
III	CH$_3$	CH$_3$	H	H	*XIII*	H	H	Br	OCH$_3$
IV	H	H	CH$_3$	CH$_3$	*XIVa*	H	CH$_3$	Br	OCH$_3$
V	CH$_3$	H	CH$_3$	CH$_3$	*XIVb*	CH$_3$	H	Br	OCH$_3$
VI	CH$_3$	CH$_3$	CH$_3$	CH$_3$	*XV*	CH$_3$	CH$_3$	Br	OCH$_3$
VII	H	H	Br	Br	*XVI*	H	H	H	OCH$_3$
VIII	CH$_3$	H	Br	Br	*XVIIa*	H	CH$_3$	H	OCH$_3$
IX	CH$_3$	CH$_3$	Br	Br	*XVIIb*	CH$_3$	H	H	OCH$_3$
X	H	H	OCH$_3$	OCH$_3$	*XVIII*	CH$_3$	CH$_3$	H	OCH$_3$

* The ethylidene derivatives *II, V, VIII,* and *XI* also belong to the point group of symmetry C_s. The symmetry of the molecule is however very slightly affected by the methyl group, in accordance with the fact that the deviation of the polarisation of the dominant π–π* transition from the direction of the longitudinal axis does not exceed the value of 7°. The parallelity of transitions in compounds *I— XII* is thus unequivocal and classification of compounds *I— XII* along with those belonging to the point group of symmetry C_{2v} is thus justified (the models of symmetrically substituted derivatives unambiguously exhibit the C_{2v} symmetry whereas a free rotation of substituents must be assumed in the case of virtual substances.

that the two longest wavelength transitions are polarised in the direction differing only a little from the longitudinal axis of the molecule. In the case of compounds *XV* and *XVIII*, they are represented by almost pure $1-1'$ and $2-1'$ transitions (weight above 90%) whereas with compounds *XIII*, *XIV*, *XVI*, and *XVII* the two longest wavelength transitions are formed from mixed $1-1'$ and $2-1'$ transitions. Their intensities vary in the range of log ε from 3 to 4. The stronger one is of the $1-1'$ type again or this type is at least predominating (except for compound *XVI*). In the discussed group of compounds it is that transition which corresponds to the observed dominant maximum on the UV absorption curve. The third transition is polarised in direction close to the transversal axis of the molecule. It is always of the $1-2'$ type (weight above 90%). Its intensity corresponds to log $\varepsilon = 3$ and it was confirmed experimentally in the case of compound *XVI* only.

Substitution on the methide $C_{(7)}$ carbon atom affects most markedly the longest wavelength transition (by a shift to longer wavelengths and a moderately increased intensity). As it may be inferred from calculated characteristics of compounds *I −III*, the magnitude of the bathochromic shift is roughly additive and the increment for one methyl group is about $2\,000\ cm^{-1}$. Position of the further band remains almost unchanged and the last $\pi - \pi^*$ transition is shifted to shorter wavelengths (see Table II). In the case of the two longest wavelength $\pi - \pi^*$ transitions, substituents at positions 2 and 6 cause a bathochromic shift whereas the position of the energetically richest transition remains almost unchanged. In the series of 2,6-disubstituted derivatives (compounds *IV*, *VII*, and *X*) the presence of two methyl groups, two bromo atoms or two methoxyl groups results in bathochromic shifts equal to $1\,700$, $2\,200$, and $3\,100\ cm^{-1}$, resp. The trend of these values might be dependent on the extent of π-electron interactions of the particular substituents with the quinone methide system. On the magnitudes of bathochromic shifts due to the methyl groups (*cf.* compounds *III* and *IV*), the much lower substitution effect on the ring may be demonstrated in comparison to substitution on the methide $C_{(7)}$ carbon atom.

In order to determine the effect of substitution at positions 3 and 5 of the quinone methide ring system, spectral characteristics of the hitherto unprepared methylene-cyclohexadienone *XIX* were theoretically examined. The calculated spectrum of compound *XIX* was very similar to that of compound *IV* but the bathochromic shift of the dominant $\pi - \pi^*$ transition was lower with compound *XIX* than in the case of compound *IV*.

Experimental absorption curves of compounds *XIII −XV* exhibit a single band, the asymmetry of which appears to suggest superposition of two transitions. These experimental observations are in accord with calculated two closely adjacent intensive transitions with compounds *XIII −XV*. With compound *XIII*, these transitions differ by about $1\,700\ cm^{-1}$; this value slightly increases by substitution on the methide $C_{(7)}$ carbon atom. With respect to the dominant transition of compound *I*, the corresponding bathochromic shifts of transitions in compound *XIII* are 2300 and

TABLE II

Calculated Characteristics of three Longest Wavelength Transitions in UV Spectra of Compounds *I–XX*

Compound	Transition symmetry[a]	Transition energy, cm^{-1} calculated	Transition energy, cm^{-1} found[b]	log f	Transition type	Weight, %
I	$^1A_1-^1A_1(z)$	34 910	35 460	0·051	*1—1'*	96
	$^1A_1-^1B_1(x)$	36 560	—	−2·512	*2—1'*	99
	$^1A_1-^1B_1(x)$	43 650	—	−1·707	*1—2'*	99
II	$^1A'-^1A'(x, \underline{z})$	32 520	33 330	0·069	*1—1'*	94
	$^1A'-^1A'(\underline{x}, z)$	37 230	—	−2·290	*2—1'*	99
	$^1A'-^1A'(\underline{x}, z)$	42 490	—	−1·650	*1—2'*	96
III	$^1A_1-^1A_1(z)$	30 940	31 450	0·117	*1—1'*	96
	$^1A_1-^1B_1(x)$	37 610	—	−2·123	*2—1'*	98
	$^1A_1-^1B_1(x)$	41 370	—	−2·940	*1—2'*	71
IV	$^1A_1-^1B_1(x)$	33 210	—	−2·110	*2—1'*	94
	$^1A_1-^1A_1(z)$	33 480	34 480	0·028	*1—1'*	96
	$^1A_1-^1B_1(x)$	41 990	—	−0·887	*1—2'*	71
V	$^1A'-^1A'(x, \underline{z})$	32 020	33 000	0·104	*1—1'*	96
	$^1A'-^1A'(\underline{x}, z)$	34 400	—	−1·982	*2—1'*	97
	$^1A'-^1A'(\underline{x}, z)$	41 560	—	−1·205	*1—2'*	88
VI	$^1A_1-^1A_1(z)$	31 180	30 670	0·123	*1—1'*	99
	$^1A_1-^1B_1(x)$	34 970	—	−2·068	*2—1'*	99
	$^1A_1-^1B_1(x)$	40 740	—	−1·161	*1—2'*	98
VII	$^1A_1-^1B_1(x)$	32 100	—	−2·218	*2—1'*	100
	$^1A_1-^1A_1(z)$	32 710	32 680	0·028	*1—1'*	96
	$^1A_1-^1B_1(x)$	42 620	—	−1·240	*1—2'*	99
VIII	$^1A'-^1A'(x, \underline{z})$	30 880	30 960	0·065	*1—1'*	96
	$^1A'-^1A'(\underline{x}, z)$	32 670	—	−2·375	*2—1'*	100
	$^1A'-^1A'(\underline{x}, z)$	41 490	—	−1·263	*1—2'*	98
IX	$^1A_1-^1A_1(z)$	29 770	29 240	0·096	*1—1'*	97
	$^1A_1-^1B_1(x)$	33 170	—	−2·771	*2—1'*	100
	$^1A_1-^1B_1(x)$	40 660	—	−1·232	*1—2'*	98
X	$^1A_1-^1B_1(x)$	30 670	—	−2·315	*2—1'*	94
	$^1A_1-^1A_1(z)$	31 830	31 550	0·013	*1—1'*	96
	$^1A_1-^1B_1(x)$	42 510	—	−0·989	*1—2'*	97
XI	$^1A'-^1A'(x, \underline{z})$	30 540	30 300	0·054	*1—1'*	97
	$^1A'-^1A'(\underline{x}, z)$	31 090	—	−2·356	*2—1'*	95
	$^1A'-^1A'(\underline{x}, z)$	41 560	—	−0·939	*1—2'*	99

TABLE II

(*Continued*)

Compound	Transition symmetry[a]	Transition energy, cm⁻¹ calculated	found[b]	log f	Transition type	Weight, %
XII	$^1A_1 - {}^1A_1(z)$	29 490	28 990	0·071	$1-1'$	98
	$^1A_1 - {}^1B_1(x)$	31 480	—	−3·076	$2-1'$	96
	$^1A_1 - {}^1B_1(x)$	40 770	—	−0·971	$1-2'$	99
XIII	$^1A' - {}^1A'(x, \underline{z})$	30 870	—	−0·598	$2-1'$	64
	$^1A' - {}^1A'(x, \underline{z})$	32 600	32 470	−0·106	$1-1'$	64
	$^1A' - {}^1A'(\underline{x}, z)$	42 400	—	−1·001	$1-2'$	96
XIVa	$^1A' - {}^1A'(x, z)$	30 370	30 770	0·006	$1-1'$	88
	$^1A' - {}^1A'(x, \underline{z})$	32 140	—	−0·804	$2-1'$	88
	$^1A' - {}^1A'(\underline{x}, z)$	41 390	—	−1·089	$1-2'$	97
XIVb	$^1A' - {}^1A'(x, \underline{z})$	30 320	30 770	−0·001	$1-1'$	87
	$^1A' - {}^1A'(x, \underline{z})$	32 200	—	−0·761	$2-1'$	87
	$^1A' - {}^1A'(\underline{x}, z)$	41 440	—	−0·923	$1-2'$	98
XV	$^1A' - {}^1A'(x, z)$	29 570	28 990	0·059	$1-1'$	95
	$^1A' - {}^1A'(x, \underline{z})$	32 570	—	−1·117	$2-1'$	94
	$^1A' - {}^1A'(\underline{x}, z)$	40 680	—	−1·095	$1-2'$	98
XVI	$^1A' - {}^1A'(x, \underline{z})$	30 080	31 090[c]	−0·338	$1-1'$	67
	$^1A' - {}^1A'(x, \underline{z})$	35 600	35 150[c]	−0·101	$2-1'$	59
	$^1A' - {}^1A'(\underline{x}, z)$	42 430	41 840[c]	−0·818	$1-2'$	92
XVIIa	$^1A' - {}^1A'(x, \underline{z})$	30 080	30 300	−0·099	$1-1'$	87
	$^1A' - {}^1A'(x, \underline{z})$	35 040	32 900	−0·440	$2-1'$	78
	$^1A' - {}^1A'(x, z)$	41 620	—	−0·999	$1-2'$	94
XVIIb	$^1A' - {}^1A'(x, \underline{z})$	30 010	30 300	−0·101	$1-1'$	86
	$^1A' - {}^1A'(x, \underline{z})$	36 130	32 900	−0·445	$2-1'$	78
	$^1A' - {}^1A'(x, z)$	41 710	—	−0·726	$1-2'$	96
XVIII	$^1A' - {}^1A'(x, \underline{z})$	29 570	29 940	−0·024	$1-1'$	92
	$^1A' - {}^1A'(x, \underline{z})$	35 160	34 600	−0·577	$2-1'$	85
	$^1A' - {}^1A'(\underline{x}, z)$	40 960	—	−0·924	$1-2'$	96
XIX[d]	$^1A_1 - {}^1B_1(x)$	33 440	—	−1·544	$2-1'$	97
	$^1A_1 - {}^1A_1(z)$	34 510	—	0·041	$1-1'$	96
	$^1A_1 - {}^1B_1(x)$	43 390	—	−2·131	$1-2'$	94
XX[g]	$^1A_g - {}^1B_{1g}$	34 260	33 900[e]	forbidden[f]	$2-1'$	99
	$^1A_g - {}^1B_{2u}(y)$	38 070	40 800[e]	−0·039	$1-1'$	94
	$^1A_g - {}^1B_{1g}$	49 960	—	forbidden	$1-2'$	99
	$^1A_g - {}^1A_g$	53 550	—	forbidden	$3-1'$	80
	$^1A_g - {}^1B_{2u}(y)$	58 480	58 300[e]	−0·029	$2-2'$	55
					$4-1'$	39

TABLE II

(*Continued*)

Com-pound	Transition symmetry[a]	Transition energy, cm^{-1}		log f	Transition type	Weight, %
		calculated	found[b]			
XX^h	$^1A_g - {}^1B_{1g}$	35 800	33 900	forbidden	$2-1'$	99
	$^1A_g - {}^1B_{2u}(y)$	39 530	40 800	-0.070	$1-1'$	93
	$^1A_g - {}^1B_{1g}$	51 040	—	forbidden	$1-2'$	99
	$^1A_g - {}^1A_g$	57 370	—	forbidden	$3-1'$	7
	$^1A_g - {}^1B_{2u}(y)$	59 550	58 300	-0.105	$2-2'$	8

[a] Direction of the predominating polarisation is underlined; [b] extinction coefficients of absorption bands of compounds $I-XVIII$ are experimentally unaccessible; [c] in cyclohexane; [d] the compound has not been so far prepared; [e] for the experimental data see ref.[23]; [f] $\log f < -10.0$; [g] $\beta_{C=O} = 1.25$ (in β units); [h] $\beta_{C=O} = 1.40$ (in β units).

4000 cm^{-1}. Calculated characteristics of the two possible positional isomers ($XIVa$ and $XIVb$) do not substantially differ. The order of magnitude of the particular transition shifts does not exceed tens of cm^{-1}. The values calculated for the model compound $XIVa$ are in a somewhat better agreement with the experimental curve than those of the model compound $XIVb$. The spectral characteristics of monosubstituted derivatives $XVI-XVIII$ are analogous to the above mentioned. Only the difference between the two intensive transitions is much higher. When compared with the dominant transition in the parent compound I, the longer wavelength transitions of compounds $XVI-XVIII$ are shifted by about 5000 cm^{-1} while the position of the shorter wavelength transition is almost equal. Both transitions correspond to the experimental almost separated absorption bands of compounds XVI and $XVIII$. Furthermore, the third experimental band of compound XVI (the spectrum was measured in cyclohexane) corresponded to the calculated transition of weak intensity at 42400 cm^{-1} (Fig. 2). With compound $XVII$, the first transition at 30300 cm^{-1} corresponds to the shoulder on the experimental curve whereas the other transition at 35000 cm^{-1} exhibits a hypsochromic shift of 2000 cm^{-1} with respect to the experimental maximum. Also the intensity of the two calculated transitions does not agree with the experimental results. This discrepancy cannot be, however, ascribed to the positional isomerism as shown by examination of the E and Z 2-methoxy-4--ethylidene-2,5-cyclohexadien-1-ones ($XVIIa$ and $XVIIb$).

The spectral characteristics calculated with the use of variable α-core integrals are in better agreement with experimental data than those calculated without varia-

tion. All the presented values were obtained by calculations with variation of α-core integrals. The difference between the two procedures is demonstrated on Fig. 3.

When compared with experimental positions of strongest absorption bands, the positions of calculated dominant transitions in quinone methides $I - XVIII$ exhibit differences not exceeding (except for compound $XVII$) the value of $1000 \, cm^{-1}$. The obtained oscillator strengths of these transitions correspond to extinction coefficients ε higher than 10000, in agreement with experimental data of stable quinone methides[20,21]. For a survey of calculated and experimental data see Table II.

Relation between the Spectral Behaviour and the Electron Structure of p-Quinonemethide (I) *and p-Benzoquinone* (XX)

The theoretical examination of the electron spectrum of p-benzoquinone (XX) has been paid considerable attention (see for example ref.[22,23]). Notwithstanding, some
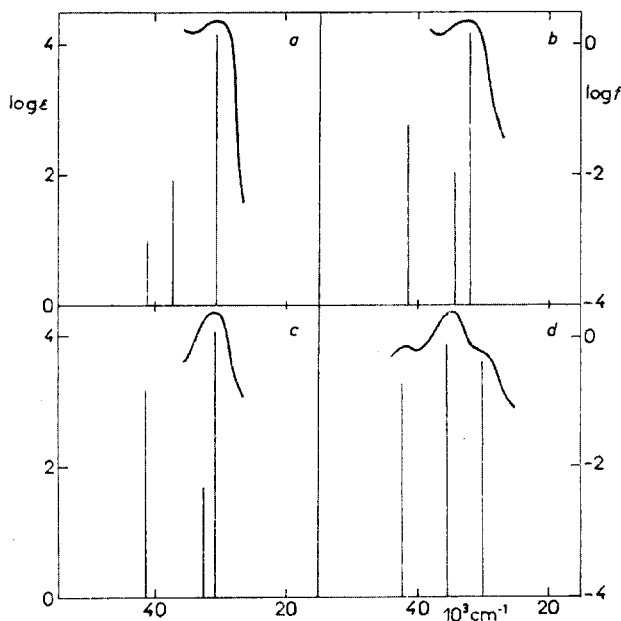
FIG. 2

Comparison of Calculated and Experimental Electron Spectra

Experimental curves are constructed for the hypothetical concentration, log ε 4·4 (dominant transition); *a* UV absorption spectrum of 4-isopropylidene-2,5-cyclohexadien-1-one (*III*), dichloromethane; *b* UV absorption spectrum of 4-ethylidene-2,6-dimethyl-2,5-cyclohexadien-1-one (*V*), dichloromethane; *c* UV absorption spectrum of 4-ethylidene-2,6-dibromo-2,5-cyclohexadien-1-one (*VIII*), dichloromethane; *d* UV absorption spectrum of 4-methylene-2-methoxy--2,5-cyclohexadien-1-one (*XVI*), cyclohexane.

recalculations have been now performed using the set of parameters derived for calculations in the quinone methide series with the aim to compare the characteristics of compounds *I* and *XX* in the ground and the excited state within a consistent set of parameters and to verify the applicability of these parameters for examination of the quinonoid ring system. The calculated data are in a satisfactory agreement with the experimental spectrum of *p*-benzoquinone. The experimental accordance with the allowed $^1A_g - ^1B_{2u}$ transition may be improved by an increase of the $\beta^c_{\mu\gamma}$ integral value for the C=O bond; however, this improvement is at expense of the $^1A_g - ^1B_{1g}$ and the short wavelength $^1A_g - ^1B_{2u}$ transition (Fig. 3). Compounds *I* and *XX* exhibit two intensive $\pi - \pi^*$ transitions (log $\varepsilon > 4$) which are polarised in direction of the C=O bond. While the position of shorter wavelength transitions is almost equal $(58\,480$ and $58\,640\ \text{cm}^{-1})$, the energetically poorer transitions are mutually shifted by almost $5000\ \text{cm}^{-1}$; this shift, however, does not exclude an identical character. With the remaining transitions, conspicuous deviations may be observed such as slightly intensive but allowed $\pi - \pi^*$ transitions (polarised perpendi-
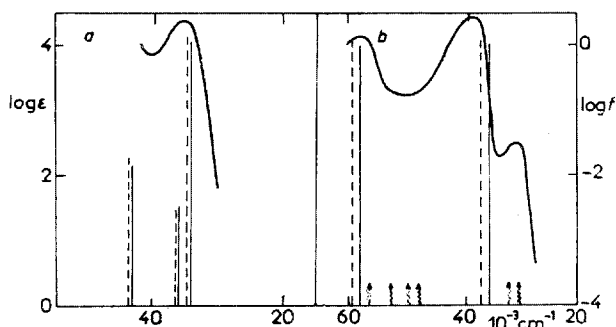

FIG. 3

Comparison of Calculated Transitions with Experimental Absorption Curves

a *p*-Quinone methide (*I*) spectrum; ——— PPP calculation without variation of α^c integrals; —————— PPP calculation with variation of α^c integrals; *b* *p*-benzoquinone (*XX*) spectrum; ——— $\beta^c_{C=O} = 1\cdot25$ (in β units); —————— $\beta^c_{C=O} = 1\cdot40$ (in β units); ⌇⌇⌇⌇, ⌇⌇⌇⌇ forbidden transitions (log $f < -10$).
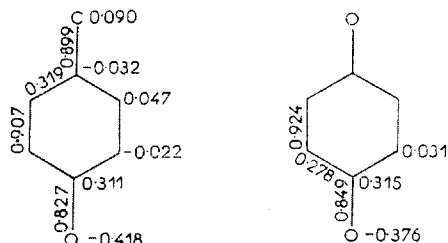

FIG. 4

SCF Molecular Diagrams of *p*-Quinone Methide (*I*) and *p*-Benzoquinone (*XX*) in Ground States

cularly to the longitudinal axis of the molecule) in the case of the quinone methide *I*
whereas forbidden transitions are involved in the case of *p*-benzoquinone. (The
$n - \pi^*$ transitions cannot be calculated by the present program version.) Fig. 4
shows the SCF molecular diagrams of compounds *I* and *XX* in the ground state.
The marked polarisation of the quinone methide system correlates with the experi-
mentally observed high reactivity of quinone methides with both electrophilic and
nucleophilic agents[6].

Changes of the π-electron distribution in the quinone methide and quinonoid ring
system of compounds *I* and *XX*, induced by transition into the first two excited states,
are shown in Table III. The absolute magnitude of values listed in Table III indicates
a higher polarisation of the quinone ring system during transition into excited states.
The parallelity between changes of charges and bond orders accompanying transition
into the first excited state with *p*-quinone methide (*I*) and values for the 2nd excited
state with *p*-benzoquinine (*XX*) is in accord with the previously observed analogy
of transitions corresponding to these excitations.

Changes in the π-electron distribution due to dominant $\pi - \pi^*$ transitions may be
detected by means of the corresponding dipole moment values. In the case of *p*-quinone
methide (*I*), the electric moment values change from 4·6 D (ground state) to 4·3 D
(excited state). With respect to the dipole moment, the whole set of compounds
I−XVIII may be evaluated as follows. Substituents on the $C_{(7)}$ methide carbon atom
increase the magnitude of the dipole moment, the value in the excited state being
higher than in the ground state; thus, *e.g.*, the values 8·4 and 9·3 D were calculated
in the case of compound *III*. On the other hand, the ring substituents (position 2
and 6) decrease the magnitude of the dipole moment in the ground state depending on
the extent of the electron interaction with the ring. Substituents CH_3, Br, and OCH

TABLE III
Changes in π-Electron Distribution Corresponding to the First Two Transitions (compounds *I*
and *XX*)

Atom	$q_i^1(I)$	$q_i^2(I)$	$q_i^1(XX)$	$q_i^2(XX)$	Bond	$p_{ij}^1(I)$	$p_{ij}^2(I)$	$p_{ij}^1(XX)$	$p_{ij}^2(XX)$
1	−0·114[a]	−0·118	−0·140	−0·112	*1 2*	0·093	0·093	0·117	0·129
2	0·067	0·172	0·152	0·031	*2 3*	−0·215	−0·335	−0·347	−0·268
3	−0·056	0·153	—	—	*3 4*	0·151	0·084	—	—
4	0·064	−0·072	—	—	*4 7*	−0·269	−0·155	−0·152	−0·153
7	−0·015	−0·331	−0·165	0·050	*1 8*	−0·118	−0·125	—	—
8	0·041	−0·130	—	—					

[a] Referred to the ground state values.

(compounds *IV*, *VII*, and *X*) exhibit the values 2·7, 2·8, and 0·8 D (ground states) and 1·3, 3·3, and 2·4 D (excited states), resp. In the case of methyl groups, the same trend may be observed as encountered with compound *I*; in the remaining cases, the excited state is more polar. Changes of π-dipole moments with disubstituted isopropylidene derivatives *VI*, *IX*, and *XII* are analogous to relative changes determined for dominant $\pi - \pi^*$ transitions in the case of the corresponding disubstituted fuchsone derivatives[24].

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