SOLVATOCHROMIC STUDY OF INTERNAL CHARGE TRANSFER IN 7,7-DISUBSTITUTED QUINONE METHIDES*

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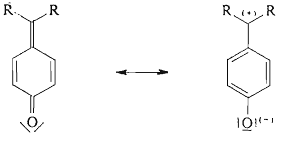
Electronic spectra of 7,7-disubstituted quinone methides *I*—*III* with substituents of various electronegativities were measured in thirteen solvents. Character of the long-wavelength transition was investigated by correlation between transition energy and ionization potential of the donor part of the molecule as well as by comparison of transition moment with $\Delta\mu$. The long wavelength absorption band of *Ia*—*Id*, *IIa* and *IV* does not correspond to a pure ($\pi-\pi^*$) transition, but it is perturbed by intramolecular charge transfer.

The chromophoric system of quinone methides is characterized by the presence of a carbonyl group (electron acceptor A), coupled by a cross-conjugated system of double bonds (C) with a group R which can be either an electron donor (D) or acceptor (A). By analogy with benzenoid compounds, the electronic state of quinone methides can be described[1,2], in the first approximation, by a resonance between nonpolar and polar structures (*e.g.* *N* and *P*), or by the total



N *P*

wavefunction

$$\psi_i = c_{iN}\psi_N + c_{iP}\psi_P \,, \qquad (1)$$

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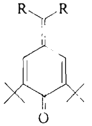
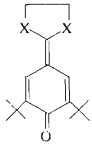
where i denotes the electronic state of the molecule. Weighted population of the nonpolar and polar structures is given by the ratio of coefficients c_{iN}/c_{iP}. This ratio depends first of all on the difference between electronegativities of the groups R and A. In the electronic ground state ($i = g$), for nonpolar compounds (electronegativity of R $\approx$ electronegativity of A) $|c_{gN}| < |c_{gP}|$ and, on the contrary, for strongly polar compounds $|c_{gN}| < |c_{gP}|$.

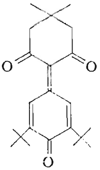
From the series of more than seventy quinone methides, prepared by us so far, we selected eight compounds for the study of properties related to charge transfer. These derivatives represented mainly the A–C–D system, *i.e.* they contain strong electron donors in the position 7,7; for illustration we included also some electron acceptors, *i.e.* compounds of the A–C–A type. The selection of models *I*, *II* and *III* was dictated, first of all, by instability of the simplest compounds (*i.e.* compounds containing no tert-butyl group in the molecule) and also by the necessity to conserve the approximate C_{2v} symmetry (collinearity of dipole moments in the ground and excited states ($\mu_g \parallel \mu_e$) throughout the whole series.



Ia; R = NC_5H_{10}
Ib; R = CH_3
Ic; R = C_6H_5
Id; R = Cl
Ie; R = CN



IIa; X = S
IIb; X = SO_2



III

In this communication we try to investigate the effect of electronegativity of the group R in quinone methides *I*, *II* and *III* on the character of the long wavelength transition. The effect of internal charge transfer on the transition type is assessed by application of the existing criteria based on (*i*) a comparison of the transition moment with the difference between the dipole moments in ground and excited states[3], (*ii*) the relationship between the transition energy, $h\nu$, and the ionization potential, I_D, of the donor component[4].

EXPERIMENTAL

Quinone methides *I*–*III* were prepared by the reported procedures[5–12] and their physico-chemical constants were in agreement with published values.

The ground state dipole moments were determined in benzene solutions at 25°C by heterodyning (1·2 MHz). Usually five measurements were carried out, concentration range $5 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$ mol l^{-1}. The total polarization P_2^0 was calculated according to Halverstadt and Kum-

TABLE I

Effect of solvent on the first absorption maximum, $\tilde{\nu} \cdot 10^{-3}$ (cm^{-1}), of quinone methides *I*—*III*

Solvent	*Ia*	*Ib*	*Ic*	*Id*	*Ie*	*IIa*	*IIb*	*III*
n-Hexane	23·52	31·43	27·28	21·23	29·60	25·22	30·80	29·32
Isooctane	23·45	31·60	27·35	31·22	29·60	25·30	30·70	29·28
Cyclohexane	23·50	31·40	27·10	31·07	29·50	25·15	30·60	29·20
Ether	23·85	31·48	27·10	31·19	29·65	24·90	30·80	29·51
Pentyl acetate	24·58	31·13	27·05	31·09	28·60	24·60	30·70	29·38
Butyl acetate	23·80	31·21	27·08	31·03	29·63	24·60	30·60	29·42
Ethyl acetate	24·00	31·20	27·10	31·10	29·65	24·58	30·70	29·44
Methyl acetate	24·20	31·15	26·95	31·08	29·75	24·48	30·72	29·44
Tetrahydrofuran	23·82	30·80	26·70	30·98	28·50	24·40	30·58	29·40
Dichloroethane	24·00	30·70	26·58	30·86	29·40	24·25	30·55	29·31
Dimethylformamide	24·30	30·52	26·68	30·51	29·50	23·80	30·52	29·38
Acetonitrile	24·58	30·90	26·90	31·00	29·73	24·08	30·80	29·58
Dimethyl sulfoxide	24·40	30·28	26·30	30·43	29·40	24·75	30·52	29·30

TABLE II

Transition moments, μ_{ge}, and differences between dipole moments in ground and excited state, $\Delta\mu$, for compounds *Ia*—*Id* and *IIa*, in isooctane

Compound	ε_{max} l mol^{-1} cm^{-1}	$A_{pract} \cdot 10^{-7a}$ l mol^{-1} cm^{-2}	f^b	$\lvert\mu_{ge}\rvert \cdot 10^{30}$ Cm	$\lvert\Delta\mu\rvert \cdot 10^{30}$ Cm
Ia	35 481	10·950	0·473	19·61	3·60
Ib	28 183	9·594	0·514	18·87	7·23
Ic	25 703	10·394	0·466	18·07	7·37
Id	27 955	8·329	0·359	14·84	7·40
IIa	39 287	7·525^c	0·325	15·74	5·17

[a] In calculation of integrated intensity the Gaussian profile was considered and the value of the integral was substituted by the practical intensity ,A_{pract}^{28}. [b] The oscillator strength was calculated[4,21] from the relationship $f_{exp} = 4\cdot32 \cdot 10^{-9} S. \int \varepsilon d\tilde{\nu}$ where S is the correction for solvent effect: $S = 9n/(n^2 + 2)^2$; [c] because the spectrum of *IIa* contains two overlapping bands, the value of $\Delta\tilde{\nu}_{1/2}$ of the first intensive absorption band was taken into account after the graphical separation.

ler[13] from the slopes α and β of the correlations of ε_{12} *vs* w_2 or d_{12}^{-1} *vs* w_2. In final calculations of μ_g the 5% correction was taken for the atomic polarization (Table I).

Dipole moments in the first excited state were determined by the method of solvent induced shifts in absorption spectra[14]. Electronic spectra were recorded on Specord UV-VIS (Zeiss, Jena) spectrophotometer in the following solvents: n-hexane, isooctane, cyclohexane, ether, pentyl acetate, butyl acetate, ethyl acetate, tetrahydrofuran, dichloroethane, dimethylformamide, acetonitrile and dimethyl sulfoxide. Wavenumbers of the first absorption maximum in these solvents are given in Table I, the molar absorption coefficients in isooctane in Table II. The data were processed on a Hewlett–Packard 9830 calculator using the multiple regression program (Hewlett–Packard Statistic Pac No 2). The cavity radius was determined by the method of apparent molal volumes[15]. The statistic data, a_0 values and dipole moments μ_e are listed in Table III.

RESULTS AND DISCUSSION

The intramolecular charge transfer CT transition is defined as an electron transition from the occupied molecular orbital, localized in one part of a conjugated system,

TABLE III

Statistics of the relationship (*3*) and dipole moments in the excited state of quinone methides *I*—*III*

Compound	E^a	K^b	L^b	M^b	$a_0 \cdot 10^{8c}$ [cm]	$\mu_e \cdot 10^{30}$ [Cm]
Ia	0·957	1 120 (106)	−2 134 (1 277)	24 007 (338)	4·70	32·38
Ib	0·977	−972 (88)	−7 418 (1 058)	33 499 (280)	4·68	22·41
Ic	0·967	−690 (81)	−6 361 (970)	28 953 (156)	5·23	22·18
Id	0·951	−494 (81)	−5 909 (972)	32 799 (257)	4·64	14·77
Ie	0·933	27 (42)	−4 091 (503)	30 666 (133)	4·69	7·67
IIa	0·989	−1 462 (68)	−4 697 (829)	26 483 (221)	4·08^d	26·38
IIb	0·920	−57 (47)	−3 462 (569)	31 619 (150)	4·65	10·20
III	0·940	217 (39)	−3 695 (478)	30 270 (126)	5·15	13·74

[a] Correlation coefficient of the double regression; [b] regression coefficients of the relationship (*3*) and their standard deviations (in parentheses); [c] a_0 calculated from apparent molal volumes[15]; [d] the value of a_0 was determined by the increment method which afford about 10% lower results as compared with the method of apparent molal volumes.

into a virtual orbital, localized in another part of the molecule[16-18]. Since spectra of most of the studied quinone methides exhibit an isolated structureless band in the long wavelength region we could approach a verification of its intramolecular character.

The often cited[3,19,20] relationship, used for classification of a charge transfer transition, is based on a close similarity of the absolute value of the transition moment to the difference between the ground and excited state dipole moments $|\mu_{ge}| \approx |\Delta\mu|$. Although this criterion possesses a certain physical substantiation, based on the assumption that the transition dipole moment μ_{ge} serves as a measure of the dynamics of the electronic process in the excitation, the result of which is the π-electron delocalization expressed by the difference $\Delta\mu$, its applicability cannot be overestimated. Particularly, we have to take with some caution the dipole moments obtained using this relation[3]. There are several reasons for this scepticism. Apart from the fact that the separation of spectral bands is usually very difficult and more or less only approximates the actual band shape, the situation is significantly complicated by inconsistency of the basic relationship[4,19-21] for oscillator strength calculation. For this reason we used the mentioned relationship only as a crude criterion for elimination of compounds exhibiting marked differences in the series under study.

The ground state dipole moments were determined by the usual technique and are listed, together with other polarization data, in Table IV. The μ_g value for 4-methylidene-2,6-ditert-butylcyclohexadien-1-one (*IV*) was determined using the value

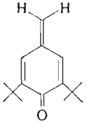
TABLE IV

Dipole moments (μ_g) of quinone methides *I*—*III* in benzene at 25°C

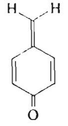
Compound	α^a	β^a	P_2^0 [cm^3]	$\mu_g \cdot 10^{30\,b}$ [Cm]
Ia	34·70	−0·465	2 503·16	35·99
Ib	9·30	−0·092	507·75	15·34
Ic	6·03	−0·167	527·67	14·81
Id	1·29	−0·235	147·43	7·37
Ie	2·44	−0·146	202·93	8·07
IIa	—	—	—	21·21^c
IIb	2·70	−0·464	264·51	9·54
III	6·49	−0·147	519·20	15·84

[a] Slopes of the Halverstadt–Kumler relationship[13]; [b] corrected, for the atomic polarization (5%) of the value of molar refraction, [c] ref.[10].

calculated (MINDO/3)[22] for 4-methylidenecyclohexadien-1-one (*V*) ($15{\cdot}34 \,.\, 10^{-30}$ Cm). After a correction for the contribution of tert-butyl groups[23] the dipole moment of the compound *IV* amounts to $(15{\cdot}34 - 3{\cdot}93) \,.\, 10^{-30} = 11{\cdot}41 \,.\, 10^{-30}$ Cm.



IV



V

In view of the close relation between the π-electron delocalization in the molecule and the ground state dipole moment it was of interest to appreciate the extent to which the μ_g value depends on the electronic effect of 7,7-substituents. The relationship between the dipole moment change and substitution parameters is best described by correlation[24] with σ_p^+ substituent constant [25], which include the inductive and mesomeric substituent effect as well as the direct polar conjugation effect. The linear relationship is expressed by the equation (*2*).

$$\mu_g = [(-7{\cdot}55 \pm 1{\cdot}2)\,\sigma_p^+ + 10{\cdot}94] \,.\, 10^{-30} \qquad (2)$$

$$(r = 0{\cdot}993;\ n = 6)$$

The substituents in compounds *Ie,IIb* and *III* do not fit the correlation and are not included. The very good correlation of these six compounds can be ascribed to the fact that the distance between the localized charges in the idealized dipole $d(\text{O—C}_{(7)})$ is constant and the internal dipole of substituent has no marked effect on the correlation. On the other hand, the failure of compounds *Ie, IIb* and *III* to fit the correlation can be caused by many factors, including the marked effect of the internal dipole of the substituent, variability of the distance *d*, and direction of the dipole. Formation of complexes in benzene during the dielectric measurements can not be exluded as well.

The first excited state dipole moments were determined by the method of solvent induced shifts in absorption spectra[14], as modified by Bilot, Kawski[14] and Bakhshiev[26] (for spherical molecule and by approximating the mean polarizability by the expression $\alpha = a_0^3/2$). The recent statistical check[27] of solvatochromic methods of calculation of μ_e has shown optimum results with this modification. If we know the dipole moment μ_g and are capable of estimating the cavity radius a_0, we can calculate the value of μ_e from the slope K (equations (*3*) and (*4*)).

$$\tilde{\nu} = -2\mu_g(\mu_e - \mu_g)/hca_0^3 \,.\, (2n^2 + 1)/(n^2 + 2)\,[(\varepsilon - 1)/(\varepsilon + 2) - \\ - (n^2 - 1)/(n^2 + 2)] - (\mu_e^2 - \mu_g^2)/hca_0^3 \,.\, (n^4 - 1)/(n^2 + 2)^2 + M \qquad (3)$$

$$K = -2\mu_g(\mu_e - \mu_g)/hca_0^3 \qquad (4)$$

The solvent shifts for quinone methides *I*–*III* are given in Table I, while the statistical evaluation of equation (*3*), the a_0 values and the dipole moments μ_e calculated from the slope K (equation (*4*)), are listed in Table III.

The transition moment, μ_{ge}, is expressed by the relation[4]

$$\mu_{ge} = \sqrt{(f)}/4{\cdot}704 \,.\, 10^{-6}\tilde{\nu}_{max}\,, \qquad (5)$$

where f is the oscillator strength which is proportional to the integrated intensity of the absorption band. The transition moments μ_{ge}, extinction coefficients ε, integrated intensities $A_{pract.}$, and oscillator strengths f are given in Table II.

Comparison of the relationships between μ_{ge} and $\Delta\mu$ for compounds *Ib*–*Id* and *IIa* with that for *Ia* reveals a certain correspondence, particularly, if we realize that the compound *Ia* having strong electron donors at $C_{(7)}$ can be regarded as an intramolecular charge transfer complex (iCT) which is depolarized by excitation. This assumption is confirmed by the marked negative solvatochromism (the positive slope K, Table III) and the lower dipole moment in the excited state (Tables II and IV). It is obvious from the slopes K and their standard deviations (Table III) that the compounds *Ie*, *IIb* and *III* do not exhibit any significant solvatochromism in the solvents employed and this is also reflected in the low $\Delta\mu$ values (Table II). Thus, it is confirmed that in compounds *Ie* and *IIb* the nonpolar form N predominates because of the strong electron acceptor character of substituents. In compound *III* some interference of the ($n - \pi^*$) and ($\pi - \pi^*$) transitions of conjugated carbonyl groups cannot be excluded.

For weak CT interactions the transition energy is a function of ionization potential of the donor and of the electron affinity of the acceptor. The use of a simple perturbation theory[4] and application of the relationships to systems with variable donors and constant acceptors led to the simplified equation

$$h\nu_{CT} = \gamma I_D - C_1 + \frac{C_2}{I_D - C_1}\,, \qquad (6)$$

where C_1 and C_2 are constants for the given acceptor. The same reasoning was applied for *iCT* complexes[3]. Since ionization potentials of the donors in the studied series range in the narrow region 8·0–13·6 eV, it was possible to substitute, in the

TABLE V

Energy of the intensive long wavelength transitions and ionization potentials of the donor components (in neutral form) of quinone methides *Ia*—*Id*, *IIa* and *IV*

Compound	*Ia*	*Ib*	*Ic*	*Id*	*IIa*	*IV*
$h\nu$ [eV]	2·91	3·88	3·37	3·85	3·09	4·26
$I_D{}^a$, [eV]	8·01	12·99	9·24	12·74	9·44	13·60

[a] Ref.[30].

TABLE VI

Comparison of charge transfer in 7,7-disubstituted quinone methides (in thirteen solvents) with substituted tetracyanoquinodimethanes and 2-(arylmethylene)-1,3-indanones

γ^a	δ^a	r^b	Solvent
			Substituted tetracyanoquinodimethanes
0·51	1·79	—	acetonitrile
			2-(Arylmethylene)-1,3-indanones
0·59	1·84	—	chloroform
			7,7-Disubstituted quinone methides[c]
0·190	1·44	0·961	n-hexane
0·190	1·43	0·967	isooctane
0·190	1·43	0·971	cyclohexane
0·186	1·46	0·961	ether
0·171	1·63	0·951	pentyl acetate
0·184	1·46	0·960	butyl acetate
0·181	1·50	0·951	ethyl acetate
0·180	1·52	0·954	methyl acetate
0·180	1·47	0·959	tetrahydrofuran
0·171	1·50	0·957	dichloroethane
0·167	1·59	0·935	dimethylformamide
0·173	1·59	0·935	acetonitrile
0·164	1·61	0·934	dimethyl sulfoxide

[a] Coefficients of the relationship (7); [b] correlation coefficient of the single regression (7); [c] the compound *IV* was excluded from the correlation because of lack of the necessary data.

interval investigated, the nonlinear equation (*6*) by the linear approximation

$$h\nu_{\mathrm{iCT}} = \gamma I_{\mathrm{D}} - \delta \,, \qquad (7)$$

where ν_{iCT} is the frequency of the absorption *iCT* band (Hz), I_{D} is the ionization potential of the donor part of the molecule (eV) (considered in the neutral form), and the constants γ and δ relate to the properties of the invariable acceptor part. The ν values (Table V) were calculated from the wavenumbers $\tilde{\nu}_{\mathrm{max}}$ (isooctane) of the bands under study. The single correlation shows that all the compounds considered (*Ia*–*Id*, *IIa* and *IV*) obey the relationship (*7*) (for isooctane $r = 0{\cdot}967$,, $\gamma = 0{\cdot}19$, $\delta = 1{\cdot}43$). According to the MO description of CT transition[29] the slope γ indicates the charge transferred in the complex. The lower the slope value, the greater the charge transfer. In accord with this conclusion the values of γ for 7,7-disubstituted quinone methides indicate larger transfer of charge when compared with γ values for other two series of iCT complexes (Table VI) studied by other authors[3,31]. When comparing the results it is necessary to consider also the solvation energy which, particularly in more polar solvents, affects the polarity of the complex, increasing thus the charge transfer, *i.e.* lowering the slope (Table VI). Correlations of the slopes (obtained for thirteen solvents) with the solvent functions $F_2(\varepsilon, n)$ and $F_1(n)$[27] provide unequivocal information. The equation $\gamma = -(2{\cdot}48 \,.\, 10^{-2} \pm 1{\cdot}8 \,.\, 10^{-3})\, F_2(\varepsilon, n) - (1{\cdot}06 \,.\, 10^{-1} \pm 2{\cdot}15 \,.\, 10^{-2})\, F_1(n) + (2{\cdot}19 \,.\, 10^{-1} \pm 5{\cdot}6 \,.\, 10^{-3})$, ($r = 0{\cdot}983$, $n = 13$) enables to asses the magnitude of the effect of solvation energy on the intramolecular charge transfer in quinonoid iCT complexes and, moreover, knowledge of the solvent functions $F_2(\varepsilon, n)$, $F_1(n)$ and the slope γ in one molecule, makes it possible to predict the effect of solvent on the charge transfer.

REFERENCES

1. Flurry R. L. jr: J. Phys. Chem. *69*, 1927 (1965).
2. Liptay W.: Z. Naturforsch. *20a*, 272 (1965).
3. Pankratov A. A., Bespalov B. P., Lisjutenko V. N., Germanova E. V.: Opt. Spektrosk. *41*, 983 (1976).
4. Foster R.: *Organic Charge-Transfer Complexes*. Academic Press, New York 1969.
5. Pavlíčková L., Vašičková S., Souček M.: This Journal *45*, 2675 (1980).
6. Cook C. D., Norcross B. E.: J. Amer. Chem. Soc. *78*, 3797 (1965).
7. Becker H.-D.: J. Org. Chem. *32*, 2115 (1967).
8. Lyčka A., Šnobl D., Koutek B., Pavlíčková L., Souček M.: This Journal, *46*, 2083 (1981).
9. Rieker A.: Chem. Ber. *103*, 656 (1970).
10. Gompper R., Schmidt R. R., Kutter R.: Justus Liebigs Ann. Chem. *684*, 37 (1965).
11. Gompper R., Kutter R., Schmidt R. R.: Chem. Ber. *98*, 1374 (1965).
12. Pavlíčková L., Souček M.: Unpublished results.
13. Halverstadt I. F., Kumler W. D.: J. Amer. Chem. Soc. *64*, 2988 (1942).
14. Bilot L., Kawski A.: Z. Naturforsch. *17a*, 621 (1962).
15. Jolicoeur C., Boileau J.: Can. J. Chem. *56*, 2707 (1978).

16. Freimanis J.: *Progress and Some Prospect in Charge-Transfer Complex Chemistry*. Wroclaw Technical University, Wroclaw 1978.
17. Nakagura S., Tanaka J.: J. Chem. Phys. *22*, 236 (1954).
18. Aihara J., Kushibiki G., Matsunaga Y.: Bull. Chem. Soc. Jap. *46*, 3584 (1973).
19. Bakhshiev N. G.: *Spektroskopyia Mezhmolekulyarnykh Vzaimodeistvii*, p. 76. Nauka, Leningrad 1972.
20. Saidov G. V., Bakhshiev N. G.: Dokl. Akad. Nauk *175*, 1090 (1967).
21. Rabinowicz A.: Rep. Prog. Phys. *7*, 14 (1939).
22. Dits H., Nibbering N. M. M., Verhoeven J. W.: Chem. Phys. Lett. *51*, 95 (1977).
23. Koutek B., Píšová M., Souček M., Exner O.: This Journal *41*, 1676 (1976).
24. Exner O.: This Journal *25*, 642 (1960).
25. Perjéssy A.: Tetrahedron *29*, 3189 (1973).
26. Bakhshiev N. G.: Opt. Spektrosk. *13*, 192 (1962).
27. Koutek B.: This Journal *43*, 2368 (1978).
28. Horák M., Vítek A.: *Interpretation and Processing of Vibrational Spectra.* Interscience, New York 1978.
29. Flurry R. L. jr: J. Phys. Chem. *73*, 2111 (1969).
30. Vilesov F. I.: Usp. Fiz. Nauk *81*, 669 (1963).
31. Chiba K., Aihara J., Araya K., Matsunaga Y.: Bull. Chem. Soc. Jap. *53*, 1703 (1980).

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