CNDO/S MO STUDY OF THE FUCHSONE DERIVATIVES WITH STERICALLY CROWDED EXOCYCLIC DOUBLE BOND*

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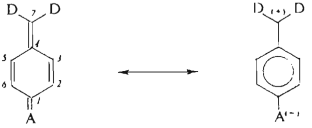
Received January 26th, 1981

The electronic absorption spectra of 2-methyl-, 3-methyl-, 2,6-dimethyl-, 3,5-dimethyl- and 2,3,5,6-tetramethylfuchsone were investigated. The interpretation was carried out by comparing the spectra with those of the suitable model compounds and by quantum chemical (CNDO/S) analysis of the chromophoric systems of 4-benzhydrylidene-, 4-benzylidene- and 4-(9-fluorenylidene)-2,5-cyclohexadien-1-one. Within this approach also the effects were investigated of torsion and distortion of the double bond on spectral parameters of ethylenic chromophore. The knowledge thus obtained allowed us to suggest a plausible mechanism of the response of fuchsone derivatives to steric crowding of the exocyclic double bond region and to explain in a reasonable way the anomalous bathochromic shift and hypochromic effect exhibited by the long wavelength UV absorption band of 3,5-dimethyl- and 2,3,5,6-tetramethylfuchsone. The suggested interpretation corresponds well also with trends of half-wave potentials of these compounds.

Within our investigations on quinone methides we paid attention to systems stabilized by two phenyl groups at the exocyclic $C_{(7)}$ carbon atom. These compounds, known from the very beginning of this century[1], constitute a large class of fuchsones. The increased π-system stability of fuchsones can be attributed, on the basis of physico-chemical studies[2], to "push-pull" effects between donor and acceptor parts of the molecule. Within the framework of Valence Bond Theory these effects can be regarded as an equilibrium between the zwitterionic *Z* form and the non-polar *N* form.



N *Z*

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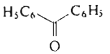
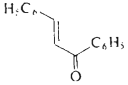
[*] Part XXIX in the series Quinone Methides and Fuchsones; Part XXVIII: This Journal *48*, 2376 (1983).

As a consequence of the resonance interactions the long wavelength band of fuchsone chromophore is shifted bathochromically by 7 500 cm^{-1} when compared with the chromophoric system of 4-methylene-2,5-cyclohexadien-1-one. The investigation of electronic absorption spectra of 2,6-disubstituted fuchsones revealed[3] that the shift is controlled mainly by the inductive effect of substituents. The steric effect, causing interestingly a red shift, applies to a lesser extent. Recently, this effect started to attract a considerable attention. Synthesis and properties of sterically crowded organic molecules were summarized in a review article[4]. In last years, sterically crowded ethylenes have been thoroughly investigated with the particular interest applied to electronic spectra[5], dynamic stereochemical behaviour[6,7], thermochromic[8] and chiroptical[9,10] properties. The 3,5-disubstituted derivatives seem to be rather attractive substrates with respect to the possibility of steric crowding in the region of exocyclic fuchsone double bond. The research of the effect of steric crowding on absorption spectra of fuchsone derivatives requires a detailed knowledge of spectroscopic properties of the non-perturbed chromophore. However, there is still no quantum chemical study of fuchsones and, similarly, no attention has been paid to related topological and conformational effects.



I



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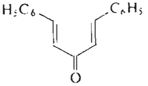

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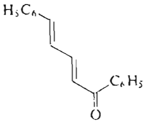

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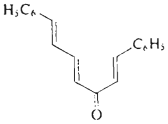

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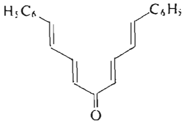
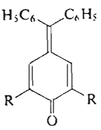
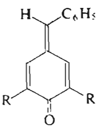


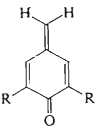
VI



VIIa; R = H
VIIb; R = t-C$_4$H$_9$



VIIIa: R = H
VIIIb; R = t-C$_4$H$_9$



IXa; R = H
IXb: R = t-C$_4$H$_9$

In a previous paper we reported syntheses of several 3,5-disubstituted fuchsone derivatives[11] together with their characterization by UV spectra, ^{13}C NMR spectra and dipole moments related to ground state and first $^1\pi-\pi^*$ state. In the present study we pay attention to the nature of absorption spectra of cross-conjugated systems *I*–*VI* as compared with the spectrum of fuchsone (from the π-system topology viewpoint). The effect of phenyl group torsion is investigated on the basis of quantum chemical calculations and comparison of spectra of *VII*–*X*. We also evaluate the influence of number and location of methyl groups on spectral parameters of compounds *XI*–*XII*. Finally, the anomalous bathochromic shift and hypochromic effect exhibited by the long wavelength absorption band of compounds *XId*,*e* is analysed on the basis of CNDO/S calculations compared with the experimentally accessible photoelectron spectra and half-wave reduction potentials of the selected fuchsone derivatives *XIa-e*.

EXPERIMENTAL

The compounds *VII*–*XII* were prepared according to reported procedures[11–14]. Electronic absorption spectra were recorded on Specord UV-VIS (Carl Zeiss, Jena) spectrophotometer at 25°C (scan speed 151·5 $\text{cm}^{-1}\,\text{s}^{-1}$) in n-hexane and isooctane ($c = 1 - 5 \cdot 10^{-5}$ mol l^{-1}). Half-wave reduction potentials were measured in 0·1M tetrabutylammonium perchlorate solution using the instrumentation and experimental conditions as described in ref.[15]. Dimethylformamide was purified by shaking with molecular sieves and subsequent distillation in vacuo. He(I) Photoelectron spectra were measured in the gas phase with the aid of UVG 3 (VG Scientific, England) instrument equipped with a heated cell (temperature range 190–210°C). The spectra were calibrated using Ar lines.

Quantum chemical calculations were performed using the methods CNDO/2 (ref.[16]) and CNDO/S (ref.[17]). Standard parameter values and standard computer programs were used. Limited configuration interaction involving 54 singly excited configurations (9 highest occupied and 6 lowest virtual MOs) was utilized for the calculation of electronic absorption spectra. Numerical calculations were executed on IBM 370/135 (UTIA, ČSAV) computer. Spectral and polarographic curves were analysed on Hewlett-Packard 9830 calculator. All graphs were drawn using H-P 9871A digital $x-y$ plotter.

RESULTS AND DISCUSSION

Effect of Topology of the π-Electron System on the Positions of Absorption Maxima

Firstly, let us examine the positions of long wavelength absorption maxima in electronic spectra of compounds *I*–*VII* (Table I). The π-electron systems of reference compounds *I*–*VI*, fulfil, in the rigorous way, the conditions imposed by a definition of the cross-conjugated system[18]. The analysis of electronic spectra of benzophenone (*I*) and its vinylogues *II*–*VI* revealed that the particular absorption bands can be identified with the transitions localized in the molecular fragments which are formed by breaking the bonds to the carbonyl carbon atom. The interaction of both fragments is weak and causes a red shift of about 2 440 – 4 460 cm^{-1} in the case of the long wavelength band. Generalization of these observations leads to a conclusion that the π-system extension achieved by cross-conjugation does not cause marked bathochromic shifts of absorption bands. On the other hand, remarkable hyperchromic effects can be observed especially with symmetric cross-conjugated skeletons.

On the contrary to planar system *I – VI* the spectroscopic behaviour of fuchsone and its derivatives is complicated by conformational effects. It follows from the recent X-Ray study of 2,6-dimethylfuchsone[20] that the diphenylmethylene fragment does not lie completely in the plane of the quinone nucleus. The deviation of phenyl groups from this plane minimizes the supposed steric interactions while decreasing simultaneously the resonance with the rest of the molecule. The consequences of this decrease can be estimated from the compared positions of long wavelength absorption maxima of compounds *VIIb – IXb*. The shifts of band maxima of compounds *VIIb* and *VIIIb* with respect to *IXb* amount to 7 190 and 5 685 cm^{-1}. These shift values together with the proved additivity of substitution effect in quinone methide spectra[14] give evidence of two facts. The single phenyl group exhibits a rather strong interaction with quinone methide skeleton in accord with the suggested equilibrium *VIIIa*, *VIIIb*, *VIIIc*. On the other hand, the introduction of two phenyl groups does not result in the theoretically calculated shift value of 10 370 cm^{-1}. The difference of 3 200 cm^{-1} is connected with the loss of resonance energy as a consequence of the supposed non-planar conformation of the molecule. We can obtain

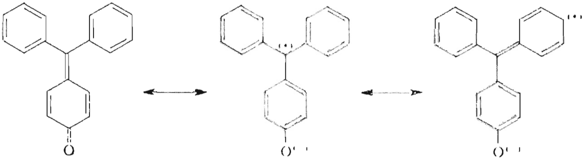
TABLE I

Positions (cm^{-1}) and intensities ($\varepsilon_{max} \cdot 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$) of bands in electronic absorption spectra of systems *I – VII*

I[a]	*II*[a]	*III*[a]	*IV*[a]	*V*[a]	*VI*[a]	*VII*[b]
40 323	33 557	31 546	30 303	29 498	28 000	27 930
(19·6)	(24·7)	(37·0)	(41·2)	(44·0)	(51·0)	(31·6)
49 751	38 461	43 859	38 461	38 759	41 494	37 453
(30·1)	(7·0)	(16·6)	(8·9)	(10·8)	(10·0)	(15·4)
—	44 643	—	43 103	42 735	—	38 461
—	(12·6)	—	(10·9)	(16·6)	—	(15·9)
—	52·631	—	—	—	—	47 620
—	(32·8)	—	—	—	—	(14·0)

[a] Spectral parameters of compounds *I — VI* as taken from ref.[19]; [b] compound *VIIa* in n-hexane.

the cyclic compound *VIIa* by formal equalization of both the terminal double bonds of the system *VI*. Under such assumption both these chromophoric systems appear to be analogous. This is further supported by almost equal positions of the corresponding long wavelength absorption maxima (28 000 cm^{-1}, resp. 27 930 cm^{-1}).



VIIIa *VIIIb* *VIIIc*

However, this situation further implies a relatively weak interaction between both branches of the quinonoid ring across the $C_{(4)}$ carbon atom. Simultaneously the gain in the resonance energy has to be compensated in the rotation of phenyl groups. Under these assumptions a red shift of 3 200 cm^{-1} corresponds to the π-interaction connected with a creation of the cyclic moiety *VII*. This value is comparable with the shift of 4 460 cm^{-1} which is ascribed to the interaction of both branches across the carbonyl carbon atom in the non-cyclic system *VI*. In other words, the π-electron system of the compound *VII* can be also classified as cross-conjugated and the compound itself can be included in the class of cyclic cross-conjugated compounds. It is worth mention that our findings are consistent with the analyses of ^{13}C NMR spectra of fuchsones and with the transmission of substituent effects across their skeletons[21].

Effect of Phenyl Group Conformation on Quinone Methide Chromophore

The detailed information related to the effect of phenyl group on the chromophoric system of *p*-quinone methide was obtained with the aid of semiempirical quantum chemical calculations. The results of the investigation of the influence of the phenyl group torsion on molecular energy and position (intensity) of the long wavelength absorption band are given in Figs 1 and 2. The energetically most advantageous conformation corresponds to a phenyl group deviation of about 8° and this finding can be ascribed to its steric interactions with the hydrogen atom in the position 3 of the quinone nucleus. However, the energy barrier separating the planar conformation is small (6·28 kJ mol^{-1}). The long wavelength transition energy decreases slightly with torsion increasing up to 10°, but any further increase of torsion is characterized by the progressive transition energy increase. On the other hand, the intensity of this transition decreases monotonously with increasing rotation of the phenyl group as follows from the calculated dependence of oscillator strength on conformation (Fig. 2). Since the electronic spectrum of compound *VIIIa* cannot be measured due to non-stability and high reactivity of the compound it is only possible to compare, in a semiquantitative way, the calculated data with the spectrum of compound *VIIIb*. According to our experience with this type of compounds[3,14] all the absorption bands of *VIIIb* should be slightly bathochromically shifted when compared with *VIIIa* and the maximal shift (about 600 cm^{-1}) should be exhibited by the long wavelength band. Calculation afforded the following transitions (experimental band positions of *VIIIb* are given in parentheses for comparison): 49 219 and 38 738 cm^{-1} (48 370 cm^{-1}), 44 699, 42 733, 40 572 and 40 141 cm^{-1} (42 000 and 40 832 cm^{-1}) and the long wavelength most intense transition at 29 044 cm^{-1} (28 880 cm^{-1}). The last mentioned transition is contributed by 97% of the HOMO-LUMO configuration and its transition moment vector is almost parallel to the orientation of the carbonyl group. Although the frontier orbitals of this molecule cannot be regarded as strictly localized in the different parts of the molecule the most significant contributions to HOMO orbital are represented by AOs of the phenyl group and the exocyclic double bond while the LUMO orbital is most significantly contributed by the AOs of the carbonyl group. The excitation is accompanied by a transfer of charge from the phenyl group to the carbonyl group. This process

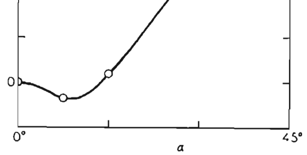


FIG. 1

Dependence of total energy of benzylidene derivative *VIIIa*, as calculated by the CNDO/2 method, on phenyl group conformation (planar conformation $a = 0°$)

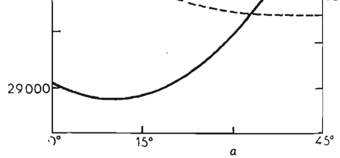


FIG. 2

Dependence of transition energy and oscillator strength of the long wavelength $\pi-\pi^*$ transition of compound *VIIIa*, as calculated by CNDO/S method, on phenyl group torsion corresponds to an increase of the dipole moment by 5 . 10^{-30} Cm in the first excited state. In addition a symmetry forbidden transition has been calculated in the long wavelength part of the spectrum (at 22 596 cm^{-1}) which is contributed by 69% of the $n-\pi^*$ type configuration. However, no such transition was detected in the spectrum of compound *VIIb*.

Introduction of a second phenyl group on the exocyclic carbon atom implies a significant steric hindrance. In order to get some insight we performed CNDO/2 calculations of the two model structures *A* and *B* in which the steric crowding within the diphenylmethane fragment is minimized in two different ways. One phenyl group of the structure *A* deviates by 60° while the second one remains in the molecular plane. In the model compound *B* both phenyl groups are deviated by 30°. Regarding the electronic energy the model *B* is strongly destabilized when compared with *A*. However, according to total energy of the system the model *B* is prefered by 75·82 kJ . . mol^{-1}. This preference of the symmetric structure *B* is in agreement with the result of X-Ray analysis of 2,6-dimethylfuchsone[20]. The computed dipole moment (19·5 . . 10^{-30} Cm) exhibits satisfactory agreement with experimental value (18·7 . 10^{-30} Cm including 5% atomic polarization correction)[2]. The computed spectral parameters of the structure *B* are compared with the electronic absorption spectrum of *VIIa* in Fig. 3 (empirical formula $\log \varepsilon = \log f + 4$ has been used in order to convert values of oscillator strengths to the corresponding molar absorption coefficients). The computed spectrum describes this real situation quite well, particularly with respect to the long wavelength absorption band which is often used for characterization of these compounds[22]. In analogy with *VIIIa* the transition is rather intense ($f = 1{\cdot}21$) and consists mainly of the HOMO-LUMO configuration (90%). It can be classified as ${}^1A_1 - {}^1A_1$ transition provided that the torsion of phenyl groups is con-

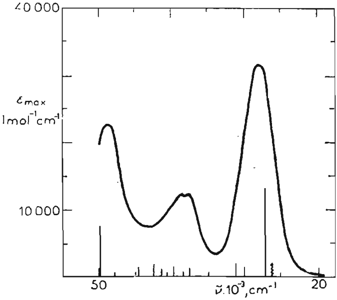
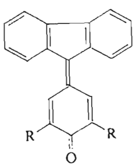


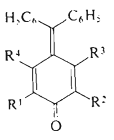
FIG. 3

Comparison of calculated transitions with experimental absorption curve of fuchsone (⇝ denotes $n-\pi^*$ transition) sidered as relatively weak perturbation of the parent quinone methide chromophore. The transition moment vector is oriented along the carbonyl group direction. Like in the case of *VIIIa* the transition exhibits partial intramolecular charge transfer character. This finding is supported by the observed trends of μ_g and μ_e values in the series of fuchsone dimethylderivative[11]. Moreover, the significant charge transfer contribution to this transition has been also proved in 2,6-ditert-butylfuchsone[23]. An additional transition exhibiting strong mixing of configurations has been calculated in the long wavelength maximum region (at 26 634 cm^{-1}). This transition is contributed by $2-1'(n-\pi^*$, 30%), $3-1'(n-\pi^*$, 38%) and $4-1'$ ($\pi-\pi^*$, 13%) configurations. It is clear from the oscillator strength value ($f = 0{\cdot}074$) that the transition is not strictly forbidden probably as a consequence of a coupling of contributing configurations. Another plausible explanation operates with a possibility to excite n-electrons from the oxygen atom into the antibonding orbital of the quinone methide nucleus. This process corresponds to a weakly allowed transition according to symmetry considerations. In accord with these calculations a small shoulder was observed inside the region of the long wavelength branch of the lowest energy transition when the measurement was performed in non-polar solvent at a concentration of about 10^{-2} mol l^{-1}.

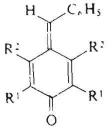
Regarding the above problems it appeared useful to investigate spectra of a model system having strictly planar fuchsone chromophore. It seems straightforward to utilize the fluorene derivative *X*. However, this model suffers the following shortcomings: *i*) a perturbation by compression of the bond angle on the sp^2 hybridized exocyclic carbon atom which corresponds to interconnection of phenyl groups by the five membered ring; *ii*) the resonance interaction between both the phenyl groups inside the fluorene fragment. The first drawback appears to be not very serious especially when X-Ray analyses of 2,6-dibromofuchsone[24] and 2,6-dimethylfuchsone[20] are taken into consideration. In these compounds markedly diminished values of the given bond angle were observed (115·0° and 116·2°) in comparison to the idealized



Xa; R = H
Xb; R = CH_3



XIa; $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$
XIb; $R^3 = CH_3$, $R^1 = R^2 = R^4 = H$
XIc; $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$
XId; $R^1 = R^2 = H$, $R^3 = R^4 = CH_3$
XIe; $R^1 = R^2 = R^3 = R^4 = CH_3$



XIIa; $R^1 = CH_3$, $R^2 = H$
XIIb; $R^1 = H$, $R^2 = CH_3$

value of 120°. The second problem seems more important since it offers a principal possibility of contaminating the investigated spectral region with other undesirable transitions. In order to exclude such a possibility we compared the spectrum of *Xb* with the quantum chemical calculation of the parent chromophore *Xa* (Fig. 4). The overall shape of the absorption curve is reproduced with a similar accuracy as in the case of fuchsone. Three transitions were calculated within the region of the long wavelength band. The first of them (at 25 160 cm^{-1}) is contributed by 95% of the $2-1'$ excitation. The transition is transversally polarized with respect to C_2 symmetry axis and consists of the excitation of the electron localized exclusively in the fluorene fragment into the delocalized LUMO orbital. The dipole moment markedly increases upon excitation ($\Delta\mu_{e-g} = 34{\cdot}9\ .\ 10^{-30}$ Cm). A similar drastic dipole moment change associated with a transition transversally polarized with respect to C_2 axis has been observed with substituted diphenylcalicenes[25]. However, the above transition is of low intensity ($f = 0{\cdot}007$) and cannot substantially influence parameters of the closely located band calculated at 25 176 cm^{-1}. The latter transition exhibits features coinciding with those of the characteristic absorption bands of quinone methides and fuchsones. Again it is a rather intense ($f = 1{\cdot}283$) almost configurationally pure transition (97% of the HOMO-LUMO configuration). The transition moment vector is collinear with C_2 axis. The change of dipole moment upon excitation is very small ($\Delta\mu_{e-g}$ $0{\cdot}33\ .\ 10^{-30}$ Cm) in agreement with the trends observed previously with the related compounds *Xb*, *XIc*. It has been deduced from solvatochromic study[11] that the $\Delta\mu_{e-g}$ value of *Xb* approaches approximately one third of that of *XIc*. The band position calculated for *Xb* by empirical summation of contributions[14] amounts to 24 117 cm^{-1} while the experimental value is 23 616 cm^{-1}. The difference of about 500 cm^{-1} can be ascribed to resonance type interactions between both "planar" phenyl groups. The third strictly forbidden transition is cal-

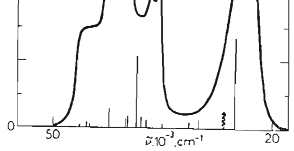


FIG. 4

Comparison of calculated transitions with experimental absorption curve of fluorenylidene derivative *Xb* ($\rightsquigarrow$ denotes $n-\pi^*$ transition) culated at 26 459 cm^{-1} and consists of 80·9% of the $n-\pi^*$ configuration. Thus the discussion pertaining to this section can be concluded in such a way that the torsion of phenyl groups around single bonds is associated with a substantial hypsochromic shift and hypochromic effect in accord with general experience[26].

Substituent Effect of Methyl Groups Attached to Quinone Nucleus

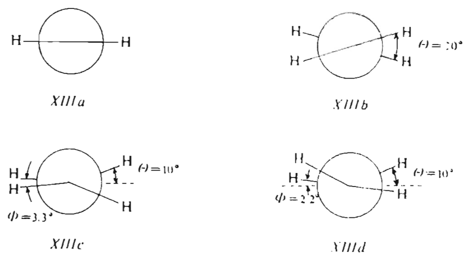
The aim of this part of our study is to investigate the effect of number and location of methyl groups on the long wavelength absorption band. The necessary spectral parameters of a set of selected compounds are given in Table II. The compounds can be approximately classified into two categories. The first of them comprises compounds which, when compared with the reference compound, exhibit simultaneous hypsochromic shift and hypochromic effect. In these cases the observed spectroscopic phenomena can be unambiguously explained as a consequence of phenyl group deviation from the plane of the quinone methide nucleus. This explanation applies both to the blue shift of 3,5-disubstituted benzylidene derivative *XIIb* and the almost negligible response of the 3-monosubstituted derivative *XIb*. However, it seems more probable for the latter compound that the observed phenomenon results from the approximate compensation of two effects involving: *i*) a blue shift induced by steric hindrance preventing conjugation between diphenylmethylene fragment and quinone nucleus; *ii*) a red shift caused by electron-donating effect of methyl groups which are more effective in the positions 3 and 5 than in the positions 2 and 6. The supposed slightly higher bathochromic shift caused by 3,5-di-

TABLE II

Spectral parameters of the long wavelength absorption band of compounds *VII*—*XII*

Compound	*VIIa*	*VIIb*	*VIIIb*	*IXb*	*Xb*	*XIa*
Band position[a], cm^{-1}	27 894	27 293	28 877	34 483	23 616	27 720
$\varepsilon_{max} \cdot 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$	31·5	25·7	31·94	[b]	36·77	28·84
Compound	*XIb*	*XIc*	*XId*	*XIe*	*XIIa*	*XIIb*
Band position[a], cm^{-1}	27 640	27 560	26 000	24 928	27 040[c]	28 976[c]
$\varepsilon_{max} \cdot 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$	25·55	30·63	16·26	12·64	[b]	[b]

[a] In iso-octane; [b] not measured; [c] measured in 0·02M-NaOH in acetonitrile.



SCHEME 1

substitution is consistent with results of the SCF PPP study of the corresponding pair of *p*-quinone methides[27]. The transition energy of 3,5-dimethyl derivative is lowered by 460 cm^{-1}. The second category involves compounds *XId*,e in the spectra of which the substitution causes a marked band intensity decrease accompanied by anomalous red shift. In this case, the steric crowding cannot be supressed by rotation of phenyl groups and, probably, other mechanisms will be operating. We tried to get some more detailed insight into these mechanisms with the use of quantum chemical calculations on the ethylenic chromophore possessing various geometric perturbations. Four basic geometric arrangements (Scheme 1) were investigated starting with optimized geometries (ref.[28]). The results of CNDO/S and CNDO/2

TABLE III

Quantum chemical parameters of systems *XIIIa*–*XIIId*

Parameter	*XIIIa*	*XIIIb*	*XIIIc*	*XIIId*
E, kJ mol^{-1} (*ab initio*)[a]	0·0	29·72	10·47	12·56
E, kJ mol^{-1} (CNDO)[a,b]	0·0	28·50	11·87	14·09
ε(HOMO) eV	−10·9248	−10·5128	−10·9028	−10·8784
ε(LUMO) eV	0·2850	0·2647	0·2067	0·1826
$E(\pi-\pi^*)$ cm^{-1}	52 020·0	45 700·0	50 620·0	49 040·0
Oscillator strength, f	0·4432	0·2579	0·3894	0·3401
Q_c, a.u.	−0·0225	−0·0242	−0·0203	−0·0236
$W_{C=C}$, a.u.[c]	2·0689	2·0676	2·0659	2·0670

[a] Relative to the energy of systems *XIIIa*; [b] optimized geometries of the systems *XIIIa*–*XIIId* were taken from ref.[28]; [c] Wiberg index.

calculations are given in Table III. Energy calculations of structures *XIIIa*–*XIIId* were performed by CNDO/2 method in order to verify the reliability of the used semiempirical procedure by means of a comparison with *ab initio* calculations. It is clear from the very good agreement between the calculated energies that, for our purpose, the utilized procedure is satisfactory. Among the possible perturbations of planar ethylene the most energetically demanding one appears to be a pure torsion causing also the largest red shift of the corresponding spectral band together with the largest intensity decrease. If the case of torsion is taken as a reference then the *cis*-distortion corresponds to about one third of its energy increase and the *trans*-distortion to about one half of it. Both these mechanisms are also associated with a red shift and intensity decrease of the corresponding absorption band. Non-planarity of the system results in a very small increase of electron density on carbon atoms and in a lowering of the bond order (see Wiberg indices in Table III). However, a substantial difference exists between the pure torsion and a distortion of the double bond which consists in their effect on the energies of frontier orbitals. The torsion causes, mainly, an increase of HOMO energy while a distortion lowers the energy of the LUMO orbital. Both these effects influence transition energy predominantly *via* the one electron term $(\varepsilon_j - \varepsilon_i)$ since the transition under study is basically of $1 - 1'$ type. A more detailed information on the mechanisms which are effective with the compounds *XId*,*e* can be obtained using half-wave reduction potentials and first ionization potentials. It has been shown in our previous paper[15] that the substituent effect is additive within the fuchsone series and that a linear correlation exists between $E_{1/2}^{red}$ and ε_{LUMO}. On the other hand, the energies of HOMO orbital when taken as negative values can be regarded as first ionization potentials according to Koopmans theorem[29]. It is interesting to note that first ionization potentials of „push-pull" ethylenes decrease with increasing torsional deformation[30]. Unfortunately, the full confrontation between experimental data and calculated results could not be carried out since it was not possible to obtained reproducible photoelectron spectra of *XId*,*e* even at 210°. The corresponding first ionization potential of 2,6-dimethylfuchsone amounts to 7·72 eV. Experimental half-wave reduction potentials are given in Table IV. Considering the proved additivity of substituent effect[15] we can estimate potentials related to structures *XIc*, *d* on the basis of potentials of *VIIa*, *XIa*,*b*. The value of −601 mV calculated empirically for *XIc* corresponds rather well to the experimental value of −582 mV. The analogous values related to *XId* amount to −337 mV resp. −219 mV. The difference of 118 mV which corresponds to a decrease of the LUMO energy gives evidence on further non-electronic effects. If, in the next stage, we calculate reduction potential of *XIe* according to a relation $E_{1/2}^{red}(XIe) = E_{1/2}^{red}(XIc) + E_{1/2}^{red}(XId) - E_{1/2}^{red}(VIIa)$ we obtain a value of −356 mV which compares favourably with the experimental value of −342 mV. The result demonstrates unambiguously that the additional anomalous contributions to the red shift in the spectrum of the *XIe*, which appears on comparison with the spectrum of *XId*, cannot be caused by a further decrease of the LUMO energy. Regarding the above results we can suggest the following explanation: as for the compound *XId* the anomalous red shift of the long wavelength band is caused by the double bond distortion while in the case of *XIe* we have to assume a perturbation by torsional mechanism. As a consequence of molecular symmetry the distortion probably proceeds by the *trans*-mechanism.

The model quantum chemical calculation of the fuchsone chromophore perturbed by the *trans*-distortion (with the geometric and steric constraints at the exocyclic double bond which are identical with those existing in structure *XIIId* affords the following results: *1*) Non-planarity of the system causes a decrease of the ground state dipole moment by about 0·8 . 10^{-30} Cm. However, experimental dipole moments of compounds *XIc* and *XId* are almost identical[11] and, consequently, we can assume that the dipole moment decrease caused by a distortion of the exocyclic bond is compensated by the partial dipole moment of methyl groups the electron-donating effect of which is slightly higher in the positions 3,5 than in the positions 2,6 in accord with the quantum chemical calculation[27]. *2*) The long wavelength transition

TABLE IV

Half-wave reduction potentials of compounds *VIIa*, *XIe*—*XIe*

Compound	*VIIa*	*XIa*	*XIb*	*XIc*	*XId*	*XIe*
$-E_{1/2}^{\mathrm{red}\,a}$, mV	445	523	391	582	219	342

[a] *vs* saturated LiCl/dimethylformamide electrode.

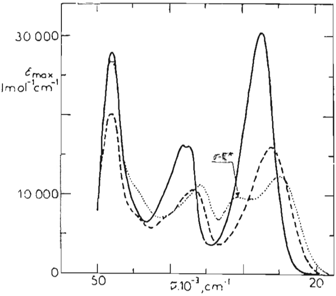


FIG. 5

Electronic absorption spectra of fuchsones (—— *XIc*, - - - - - *XId*, ······ *XIe*) measured in n-hexane is bathochromically shifted by 2 121 cm^{-1} when compared with the non-perturbed fuchsone chromophore and exhibits a decrease of oscillator strength from 1·21 to 0·916. *3*) The excited state exhibits higher polarity as follows from the compared values of $\Delta\mu_{e-g}$ corresponding to both structures ($5{\cdot}23 \, . \, 10^{-30}$ Cm and $7{\cdot}6 \, . \, 10^{-30}$ Cm). *4*) In addition to the long wavelength band, there is a relatively intense ($f = 0{\cdot}195$) strongly mixed transition at 28 145 cm^{-1} (towards the short wavelength part of the spectrum) which is contributed by configurations of the type $2-1'$ (30%) and $6-1'$ (25%). The first of these configurations is of $\sigma-\pi^*$ type and the second one of $n-\pi^*$ type. It is consistent with the above conclusions that the long wavelength band position is rather sensitive to solvent polarity, as observed with compounds *XId,e*. Somewhat different shape of absorption curves of these compounds (see Fig. 5, the band designated as $\sigma-\pi^*$) is in accord with the appearance of the aforementioned additional transition (*cf.* Robin and coworkers[31]).

The authors are indebted to Dr T. Juška, J. Heyrovský Institute of Physical Chemistry and Electrochemistry Prague, for the measurement of photoelectron spectra.

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Translated by P. Maloň.