

SUBSTITUTION EFFECT IN ELECTRONIC ABSORPTION SPECTRA OF 2- AND 2,6-SUBSTITUTED 4-BENZHYDRYLIDENE-2,5-CYCLOHEXADIEN-1-ONES*

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Electronic absorption spectra of the seventeen fuchsons derivatives Ia—Iq were recorded in n-hexane. The symmetric Gaussian function could be fitted to absorption profiles within the region of the lowest energy $\pi-\pi^*$ transition. Band parameters obtained in this way were utilized in calculation of the corresponding oscillator and dipole strengths. The effect of substitution on positions and intensities of all the observed bands was also investigated. The most sensitive response to substituent change is exhibited by the longest wavelength absorption band. The relation between the substituent nature and band position or oscillator strength may be quantified as

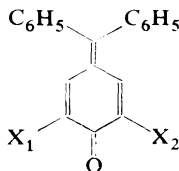
$$P = \sum_{i=1}^n \rho_i \sigma_i + P^0$$
. It follows from the analysis of variance that both the inductive and steric

effects are operating. On the other hand, for the non-symmetrically substituted fuchsons, the band intensity characterized by the molar absorption coefficient is a linear function of the inductive effect only. There is no statistically significant contribution of the resonance effect in any of the quantities investigated. The effect of solvent was followed by the separate evaluation of the wavenumbers related to maxima of the longest wavelength band of fuchsons Ia—Iq in the following series of solvents: n-hexane, cyclohexane, isooctane, tetrahydrofurane, acetone, acetonitrile and ethanol.

Up to this time little attention has been paid to quantitative evaluation of substituent effect acting on the chromophoric system of 4-benzhydrylidene-2,5-cyclohexadien-1-one (fuchson). It has been shown for the more simple *p*-benzoquinone methide chromophore¹ that a location of the long wavelength $\pi-\pi^*$ transition in 2,6 and 7,7-substituted derivatives can be determined with reasonable reliability using the additive approach. The long wavelength absorption maximum of 4-methylene-2,5-cyclohexadien-1-one serves as a reference value to which the particular substituent contributions are being added. Later on, the experimentally accessible spectral parameters of a similar set of compounds were compared with values calculated quantum chemically by the SCF PPP procedure². In many cases the interpretation of absorption curves of substituted quinone methides must be based exclusively on quan-

* Part XXX in the series: Quinone Methides and Fuchsons; Part XXIX; This Journal 48, 2825 (1983).

tum-chemical calculations due to non-stability of these compounds preventing thorough spectroscopic investigation. A slightly more favourable situation is achieved with the analogous series of fuchsons derivatives. These compounds are sufficiently stable in order to allow for the full necessary extent of spectroscopic investigation. The further need for the more detailed investigation of substituent effects on spectra of these compounds consists in the fact that the fuchson skeleton itself is the basic chromophoric system of triphenylmethane compounds^{3,4}, many of which have found their practical use *e.g.* in analytical chemistry⁵ and dyes industry⁶. Qualitatively, it has been already shown that in the case of 4-bis(4-dimethylaminophenyl-methylene-3,5-dimethyl-2,5-cyclohexadien-1-one) and some 2,6-disubstituted fuchsons the changes of spectral parameters are influenced by steric^{7,8} as well as electronic substituent effects. However, a systematic study providing quantification of substituent effects has yet to be reported and this is the aim of our present work. For this purpose the electronic absorption spectra of seventeen fuchsons *Ia–Iq* were measured and analysed with the main interest applied to: *a*) the effect of substituents on position and intensity of particular absorption bands; *b*) the quantitative evaluation of the extent to which the total substituent effect is contributed by the respective electronic and steric contributions; *c*) the effect of solute-solvent interactions on the form of the found relations.



| | |
|--|---|
| <i>Ia</i> ; X ₁ = H, X ₂ = CH ₃ | <i>Ii</i> ; X ₁ = H, X ₂ = COOH |
| <i>Ib</i> ; X ₁ = H, X ₂ = C ₂ H ₅ | <i>Ij</i> ; X ₁ = CH ₃ , X ₂ = <i>p</i> -C ₄ H ₉ |
| <i>Ic</i> ; X ₁ = H, X ₂ = <i>i</i> -C ₃ H ₇ | <i>Ik</i> ; X ₁ = X ₂ = H |
| <i>Id</i> ; X ₁ = H, X ₂ = <i>t</i> -C ₄ H ₉ | <i>Il</i> ; X ₁ = X ₂ = CH ₃ |
| <i>Ie</i> ; X ₁ = H, X ₂ = Br | <i>Im</i> ; X ₁ = X ₂ = C ₂ H ₅ |
| <i>If</i> ; X ₁ = H, X ₂ = OCH ₃ | <i>In</i> ; X ₁ = X ₂ = <i>i</i> -C ₃ H ₇ |
| <i>Ig</i> ; X ₁ = H, X ₂ = NO ₂ | <i>Io</i> ; X ₁ = X ₂ = <i>t</i> -C ₄ H ₉ |
| <i>Ih</i> ; X ₁ = H, X ₂ = OH | <i>Ip</i> ; X ₁ = X ₂ = Br |
| | <i>Iq</i> ; X ₁ = X ₂ = OCH ₃ |

EXPERIMENTAL

The fuchsons *Ia–Iq* were prepared according to known procedures^{9–11}. Electronic absorption spectra were measured on SPECORD UV-VIS Zeiss, Jena spectrophotometer at 25°C (scan speed 151.5 cm⁻¹ s⁻¹) in *n*-hexane, cyclohexane, isooctane, tetrahydrofuran, acetone, acetonitrile and ethanol (*c* 1–5 · 10⁻⁵ mol l⁻¹). Ethanol was dried according to the recommended procedure¹².

The shape of absorption curves in the region of the lowest energy band was fitted by the symmetric Gaussian function:

$$\varepsilon_{\tilde{\nu}} = \varepsilon_0 \cdot \exp \left[-\frac{(\tilde{\nu} - \tilde{\nu}_0)^2}{\theta^2} \right], \quad (1)$$

where $\varepsilon_{\tilde{\nu}}$ denotes the actual value of the molar absorption coefficient corresponding to the wave-number $\tilde{\nu}$ and ε_0 , $\tilde{\nu}_0$ are the respective position and molar absorption coefficient of the band maximum. θ is the band half-width. The oscillator strength (f) and the dipole strength (D) were calculated according to relations (2) and (3),

$$f = 4.315 \cdot 10^{-9} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \varepsilon_{\tilde{\nu}} d\tilde{\nu} = 4.6 \cdot 10^{-9} \varepsilon_0 \theta \quad (2)$$

$$D = 0.10204/\tilde{\nu}_0 \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \varepsilon_{\tilde{\nu}} d\tilde{\nu} = 0.108619 \varepsilon_0 \theta / \tilde{\nu}_0. \quad (3)$$

The obtained spectral parameters were subjected to multiple linear regression. The quality of particular correlations was appreciated on the basis of correlation coefficients, normalized standard deviations and total F-tests. Statistical significance of particular independent variables was tested by a comparison of the relevant partial F- and t-tests with the corresponding critical values at the 5% significance level. Hewlett-Packard 9830 calculator was utilized for numerical data processing and for the analysis of spectral curves. The graphical recordings were drawn on HP 9781A digital $x-y$ plotter.

The values of substituent constants were taken from refs¹³⁻¹⁸.

RESULTS AND DISCUSSION

Spectral Parameters of Compounds under Study

Four absorption bands ($A-D$) are visible in electronic absorption spectra of fuchsones $Ia-Iq$. Two of them (A, D) are separated while the other two (B, C) exhibit considerable overlapping. Spectral curves of these compounds are very similar (the typical example is shown in Fig. 1). The most important parameters of all the observed bands are summarized in Table I. It follows from these values that the band intensities are more sensitive to substituent effect than the corresponding band positions. The most sensitive response to substituent change is achieved with the A band which is also frequently utilized for the spectral characterization of fuchsones and quinone methides¹⁹. We analyzed this band in detail, firstly by fitting the symmetric Gaussian function to its absorption profile (minimizing the sum of squares of residuals between the calculated and experimental spectrum). Using the band parameters thus obtained we subsequently evaluated the corresponding oscillator and dipole strengths (Table II). These values do not exhibit substantial changes for various substituents and provide thus some evidence on a similar nature of the corresponding transition within the series of compounds under study. Nevertheless, it is evident from the magnitudes of spectral parameters that we cannot exclude

splitting of these data into two groups pertaining to symmetrically and non-symmetrically substituted fuchsones. On the other hand, the shifts of the *A* band maximum when compared with the non-substituted compound are not too large. The maximal shift value amounts to $2\,160\text{ cm}^{-1}$ favouring thus rather weak interactions of substituents with MO levels of the basic chromophoric system. Hence, it can be assumed that the ordering of molecular orbitals is not changed and the interactions can be classified as second order perturbations. In such a case it seems not very risky to generalize the results afforded by the recent CNDO/S study²⁰ of the chromophoric system of *Ik*. The lowest energy absorption band is ascribed to a single $\pi-\pi^*$ transition which is almost purely of $n-V_1$ type (HOMO-LUMO). According to symmetry classification it belongs to ${}^1A_1-{}^1A_1$ representation with the transition moment oriented along the C_2 symmetry axis. In analogy such a transition can be ascribed to all fuchsones belonging to C_{2v} symmetry group, while in the remaining cases the transition should be of the ${}^1A'-{}^1A'$ symmetry. Moreover, on the basis of quantum chemical calculations and in agreement with recent solvatochromic study²¹ of *Io* some intramolecular charge-transfer character can also be ascribed to this transition.

Effect of Substituents on Electronic Absorption Spectra

The rigorous treatment of substituent effects requires experimental determination of the 0-0 vibronic component of the electronic transition under study. However, it is more usual in chemical applications to utilize the position of the band maximum and it has been shown that such a procedure is acceptable²². The other serious requirement is connected with the method used for the evaluation of substituent effect²³. It consists in a necessity to divide the molecule into parts comprising variable substituent and non-varying framework possessing a suitable physico-chemical

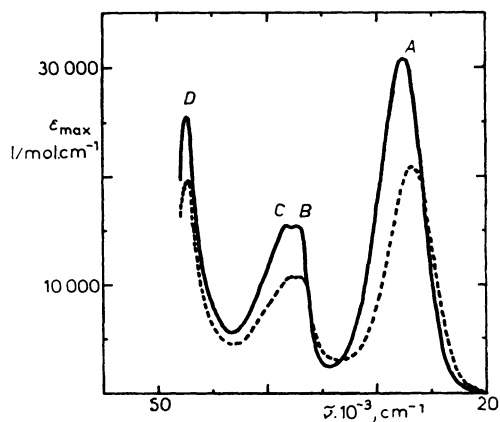


FIG. 1
Electronic absorption spectra of the fuchsones *II* (—) and *Ie* (-----)

TABLE I
Spectral parameters of the four long wavelength $\pi - \pi^*$ transitions A—D observed in electronic absorption spectra of the fuchsones I

| Compound | A | | B | | C | | D | |
|-----------|-----------------------------------|---|-----------------------------------|---|-----------------------------------|---|-----------------------------------|---|
| | $\tilde{\nu}$ cm ⁻¹ | ϵ_{\max} l mol ⁻¹ cm ⁻¹ | $\tilde{\nu}$ cm ⁻¹ | ϵ_{\max} l mol ⁻¹ cm ⁻¹ | $\tilde{\nu}$ cm ⁻¹ | ϵ_{\max} l mol ⁻¹ cm ⁻¹ | $\tilde{\nu}$ cm ⁻¹ | ϵ_{\max} l mol ⁻¹ cm ⁻¹ |
| <i>Ia</i> | 27 760 | 22 467 | 37 600 | 11 623 | 38 400 | 11 706 | 47 600 | 17 202 |
| <i>Ib</i> | 27 734 | 22 549 | 37 520 | 11 819 | 38 400 | 11 977 | 47 600 | 17 917 |
| <i>Ic</i> | 27 664 | 22 801 | 37 480 | 11 859 | 38 340 | 12 012 | 47 584 | 18 434 |
| <i>Id</i> | 27 624 | 22 801 | 37 440 | 11 601 | 38 320 | 11 791 | 47 584 | 17 947 |
| <i>Ie</i> | 26 800 | 20 056 | 37 070 | 10 458 | 38 160 | 10 274 | 47 504 | 19 910 |
| <i>If</i> | 26 960 | 19 987 | 37 180 | 11 879 | 38 272 | 12 297 | 47 552 | 20 163 |
| <i>Ig</i> | 26 224 | 18 130 | 36 750 | 8 765 | 83 128 | 8 885 | 25 392 | 25 694 |
| <i>Ih</i> | 25 680 ^a | 15 349 ^b | 36 830 | 11 567 | 37 830 | 12 079 | 47 500 | 21 690 |
| <i>Ii</i> | 23 184 | | | | | | | |
| <i>Ij</i> | 27 536 | 23 017 | 37 300 | 11 508 | 38 296 | 11 610 | 47 568 | 18 739 |
| <i>Ik</i> | 27 920 | 31 574 | 37 472 | 15 374 | 38 512 | 15 946 | 47 472 | 13 976 |
| <i>Il</i> | 27 632 | 30 927 | 37 328 | 15 402 | 38 400 | 15 525 | 47 456 | 18 394 |
| <i>Im</i> | 27 560 | 30 967 | 37 296 | 15 633 | 38 352 | 15 746 | 47 424 | 16 871 |
| <i>In</i> | 27 484 | 29 107 | 37 248 | 14 659 | 38 320 | 14 818 | 47 408 | 13 230 |
| <i>Io</i> | 27 328 | 25 707 | 37 264 | 13 071 | 38 256 | 13 306 | 47 400 | 13 876 |
| <i>Ip</i> | 25 760 | 24 140 | 36 416 | 12 714 | 37 712 | 12 230 | 47 184 | 29 934 |
| <i>Iq</i> | 26 760 | 28 520 | 36 912 | 13 043 | 37 936 | 13 043 | 47 312 | 27 477 |

^a Wavenumbers of the separated bands amount to 25 644 and 29 518 cm⁻¹; ^b intensities of the separated bands in 1 mol⁻¹ cm⁻¹ amount to 14 799 and 5 000; ^c not measured.

property which is accessible to experimental investigation. From the practical viewpoint the latter requirement imposes certain limitations on the utilization of electronic spectroscopy since, in principle, the substituent forms the non-separable part of the chromophoric system. However, we can assume that for $\pi-\pi^*$ (and also $n-\pi^*$) transitions the above requirements are approximately fulfilled provided that either the substituent is not bonded directly to the chromophore or the two units are not conjugated. Our set of compounds satisfies these conditions in slightly better way than benzene derivatives used up to this time for quantitative evaluation of substituent effect in electronic absorption spectra²⁴. It is therefore not surprising that some formerly derived conclusions^{25,26} might be disproved on the basis of critical evaluation using correct statistical methods.

Our initial hypothesis starts with the assumption that substituent effect is additive and reflects electronic effects as well as steric requirements of the attached substituent.

TABLE II

Half-widths, oscillator and dipole strengths of the transition corresponding to the long wavelength *A* band in the fuchsone series *I*

| Compound ^a | Half-width cm ⁻¹ | Oscillator strength <i>f</i> | Dipole strength C ² m ² · 10 ⁶⁰ |
|-----------------------|--------------------------------|------------------------------------|--|
| <i>Ia</i> | 4 400 | 0.4547 | 386.82 |
| <i>Ib</i> | 4 400 | 0.4564 | 388.60 |
| <i>Ic</i> | 4 320 | 0.4531 | 386.71 |
| <i>Id</i> | 4 256 | 0.4464 | 381.60 |
| <i>Ie</i> | 4 480 | 0.4133 | 364.15 |
| <i>If</i> | 4 730 | 0.4349 | 380.93 |
| <i>Ig</i> | 4 560 | 0.3803 | 342.47 |
| <i>Ih</i> | 7 600 | 0.5331 | 493.41 |
| | (5 789) ^b | (0.3941) ^b | (362.87) ^b |
| | (4 644) ^b | (0.1068) ^b | (85.44) ^b |
| <i>Ij</i> | 4 128 | 0.4371 | 374.82 |
| <i>Ik</i> | 4 480 | 0.6507 | 550.33 |
| <i>Il</i> | 4 192 | 0.5964 | 509.65 |
| <i>Im</i> | 4 128 | 0.5880 | 503.76 |
| <i>In</i> | 4 120 | 0.5570 | 473.97 |
| <i>Io</i> | 4 096 | 0.4844 | 418.50 |
| <i>Ip</i> | 4 224 | 0.4690 | 429.95 |
| <i>Iq</i> | 4 128 | 0.5416 | 477.86 |

^a Excluding derivative *Ii*; ^b values related to separated bands (Fig. 3).

tents. We do not suppose significant application of resonance contribution within the framework of electronic effect. The general approach^{27,28} to quantitative evaluation of substituent effects using spectroscopic data is based on a correlation equation of the type (4):

$$\Delta P^X = P^X - P^H = \sum_{i=1}^n \rho_i \sigma_i + C, \quad (4)$$

where the property P is represented either by the frequency $\tilde{\nu}$ or by a value related to band intensity (ϵ_{\max} , f). In the first step the data were tested using the equation (4) with inclusion of inductive, resonance and steric effects. Statistical evaluation of the A band position affords the following relation: $\tilde{\nu}_{\text{abs}}^X = -1\,914.8\sigma_I - 37.1\sigma_R - 316.5\vartheta + 27\,812.6$ ($r = 0.994$, $s_{\text{stand}} = 0.0028$, $F_i(828.8, 0.3, 87.7)$, $t_i(-27.0, -0.5, -9.4)$). It is obvious from the comparison of partial F- and t-tests with the appropriate critical values that the resonance contribution is not statistically significant and can be omitted from further considerations. This finding supports our starting assumption and, simultaneously it is in agreement with the modified requirements imposed on the model. Hence, further analyses of our experimental data were carried out for the two parameter equation of the type (5):

$$P^X = \rho_I \sigma_I + \rho_S \chi_S + P^H. \quad (5)$$

For the steric constants χ_S we tested both the classical E_S set¹⁸ and the ϑ set recommended by Charton¹⁵. Despite some deficiencies of both these sets of steric constants^{17,29}, we feel that steric requirements are described more satisfactorily by the ϑ constants since these were derived from van der Waals volumes of substituents. Our opinion is supported by slightly better statistical results obtained for the A band position with the use of ϑ set ($r = 0.994$, and 0.992 , $s_{\text{stand}} = 0.027$ and 0.0031 , $F_i = 387.2$ and 381.9).

In the next step we analysed the effect of substituents on the position of absorption bands $A-D$. Experimental data were evaluated either as a whole (set I) or with separate consideration of non-symmetrically (set II) and symmetrically (set III) substituted fuchsones (in all cases excluding compounds Ih,i). The results are given in Table III. The susceptibility of band positions to particular substituent contributions was evaluated on the basis of the analysis of variance by the procedure of Swain-Lupton³⁰. The found sensitivity factors are summarized in Table IV. The course of the regression between $\tilde{\nu}_{\max}$ of the A band and the substituent constants σ_I and ϑ is shown in Fig. 2. The drawing includes also the $\tilde{\nu}_{\max}$ values pertaining to compounds Ih,i . Their exceptional character is documented by marked deviations from the regression which can probably be ascribed to a formation of intramolecular H-bond (see IV, V). Simultaneously, the marked bathochromic shift gives evidence on higher

strength of the H-bond in excited state in accord with the transition moment direction²⁰ as well as with the found polarization of this type of compounds on transition to the first excited π, π^* state¹¹. In addition, we cannot exclude the tautomerism $V \rightleftharpoons VI$ for the hydroxyderivative *Ih*. Its potential presence is supported by curve-

TABLE III

Statistical treatment of the substituent effect on the position of electronic absorption bands *A–D* in the fuchsones series *I* (using equation (5))

| Series ^{a,b} | ϱ_1^c | t^d F ^d | ϱ_S^c | t^d F ^d | $\tilde{\nu}_H^c, \text{cm}^{-1}$ | F_t^e | s^f | r^g |
|-----------------------|-----------------------|-------------------------|---------------------|-------------------------|-----------------------------------|---------|--------|-------|
| <i>IA</i> | – 1 897.41 (61.08) | 31.07 881.08 | – 316.10 (32.43) | 9.66 93.29 | 27 820.30 (40.09) | 487.18 | 0.0027 | 0.994 |
| <i>IIA</i> | – 1 987.08 (70.30) | 28.26 775.86 | – 242.43 (44.23) | 5.48 30.05 | 2 7764.25 (45.24) | 402.95 | 0.0019 | 0.997 |
| <i>IIIA</i> | – 1 832.74 (37.64) | 22.15 439.67 | – 352.39 (42.93) | 8.21 67.37 | 27 860.16 (60.80) | 253.52 | 0.0029 | 0.996 |
| <i>IB</i> | – 933.69 (64.22) | 14.54 186.01 | – 195.92 (34.75) | 5.64 31.79 | 37 541.73 (42.61) | 108.90 | 0.0021 | 0.974 |
| <i>IIB</i> | – 993.54 (57.79) | 17.19 256.65 | – 234.33 (36.36) | 6.44 41.54 | 37 626.75 (37.19) | 149.09 | 0.0012 | 0.992 |
| <i>IIIB</i> | – 888.23 | 12.16 | – 148.21 | 3.85 | 37 429.67 | 74.95 | 0.0019 | 0.987 |
| <i>IC</i> | – 572.17 (54.79) | 10.44 93.78 | – 128.23 (29.30) | 4.38 19.15 | 38 464.19 (36.76) | 56.47 | 0.0018 | 0.951 |
| <i>IIC</i> | – 345.37 (38.36) | 9.00 68.93 | – 88.72 (24.13) | 3.68 13.52 | 38 411.86 (24.68) | 41.22 | 0.0007 | 0.971 |
| <i>IIIC</i> | – 708.43 | 13.95 | – 129.61 | 4.99 | 38 466.17 | 99.06 | 0.0013 | 0.990 |
| <i>ID</i> | – 260.47 (68.22) | 3.82 11.62 | – 83.34 (36.91) | 2.26 5.10 | 47 588.00 (45.26) | 8.36 | 0.0018 | 0.763 |
| <i>IID</i> | – 242.45 (26.97) | 8.99 70.97 | – 54.39 (16.97) | 3.21 10.27 | 47.627.20 (17.36) | 40.62 | 0.0004 | 0.971 |
| <i>IIID</i> | – 247.68 (17.70) | 13.99 175.95 | – 46.73 (9.33) | 5.01 25.09) | 47 468.18 (13.24) | 100.52 | 0.0004 | 0.990 |

^a Excluding derivatives *Ih*, ^b the series designation *A, B, C, D* specifies the absorption bands *A–D*; series *I* (fuchsones *Ia–Ig, Ij–Iq*), series *II* (non-symmetrically substituted fuchsones *Ia–Ig, Ij*), series *III* (symmetrically substituted fuchsones *Ij–Iq*); ^c coefficients of the equation (5) with the standard deviations in parentheses; ^d partial Student t- and Fisher Snedecor F-tests; ^e the value of total Fischer Snedecor F-test; ^f normalized standard deviation; ^g multiple correlation coefficient.

-fitting of two absorption bands to the unusually broad *A* band (Fig. 3). The most detailed analysis of substituent effects was carried out for the *A* band which is a characteristic feature of this class of compounds. Its position (Tables III and IV)

TABLE IV

Quantitative evaluation of the effect of particular independent variables on the position of absorption bands *A–D* in the fuchsones series *I*

| Series ^{a,b} | $\eta_v^2, \%$ ^c | $\eta_\Delta^2, \%$ ^d | $\eta_I^2, \%$ ^e | $\eta_S^2, \%$ ^e | $\varphi(I), \%$ ^f | $\varphi(S), \%$ ^f |
|-----------------------|-----------------------------|----------------------------------|-----------------------------|-----------------------------|-------------------------------|-------------------------------|
| <i>IA</i> | 98.8 | 1.2 | 89.3 | 9.5 | 78.4 | 21.6 |
| <i>IIA</i> | 99.4 | 0.6 | 95.7 | 3.7 | 85.2 | 14.8 |
| <i>IIIA</i> | 99.2 | 0.8 | 86.0 | 13.2 | 69.8 | 30.2 |
| <i>IB</i> | 94.8 | 5.2 | 80.9 | 13.9 | 74.2 | 25.8 |
| <i>IIB</i> | 98.4 | 1.6 | 84.7 | 13.7 | 75.0 | 25.0 |
| <i>IIIB</i> | 97.4 | 2.6 | 87.8 | 9.6 | 72.7 | 27.3 |
| <i>IC</i> | 90.4 | 9.6 | 75.1 | 15.3 | 73.0 | 27.0 |
| <i>IIC</i> | 94.3 | 5.7 | 78.8 | 15.5 | 73.3 | 26.7 |
| <i>IIIC</i> | 98.0 | 2.0 | 85.7 | 12.3 | 70.8 | 29.2 |
| <i>ID</i> | 58.2 | 41.8 | 40.5 | 17.7 | 65.4 | 34.6 |
| <i>IID</i> | 94.2 | 5.8 | 82.3 | 11.9 | 75.9 | 24.1 |
| <i>IIID</i> | 98.0 | 2.0 | 85.8 | 12.2 | 70.2 | 29.8 |

^a Excluding derivatives *Ih, i*; ^b see note ^b to Table III; ^c variance of the dependent variable caused by the independent variables; ^d variance of the dependent variable caused by random factors; ^e participation of inductive and steric effects on the variance given in the column^c; ^f susceptibility to inductive and steric effects as determined by the procedure recommended by Swain Lupton³⁰.

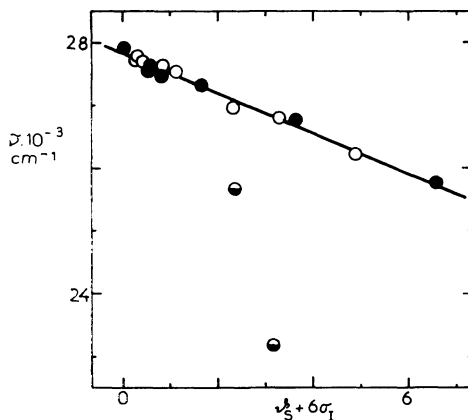


FIG. 2

Dependence of $\tilde{\nu}_{\max}$ of the long wavelength absorption band of the fuchsones *I* on the substituent constants σ_I and ϱ_S ; ○ non-symmetrically substituted fuchsones, ● symmetrically substituted fuchsones, ◐ fuchsones *Ih, i*

is predominantly determined by inductive contribution. The slight break of the correlation into two separate series (*II* and *III*) gives evidence on the more significant contribution of steric effect when compared with disubstituted derivative. In other words, this is an indication of slight non-additivity of this effect. Quantitative contribution of steric effect to the total transmission amounts to 14.8% for non-symmetrically substituted fuchsones and 30.2% for symmetrically substituted fuchsones. The *I* and *S* effects act in opposite directions. This finding is not surprising. Substituents having electron donating potency diminish the inherent polarization of the transition towards the carbonyl oxygen atom and, consequently, cause an increase of the transition energy. On the other hand, an increase of the steric volume of the substituent causes a bathochromic shift. Generally, any steric crowding within a conjugated system results in its destabilization. The relaxations related to deformation of π -bonds cause an increase of the corresponding occupied molecular orbitals³¹. On the other hand, either nonbonded interactions caused by steric effect or charge repulsions in the excited state induce a blue shift of the corresponding absorption band³². Substituents exhibiting a positive *I* effect cause a decrease of the first ionization potential³³ and an increase of the half wave reduction potential³⁴. These findings allow to analyse substituent effects in both the ground and excited states. For the *A* band the energy of the corresponding singlet transition is given by the relation³⁵ $\Delta E_{i-j} = \epsilon_j - \epsilon_i - J_{i,j} + 2K_{i,j}$ ($i = \text{HOMO}, j = \text{LUMO}$). If the contribution of the term $2K_{i,j} - J_{i,j}$ is approximately constant (in the series of structurally related compounds) then any change of transition energy is predominantly caused by variation of energies of the molecular orbitals i and j . CNDO/2 calculation on two simple models *VII* and *VIII* affords the following energies of frontier orbitals: -12.0313 eV (HOMO), 0.7442 eV (LUMO) for *VII* and -11.1742 eV

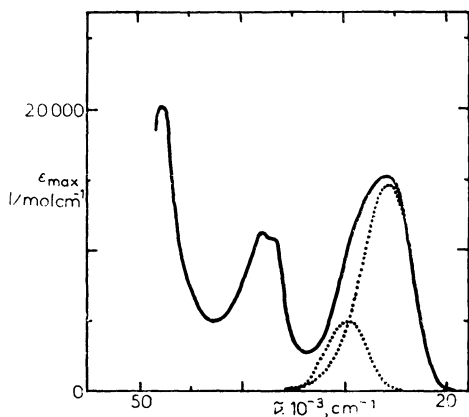
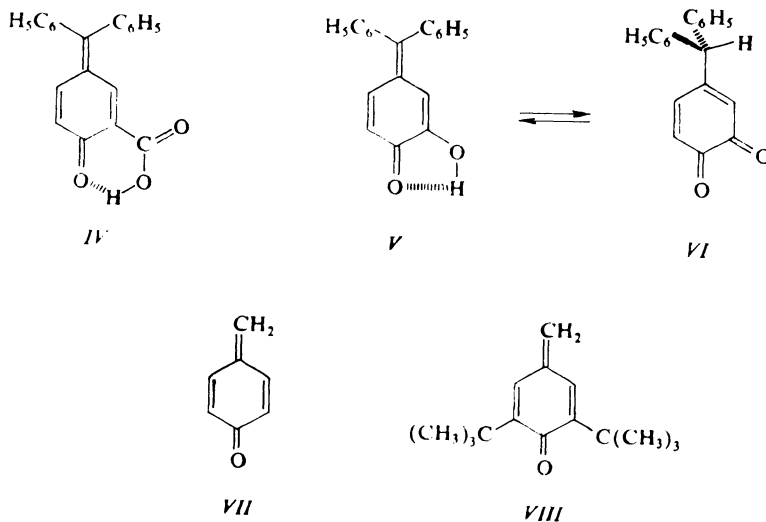


FIG. 3
Electronic absorption spectrum of the hydroxy derivative *Ih* (the dotted curves denote separated bands)

(HOMO), 0.8082 eV (LUMO) for *VIII*. It is clear that the substituent effect acting on individual MO levels is partially compensated in the resulting transition energy. This compensation can explain the rather low bathochromic shift of the *A* band in *Io* when compared with *Ik*. In addition the sterically conditioned destabilization of the π -system (especially in the ground state) is further evidenced by the observed $\bar{\nu}_{C=O}$ decrease of fuchsones⁹. On the other hand, the increase of LUMO energy, which is caused presumably by the inductive effect, is confirmed by an increase of $E_{1/2}^{red}$ potential in this series of compounds³⁶.



The positions of absorption bands *B* and *C* exhibit almost identical response to substitution. However, as compared to the *A* band, the shifts caused by substitution are much lower. Positional changes of both these bands are again predominantly determined by the inductive effect. The contribution of steric effect is approximately the same for both bands and there is no marked difference between the series *II* and *III*. This result is in agreement with the suggested polarization of the transition (transversal to the longitudinal chromophore axis) as well as with the direction of transition moments calculated by the CNDO/S method for *Ik* (ref.²⁰). The short wavelength *D* band exhibits little variability with substituent changes. Its position is determined with the relatively large error and therefore the corresponding statistical evaluation is given for completeness only (Tables III and IV). We presume, on the basis of a similarity between the sets *IIIA* and *IIID* (Table IV), that the transition possesses analogous direction of polarization. This assumption is not in contrast with the results of CNDO/S calculations on the chromophoric grouping of *Ik*.

Band intensities in electronic absorption spectra are usually expressed as the cor-

responding molar absorption coefficients. However, these values cannot be directly related to any spectral parameter derived theoretically. The more suitable reference value is represented by the integrated intensity which is proportional to oscillator strength f (ref.³⁷). The exact evaluation of integrated intensity is possible only for isolated bands. In other cases, it is necessary to perform a band separation which is always somewhat arbitrary. Moreover, the parameters obtained in this way suffer certain error which may cause failure of their correlation with substituent constants. Due to this fact we limited the analysis of the relation between intensity and substituent effect to the long wavelength A band affording relatively reliable spectral parameters.

It is not surprising that the intensity of a band is much more sensitive to substituent changes than the position and that the series of compounds under study is split into the two already mentioned groups *II* and *III*. With these compounds, we have already observed the analogy of this splitting upon evaluation of IR band intensities of the carbonyl stretching vibration⁹. For the groups *II* and *III*, the effect of substituent has been investigated on both the molar absorption coefficient and the oscillator strength. The results of statistical evaluation based on the equation (5) are summarized in Table V and the corresponding sensitivity factors in Table VI. It is clear that, for non-symmetrically substituted fuchsones *II*, the steric contribution is not statistically significant and, consequently, ϵ_{\max} is a linear function of the induc-

TABLE V

Statistical treatment of the substituent effect on the intensity of the long wavelength A band in the fuchsones series *I* (using the equation (5))

| Series ^{a,b} | ρ_1^c | t^d F ^d | ρ_s^c | t^d F ^d | ϵ_{\max}/f l mol ⁻¹ cm ⁻¹ | F _t ^e | s ^j | r ^g |
|-----------------------|-------------------------|-------------------------|-------------------------|-------------------------|---|-----------------------------|----------------|----------------|
| <i>IIE</i> | -6 159.78 (352.99) | 17.45 335.33 | 84.54 (222.06) | 0.38 0.14 | 22 243.52 (227.14) | 167.70 | 0.0122 | 0.993 |
| <i>IIIE</i> | -5 308.86 (957.89) | 5.54 20.39 | -2 838.26 (504.96) | 5.62 31.59 | 32 733.51 (716.82) | 25.99 | 0.0324 | 0.964 |
| <i>IIIF</i> | -0.091371 (0.005358) | 17.05 247.54 | -0.023365 (0.003370) | 6.93 48.06 | 0.466806 (0.003447) | 147.80 | 0.0092 | 0.992 |
| <i>IIIF</i> | -0.109184 (0.007536) | 14.49 122.92 | -0.072413 (0.003973) | 18.23 332.25 | 0.654377 (0.005639) | 227.58 | 0.0113 | 0.996 |

^a Excluding derivatives Ih, i ; ^b the series designation *E, F* denotes molar absorption coefficient ϵ_{\max} and oscillator strength f of the A band, for the designation *II* and *III* see note^b to Table III; ^{c-g} see notes^{c-g} to Table III.

tive effect. The single parameter equation affords the relation: $\varepsilon_{\max}^X = -6\,197.93 (\pm 313.42) \sigma_1 + 22\,320.47 (\pm 95.95)$, ($s_{\text{stand}} = 0.0113$, $t = 19.8$, $F = 391.1$, $r = 0.992$). On the other hand, ε_{\max} of symmetrically substituted fuchsones is influenced by both these effects with the dominant contribution of steric effect (weight 54.5%). The value of oscillator strength involves, besides ε_{\max} , also the band width parameter causing the significant contribution of the steric effect in both groups. For the group *II*, the steric contribution amounts only to 26.6%, while in the case of *III* it is again a dominating contribution (59.9%). Substituents with electron donating potency cause an increase of band intensity while an increase of steric volume results in its decrease. The action of steric effect is in agreement with the suggested means of the π -skeleton destabilization. If the steric crowding causes a bathochromic shift of a band then the same effect has to be manifest also by a decrease of band intensity³⁸.

Effect of Interactions in Solution on the Form of Obtained Correlations

In the majority of reports dealing with quantitative evaluation of substituent effects it is not usual to stress that the found correlation equations are valid only for the defined phase conditions and/or for the given solvent. Hence, using strict terms, it seems that statistical evaluation of electronic absorption parameters, averaged for a series of solvents³⁹, is not quite correct and, moreover, that the procedure is of no value for the possible practical use. On the other hand, besides prediction of properties of the still unknown derivative, there is another interesting aspect. It consists in the possibility to use the found relation quite generally, *e.g.* for various solvents. The passage from one solvent to another is really common, namely in the electronic absorption spectroscopy. The problem thus suggested consists in finding the necessary transformation equations which are capable to guarantee the universal-

TABLE VI

Quantitative evaluation of the effect of particular independent variables on the intensity of the *A* band in the fuchsones series *I*

| Series ^{a,b} | $\eta_V^2, \%^c$ | $\eta_{\Delta}^2, \%^d$ | $\eta_1^2, \%^e$ | $\eta_S^2, \%^e$ | $\varphi(I), \%^f$ | $\varphi(S), \%^f$ |
|-----------------------|------------------|-------------------------|------------------|------------------|--------------------|--------------------|
| <i>IIE</i> | 98.5 | 1.5 | 98.4 | 0.1 | 98.1 | 1.9 |
| <i>IIIE</i> | 92.9 | 7.1 | 36.5 | 56.4 | 45.5 | 54.5 |
| <i>IIF</i> | 98.0 | 2.0 | 81.3 | 16.7 | 73.4 | 26.6 |
| <i>IIIF</i> | 99.2 | 0.8 | 27.0 | 72.2 | 40.1 | 59.9 |

^{a,b} See notes^{a,b} to Table V; ^{c-f} see notes^{c-f} to Table IV.

ity of the found relation. In advance of this step, let us analyse the influence of particular solvents on correlation equations within the general RS ("reactivity - selectivity") principle⁴⁰. Application of the principle to our correlation relations for the given series of solvents is presented in Fig. 4. It is clear that the search for the transformation equations must be limited solely to solvents possessing non-specific interactions. We used the theory of universal intermolecular interactions. The band shifts caused by particular solvents were treated by the relation of Bilot and Kawski⁴¹. If the shift of the absorption maximum of the compound *i* caused by a passage from the gas phase (*g*) into the solvent α is defined by a value of $\Delta\tilde{\nu}_\alpha^i = \tilde{\nu}_\alpha^i - \tilde{\nu}^i(g)$ then we can write:

$$\Delta\tilde{\nu}_\alpha^i = \frac{-2\mu_g^i(\mu_e^i - \mu_g^i)}{hca_i^3} \left[\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right) \frac{2n^2+1}{n^2+2} + 3/2K \frac{n^4-1}{(n^2+2)^2} \right]. \quad (6)$$

If we define a value $A^i = -\frac{2\mu_g^i(\mu_e^i - \mu_g^i)}{hca_i^3}$ representing the properties of the molecule *i* independently on the used solvent and if the expression in square brackets is replaced by a function ϕ_α describing the solvent α then we have the following simple relation

$$\Delta\tilde{\nu}_\alpha^i = A^i \phi_\alpha \quad (7)$$

for the solvent α and the compound *i*. The position change of the absorption band related to a passage between the solvents α and β is then given by the equation (8):

$$\Delta \Delta\tilde{\nu}_{\alpha,\beta}^i = A^i \Delta\phi_{\alpha,\beta}. \quad (8)$$

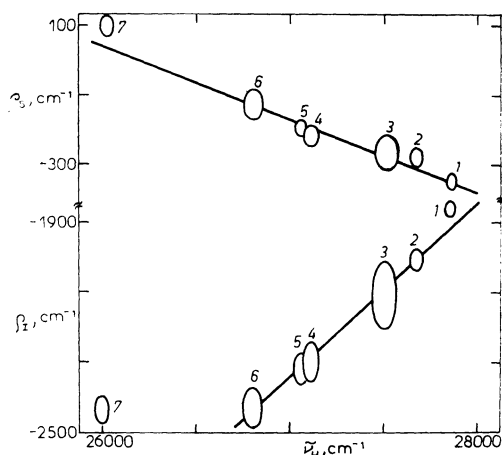


FIG. 4

Graphical demonstration of the dependencies $\rho_1^i = f(\tilde{\nu}_H^i)$ and $\rho_2^i = f(\tilde{\nu}_H^i)$. The coefficients ρ_1^i , ρ_2^i , $\tilde{\nu}_H^i$ pertaining to the equation (5) were obtained by the statistical treatment of data recorded in the following solvents *i*: 1 n-hexane, 2 isooctane, 3 cyclohexane, 4 tetrahydrofuran, 5 acetone, 6 acetonitrile, 7 ethanol

Further on, the equation (9) relates the shift of the absorption maximum of the compound i to the compound j in the solvent α :

$$\Delta \tilde{\nu}_{\alpha}^{i,j} = \varrho(\text{I})_{\alpha} \sigma_1^{i,j} + \varrho(\text{S})_{\alpha} \vartheta_S^{i,j}. \quad (9)$$

The equation (10) describes the passage from the solvent α to β :

$$\Delta \Delta \tilde{\nu}_{\alpha,\beta}^{i,j} = \Delta \varrho(\text{I})_{\alpha,\beta} \sigma_1^{i,j} + \Delta \varrho(\text{S})_{\alpha,\beta} \vartheta_S^{i,j} \quad (10)$$

Combination of the equations (8) and (10) results in the equation (11):

$$\Delta A^{i,j} \Delta \phi_{\alpha,\beta} = \Delta \varrho(\text{I})_{\alpha,\beta} \sigma_1^{i,j} + \Delta \varrho(\text{S})_{\alpha,\beta} \vartheta_S^{i,j}. \quad (11)$$

Rearrangement of this equation leads to the final relation (12)

$$A^i = \frac{\Delta \varrho(\text{I})_{\alpha,\beta}}{\Delta \phi_{\alpha,\beta}} \sigma_1^{i,j} + \frac{\Delta \varrho(\text{S})_{\alpha,\beta}}{\Delta \phi_{\alpha,\beta}} \vartheta_S^{i,j} + A^j, \quad (12)$$

which represents the necessary transformation equation. The parameters A^i were obtained using the recommended procedure^{4,1}. Their statistical evaluation with the aid of the equation (12) afforded numerical values of universal sensitivity factors $R(\text{I}) = \Delta \varrho(\text{I})_{\alpha,\beta} / \Delta \phi_{\alpha,\beta}$ and $R(\text{S}) = \Delta \varrho(\text{S})_{\alpha,\beta} / \Delta \phi_{\alpha,\beta}$. If the base member of the series ($X = \text{H}$) serves as the reference compound j then the following equation is valid for the compound possessing substituent X :

$$A^X = -613.01 (\pm 140.70) \sigma_1 + 163.36 (\pm 73.00) \vartheta_S - 1115.56 (\pm 103.38). \quad (13)$$

We can easily calculate corrections to sensitivity factors $\Delta \varrho(\text{I})_{\alpha,\beta}$ and $\Delta \varrho(\text{S})_{\alpha,\beta}$ from the calculated change of the solvent function for the given solvent β in relation to the reference compound α with the aid of universal sensitivity factors $R(\text{I})$ and $R(\text{S})$. Introduction of the corrections into the equation (9) provides the transformation for the calculation of $\tilde{\nu}_{\max}$ in the solvent β .

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