PERTURBATION OF THE FUCHSONE CHROMOPHORE
BY 3,5-METHYL SUBSTITUTION. STERICALLY CROWDED
EXOCYCLIC DOUBLE BOND*

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Several 3,5-methyl substituted fuchsones have been synthesized and characterized by means of UV and NMR spectroscopy as well as dipole moment measurements. Two basic types of behaviour of the longest wavelength band have been found for these derivatives in comparison to 2,6-substituted analogues *i.e.* hypochromic effect and bathochromic shift. These effects can be attributed to a steric crowding of the $C_{(4)}$—$C_{(7)}$ double bonds. The role of the steric interactions in the ground state and in the excited state is discussed.

In connection with our studies concerning the physical and chemical properties of 2,6-substituted fuchsones (A), a considerable degree of charge separation in the methylenecyclohexadienone moiety have invariably been found[1-3] and the same
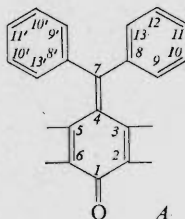

results seem to have been reached by other workers[4,5]. Incorporation of the exocyclic double bond π-electrons into the quinonoid ring results in creation of an aromatic phenolate system, and dipolar stabilization of the twisted transition state to rotation around the exocyclic double bond might be envisaged in the same way as for push-pull substituted ethylenes[6] and quinone methides[7], which show low rotational barriers. It is supposed[8,9], that the potential energy curve for rotation around the olefinic

double bond may be regarded as the superposition of a π-electron and steric strain energy terms. When the steric interactions in the ground state become important, the molecule will deviate from planarity often by twisting aroung the double bond[10,11]. Permanently twisted polarized ethylenes in which steric barriers exceed π-electronic barriers have recently evoked considerable interest[12-14].

For systems such as A it may be supposed that the twisting around the exocyclic double bond will strongly depend on the position and nature of substituent(s) of the quinonoid ring. The ground state geometry in the vicinity of the double bond for 2,6-substituted fuchsones seems to be well characterized by X-ray analysis of the 2,6-dibromo and 2,6-dimethyl derivatives[15,16]. It follows from these studies, that 1) there are significant deviations from idealized planar geometry at the sp^2 centers $C_{(4)}$ and $C_{(7)}$, presumably to relieve steric overcrowding of the α,α-diphenylmethylene functionality; the $C_{(3)}$—$C_{(4)}$—$C_{(5)}$ and $C_{(8)}$—$C_{(7)}$—$C_{(8')}$ angles are compressed ($\approx 116°$) with concomitant increase in the other angles at these centers; 2) this angular distortion, combined with lengthening of the $C_{(4)}$—$C_{(7)}$ bond relative to the $C_{(2)}$—$C_{(3)}$ and $C_{(5)}$—$C_{(6)}$ bonds, places both phenyl substituents as far away as possible from the quinonoid ring, and 3) the $C_{(7)}$, $C_{(8)}$, $C_{(8')}$ plane makes the twist angles approximately 43° with the phenyl rings.
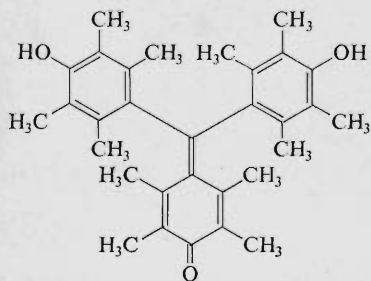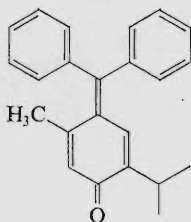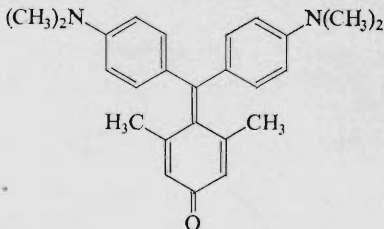

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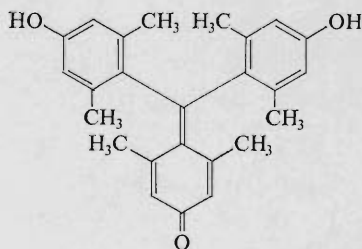
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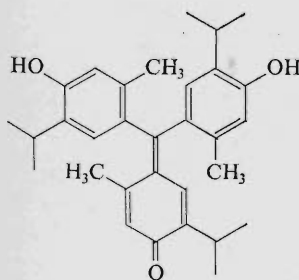
III

IV

V

Still greater deviation from an idealized planar geometry could be expected in the case of 3,5-substituted fuchsones. To our knowledge, only the fuchsones $I - VI$ having a substituent in 3,5-positions have been prepared[17-21]. Unfortunately, the poly-substitution of these derivatives and/or the absence of suitable experimental data makes quantitative interpretation of the 3,5-substituent effect impossible. It is interesting to note that an unsuccessful attempt was made[22] to prepare the 2,3,5,6--tetramethylfuchsone by oxidation of the corresponding phenol.
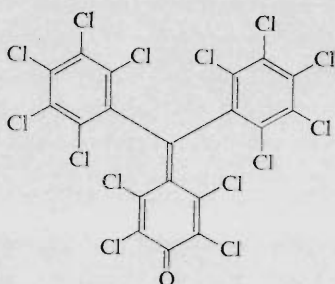
VI

In the present study our work on fuchsones is extended in two directions: *a*) Synthesis and characterization of new 3,5-methylsubstituted fuchsones *VII* and *VIII* and *b*) comparison of some physico-chemical properties of these compounds and corresponding 2,6-methylsubstituted derivatives *IX*. We assume that the combination of evidence from UV and ^{13}C-NMR spectroscopic data, together with the ground state and excited state dipole moment measurements should allow for a more detailed classification of the 4-alkylidene-2,5-cyclohexadien-1-one moiety.
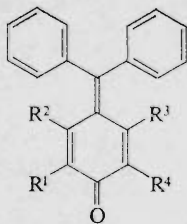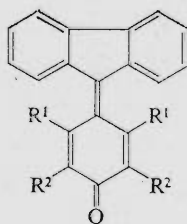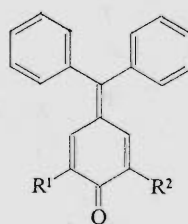
VII   *VIII*   *IX*

VIIa; $R^1 = R^2 = R^4 = H$, $R^3 = CH_3$ *VIIIa*; $R^1 = H$, $R^2 = CH_3$
VIIb; $R^1 = R^4 = H$, $R^2 = R^3 = CH_3$ *VIIIb*; $R^1 = CH_3$, $R^2 = H$
VIIc; $R^1 = R^2 = R^3 = R^4 = CH_3$

IXa; $R^1 = R^2 = H$
IXb, $R^1 = CH_3$, $R^2 = H$
IXc; $R^1 = R^2 = CH_3$
IXd; $R^1 = R^2 = t\text{-}C_4H_9$

EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. The analytical samples were dried at room temperature and 13·3 Pa for 7 h.

Physical Measurements

The infrared absorption spectra were recorded on Perkin Elmer 580 spectrophotometer in a 0·1 mm cell. The concentration of the tetrachloromethane solution was 0·03 mol l^{-1}. Electronic spectra were recorded on a Specord UV-VIS spectrophotometer ($\tilde{v}_{max}$ given in cm^{-1}) at a scan speed 16·7 cm^{-1}/s in following solvents: n-hexane, isooctane, diethyl ether, methyl acetate, ethyl acetate, n-butyl acetate, n-pentyl acetate, tetrahydrofurane, dichloroethane, acetone, N,N-dimethylformamide, acetonitrile and dimethyl sulfoxide. Mass spectra were measured on an AEI MS 902 mass spectrometer (70 eV; source temperature 110—230°C). ^{1}H-NMR spectra were taken in deuteriochloroform on a Varian HA-100 instrument (tetramethylsilane as internal standard; δ in ppm, J in Hz). ^{13}C-NMR spectra were obtained at 25·047 MHz in 10 mm tubes using a JNM-FX 100 (JEOL) spectrometer. All spectra were recorded at the 35°C, for approximately 0·4 mol l^{-1} solutions in deuteriochloroform using tetramethylsilane as internal standard. Field frequency lock was established on the deuterium resonance of the solvent. Typical settings for the FT parameters were: spectral width 5 000 Hz; pulse width 7 μs (flip angle c. 30°); 8 K data points and pulse repetition time 3 s. The ^{13}C chemical shifts were determined under proton-noise decoupled conditions and the ^1J(CH) coupling constants were measured with the gated decoupling technique using digital resolution 0·244 Hz/point. The standard measurement error was ±0·05 ppm for the chemical shifts and ±0·5 Hz for the ^1J(CH) coupling constants. Dipole moments in the ground state were determined from dielectric measurements of benzene solutions at 25°C using a heterodyne apparatus (frequency 1·2 Mc s^{-1}). Usually five measurements were carried out in the concentration range 5 . 10^{-3} to 5 . 10^{-2} mol l^{-1}. The overall polarizations P_2^0 were calculated according to Halverstadt and Kumler from the slopes α and β of the plots ϱ_{12} vs w_2 and d_{12}^{-1} vs w_2, respectively. Within the concentration range given linear dependences of ϱ and d against weight fraction of the dissolved compound were obtained. The statistical treatment of the data was carried out using program for multiple regression (Hewlett–Packard Standard Statistics Pac No 2).

Intermediates

2,3,5,6-*Tetramethylphenol*: A solution of bromodurene[23] (20 g, 0·09 mol) in sodium hydroxide (2·5M, 250 ml) was added in a steel bomb to a mixture of cuprous oxide (3 g) and bronze (1 g). The bomb was closed and heated to 260°C for 3 h. After cooling the mixture was filtered from the solid and filtrate was acidified with 30% sulfuric acid. The precipitate after crystallization from a mixture of isooctane and chloroform afforded 6·1 g (43%) of 2,3,5,6-tetramethylphenol, m.p. 116—117°C (reported[24] 118°C) and 0·64 g (2·3%) of 4,4'-dihydroxy-2,2',3,3',5,5',6,6'-octamethylbiphenyl, m.p. 205—207°C. For $C_{20}H_{26}O_2$ (298·4) calculated: 80·49% C, 8·78% H; found: 80·26% C, 8·84% H. Mass spectrum: M$^+$ 298.

4-*Iodo*-3,5-*dimethylphenol* was prepared by the known procedure and its physical constants agreed with those reported[20] in literature.

4-*Iodo*-2,3,5,6-*tetramethylphenol* was prepared in the same way. Crystallization from isooctane afforded 7·2 g (55·4%), m.p. 110—112°C. For $C_{10}H_{13}IO$ (276·1) calculated: 43·50% C, 4·74% H; found: 43·32% C, 4·80% H. ^{1}H-NMR spectrum: 2·14 (s, 6 H), 2·46 (s, 6 H), 4·64 (s, 1 H). Mass spectrum: M$^+$ 276.

3-Methyl-4-benzhydrylidene-2,5-cyclohexadien-1-one (*VIIa*)

A solution of 3-methylphenol (1·37 g, 13 mmol) in dichlorodiphenylmethane[25] (2·37 g, 10 mmol) was set aside at room temperature for 72 h in argon atmosphere. The mixture was then poured into ice-cold water (100 ml), extracted with three 25 ml portions of ether, dried ($MgSO_4$) and evaporated *in vacuo*. The crude product was purified by column chromatography on silicagel (300 g) with light petroleum–ether (5 : 1). Recrystallization from chloroform–hexane afforded 1·74 g (50·2%) of *VIIa*, m.p. 194—196°3. For $C_{20}H_{16}O$ (272·3) calculated: 88·20% C, 5·92% H; found: 88·34% C, 5·87% H. UV spectrum (hexane): 27 500 cm^{-1}. IR spectrum (CCl_4): 1 633 cm^{-1} (conjugated C=O). ^{1}H-NMR spectrum: 2·1 (s, 3 H), 7·05—7·45 (m, 10 H). Mass spectrum: $M^{\ddagger}$ 272. 2-Methyl-4-benzhydrylidene-2,5-cyclohexadien-1-one and 2,6-dimethyl-4-benzhydrilidene-2,5-cyclohexadien-1-one were prepared in the same way and their physical constants agreed with those reported[26,27] in literature.

3,5-Dimethyl-4-benzhydrylidene-2,5-cyclohexadien-1-one (*VIIb*)

A solution of n-butyllithium (4·42 g, 69 mmol) in ether (150 ml) was added dropwise to a stirred solution of 4-iodo-3,5-dimethylphenol (8·45 g, 34 mmol) in ether (50 ml). The mixture was refluxed for 2 h and after cooling a solution of benzophenone (6·19 g, 34 mmol) in ether (100 ml) was slowly added. After 2 h of additional reflux the mixture was allowed to stand overnight, poured into saturated aqueous solution of citric acid (100 ml) and extracted with ether (3 × 25 ml) The extracts were combined, washed with water (5 × 10 ml), dried ($MgSO_4$) and evaporated *in vacuo*. The residue was triturated with hexane to give 7·43 g (80%) of diphenyl (4-hydroxy--2,6-dimethylphenyl)methanol, m.p. 164—166°C. For $C_{21}H_{20}O_2$ (304·4) calculated: 82·86% C, 6·62% H; found: 82·81% C, 6·51% H. ^{1}H-NMR spectrum: 1·63 (s, 6 H), 4·90 (s, 1 H), 6·29 (s, 2 H), 7·17 (m, 10 H), 8·40 (s, 1 H). Mass spectrum: $M^{\ddagger}$ 304. Stirred mixture of diphenyl-(4-hydroxy-2,6-dimethylphenyl)methanol (0·5 g, 1·6 mmol), magnesium sulfate (0·20 g) and activated charcoal (0·10 g) in benzene (30 ml) was refluxed for 15 min, cooled and filtered through a small column of Cellite. Removal of the solvent furnished red crystals (0·30 g, 65%) of *VIIb*, m.p. 175—178°C. For $C_{21}H_{18}O$ (286·4) calculated: 88·07% C, 6·33% H; found: 87·92% C, 6·30% H. UV spectrum (hexane): 26 000 cm^{-1}. IR spectrum (CCl_4): 1 626 cm^{-1} (conjugated C=O). ^{1}H-NMR spectrum: 1·52 (s, 6 H), 6·08 (s, 2 H), 7·05—7·45 (m, 10 H). Mass spectrum: $M^{\ddagger}$ 286.

2,3,5,6-Tetramethyl-4-benzhydrylidene-2,5-cyclohexadien-1-one (*VIIc*)

The fuchsone *VIIc* was prepared analogously to *VIIb*, but the intermediate alcohol was not isolated. Crystallization from ether–hexane gave red crystals (0·20 g, 58%), m.p. 175—176°C. For $C_{23}H_{22}O$ (314·4) calculated: 87·86% C, 7·05% H; found: 87·62% C, 6·82% H. UV spectrum (hexane): 24 900 cm^{-1}. IR spectrum (CCl_4): 1 625 cm^{-1} (conjugated C=O). ^{1}H-NMR spectrum: 1·5 (s, 6 H), 1·95 (s, 6 H), 7·1—7·45 (m, 10 H). Mass spectrum: $M^{\ddagger}$ 314.

Fuchsones *XIa—XIc*

Solution of 4-iodo-3,5-dimethylphenol (4·22 g, 18 mmol) in ether (25 ml) was added slowly to a stirred solution of n-butyllithium (38 mmol) in ether (60 ml) under nitrogen. The mixture was refluxed for 2 h and after cooling a solution of substituted benzophenone (8·5 mmol) in ether (25 ml) was added. After additional reflux for 2 h the mixture was kept overnight at room tempera-

ture and worked up by diluting with saturated aqueous solution of citric acid (50 ml) and extraction with ether. The ethereal extracts were washed with water and dried over magnesium sulfate. Removal of the solvent *in vacuo* left a solid, which was further purified by trituration with hexane.

4-[*Phenyl-(4-hydroxy-2,6-dimethylphenyl*)]*methylene-2,5-cyclohexadien-1-one* (XIa) was prepared from 4-hydroxybenzophenone in 20% yield, m.p. 223—225°C. For $C_{21}H_{18}O_2$ (302·4) calculated: 83·41% C, 6·00% H; found: 83·21% C, 6·12% H. UV spectrum (hexane): 27 100cm^{-1}, 29 900 (sh) cm^{-1}. IR spectrum (CCl_4): 1 629·5 cm^{-1} (conjugated C=O). Mass spectrum: M$^+$ 302.

4-[*Phenyl-(4-hydroxy-2,6-dimethylphenyl*)]*methylene-2,6-dimetyl-2,5-cyclohexadien-1-one* (XIb) was prepared from 3,5-dimethyl-4-hydroxybenzophenone in 23% yield, m.p. 167—170°C. For $C_{23}H_{22}O_2$ (330·4) calculated: 83·61% C, 6·71% H; found: 83·48% C, 6·73% H. UV spectrum (hexane): 27 100, 29 600 (sh) cm^{-1}. IR spectrum ($CHCl_3$): 1 604 cm^{-1} (conjugated C=O). Mass spectrum: M$^+$ 330.

4-[*Phenyl-(4-hydroxy-2,6-dimethylphenyl*)]*methylene-2,6-ditert-butyl-2,5-cyclohexadien-1-one* (XIc) was prepared from 3,5-ditert-butyl-4-hydroxybenzophenone in 17% yield, m.p. 254—255°C. For $C_{29}H_{34}O_2$ (414·6) calculated: 84·01% C, 8·26% H; found: 84·15% C, 8·11% H. UV spectrum (hexane): 26 900, 28 500 (sh) cm^{-1}. IR spectrum ($CHCl_3$): 1 604·5 cm^{-1} (conjugated C=O). Mass spectrum: M$^+$ 414.

2,6-Dimethyl-4-(9-fluorenyliden)-2,5-cyclohexadien-1-one (*VIIIa*)

A) To the solution of 9,9-dichlorofluorene[28] (3 g, 12 mmol) and 2,6-dimethylphenol (1·55 g, 12 mmol) in carbon disulfide (20 ml) pulverized aluminium chloride (0·35 g, 2·6 mmol) was added and the progress of reaction was checked by thin-layer chromatography in light petroleum—–ether (1 : 4). When the reaction was complete the mixture was acidified with ice-cold saturated aqueous solution of citric acid and extracted with ether (3 × 50 ml). Combined extracts were evaporated *in vacuo*. Chromatography on silicagel (300 g, light petroleum–ether 8 : 1) afforded red crystals (0·72 g, 20%) of *VIIIa*, m.p. 211°C (reported[2]; 210—211°C) and 9,9-bis(3,5-dimethyl--4-hydroxyphenyl)fluorene (*XIII*) (3·6 g, 70%), m.p. 279—281°C (ethanol). For $C_{29}H_{26}O_2$ (406·5) calculated: 85·70% C, 6·44% H; found: 85·61% C, 6·32% H. ^{1}H-NMR spectrum: 2·1 (s, 12 H), 4·45 (s, 2 H), 6·75 (s, 4 H), 7·21—7·45 (m, 6 H), 7·65—7·81 (m, 2 H). Mass spectrum: M$^+$ 406.

B) Diarylfluorene *XIII* (3·6 g, 8·9 mmol) was dissolved in concentrated sulfuric acid (15 ml). The stirred mixture turned deep purple and after one hour was poured into ice-cold water and extracted with ether (4 × 50 ml). The combined ethereal extracts were washed with water, dried (MgSO$_4$) and evaporated *in vacuo*. Crystallization from ethanol in the presence of charcoal gave 2·2 g (82%) of 9-hydroxy-9-(3,5-dimethyl-4-hydroxyphenyl)fluorene, m.p. 132—134°C. For $C_{21}H_{18}O_2$ (302·4) calculated: 83·41% C, 6·00% H; found: 83·34% C, 5·87% H. ^{1}H-NMR: spectrum: 2·15 (s, 6 H), 4·45 (s, 1 H), 7·22—7·40 (m, 6 H), 7·69—7·80 (m, 2 H). Mass spectrum: M$^+$ 302. A solution of 9-hydroxy-9-(3,5-simethyl-4-hydroxyphenyl)-fluorene (2·2 g, 7·3 mmol) and sodium benzenesulfinate (1·82 g, 9·0 mmol) in acetic acid was refluxed 5 h. Usual[30] work-up furnished 2·54 g (82%) 9-(3,5-dimethyl-4-hydroxyphenyl)-9-phenylsulfonylfluorene, m.p. 210 to 212°C (ethanol). For $C_{27}H_{22}O_3S$ (426·5) calculated: 76·03% C, 5·19% H; found: 77·02% C, 5·15% H. Mass spectrum: M$^+$ 426. The sulfone (2·50 g, 5·9 mmol) was converted to *VIIIa* (1·54 g, 92%) by the standard procedure[31]. In this way the overall yield of *VIIIa* was improved to 62%.

Attempted Preparation of the 3,5-Dimethyl-4-(9-fluorenyliden)-2,5-cyclohexadien-1-one (*VIIIb*)

Reaction of dilithium salt of 3,5-dimethylphenol (17 mmol) with fluorene (3·1 g, 17·2 mmol) in ether (50 ml) afforded 4·29 g (52·5%) of 9-hydroxy-9-(2,6-dimethyl-4-hydroxyphenyl)fluorene (*XIV*), m.p. 233—235°C (ethanol). For $C_{21}H_{18}O_2$ (302·4) calculated: 83·4% V, 5·99% H; found: 83·36% C, 6·15% H. ^{1}H-NMR spectrum: 2·6 (s, 6 H), 3·8 (s, 1 H), 7·2—7·45 (m, 6 H), 7·55—7·75 (m, 2 H). Mass spectrum: M$^+$ 302. 9-(2,6-Dimethyl-4-hydroxyphenyl)-9-phenylsulfonylfluorene (*XV*) was prepared by reported[30] procedure in 89% yield, m.p. 246—248°C (ethanol). For $C_{27}H_{22}O_3S$ (426·5) calculated: 76·03% C, 5·19% H; found: 76·12% C, 5·25% H. Mass spectrum: M$^+$ 426. All attempts to generate *VIIIb* either by the pyrolysis of carbinol *XIV* or by the hydrolysis[31] of sulfone *XV* with dilute sodium hydroxide in the presence of an extracting solvent failed.

RESULTS AND DISCUSSION

The synthesis of 3,5-methylsubstituted fuchsones was based on the recently published[20] reaction of 4-lithio-3,5-dimethylphenoxide with Michler's ketone. The derivatives *VIIb* and *VIIc* were prepared in good yields according to Scheme 1.
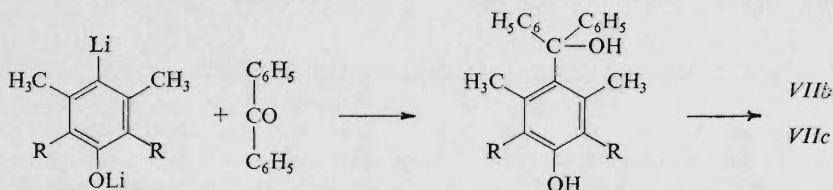
SCHEME 1

In order to compare the influence of 2,6- and 3,5-substitution on thermodynamic stability of fuchsone moiety we selected the elimination of water from carbinol *Xa* as a model reaction (Scheme 2). To decide between structures *XI* and *XII* we eva-

XII

Xa; R = H
Xb; R = CH₃
Xc; R = t-C₄H₉

XI
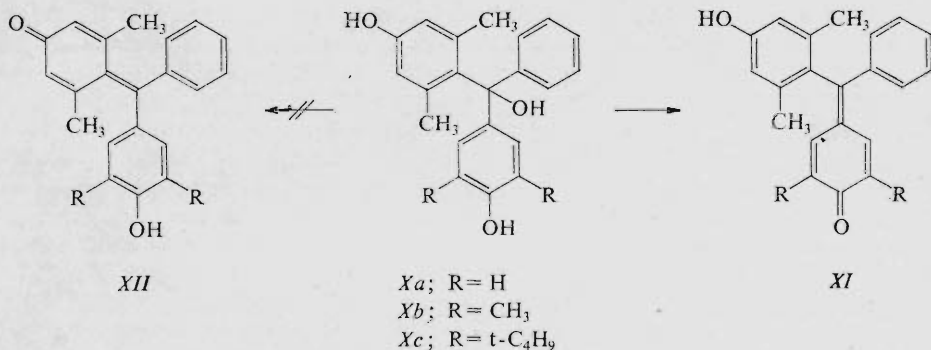
SCHEME 2

luated ^{1}H-NMR spectrum of the single reaction product (Table I). The structure *XII* could be unambiguously excluded by the presence of fourspin system of nonequivalent protons of quinonoid ring in *XI*. This system is composed from two pairs multiplets with splitting $J = 10$ Hz, the magnitude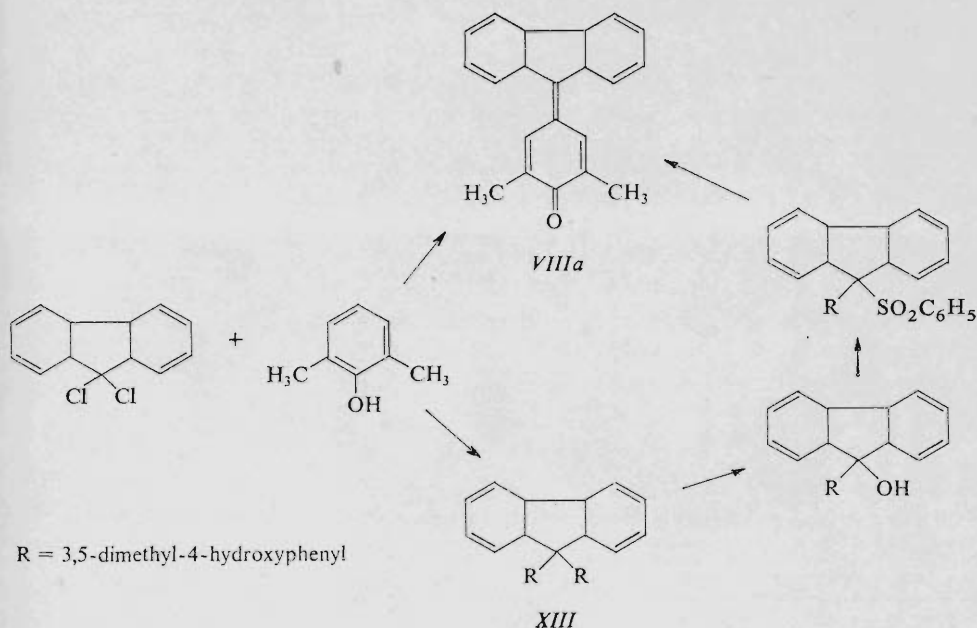 of which corresponds to vicinal interaction in *cis* olefinic double bond, and other long-range splittings (about 2 Hz). The synthesis of the fluorenylidene compound *VIIIa* is outlined in Scheme 3. We have failed to prepare derivative *VIIIb*.

SCHEME 3

The longest wavelength transition of parent 4-methylene-2,5-cyclohexadien-1-one has been interpreted[32] as a symmetrically allowed $^1A_1 - {}^1A_1$ transition with the polarization vector identical with the rotational axis of symmetry C_{2v}. The $^1A_1 - {}^1B_1$ bands predicted in the same region ($\varepsilon < 100$) cannot enhance the observed intensity. We assume that the longest wavelength transitions of the derivatives *VII* − *IX* are of the same types.

As demonstrated by Fig. 1, the 1st absorption bands of both the 3,5-dimethyl (*VIIb*) and 2,6-dimethyl (*IXc*) fuchsones reveal a considerable hypsochromic shift when compared to the "inherently planar"[29] fluorenyl derivative *VIIIa*. On the other hand, the bathochromic shift of 1600 cm^{-1} may be observed on going from 2,6-dimethylfuchsone to its 3,5-dimethyl analogue. It follows that two basic ways in which

the steric crowding can be relieved or minimalized should be operative for the compounds under study: *1*) rotation around the single bond $C_{(7)}$—C_{aryl} and *2*) twisting around the exocyclic $C_{(4)}$—$C_{(7)}$ double bond. In accordance with the theoretical

TABLE I
^{1}H-NMR data of benzaurines *XI* and fuchsones *IXa*, *IXc* and *IXd*

Compound[a]	$C_{(6)}$—R	$C_{(5)}$—H	$C_{(3)}$—H	$C_{(2)}$—R	$C_{(10')}$—H $C_{(12')}$—H	$C_{(9')}$—CH$_3$ $C_{(13')}$—CH$_3$
XIa	6·41 m $J_{6,5} = 10$ $J_{6,2} = 2·5$	7·07 m $J_{5,6} = 10$ $J_{5,3} = 2·5$	7·67 m $J_{3,2} = 10$ $J_{3,5} = 2·5$	6·55 m $J_{2,3} = 10$ $J_{2,6} = 2·5$	6·66 s	1·95 s
XIb	1·97 d $J_{CH_3,H_5} = 1·25$	6·81 m $J_{5,3} = 2·5$	7·44 m $J_{3,5} = 2·5$	2·07 d $J_{CH_3,H_3} = 1·25$	6·67 s	1·97 s
XIc	1·16 s	6·76 d $J_{5,3} = 2.5$	7·46 d $J_{3,5} = 2·5$	1·29 s	6·61 s	1·99 s
IXa	6·40 m $J_{6,5} = 10$	7·36 m $J_{5,6} = 10$	7·36 m $J_{3,2} = 10$	6·40 m $J_{2,3} = 10$	—	—
IXc	2·02 d $J_{CH_3,H} = 1·2$	7·15 m	7·15 m	2·02 d $J_{CH_3,H} = 1·2$	—	—
IXd	1·23 s	7·17 s	7·17 s	1·23 s	—	—

[a] Chemical shifts in ppm (δ) from internal tetramethylsilane; coupling constants in Hz.
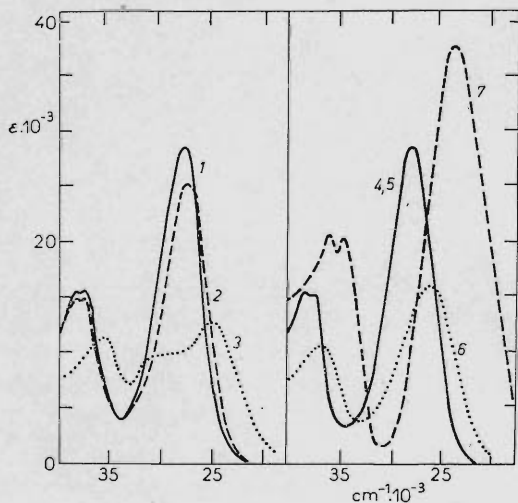

FIG. 1

Electronic spectra of fuchsones: *1* (*VIIa*), *2* (*IXb*), *3* (*VIIc*), *4* (*IXa*), *5* (*IXc*), *6* (*VIIb*) and *7* (*VIIIa*) measured in hexane

prediction[33] both types of the twisting are associated with a hypochromic effect.

It is well known that in analysis of the spectral effects of the steric crowding, attention should be focused on the molecular properties of the ground state as well as that of excited state. For that reason, knowledge of the ground (μ_g) and excited state (μ_e) dipole moments may be of great importance. Accordingly, the forthcoming discussion will deal firstly with the ground state dipole moments of fuchsones $VII-IX$ (Table II). When compared to the moment of parent fuchsone[1] $(18\cdot75\cdot10^{-30}$ C m) the dipole moments of both 3,5-dimethyl $(VIIb)$ and 2,6-dimethyl (IXc) derivatives reveal the increment of $2\cdot5\cdot10^{-30}$ C m, which one could accept by taking into account the σ and π donor properties of methyl groups. Furthermore, negligibe difference of dipole moments of 3,5- and 2,6-dimethyl isomers suggests approximately equal contributions of the dipolar mesomeric structures $VIIb'$ and IXc'. This result is, however, rather surprising. As can be expected from the van der Waals radii of hydrogen $(0\cdot12$ nm) and methyl group $(0\cdot20$ nm) the introduction of methyl groups into 3,5-positions must drastically change the molecular geometry in the vicinity of the $C_{(4)}$—$C_{(7)}$ double bond.
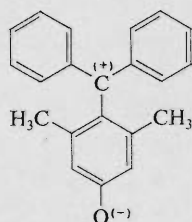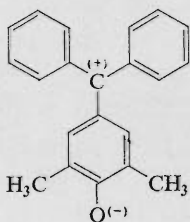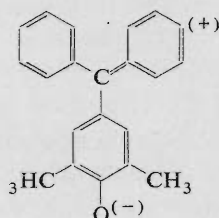
VIIb'   IXc'   IXc''

TABLE II

Polarization data of fuchsones $VII-IX$

Compound	α^a	β^a	P_2^0 cm^3	μ_g (5%)^b Cm . 10^{30}
VIIb	16·00	−0·320	924·09	21·31
VIIc	16·00	−0·160	1 043·54	22·68
VIIIa	6·22	−0·560	516·09	14·61
IXa^c	13·72	−0·300	730·50	18·75
IXc^c	15·87	−0·258	929·10	21·28

^{a} Slopes of the Halverstadt–Kumler[37] plots; ^{b} correction for the atomic polarization of 5% R_D value; ^{c} taken from ref.[1].

Two tentative explanations of the data can be considered. One is that the $C_{(4)}$—$C_{(7)}$ bond length and charge population do not change greatly on going from "planar" to the twisted (B) or folded (C) conformation;

$$B \qquad\qquad\qquad C$$
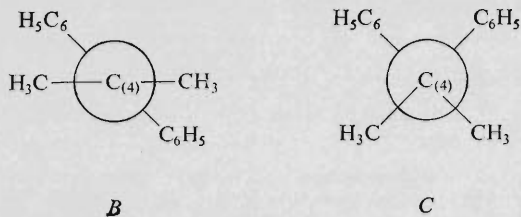
The total electronic effect of methyl groups on the gross electron delocalization is assumed to be approximately equal irrespective of their position. The other explanation, which we favour, is the cancelation of expected effect by some other factor. Most plausibly the contribution of "planar" mesomeric structures such as *IXc″* will be no more important for *VIIc* as a consequence of removal of steric interactions between 3,5-methyl groups and aromatic protons by twisting the exocyclic double bond out of quinonoid ring plane. The net result of these opposing effects is the negligible change of the dipole moment.

The dipole moment of the tetramethyl derivative *VIIc* may be simply derived from the dipole moment of *VIIb* by correcting for the contribution of 2,6-methyl groups (addition of $2 \cdot 53 . 10^{-30}$ C m). The calculated value of $23 \cdot 84 . 10^{-30}$ C m is comparable with the experimental value $\left(\mu_{\text{calc}}^{\text{VIIc}} - \mu_{\text{exp}}^{\text{VIIc}} = 1 \cdot 16 . 10^{-30} \text{ C m}\right)$.

To understand in detail the influence of substituent position on fuchsone π-system, we have studied methyl substituent effects on its ^{13}C-NMR chemical shifts, since these shifts are generally conceded to be at least indicative of electron density variations in π-systems.

^{13}C Chemical shifts and $^1J(CH)$ coupling constants are summarized in Table III. The assignments of chemical shifts were based on our previous ^{13}C-NMR work in the fuchsone series[34] and on an analogy with spectra of substituted fluorenones[35] (in the case of *VIIIa*). The most noteworthy feature of ^{13}C chemical shift data is the increased deshielding of $C_{(7)}$ to $C_{(11)}$ atoms in *VIIa* and *VIIb* when compared to their analogues *IXb* and *IXc*, indicating a more positively charged $C_{(7)}$ for twisted compounds. Moreover, it may be observed from the Table IV that introduction of the second group doubles the effect of the first methyl group. If the twist of the exocyclic double bond approaches 90° complete polarization of π-electrons in double bonds would take place and a structure like that represented by *VIIb′* would arise. However, this picture may be oversimplified, since $\sigma - \pi$ separation breaks down when the molecule is twisted. Dewar and Kohn[36] have calculated the electronic structures of planar and 90° twisted calicene by the MINDO/2 method, and they report a larger

polarization (about 0·3 electron) in the twisted than in the planar molecule, but their result is far from the complete polarization depicted in *VIIb'*. We were not able to understand completely the ^{13}C-NMR spectra of the tetramethyl derivative *VIIc*, but it is well known[38] that the effect of methyl groups in durenes is of complicated nature and so the arisen difficulties were anticipated.

As can be seen from Table V the longest wavelength absorption maximum showed a red shift on going from less polar to polar solvent indicating a larger contribution of the dipolar structure to the excited state rather than the ground state for all compounds under study. The theory[39-41] of the solvent induced shift of absorption

TABLE III
^{13}C Chemical shift values and ^1J(CH) coupling constants (in parentheses) for compounds *VII* and *VIIIa*

Carbon	VIIa	VIIb	VIIc	VIIIa
$C_{(1)}$	186·2	186·0	184·7	187·3
$C_{(2)}$	131·6[a] (160·0)	130·1 (161·1)	133·9	137·1
$C_{(3)}$	147·2	149·1	144·0	132·8 (156·7)
$C_{(4)}$	132·4	135·9	138·5	132·5
$C_{(5)}$	142·6 (160·0)	149·1	144·0	132·8 (156·7)
$C_{(6)}$	126·2[a] (163·6)	130·1 (161·1)	133·9	137·1
$C_{(7)}$	161·6	162·5	154·9	146·4
$C_{(8)}$	142·2[b] 141·7[b]	144·4	145·3	137·8
$C_{(9)}$	132·1[b,c] 131·1[b,c]	132·3 (161·4)	131·7 (161·0)	130·1[d] (161·1)
$C_{(10)}$	128·2[b,c] 128·0[b,c]	128·3 (161·6)	128·3 (161·0)	127·9[d] (161·1)
$C_{(11)}$	129·9[c]	130·6 (161·6)	129·2 (161·5)	127·7[d] (162·4)
Others	23·5 (CH$_3$) (128·6)	24·7 (CH$_3$) (127·8)	21·4 (3,5-CH$_3$) (127·5); 12·7 (2,6-CH$_3$) (128·5)	16·9 (CH$_3$); 120·3 ($C_{(12)}$); (159·9) 142·1 ($C_{(13)}$)

[a] The assignment may be reversed; [b] or primed carbon atoms of the same number; [c] ^1J(CH) = = 161·5 ± 1 Hz for atoms $C_{(9)}$ to $C_{(11)}$ and $C_{(9')}$ to $C_{(11')}$; [d] the assignment may be reversed.

maxima enables us to discuss above mentioned finding more quantitatively in terms of ground (μ_g) and excited state (μ_e) dipole moments.

For polar solutes, Eq. (I) was developed[41] to describe the shift $\Delta\tilde{\nu}$ of the wavenumber $\tilde{\nu}$ of the transition in a solvent of dielectric constant ε and refractive index n

TABLE IV

The effects of methyl substitution on the ^{13}C chemical shifts of fuchsone

Substituent[a]	$C_{(4)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(11)}$
2-Methyl[b]	0·3	− 1·4	0·4	0· −	0·1	−0·3
3-Methyl	3·1	1·5	2·5	0·2	0·2	0· −
2,6-Dimethyl[b]	0·3	− 3·7	0·7	−0·1	−0·1	−0·8
3,5-Dimethyl	6·6	2·4	4·7	0·5	0·3	0·7
2,3,5,6-Tetramethyl	9·2	− 5·2	5·6	−0·2	0·3	−0·7
2,6-Dimethyl[c]	3·2	−13·7	—	—	—	—

[a] Values are in ppm relative to the corresponding carbon atom in fuchsone; negative values denote increased shielding; [b] taken from ref.[34]; [c] derivative *VIIIa*.

TABLE V

Solvent effects on the lowest singlet-singlet electronic transitions in the symmetrically substituted fuchsones

No	Solvent	ε	n	$\tilde{\nu}_{max}$, cm^{-1}				
				VIIb	*VIIc*	*VIIIa*	*IXc*	*IXa*
1	n-Hexane	1·89	1·3748	26 100	25 040	23 640	27 730	27 920
2	Isooctane	1·94	1·3915	26 000	24 920	23 620	27 680	27 910
3	Cyclohexane	2·02	1·4266	25 920	24 880	23 540	27 500	27 750
4	Diethyl ether	4·33	1·3526	25 780	24 810	23 680	27 460	27 500
5	Methyl acetate	6·68	1 3602	25 180	24 290	23 460	27 190	27 280
6	Ethyl acetate	6·09	1·4109	25 220	24 250	23 340	27 210	27 250
7	n-Butyl acetate	5·01	1·3701	25 290	24 420	23 400	27 220	27 270
8	n-Pentyl acetate	4·75	1·4028	25 200	24 340	23 420	27 230	27 290
9	Tetrahydrofurane	7·25	1·4076	25 260	24 160	23 400	27 040	27 010
10	Dichloroethane	10·65	1·4448	24 720	23 920	23 000	26 740	26 720
11	Acetone	20·70	1·3570	25 250	24 130	23 300	27 120	26 900
12	N,N-Dimethylformamide	36·70	1·4269	24 800	23 950	23 160	26 670	26 510
13	Acetonitrile	37·50	1·3420	24 940	24 190	23 420	26 960	26 800
14	Dimethyl sulfoxide	48·90	1·4782	24 510	23 570	22 830	26 480	26 300

in terms of five solute and transition dependent paramaters, v_0, A, B, C and D. For the absorption transition from the ground (g) to excited (e) state (corresponding to the $0-0$ transition), the parameters A, B, C and D are related to other parameters of the model by equations $(2)-(5)$

$$\tilde{v} = \tilde{v}_0 + (A + C)\left[(n^2 - 1)/(2n^2 + 1)\right] + B\left[(\varepsilon - n^2)(2\varepsilon + n^2)/(n^2 + 2)^2 \varepsilon\right] +$$
$$+ D\{[(\varepsilon - 1)/(\varepsilon + 2)] - [(n^2 - 1)/(n^2 + 2)]\} \tag{1}$$

$$A = -\{[\sum A_e(\mu_e)^2] - [\sum A_g(\mu_g)^2]\}/a^3 \tag{2}$$

$$B = -\{108[\ln^2(R/a)]\,kT(\alpha_e - \alpha_g)\}/R^3 \tag{3}$$

$$C = -[(\mu_e)^2 - (\mu_g)^2]/a^3 \tag{4}$$

$$D = -2[(\mu_g\mu_e) - (\mu_g)^2]/a^3 . \tag{5}$$

Here, α, a, k, T are the polarizability, Onsager cavity radius, Boltzmann constant and the Kelvin temperature of the solution, respectively.

TABLE VI

Statistics of Eq. (2) for longest wavelength band of some symmetrically substituted derivatives $VII-IX$

Compound[a]	$\tilde{v}_0$ cm^{-1}	$-(A + C)$ cm^{-1}	B cm^{-1}	$-D$ cm^{-1}	r[b]	$t_{(A+C)}$[c]	$t_{(B)}$[c]	$t_{(D)}$[c]
VIIb	28 721	14 107 (3 172)	44 (38)	1 989 (294)	0·964	4·5	1·1	6·7
VIIc	27 560	13 449 (2 290)	32 (27)	1 685 (213)	0·975	5·9	1·1	7·9
VIIIa	25 895	11 755 (1 695)	5 (20)	669 (157)	0·957	6·9	0·2	4·2
IXa	30 291	12 552 (1 218)	−12 (14)	1 757 (113)	0·995	10·3	0·8	15·5
IXc	30 079	12 616 (1 481)	3 (17)	1 261 (137)	0·986	8·5	0·1	9·2

[a] Standard deviation in parentheses; [b] multiple correlation coefficient; [c] t-tests.

Due to the lack of clear vibronic structure of the absorption spectra it was impossible to determine the energy shifts of the $0-0$ transitions for compounds $VII-IX$. Therefore, the changes of transition energies were estimated from the shifts of absorption maxima of particular bands. The wavenumbers of the absorption maxima of $VIIb$, $VIIc$, $VIIIa$, IXb and IXc in 14 solvents used are listed in Table V. A linear least squares program was used to fit Eq. (I) to these data in order to evaluate the parameters $\tilde{v}_0$, $(A + C)$, B and D. The values obtained are summarized in Table VI. It may be seen from these data that the shift of $\pi-\pi^*$ bands is mainly due to the interactions decscribed by $(A + C)$ and D terms. The constant B, which describes the solvent Stark shift, is over a hundred times smaller than constant D. Moreover, both the values of standard deviations and t-tests indicate the constants B to be statistically unsignificant for all compounds considered. The constant D, which describes the interaction between permanent dipole moments of solute and solvent molecules is related to dipole moments of the molecule in the ground and excited states, and to the cavity radius a. Assuming that the cavity radius can be evaluated on the basis of molal volume and also that the μ_e and μ_g are colinear, we were able to determine the dipole moments in excited $\pi-\pi^*$ states (Table VII). From the comparison of the degree of dipole moment increase in the excited $\pi-\pi^*$ state $(\Delta\mu = \mu_e - \mu_g)$, it follows that the degree for $VIIb$ and $VIIc$ is about 1·5 times as great as that of IXc. Consequently the main factor causing the red shift of the $\pi-\pi^*$ absorption of fuchsones in polar solvents $(i.e.$ stabilization due to electrostatic interactions between solute and solvent molecules$)$ become more important in the case of twisted molecules $VIIb$ and $VIIc$.

It is instructive to compare the results of calculation separately for non polar and polar solvents. As typical examples let us compare the nature of the shift difference

TABLE VII
Excited state dipole moments of some derivatives $VII-IX$ having approximately C_{2v} symmetry

Compound	a^a .nm	$\Delta\mu$ Cm . 10^{30}	μ_e Cm . 10^{30}
$VIIb$	0·464	10·31	31·62
$VIIc$	0·485	9·37	32·05
$VIIIa$	0·405	3·33	17·94
IXa	0·442	8·93	27·68
IXc	0·463	6·50	27·78

[a] Onsager cavity radius was estimated from the apparent molal volume Φ_v. The Φ_v is defined by the relation: $\Phi_v = M/d - 10\,00(d - d_0)/mdd_0$, where d_0 and d are the densities of the solvent and the solution of molality m of the solute having molecular weight M, respectively.

(red shift) between *VIIb* and *IXc* in hexane with the same shift in acetonitrile. According to Eq. (*I*) this shift may be separated into a linear sum of terms, *i.e.* $\Delta\tilde{v} =$ $= \tilde{v}^{VIIb} - \tilde{v}^{IXc} = \Delta\tilde{v}^0 + \Delta\tilde{v}_{P-D} + \Delta\tilde{v}_{DIP}$ (where $\Delta\tilde{v}_{P-D}$ and $\Delta\tilde{v}_{DIP}$ denote the changes in the polarizability-dispersion and dipole–dipole interaction, respectively) on going from *VIIb* to *IXc* in identical solvent. From comparison of the weight of individual terms in hexane $(\Delta\tilde{v}^0 = 84\%,\ \Delta\tilde{v}_{P-D} = 16\%,\ \Delta\tilde{v}_{DIP} = 0\%)$ to that in acetonitrile $(67\%,\ 13\%,\ 20\%)$ it follows the enhanced participation of the dipolar term in the latter solvent. In spite of this the contribution of the $\Delta\tilde{v}^0$ term remains decisive. This finding indicates that the solvation energy has not the dominating influence on the magnitude of the red shift. In accordance with the previous MO calculations[32] it is most reasonable to conclude that the $\pi - \pi^*$ bands that are the subject of discussion belong to the group species $^1A_1$ and consist a very large contribution of the single configuration which corresponds to one electronic excitation from the highest occupied orbital to the lowest empty orbital.

Regarding the considerable intermolecular charge transfer (ICT) character of the first electronic transition in fuchsones[42] we assume that the structural feature of *VIIb* and *VIIc* are still more favourable[43] to the HOMO-LUMO separation thus enhancing the intramolecular CT character of their first absorption band.

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