BENZOANNELATED QUINONE METHIDES*

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On the basis of detailed study of UV, IR, ^{13}C NMR and $E_{1/2}$ data of quinone methides *V— VII* three dominant factors influencing the behaviour of benzoannelated compounds must be considered: *1*) electronic effects of both the exocyclic carbon substituents and the fused rings, *2*) the extent to which the substituents are displaced out of the plane of the exocyclic double bond through steric interference between the side-chain substituents and *peri*-hydrogens and *3*) the extent of the angular distorsion of the quinone-like rings. The ground state charge separation (∼0·2e) in nonannelated derivatives was found to be strongly minimized by annelation of two benzene units to the parent systems. Near parallelism with this phenomenon was also observed in both the carbonyl vibration frequency and ^{13}C NMR data.

Although many highly substituted *para*-quinone methides are well authenticated compounds the parent methide *I* has not yet been isolated because of its high reactivity[1-3]. Being antiaromatic Hückel pseudo $4n$ π-electron system it could only be subjected to spectroscopic studies at very low temperature, with the aid of matrix isolation techniques[4,5].

I   *II*
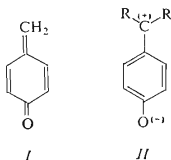
Various experimental approaches have been devised in attempts to stabilize the reactive π-electron system of *I*. The most successful ones include (*i*) introduction of bulky substituents in the *ortho* positions to the carbonyl group[6,7]; (*ii*) replacement of exocyclic methylene hydrogens by electron-donating groups[8-12] and (*iii*) annelation of an aromatic π-electron system to the six membered quinonoid ring[13,14].

The compounds *III – V* represent examples of relatively stable quinone methides, each of them illustrating one of the above mentioned possiblity of stabilization. While the compounds *IV* and *V* have been known for a long time[9,13], the isolation of ditert-butyl derivative *III* in its crystalline state (m.p. 48 – 50°C) has been realized only recently[15].
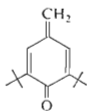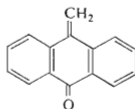

III   *IV*

Although many experimental techniques including UV (ref.[16-19]), IR (ref.[6,20]), ^{1}H and ^{13}C NMR spectroscopic methods[22-27], X-ray diffraction[28-30] and dipole moment as well as polarographic measurements[31-33] have been used to characterize quinone methides stabilized by methode (*i*) and/or (*ii*), little is known about the physico-chemical properties of annelated derivatives. Only scarce studies concerning ^{1}H NMR spectra and X-ray study of naphthofuchsones[22,30] as well as some UV and IR data of several derivatives[30,32,33] have been reported. To our knowledge no attempt has been made to study any annelation effect.
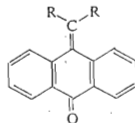
In continuation of our previous work on quinone methides we try to follow changes in their quinonoid character caused by the annelation of a benzo group. In this respect, experimental quantities connected with the carbonyl function of these molecules such as carbonyl stretching frequencies, ^{13}C=O chemical shifts and half-wave reduction potentials may prove to be of interest. The substituents on the exocyclic carbon were chosen so as to differ strongly in their electronic character. Whereas phenyl group (series *a*) can conjugatively stabilize the unsaturated system, and yet exerts only little inductive perturbation, thio group (series *b*) reinforces the molecular polarization in favor of the marked push-pull effect. Both these series are expected to be suitable models for a detailed investigation of the inherent properties of the quinone methide π-systems. Additionally, it was important to find out whether there is any similarity between annelated quinone methides and more thoroughly studied quinones.
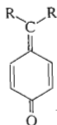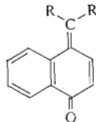
Va; R = C$_6$H$_5$ *VIa*; R = C$_6$H$_5$ *VIIa*; R = C$_6$H$_5$
Vb; R = S(CH$_2$)$_2$S   *VIb*; R = S(CH$_2$)$_2$S   *VIIb*; R = S(CH$_2$)$_2$S

EXPERIMENTAL

Materials. The quinone methides *V—VII* were prepared by known methods[8,31] from the corresponding phenols and their physico-chemical constants agreed with those reported[8,31,32].

Physical measurements. Infrared absorption spectra were recorded on Perkin–Elmer 580 spectrophotometer in a 0.1 mm cell. Concentration of the chloroform solution was 0·03 mol dm^{-3}. Electronic spectra were recorded on Specord UV VIS spectrophotometer in dichloromethane. ^{1}H NMR spectra were taken in deuteriochloroform on Varian HA-100 instrument (tetramethylsilane as internal standard; *J* in Hz). ^{13}C NMR spectra were recorded on JNM-FX 100 (JEOL) spectrometer working at 25·047 MHz using an 8 K transform. Pulse width of 7 μs (flip angle ∼30°) was used with a 3 s pulse repetition time. All spectra were measured in deuteriochloroform at ambient probe temperature (25°C). Tetramethylsilane was used as the internal standard and field frequency lock was established on the deuterium resonance of the solvent. The digital resolution of computer data was 1·220 Hz/point which, combined with the averages, allows the estimation of the chemical shifts accuracy as better than ±0·10 ppm. Electrochemical data were obtained using the polarographic technique, details of which have been described in a previous paper[33]. The measurements were performed on a digital polarograph using two-electrode arrangement with a modified (lithium salt was used instead of sodium chloride) saturated calomel electrode as the reference electrode. The dropping mercury electrode had the controlled drop life t_1 = 4.4 s. All experiments were carried out at 25 ± 0·1°C in N,N-dimethylformamide containing 0·1 mol cm^{-3} tetrabutylammonium perchlorate as supporting electrolyte.

RESULTS AND DISCUSSION

From the inspection of space-filling models as well as X-ray data previously reported[28,30], it is clear that annelation effect has to be connected with changes in molecular geometries. As the geometrical factors do not change continuously when the number of annelated benzene units rises from 1 to 2, the picture that emerges on combining both the geometrical and electronic factors may be of rather complicated nature. This situation is well-documented by UV spectra of the compounds studied in the 18 000 to 30 000 cm^{-1} region (Fig. 1). A number of these spectra have been observed previously. We decided to remeasure them in order to provide a greater degree of internal consistency inside the data set.

The long wavelength absorption bands recorded in Fig. 1 have in all cases extinction coefficients higher than 10 000 and are ascribed to allowed $\pi - \pi^*$ transitions. These bands exhibit a distinct bathochromic shift upon increasing the solvent polarity which is a clear indication of increased polarity of quinone methides *V—VII* in the excited state. In the fuchsone *a* series, 1st absorption band of the derivative *VIa* reveals a considerable bathochromic shift (1 900 cm^{-1}) when compared to *Va*, whereas the hypsochromic shift of 1 300 cm^{-1} on going from *Va* to its diannelated analogue *VIIa* is observed. The corresponding absorption intensity decreases in order *Va* > *VIa* > *VIIa*, indicating an increased steric inhibition of resonance in the same order. The above shifts are analogous to those found in sesquifulvalene[34] and calicene[35] systems. On the other hand, the annelation of each benzene unit to *para*-benzoquinone causes a bathochromic shift of about 950 cm^{-1}. However, in this case

the planarity of the quinone systems remains unchanged[36] and the annelation effect may be regarded as purely electronic. Comparing the positions of the 1st intense band of fuchsones $Va - VIIa$ with those of $Vb - VIIb$ the latter bands are displaced to longer wavelengths, reflecting the capability of the dithiolane ring to stabilize zwitterionic excited states. Perhaps the most interesting difference between the *para*-fuchsone and *para*-dithiolane series consists in the absence of any wavenumber shift in the latter series, suggesting apparently the same extent of conjugation for nonannelated as well as annelated compounds. On closer examination, however, this model must be regarded as unlikely for several reasons. Firstly, the difference of 37 cm^{-1} in the carbonyl stretching frequencies $\tilde{v}(C{=}O)$ between Vb and $VIIb$ (Table I) indicates that substantially more single bond C—O character is present in the carbonyl group of Vb compared with that of $VIIb$. Secondly, the upfield shift of the exocyclic carbon NMR signal (Table II) from 170·1 ppm (Vb) to 146·4 ppm ($VIIb$) provides further evidence for less effective conjugation in $VIIb$ compared to Vb, at least in sense of delocalized structures such as II. Thirdly, the hyperchromic effect in the dithiolane series follows the same order as found in the fuchsone series, *i.e.* $\varepsilon(Vb) > \varepsilon(VIb) > \varepsilon(VIIb)$.
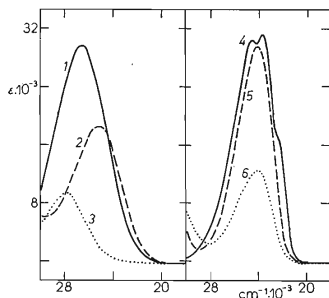

FIG. 1

Long-wavelength part of absorption spectra of quinone methides: *1* (Va), *2* (VIa), *3* ($VIIa$), *4* (Vb), *5* (VIb), *6* ($VIIb$)
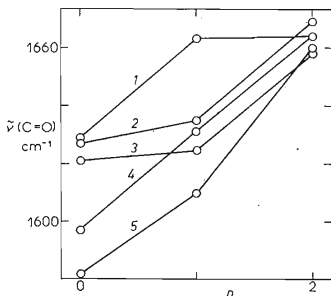

FIG. 2

Carbonyl vibration frequency as a function of the number of annelated units: *1* (pyrones), *2* (fuchsones), *3* (dithiolanes), *4* (thiopyrones), *5* (tropones)

It seems reasonable to conclude that two dominant factors governing the position of the UV maxima of fuchsones are: (*i*) twisting around the exocyclic double bond (decisive factor for *VIa*) and (*ii*) out-of-plane distorsion of the quinonoid ring in such a way as to form "butterfly shaped" skeleton (decisive factor for *VIIa*). A support for the second way can be found in X-ray analysis of 9-dicyanomethyleneanthrone, the central ring of which was found to exist in the boat form[30] (the C—C(O)—C plane is bent about 11° from the central ring plane, while the dicyanomethylene group is tilted by 36·5° from this plane).

TABLE I

^{13}C Chemical shifts of quinone methides *V—VII*

Compound	C=O	R R C	R R C || CH$_2$	$^3J(H_A, H_B)$
Va[a]	186·8	129·3	160·1	—	10·0
Vb	186·7	121·2	170·1	38·9	9·8
VIa	184·4	[b]	155·9	—	10·2
VIb	184·3	119·6	161·2	40·6	9·9
				35·6	
VIIa	185·8	[b]	146·1	—	—
VIIb	184·1	120·7	146·4	37·9	—

[a] Ref.[26]; [b] not determined.

TABLE II

C=O Stretching vibrations and half-wave potentials of quinone methides *V—VII*

Compound	$\bar{v}$(C=O)[a] cm^{-1}	$-E_{1/2}$[b] mV	Slope[c]
Va	1 627·0	445	59
Vb	1 621·0	661	72
VIa	1 635·0	508	62
VIb	1 625·5	790	56
VIIa	1 669·0	597	61
VIIb	1 658·0	990	70

[a] In CHCl$_3$; [b] in dimethylformamide; [c] in milivolts referred to logarithmic unit.

When applying related reasoning to *para*-dithiolanes we may state that apparent absence of a wavelength displacement of the $\pi - \pi^*$ band in these compounds is due to a compensation of several opposing processes: (*i*) as can be expected from the van der Waals radii of hydrogen (0·12 nm) and sulphur (0·18 nm) atoms the annelation of the benzene unit to the quinone methide ring must result in a steric interference between the sulphur atom(s) and the *peri* hydrogen(s). This interference might tend to rotate the dithiolane ring out of the quinonoid ring plane and so cause a bathochromic shift of the $\pi - \pi^*$ band. The "pure" electronic effect of the annelated ring should operate in the same direction. (*ii*) These effects are counterbalanced by the out-of-plane distorsion of the quinonoid ring and by a subsequent loss of resonance. The net effect of these opposing factors upon the position of the $\pi - \pi^*$ band is small and so little change in the maximum should be observed upon annelation of benzene units into *Vb*.

The exocyclic carbon atom resonance of *VIIb* (146.4 ppm) is very close to the same carbon atom resonance of *VIIa* (146·1 ppm) indicating similar charge densities at C_{exo} atom for both diannelated derivatives. In contrast, the C_{exo} atom chemical shifts of parent compounds *Va* and *Vb* differ by 10 ppm. Hence the differences in polarities (as measured by the charge density at C_{exo} atom) are almost completely wiped out by annelation of two benzene units. Furthermore, the carbonyl carbon chemical shifts remain essentially constant throughout both the fuchsone and the dithiolane series (186·7 − 184·1 ppm and 186·8 − 184·4 ppm respectively). However, this apparent paradox may be explained[37] in terms of a net loss of electron density from the core of the conjugated system to the oxygen end of the dipole. A support for this explanation is found in the frequencies of the C=O stretching absorption in the IR spectra

TABLE III

Dipole moments and charge separations of some quinone methides

Compound	μ C m . 10^{-30}	Reference	Charge separation e
I	15·34	45	0·17
Va	18·74	31	0·21
Vb	25·14	*a*	0·25
VIIa	12·07	31	0·14
VIIb	16·00	9	0·15

a Derived from the known dipole moment of the 2,6-ditert-butyl derivative ($\mu = 21·21$. 10^{-30} C m) (ref.[9]) by addition of 3·93 . 10^{-30} C m (correction for the two tert-butyl groups[31]).

of the compounds. A useful visualization of these results is obtained by plotting the $\tilde{v}(C=O)$ values as a function of the number of annelated units, as shown in Fig. 2. For comparison, the $\tilde{v}(C=O)$ of some other benzoannelated cross-conjugated systems, such as tropones[38], 4-pyrones[39] and 4-thiopyrones[39] are also presented. Disregarding some inconsistencies inside the data (solvent effects) the significant increase of the C=O frequency by annelation indicates that the associated force constant has increased upon this process with a concomitant decrease in the carbonyl bond length. Moreover, the $\tilde{v}(C=O)$ values of all diannelated derivatives appear in a narrow region of about $1\,660-1\,670\ cm^{-1}$ independent of marked difference in $\tilde{v}(C=O)$ of the parent members. It follows that the conjugation between carbonyl group and methide carbon atom (as measured by the C=O bond polarity) is almost absent in diannelated derivatives. This conclusion is supported by IR spectrum of anthrone[3] : ($\tilde{v}(C=O)\ 1\,667\ cm^{-1}$).

Additional information on the charge separation magnitudes were obtained from ground state dipole moments (Table III). Prior to discussing the data it should be noted that dipole moments of dithiolanes *Vb* and *VIIb* include the σ-moments of C—S—C bonds; only after correcting for this contribution (substraction of of $3\cdot00 \times 10^{-30}$ C m*) the values are comparable to the corresponding fuchsones. Interestingly, there are striking dipole moment differences between the parent members *Va* and *Vb* on the one hand and their diannelated analogues *VIIa* and *VIIb* on the other. Whereas the relatively high dipole moment values of the former compounds ($18\cdot74\,.\,10^{-30}$ C m and $25\cdot14\,.\,10^{-30}$ C m, respectively) seem to demonstrate a considerable contribution of the zwitterionic structure *II* to the ground state of the molecules, the dipole moments of *VIIa* and *VIIb* do not reveal any additional conjugation when compared to the moment of anthrone ($12\cdot20\,.\,10^{-30}$ C m) (ref.[42]) and are to be viewed as simple aromatic ketones. However, even in the case of *Va* and *Vb*, the proposed contribution of the charge separated forms shoud be considered with some caution. It has been argued[43] that a dipole moment of $9\cdot33 \pm$ $\pm\ 0\cdot66\,.\,10^{-30}$ C m is the property of the carbonyl group itself and that the enhanced moments observed in some unsaturated carbonyl compounds merely reflects the increased distance between the centers of negative (oxygen atom) and positive charge. Using this hypothesis, charge separation of 0.49 e for acetone (from $d_{C=O} =$ $=\ 0\cdot12122$ nm, $\mu = 9\cdot50\,.\,10^{-30}$ C m) has been calculated[44]. Similarly, based on the known geometries of 4-methylene-2,5-cyclohexadien-1-one[45], 2,6-dimethylfuchsone[29], 8-dicyanomethylenanthrone[30] and 6,6-(ethylenedithio)fulvene[41] a charge separation of c. $0\cdot20-0\cdot25$ e for the compounds *Va* and *Vb* and c. $0\cdot13-0\cdot15$ e for anthraderivatives *VII* were estimated. In spite of the fact that all such models are not very accurate since they depend on approximate geometries of the compounds *V*

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*   Based on the σ-moment of C-S bond ($4\cdot50\,.\,10^{-30}$ C m) (ref.[40]) and the X-ray geometry of 6,6-(ethylenedithio)fulvene[41].

and *VII* the extent of contribution of the dipolar resonance form *II* to the overall structure of *VII* appears to be small; the near parallelism of the dipole moment and IR data is obvious. However, a certain degree of cross-conjugation between the ylidene groups and benzene rings must occur in *VII* to account for the electronic spectrum, which shows considerable bathochromic shifts of absorption bands relative to methyleneanthrone.

Another interesting feature of the data in Table II is the dependence of the half-wave reduction potentials $(E_{1/2})$ of quinone methides on annelation effects. For all compounds the λ values $(\lambda = \alpha F/2 \cdot 303\ RT)$ of the first polarographic wave are close to the value corresponding to one-electron reversible reduction. Considering the $E_{1/2}$ values of annelated derivatives one can conclude that an annelation of benzene ring renders the $E_{1/2}$ to be shifted to more negative values in both series *a* and *b*. Whereas dithiolanes *b* have their $E_{1/2}$ in the range of 661 − 990 mV, $E_{1/2}$ values of fuchsones appear in the narrower region $(445 − 597\ \text{mV})$. Although only three points are available, approximately linear trend between $E_{1/2}$ and a number of annelated rings may be observed for both the series considered, indicating also a linear dependence of the LUMO orbital energy on the number of fused rings.

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