Tetrahedron. Vol. 25, pp. 4781 to 4796. Pergamon Press 1969. Printed in Great Britain

CONJUGATED RADICALS

THEORETICAL STUDY OF REDOX EQUILIBRIA

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(*Received in the UK* 26 *March* 1969; *Accepted for publication* 17 *June* 1969)

Abstract—Possibilities and limitations of the Coulomb repulsion integrals to estimate semiquinone formation constants of radicals are discussed. Elucidation of general dependency of semiquinone formation constants for violenes on the size of molecules and the aza-substitution is given.

REACTIVITY of closed shell systems and open shell systems[1] (radicals) is governed by both kinetic and thermodynamic factors. Kinetic aspects have been studied in reactions of a definite radical (e.g. phenyl- or trichloromethyl radical[2,3]) with various non-radical species (e.g. conjugated hydrocarbons). Theoretical analysis of these results can in general proceed along the same lines as with closed shell systems.[4,5] Thermodynamic stability can be investigated in all cases where the radical (Sem) reversibly disproportionates according to the following equilibrium

$$\mathrm{Ox} + \mathrm{Red} \overset{K}{\rightleftharpoons} 2\,\mathrm{Sem} \tag{1}$$

where the semiquinone formation constant, K, is defined as:*

$$K = \frac{[\mathrm{Sem}]^2}{[\mathrm{Ox}]\,[\mathrm{Red}]} \tag{2}$$

and where Ox, Sem and Red denote three oxidation levels of the redox systems with n, n + 1 and n + 2 π-electrons respectively. Provided, all three members of the redox system are appreciably stable towards the solvent, K can be determined experimentally without difficulty. A classical system of this type is formed by quinone (8 π-electrons), semiquinone anion (9 π-electrons) and hydroquinone dianion (10 π-electrons), where a reversible abstraction or addition of one electron occurs within the same molecular framework. Such systems can be generalized as:[6,7]

$$\bar{X}\text{—}(CH{=}CH)_{n}\bar{X} \rightleftharpoons \bar{X}\text{—}(CH{=}CH)_{n}\dot{X} \rightleftharpoons X{=}(CH\text{—}CH{=})_{n}X$$

$$\begin{array}{llll} & \mathrm{Red} & \mathrm{Sem\,(I)} & \mathrm{Ox} \\ \text{charge} & y-1 & y & y+1 \end{array}$$

where $y = -5, -3, -1, +1, +3, +5$.

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* With respect to the approximate nature of the correlations studied in this paper, the expression of the equilibrium constants with the aid of concentrations is sufficient.

We are interested in those redox systems where X represents heteroatoms or cyclic π-systems and where the vinylene groups may have been substituted by nitrogen (aza derivatives) or incorporated into aromatic rings (cf. Chart).

Theory of disproportionation

We shall treat disproportionation equilibria in the simplified model represented by Eq. 1, i.e. charged species in Eq. 1 will be regarded as dissociated and the effect of the counterions[9, 10] will be ignored. The nature of the energy change ΔE accompanying the disproportionation was described by Hush and Blackledge.[11] These authors suppose that ΔE consists of the two contributions:

$$\Delta \mathrm{E} = \mathrm{R} + \Delta \mathrm{E}_{\mathrm{solv}} \tag{3}$$

where R is the repulsion term and $\Delta \mathrm{E}_{\mathrm{solv}}$ is solvation energy change. Experimental evidence for the latter has already been accumulated: disproportionation of the tetraphenylethylene radical anion was studied in various ethers and considerable solvent effect was found;[12] benzenoid and polyphenyl radical anions disproportionated in 2-methyltetrahydrofuran at room temperature but not (or to a lesser extent) in dimethoxyethane or tetrahydrofuran;[8, 10] a significant temperature dependence was found[8, 9, 13] with a decreasing tendency to disproportionation at lower temperature. Attempts were made to employ MO data for the estimation both of the repulsion and solvation contributions in disproportionations of the benzenoid and α, ω-diphenylpolyene radical anions, although the agreement with experimental data was not satisfactory. It was concluded[14] that in the above systems both the energy terms were roughly of the same magnitude but of opposite sign and that the estimation of ΔE_{solv} was too approximate. In this paper we tried to find series of systems having a solvation term either similar or linearly proportional to the R term in order to avoid taking the solvation energy changes explicitly into consideration. Thus we were able to study the repulsion term in more detail. We believe that violenes (I) form such a suitable series.

MO description starts from the well-known relations of the chemical thermodynamics and adopts the usual assumptions[4] [(i) the dependence of ΔH on ΔS within one class of compounds is linear, (ii) π-electron contribution determines the total electron energy change]:

$$\Delta F = -RT \ln K \tag{4}$$

$$\Delta F = \Delta H - T\Delta S \tag{5}$$

$$\Delta H \sim -\log K \tag{6}$$

$$\Delta H = \Delta E_{\mathrm{i}} + \Delta E_{\sigma} + \Delta E_{\pi} + \Delta E_{\mathrm{solv}} \tag{7}$$

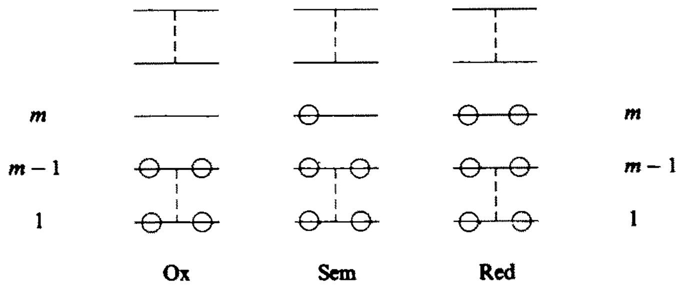
where i, σ and π concern inner shells, σ, and π-electrons, respectively. The change in the π-electron energy can be expressed as:

$$\Delta E_{\pi} = 2\,E_{\pi}^{\mathrm{Sem}} - E_{\pi}^{\mathrm{Ox}} - E_{\pi}^{\mathrm{Red}} \tag{8}$$

and regarding the assumptions mentioned above we obtain:

$$\log K \sim E_{\pi}^{\mathrm{Ox}} + E_{\pi}^{\mathrm{Red}} - 2\,E_{\pi}^{\mathrm{Sem}} \tag{9}$$

Thus, the estimation of the relative values of the semiquinone formation constants K requires calculation of the π-electron energies of all three oxidation levels of the redox system. In the HMO framework this problem cannot be solved because the expression $E_\pi^{\mathrm{Ox}} + E_\pi^{\mathrm{Red}} - 2\,E_\pi^{\mathrm{Sem}}$ equals zero for any system (with systems containing heteroatoms using the same parameters in Ox, Sem and Red form is supposed). Failure of the simple theory is caused by the neglect of the electronic repulsion term in the Hamiltonian, therefore a SCF method has to be used. However, this quantum chemical description is inconvenient because of the necessity to carry out three SCF calculations for any one system. The problem becomes more simple, if the wave functions of all three oxidation levels are considered to be built up from the same molecular orbitals. Adopting this approximation Hush and Blackledge[11] showed that the π-electron energy change was represented by the electronic repulsion in the singly occupied *MO* of the Sem form:



$$\begin{aligned}\Psi_{\mathrm{Ox}} &= |\varphi_1\bar{\varphi}_1 \cdots \varphi_{m-1}\bar{\varphi}_{m-1}|\\ \Psi_{\mathrm{Sem}} &= |\varphi_1\bar{\varphi}_1 \cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m|\\ \Psi_{\mathrm{Red}} &= |\varphi_1\bar{\varphi}_1 \cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m\bar{\varphi}_m|\end{aligned}$$

$$E_\pi^{\mathrm{Ox}} + E_\pi^{\mathrm{Red}} - 2\,E_\pi^{\mathrm{Sem}} = J_{\mathrm{mm}} \tag{10}$$

where

$$J_{\mathrm{mm}} = \iint \varphi_{\mathrm{m}}(1)\,\varphi_{\mathrm{m}}(2)\,e^2/r_{12}\,\varphi_{\mathrm{m}}(1)\,\varphi_{\mathrm{m}}(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \tag{11}$$

Considering the *LCAO* form of *MO*'s

$$\varphi_{\mathrm{i}} = \sum_\mu c_{\mathrm{i}\mu}\chi_\mu \tag{12}$$

we may write:

$$J_{\mathrm{mm}} = \sum_\mu \sum_\nu c_{\mathrm{m}\mu}^2\,c_{\mathrm{m}\nu}^2\,\gamma_{\mu\nu} \tag{13}$$

where $\gamma_{\mu\nu}$ are the electronic repulsion integrals over atomic orbitals. Hush and Blackledge calculated J_{mm} with the aid of *HMO* expansion coefficients and $\gamma_{\mu\nu}$ integrals evaluated according to Pariser and Parr.[15] The values of the electronic repulsion integrals, $\gamma_{\mu\nu}$, decrease rapidly with the distance between the centres μ and ν. This fact was used in some simplified semiempirical calculations[16-18] of the electronic spectra, in which only repulsion integrals for one centre and neighbouring centres were retained. Under such conditions J_{mm} can be expressed as:

$$J_{mm} = \sum_{\mu = \nu}\sum c^2_{m\mu}\, c^2_{m\nu}\, \gamma_{\mu\nu} \tag{14}$$

where evaluation of the $\gamma_{\mu\nu}$ integrals due to Mataga and Nishimoto[19] leads to the form:

$$J_{mm} = \sum_{\mu} c^4_{m\mu}(I_\mu - A_\mu) + \sum_{\mu = \nu}\sum c^2_{m\mu}\, c^2_{m\nu} \times \frac{14{\cdot}3986}{1{\cdot}4 + 2 \times 14{\cdot}3986/(I_\mu + I_\nu - A_\mu - A_\nu)} \tag{15}$$

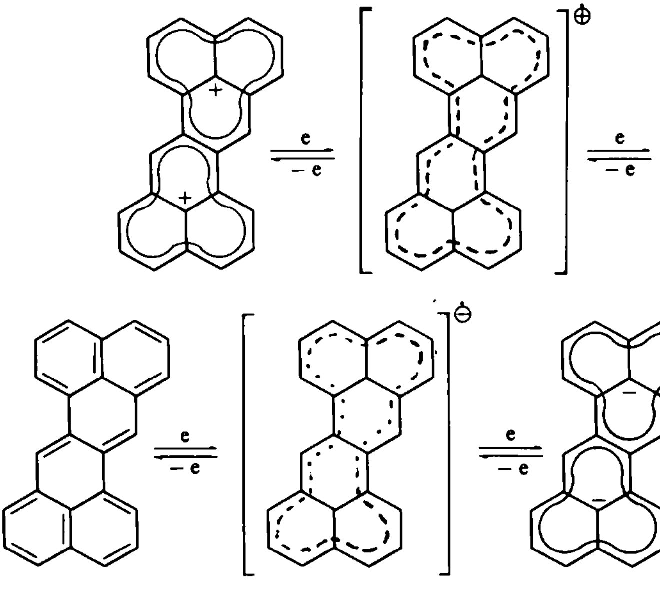
in which I_μ and A_μ stands for the ionization potential and electron affinity of the centre μ, respectively. Using our semiempirical parameters (cf. Table 1), Eq. 15 for hydrocarbons can be rewritten as:

$$J_{mm} = 10{\cdot}53 \sum_{\mu} c^4_{m\mu} + 5{\cdot}20 \sum_{\mu = \nu}\sum c^2_{m\mu}\, c^2_{m\nu} \tag{16}$$

This expression becomes very simple for the alternant odd hydrocarbons. In these systems the unpaired electron occupies the nonbonding MO, the properties[20] of which enable Eq. 16 to be written as:

$$J_{mm} = 10{\cdot}53 \sum_{\mu} c^4_{m\mu} \tag{17}$$

More complex redox systems can be treated in terms of overlapping two-step systems. In these cases MO theory also allows some reasonable predictions. Thus, for the benzenoid hydrocarbon zethrene the following redox system can be derived:



Zethrene is an alternant hydrocarbon, therefore due to the pairing properties of MO's the magnitude of the repulsion integral is the same both for a radical anion and radical cation. Eq. 16 gives us the value 1·065, which is extremely low as can be inspected from the Fig. 3.

Experimental values

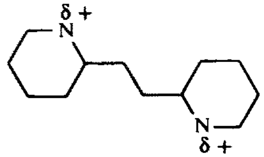
Semiquinone formation constants (Eq. 1) were determined from polarographic data according to Brdička[21, 22] (using the procedure originally suggested by Michaelis[23] for potentiometric data) with the aid of the following expression:

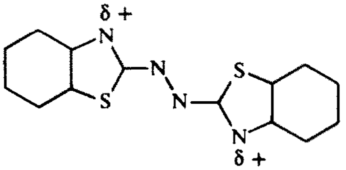
$$\Delta E_{1/2}\,(V) = 0{\cdot}06 \log K \qquad (18)$$

where $\Delta E_{1/2}$ is the half-wave potential difference of the two one-electron waves, corresponding to the reversible two-step redox process Ox $\rightleftharpoons$ Sem $\rightleftharpoons$ Red.

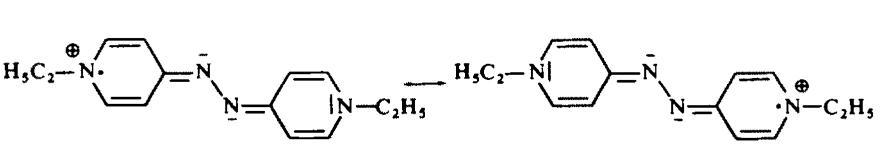
Semiempirical calculations

Closed shell systems were calculated by the method according to Pople[24] and open shell systems by the Longuet-Higgins and Pople[25] method. In both the procedures the common approximations by Pariser, Parr and Pople[15, 24] were used. Electronic repulsion integrals were evaluated according to Mataga and Nishimoto.[19] For all systems an idealized geometry was considered, i.e. bond lengths being 1·40 A and bonding angles 120°. The geometry of violenes was chosen so that the charges on the N atoms were as far apart as possible, e.g.:





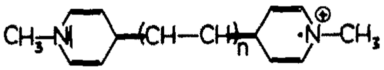
Violenes II–V (Chart) were also calculated by the LCI–SCF method, the description of which is given elsewhere. The nature of the alkylated N atoms in violenes was regarded as lying somewhere between the properties of the nitrogen in the oxidized and reduced forms, respectively. Therefore, the semiempirical parameters of the alkylated N atoms in violenes were taken as an arithmetic average of the values, valid for the protonated pyridine-like nitrogen (in Ox) and amine-like nitrogen (in Red):



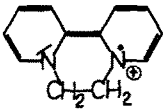
For the N atom in the polyenic part of molecules, the same parameters as in the pyridine-like compounds were used. In general, the parameters (Table 1) were the same or similar to those used in the interpretation of electronic spectra of systems having a closed shell configuration in the ground state. Calculations were carried out on the EL X8 computer in Rechenzentrum der Universität Würzburg (Germany).

DISCUSSION

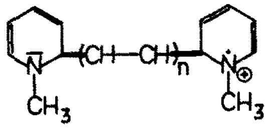
For correlation of the experimental data it is difficult to decide, *a priori*, whether the ΔE_π values (Eq. 8) have to be calculated or whether the J_{mm} (Eq. 11) values are



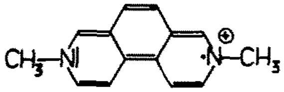
II, n = 0
III, n = 1
IV, n = 2
V, n = 3



VI



VII, n = 1
VIII, n = 3



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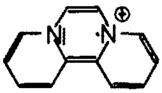

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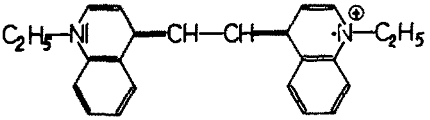
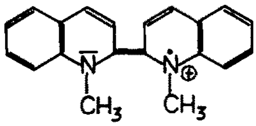


XI



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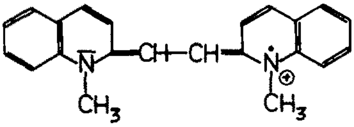

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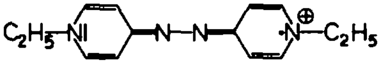

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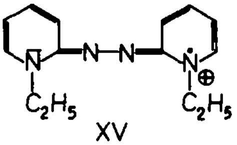
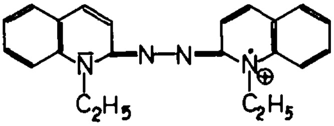
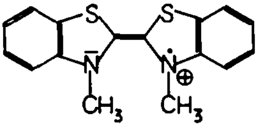


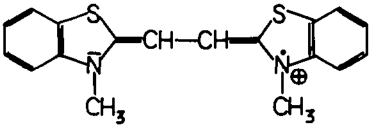
XV



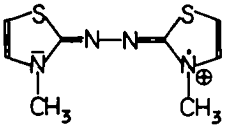
XVI



XVII



XVIII



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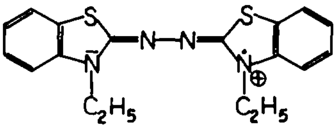
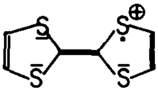
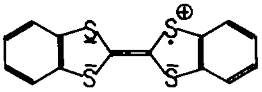


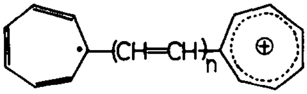
XX



XXI



XXII



XXIII, n = 0
XXIV, n = 1
XXV, n = 2
XXVI, n = 3

sufficient. Therefore, in the homologous series II–V we calculated several characteristics which, according to the theory, could be expected to correlate with the log K values (Table 2). ΔE_π (Eq. 8) was calculated using the same parameters of nitrogen in the Ox, Sem and Red forms. $\Delta E'_\pi$ is an analogous value, but calculated using different parameters for each oxidation level. In the latter case the energy contribution arising

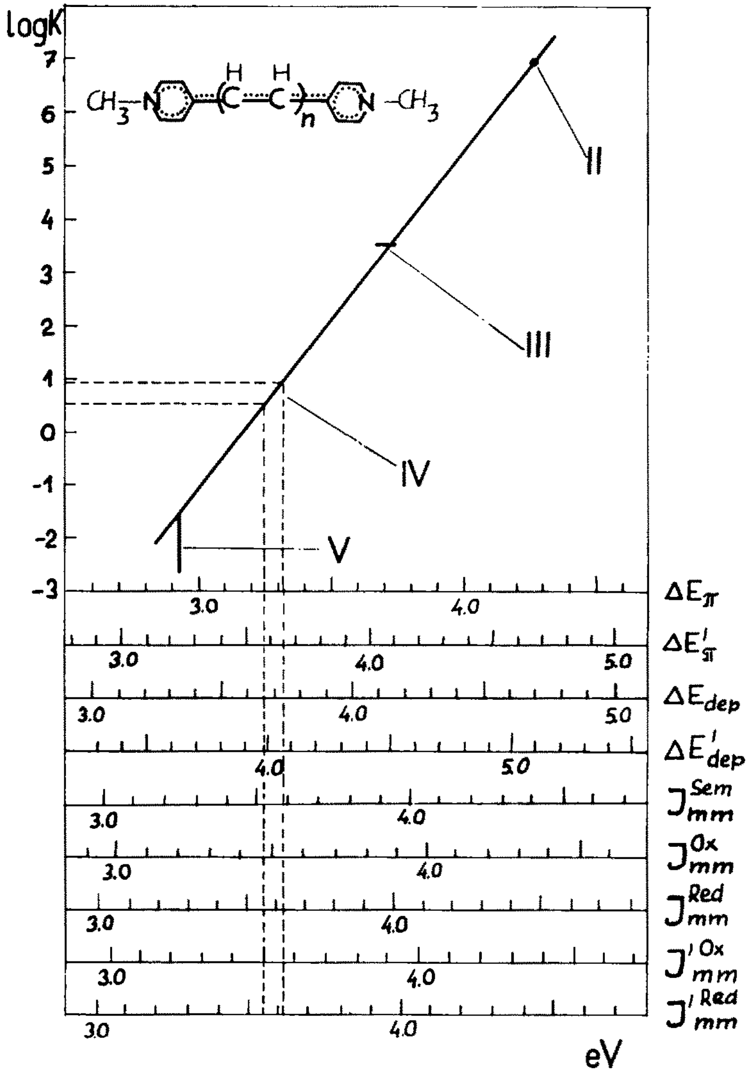


FIG. 1 Plot of the logarithms of semiquinone formation constants *vs* the MO data (for details see text) for pyridine-type violenes II–V. First, the log K values were plotted against the ΔE_π values. Scales of the other theoretical characteristics were then adjusted on the experimental values of systems II and V and accordingly shifted to the ΔE_π scale. Dashed lines indicate the region, where the log K value for the unknown IV is to be expected.

from the repulsion of nuclei also had to be taken into account, because this term cancels in Eq. 8 only if the same parameters in Ox, Sem and Red forms are used. In the LCI–SCF open shell calculations we found that a considerable depression of the

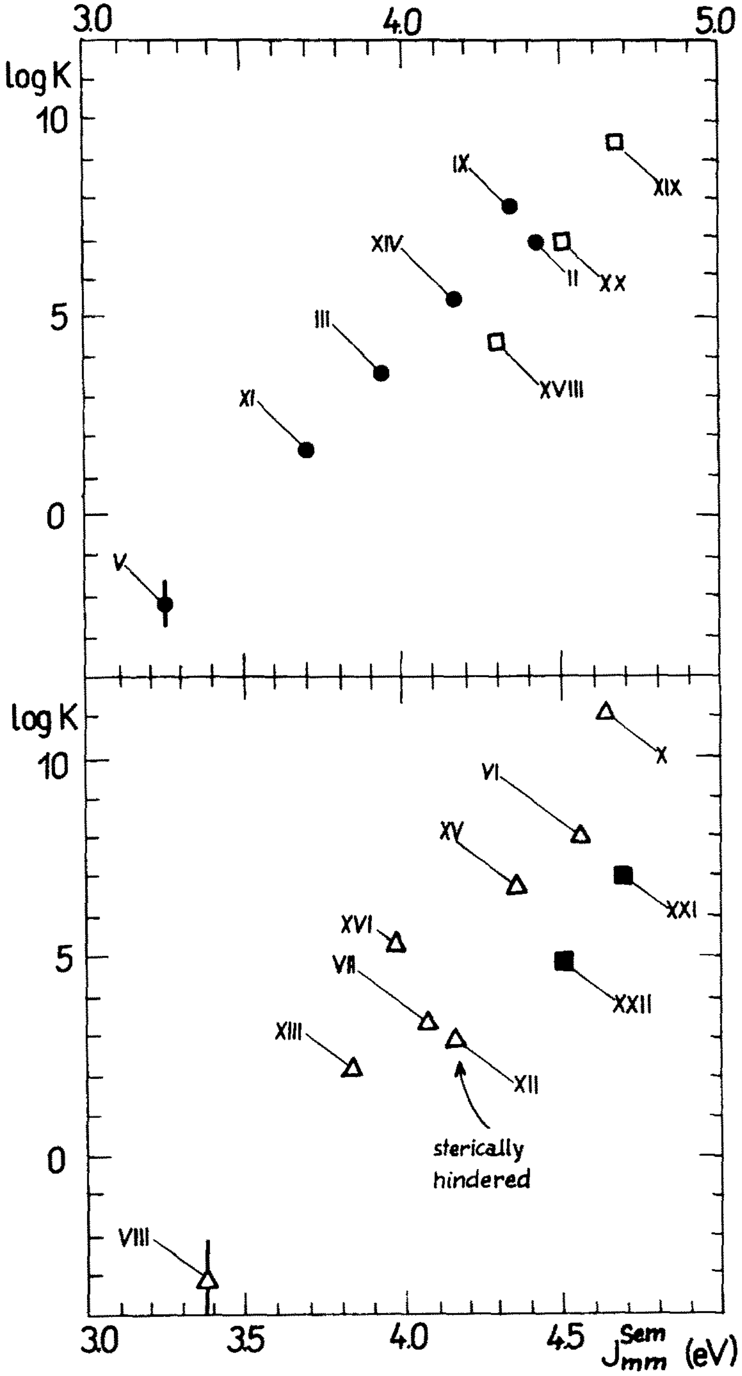


FIG. 2. Plot of the logarithms of semiquinone formation constants *vs* the repulsion integrals (J_{mm}^{Sem}) calculated by the Eq. 13 using the open shell SCF expansion coefficients. Violenes are divided into four classes according to the nature of the heterocyclic groups: ● pyridine-4 and quinoline-4, □ thiazol and benzthiazol, △ pyridine-2 and quinoline-2, ■ dithiolene and benzodithiolene.

ground state occurs. Thus, the question can be asked, whether in Eq. 8 the one determinant description of Sem is sufficient and consequently whether the expressions ΔE and $\Delta E'_\pi$ are suitable for correlations. If a depression of the ground state of Sem is taken into account,* this problem should be removed: then expressions ΔE_{dep} and $\Delta E'_{dep}$ result from Eq. 8 instead of ΔE_π and $\Delta E'_\pi$, respectively. Finally, the integrals representing electronic repulsion in the singly occupied MO of Sem (Eqs 11 and 13) were calculated. The expansion coefficients resulting from the calculations for the Ox, Sem or Red forms can be substituted in Eq. 13 and one gets integrals J^{Ox}_{mm}, J^{Sem}_{mm} or J^{Red}_{m} accordingly. If the Ox and Red forms are calculated with the parameters different from those used in the calculations of Sem, then the resulting repulsion integrals are denoted as J'^{Ox}_{mm} and J'^{Red}_{mm}.

In Fig. 1 all considered theoretical characteristics are plotted against the experimental data and, as can be seen, give practically the same results. In spite of the very limited extent of this series the plot indicates that the J_{mm} integrals can be suitable for correlations as well as the ΔE_π characteristics, which from the theoretical point of view, are more accurate. This gives an advantage because for the evaluation of a J_{mm} integral one SCF calculation is enough in contrast to the ΔE_π values, for which three SCF calculations must be performed. The plot in Fig. 1 enables us to predict for the violene IV the logarithm of the semiquinone formation constant to be 0·5–1·0. For a correlation of the larger series of compounds the integral J^{Sem}_{mm} was chosen. Its values together with the experimental data on systems II, III, V–XXII (Chart) are given in Table 3 and the respective plot is given in Fig. 2. For the sake of clarity the data are divided into two groups (upper and lower plot in Fig. 2). Roughly speaking the linear dependence as predicted by the Eqs 9 and 10 was obtained. However, the split of data which is observed could be caused by several reasons: (i) the assumption about the constant or proportional solvation energy changes need not be valid within the whole series of considered violenes but only in the series of more closely related compounds or in the series of vinylogs, (ii) the same could be true of the dependence of ΔS on ΔH, (iii) some systems (e.g. XII) cannot be expected to be planar owing to a steric hindrance, (iv) the correlation contains systems with different heteroatoms (N, S) and therefore it could be influenced by the choice of semiempirical parameters, (v) molecular diagrams of some violenes (XVII, XXI, XXII) exhibit great differences in the π-bond orders; calculations, in which resonance integrals are corrected according to bond orders in an iterative way, could provide more realistic values.

Suggestion for practical use of repulsion integrals. For the calculation of the J^{Sem}_{mm} integrals one must have a special computer program. This restricts widespread application of repulsion integrals. Therefore we tried to find a simple way of calculation, using only the now commonly used Hückel theory (HMO). We think that such calculations could be done using the simplified Eq. 15 instead of the Eq. 13 and the Hückel expansion coefficients instead of the SCF ones. In spite of the expected decrease in accuracy, we think that repulsion integrals calculated in this approximate way (J^{HMO}_{mm}) will provide reasonable results for practical purposes. To make certain we compared the J^{HMO}_{mm} integrals with the precise J^{Sem}_{mm} integrals for the series of hydrocarbon radicals and violenes. The results are given in Table 4 and the respective plot in Fig. 3. Excepting data for the even polyene anion radicals a reasonable linear dependence is obtained.

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* i.e. the LCI ground state energies are used in Eq. 9 instead of the SCF ones.

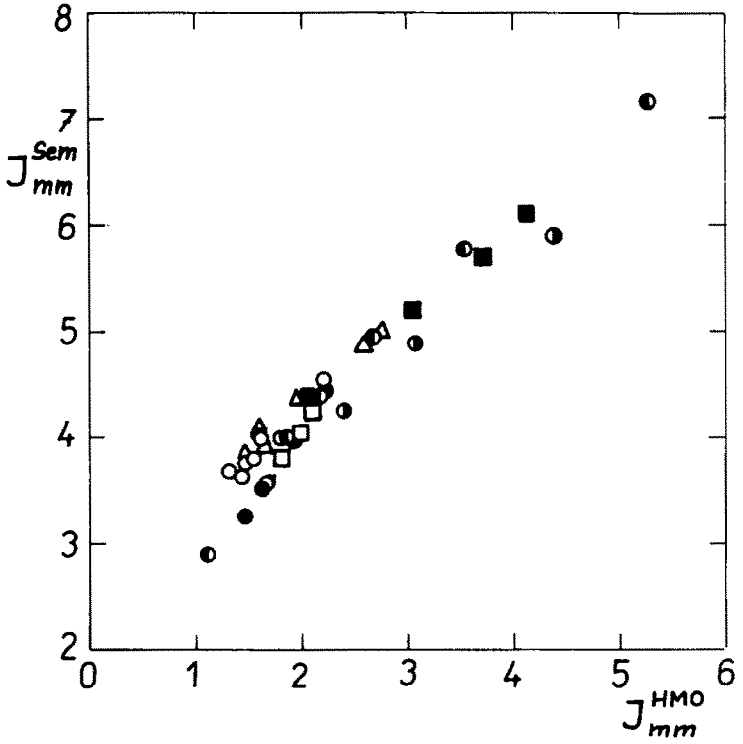


FIG. 3. Plot of the J_{mm}^{Sem} repulsion integrals calculated by the Eq. 13 using the open shell SCF expansion coefficients *vs* the approximate J_{mm}^{HMO} repulsion integrals calculated by the Eq. 15 using the Hückel expansion coefficients; ◑ even polyene radical anions, ◐ odd polyene radicals, □ even α, ω-diphenylpolyene radical anions, ○ radical anions of the benzenoid hydrocarbons, ■ benzyl-type radicals, △ radical anions and cations of the non-alternant hydrocarbons, ● violenes II–V.

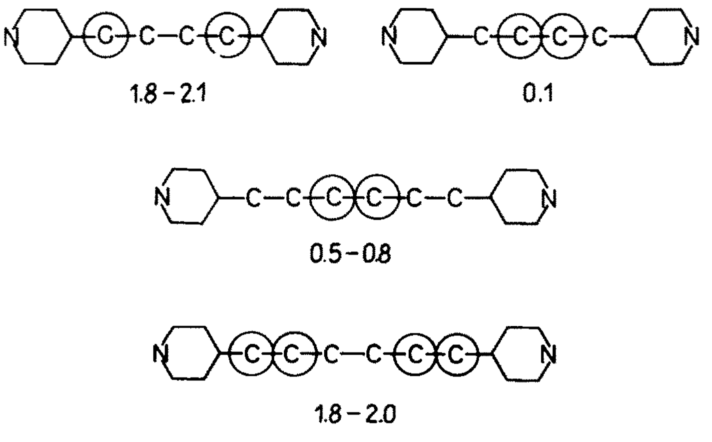


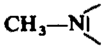
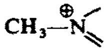
FIG. 4. Effect of the aza-substitution on the semiquinone formation constants (*K*). The positions of the aza-substitution are denoted by circles and the respective predicted increases in log *K* are given below the formulas.

CONCLUSIONS

If the solvation energy term in (1) is ignored, interpretation of semiquinone formation constants becomes crude or in some cases perhaps even impossible. However, results obtained with the violenes indicate that the calculated repulsion terms could be of some practical use:

(1) In general, the decreasing tendency of the semiquinone formation with the increasing size of the conjugated system in the calculations of homologous series was found (e.g. in polyenes or polyacenes). This trend has been demonstrated with violenes where semiquinone formation constants decrease with the increasing length of the polyenic part and where benzo derivatives disproportionate more easily than the "parent" systems (e.g. quinoline systems with respect to the pyridine systems).

TABLE 1. PARAMETERS USED IN CALCULATIONS

Atom	Ionization potentials	Electron affinities	Resonance integrals
C	11·22	0·69	2·318
	27·3	9·3	1·854
	32·9	10·0	1·854
N (violene)	30·1	9·7	1·854
$-\overline{N}=$	14·1	1·8	2·318 ($\beta_{N=N} = \beta_{C-C}$)
$-\underline{\overline{S}}-$	20·0	9·16	1·623

(2) Regardless of the nature of the heterocycles, violenes, if J_{mm}^{Sem} is greater than 4 eV (this corresponds to log $K > 3$), are expected to be stable in respect of Eq. 1. If the value of J_{mm}^{Sem} is less than 3·5 eV the semiquinone formation constant would be small and hence isolation of the respective violene would be uncertain.

(3) Aza-substitution in the polyenic part of violenes leads to the higher values of semiquinone formation constants. Predictions for some pyridine-type violenes are given in Fig. 4.

(4) In the homologous series of XXIII–XXVI (Chart) we predict that only the first member (XXIII, n = 0) and perhaps the second (XXIV, n = 1) has a reasonable chance to be synthesized.

TABLE 2. EXPERIMENTAL AND THEORETICAL DATA FOR SEMIQUINONE FORMATION CONSTANTS (MEANING OF SYMBOLS IS DESCRIBED IN TEXT, ALL THEORETICAL DATA ARE GIVEN IN eV)

System	log K	ΔE_π	$\Delta E'_\pi$	ΔE_{dep}	$\Delta E'_{dep}$	J^{Sem}_{mm}	J^{Ox}_{mm}	J^{Red}_{mm}	J'^{Ox}_{mm}	J'^{Red}_{mm}
II	7·0	4·276	4·684	4·690	5·098	4·407	4·355	4·483	4·378	4·443
III	3·6	3·727	4·094	4·101	4·468	3·929	3·890	3·977	3·908	3·949
IV	—	3·287	3·621	3·667	4·001	3·551	3·513	3·589	3·527	3·569
V	− 2·6 to − 1·5	2·931	3·244	3·325	3·638	3·252	3·212	3·285	3·224	3·270

TABLE 3. EXPERIMENTALLY FOUND LOGARITHMS OF SEMIQUINONE FORMATION CONSTANTS (K) AND REPULSION INTEGRALS CALCULATED WITH THE AID OF Eq. 13 USING THE OPEN SHELL SCF EXPANSION COEFFICIENTS (J_{mm}^{Sem})

System	log K	Medium	J_{mm}^{Sem}
II	7·0	CH_3CN	4·407
III	3·6	CH_3CN	3·929
V	− 2·6 to − 1·5	CH_3CN	3·252
VI	8·0	CH_3CN	4·545
VII	3·3	CH_3CN	4·071
VIII	− 4 to − 2	CH_3CN	3·369
IX	7·95	CH_3CN	4·326
X	11·3	CH_3CN	4·620
XI	1·78	CH_3CN	3·694
XII	2·9	CH_3CN	4·164
XIII	2·3	CH_3CN	3·808
XIV	5·62	CH_3CN	4·184
XV	6·84	H_2O	4·332
XVI	5·33	H_2O	3·946
XVII	3·0	CH_3CN	4·801
XVIII	4·48	CH_3CN	4·304
XIX	9·61	CH_3CN	4·668
XX	6·97	H_2O	4·525
XXI	6·9	CH_3CN	4·699
XXII	4·84	CH_3CN	4·495

TABLE 4. REPULSION INTEGRALS CALCULATED BY THE Eq. 15 USING THE HÜCKEL EXPANSION COEFFICIENTS (J_{mm}^{HMO}) AND Eq. 13 USING THE OPEN SHELL SCF EXPANSION COEFFICIENTS (J_{mm}^{Sem}). PRESENTED DATA CONCERN RADICALS (R), RADICAL ANIONS (A) AND RADICAL CATIONS (C)

System	J_{mm}^{HMO}	J_{mm}^{Sem}
Odd polyenes		
C_3 (R)	5·265	7·163
C_5 (R)	3·539	5·772
C_7 (R)	2·684	4·953
C_9 (R)	2·177	4·399
C_{11} (R)	1·842	3·995
C_{21} (R)	1·108	2·937
Even polyenes		
C_4 (A)	4·388	5·886
C_6 (A)	3·070	4·899
C_8 (A)	2·380	4·278
Even α, ω-diphenylpolyenes		
Diphenyl (A)	2·077	4·255
1,2-Diphenylethylene (A)	1·975	4·055
1,4-Diphenylbutadiene (A)	1·819	3·824
1,6-Diphenylhexatriene (A)	1·649	3·587
Benzenoid hydrocarbons		
Naphthalene (A)	2·208	4·555
Anthracene (A)	1·614	4·036
Phenanthrene (A)	1·796	4·035
Tetracene (A)	1·304	3·703
Pyrene (A)	1·534	3·779
Benzo[a]anthracene (A)	1·488	3·758
Chrysene (A)	1·376	3·639
Benzyl-type systems		
Benzyl (R)	4·083	6·083
1-Naphthylmethyl (R)	3·054	5·197
2-Naphthylmethyl (R)	3·680	5·677
9-Anthrylmethyl (R)	2·041	4·412
Non-alternant hydrocarbons		
Azulene (A)	2·586	4·882
Azulene (C)	2·759	5·020
Acehepthylene[a] (A)	1·964	4·370
Acehepthylene[a] (C)	1·627	4·090
Fluoranthene (A)	1·636	3·967
Fluoranthene (C)	1·466	3·815
Violenes		
II	2·211	4·407
III	1·897	3·929
IV	1·655	3·551
V	1·458	3·252

[a] Acehepthylene is a tricyclic peri-condensed system consisting of the heptalene and the ethylene bridge.

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