

## CONJUGATED RADICALS. X.\*

## BISAZULENYLETHYLENE AND RELATED SYSTEMS

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Electronic spectra and some chemical properties of bisazulenylethylene and mono- and dication thereof were discussed in terms of open and closed shell LCI-SCF methods. Calculations performed for a series of anions derived from bisazulenylethylene, which have not yet been prepared, indicate low chemical stability and occurrence of their first electronic transitions in the infrared region. It is expected that the dianion could be in a triplet ground state.

The subject of this paper is a theoretical study of the oxidation-reduction system *Ia*–*Ig* and experimental study of its three oxidation levels *Ia*–*Ic* (Chart I).

The hydrocarbon radical cation *Ib* has been isolated as a perchlorate<sup>1,2</sup> (see also<sup>3</sup>). The synthesized hydrocarbon *Ic* and its dication perchlorate *Ia* are also fairly-stable compounds<sup>2</sup>, although the former undergoes ready oxidation whereas the latter is, of course, readily reducible.

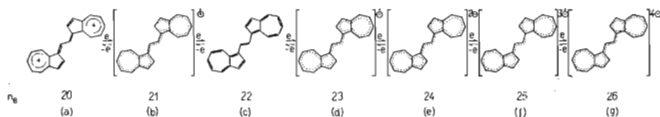


CHART I

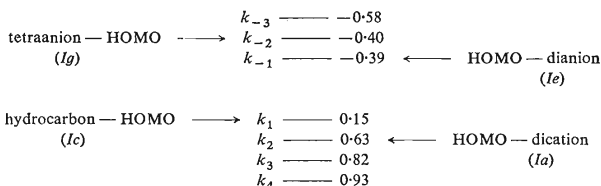
## METHODS

**Absorption curves.** Before recording the absorption curves the samples of cation perchlorates *Ia* and *Ib* and hydrocarbon *Ic* were recrystallized from methylene chloride. The same solvent was used for spectral measurements, the dication *Ia* was also measured in 90% H<sub>2</sub>SO<sub>4</sub>.

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respectively; Fig. 1) indicate the location of the first absorption band in the long-wave region of the electronic spectrum with all three compounds. In systems *Ia* and *Ib* there is an unoccupied bonding orbital, therefore for both systems one can expect a high electron affinity (easy polarographic reduction). At the same time the energy value of that orbital indicates a low ionization potential of the neutral hydrocarbon *Ic* and thus its facile polarographic oxidation and strong donor behaviour in charge-transfer complex formation can be expected. The HMO description given for systems *Ia–Ic* is in agreement with their observed properties. The energies of the two lowest antibonding MO's of the hydrocarbon *Ic* are seen, from Fig. 1, to be computed as  $-0.39$  and  $-0.40\beta$  respectively. Thus the hydrocarbon *Ic* should also be easily reducible and formation of the radical trianion *If* and perhaps even the tetraion *Ig* together with the dianion *Ie* appears to be possible in view of the very narrow gap between the first and the second antibonding MO's. This gap provides a further information<sup>7</sup> concerning the dianion *Ie*, viz. its lowest triplet state can be anticipated to be a ground state or a thermally excited state.



From the inspection of molecular diagrams\* (Fig. 2) one can expect that the systems *Ia–Ic* possess a considerable sensitivity to nucleophilic, electrophilic and radical agents. The nature of the highest bonding MO determines that the passage from the hydrocarbon *Ic* to its dication, *Ia*, is accompanied by a decrease in electron density in the centres of electrophilic reactivity rather than with a further accumulation of a positive charge on nucleophilic positions.

As the compounds *Ia–Ic* studied experimentally bear six alkyl groups (Fig. 1), we used the perturbation treatment to estimate the effect of this substitution upon the location of the first band in the electronic spectra. If all alkyl groups are treated as methyl groups the perturbation treatment leads to a bathochromic shift of  $640\text{ cm}^{-1}$  for the dication and to a hypsochromic shift of  $60\text{ cm}^{-1}$  for the hydrocarbon.

Let us now continue the discussion exploiting the more quantitative LCI–SCF data.

\* The respective differences between the HMO and SCF molecular diagrams are unimportant; Fig. 2 presents the SCF values.

**Disproportionation equilibria.** We found a linear dependence between the logarithms of the semiquinone formation constants and coulomb integrals  $J_{mm}$  for a series of violenes<sup>6</sup>. The higher the  $J_{mm}$  value, the higher the semiquinone formation constant that is encountered. On the basis of empirical experience<sup>6</sup> a  $J_{mm}$  value higher than 3.5 eV should indicate that the radical is thermodynamically stable. Provided its kinetic stability is also sufficient and that both oxidized and reduced forms taking part in the oxidation-reduction equilibrium are stable, it should be

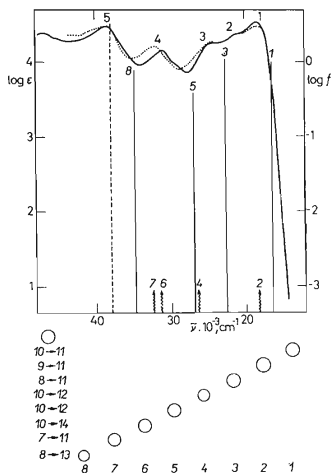


FIG. 3

Absorption Curve of the Dication *Ia* in 90%  $H_2SO_4$  (—) and in  $CH_2Cl_2$  (-----)

Positions and intensities ( $\log f$ ) of the LCI SCF transition energies are indicated by vertical lines, forbidden ones by wavy lines with arrows. At  $3.8 \cdot 10^4 \text{ cm}^{-1}$  two transitions are present (-----), the intensity of which was not computed. Below the figure the weights of main configurations are presented. The circle above the column of configuration numeral designations corresponds to a state, which is due to a pure transition.

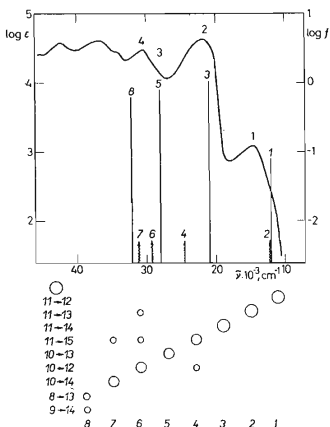


FIG. 4

Absorption Curve of the Hydrocarbon *Ic* in  $CH_2Cl_2$

Positions and intensities ( $\log f$ ) of the LCI SCF transition energies are indicated by vertical lines, forbidden ones by wavy lines with arrows. Below the figure the weights of main configurations are presented. The circle above the column of configuration numeral designations corresponds to a state which is due to a pure transition.

TABLE I

Coulomb Repulsion Integrals  $J_{mm}$  Calculated from HMO Expansion Coefficients ( $m$  is an index for the singly occupied MO)

Radical	$Ib$	$Id$	$If$
$J_{mm}$ , eV	3.47	3.14	3.18

TABLE II

Spectral LCI-SCF Characteristics for Bisazulenylethylene Cation Radical

Longuet-Higgins and Pople <sup>a</sup>			Roothaan <sup>a</sup>		
$\nu$ (cm <sup>-1</sup> ) · 10 <sup>-3</sup>	log $f^b$	weight <sup>c</sup>	$\nu$ (cm <sup>-1</sup> ) · 10 <sup>-3</sup>	log $f^b$	weight <sup>c</sup>
11.96	-0.825	A (10-11) 70.5	11.79	-0.785	A (10-11) 72.2
13.64	—	B (11-13) 80.7	13.51	—	B (11-13) 76.4
13.78	-0.889	B (11-12) 63.7	13.66	-0.864	B (11-12) 35.1
16.78	—	A (9-11) 80.6	16.45	—	A (9-11) 77.4
18.26	-0.146	B (11-14) 66.9	17.92	-0.100	B (11-14) 44.5
19.94	-0.383	A (8-11) 74.4	19.35	-0.472	A (8-11) 68.2
21.75	—	B (11-15) 55.2	22.05	—	B (11-15) 38.3
23.43	—	C <sub><math>\alpha</math></sub> (10-12) 38.7	23.14	-1.413	C <sub><math>\alpha</math></sub> (10-13) 38.6
23.52	-1.236	C <sub><math>\alpha</math></sub> (10-13) 40.2	23.17	—	C <sub><math>\alpha</math></sub> (10-12) 21.5
25.07	—	C <sub><math>\beta</math></sub> (8-12) 27.3	24.77	—	C <sub><math>\beta</math></sub> (8-14) 15.7
25.31	-1.128	C <sub><math>\beta</math></sub> (8-13) 33.2	24.86	-1.322	C <sub><math>\beta</math></sub> (8-13) 30.5
29.67	—	A (7-11) 41.8	29.02	—	A (7-11) 52.4
31.51	—	C <sub><math>\alpha</math></sub> (10-14) 58.2	31.28	—	C <sub><math>\alpha</math></sub> (10-12) 33.3
32.91	-0.240	C <sub><math>\alpha</math></sub> (8-13) 29.3	33.12	-0.252	C <sub><math>\alpha</math></sub> (9-14) 35.7
35.12	-0.490	C <sub><math>\beta</math></sub> (9-14) 30.3	35.40	-0.538	C <sub><math>\alpha</math></sub> (9-12) 31.1
35.27	—	C <sub><math>\alpha</math></sub> (8-12) 14.2	35.48	—	C <sub><math>\alpha</math></sub> (8-12) 26.6
38.56	-0.373	C <sub><math>\alpha</math></sub> (9-12) 14.2	38.25	—	C <sub><math>\alpha</math></sub> (9-13) 40.9
38.67	—	C <sub><math>\alpha</math></sub> (10-12) 16.2	38.49	-0.617	C <sub><math>\alpha</math></sub> (9-12) 37.9
39.13	-1.110	C <sub><math>\alpha</math></sub> (10-13) 23.2	39.58	—	C <sub><math>\alpha</math></sub> (10-12) 20.0
39.32	—	C <sub><math>\alpha</math></sub> (9-13) 42.1	39.84	-1.111	C <sub><math>\beta</math></sub> (10-13) 44.0
41.12	—	C <sub><math>\alpha</math></sub> (8-12) 30.1	40.48	—	C <sub><math>\beta</math></sub> (10-12) 21.2
41.43	-0.209	C <sub><math>\alpha</math></sub> (10-15) 50.5	41.06	-0.129	C <sub><math>\alpha</math></sub> (8-13) 35.1
			41.39	-0.393	C <sub><math>\alpha</math></sub> (10-15) 46.7

<sup>a</sup> MO basis used, 41 configurations. <sup>b</sup>  $f$  stands for the oscillator strengths. <sup>c</sup> Weights of singly excited configurations of the A, B, C <sub>$\alpha$</sub> , and C <sub>$\beta$</sub>  types in %.

possible to isolate the radical. The  $J_{mm}$  value for the isolated radical cation *Ib* (perchlorate) is seen, from Table I, to lie just on the border where radicals can be isolated. It is noteworthy that the  $J_{mm}$  value calculated from the SCF MO (Longuet-Higgins and Pople) amounts to 3.51 eV. Preparation of radical anions *Id* and *If* due to their low  $J_{mm}$  values appears to be uncertain.

*Electronic spectra and multiplicity of the ground states.* Figs 3 and 4 present the absorption curves of the dication *Ia* and the neutral hydrocarbon *Ic* together with the results of LCI-SCF calculations. Besides the usual indication of wavenumbers and oscillator strengths of theoretical transitions, the figures also contain data on the composition of the LCI wave functions for eight excited singlet states. These data indicate rather pure transitions, which reflects an unimportant role of configuration interaction in this case. The agreement between calculations and absorption curves is somewhat less satisfactory than that usually found. The same

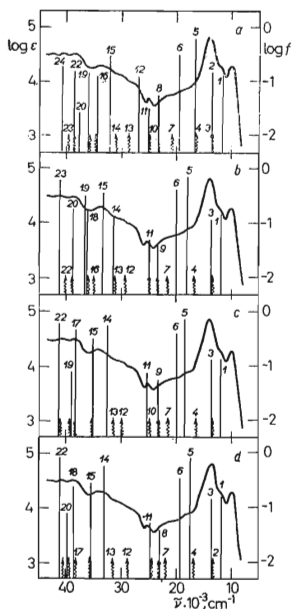


FIG. 5

Absorption Curve of Bisazulenylethylene Cation Radical and Results of LCI SCF Calculations

Calculated transition energies and oscillator strengths ( $f$ ) are indicated by vertical lines (for allowed transitions) and by wavy lines with arrows (for forbidden transitions). Calculations differ in the MO basis used and in the number of states considered in configuration interaction: a) Longuet-Higgins and Pople, 61 configurations, b) Longuet-Higgins and Pople, 50 configurations, c) Longuet-Higgins and Pople, 41 configurations, d) Roothaan, 41 configurations.

picture is obtained with the radical cation *Ib*. The reason for the observed discrepancies appears to lie with the difficulties which generally occur in the interpretation of electronic spectra of large conjugated systems<sup>8</sup> with the aid of the PPP method, rather than a special feature of bisazulenylethylene and its derivatives.

We tried to improve the agreement for the radical cation by taking a larger number of singly excited states in the configuration interaction calculation. However the ten lowest transitions are seen, (Fig. 5) to be nearly unaffected by an extension of configuration interaction from 41 to 61 states. Use of the Roothaan MO's instead of those of Longuet-Higgins and Pople is also ineffective. Weights of configurations in LCI wave functions are listed in Table II.

With the dianion *Ie* a divergence of the SCF procedure was encountered. On the basis of our experience with systems of that type, we tried to overcome this difficulty with the aid of changed parametrization. Using those parameters which were successful in the calculations of **S** - **T** and **T** - **T** transitions<sup>7</sup> ( $\gamma_{CC} = 8.2$  eV,  $\beta_{CC} = -2.5$  eV), a slow convergence in the SCF procedure was achieved. The result yielded by the LCI-SCF calculation is interesting: the first triplet state lies 1.22 eV (nearly 10000  $\text{cm}^{-1}$ ) below the first singlet state. As this difference is so great, the prediction that the dianion *Ie* should possess a triplet ground state appears to be reasonable.

The lowest HMO transition energies in the radical anion *Id* and radical trianion *If* amount to only 0.01 $\beta$  and can therefore be assumed<sup>7</sup> to correspond to absorption in the infrared region.

Finally, we mention the LCI-SCF calculation on the tetraion *Ig* (standard parametrization), which predicts the first triplet state to lie only 0.04  $eV$  above the singlet ground state. Although the theory under-estimates the singlet-triplet separation it appears the triplet state could be thermally populated. However, all theoretical data for anions *Id*-*If* presented in this paper remain to be verified experimentally and represent therefore an impulse for the experimental study.

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