Conjugated Radicals

XII.* CNDO Calculations on the Electronic Spectra of Butadiene Cation and Anion Radicals

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Restricted open shell CNDO calculations have been carried out on butadiene anion radical (M^-), butadiene cation radical (M^+), and butadiene dimer cation radical (M_2^+). Calculated transition energies are in agreement with the experimental data. Formation of M_2^+ and unsuccessful attempts to detect M_2^- have been interpreted by the CNDO and extended Hückel calculations, in light of which the $M + M^+ \to M_2^+$ process is energetically favourable while the $M + M^- \to M_2^-$ process is connected with an energy loss. CNDO calculations support the assumed sandwich structure of M_2^+.

"Restricted open shell" CNDO-Rechnungen für das Butadien-Radikalanion (M^-), das Butadien-Radikalkation (M^+) und das dimere Butadien-Radikalkation (M_2^+) wurden durchgeführt. Die berechneten Übergangsenergien stimmen mit den experimentellen Daten überein. Die Bildung von M_2^+ einerseits und die erfolglosen Versuche, das dimere Radikalanion M_2^- herzustellen, andererseits wurden mittels CNDO- und EHT-Berechnungen gedeutet. Es zeigte sich hierbei, daß der Prozeß $M + M^+ \to M_2^+$ energetisch möglich sein, die Reaktion $M + M^- \to M_2^-$ dagegen mit einem Energieverlust ablaufen sollte. Die CNDO-Rechnungen sprechen für die Annahme einer Sandwich-Struktur von M_2^+.

On a effectué des calculs avec "restricted open shell" d'après la méthode CNDO sur l'anion radical du butadiène (M^-) sur le cation radical du butadiène (M^+) et sur le cation radical du dimère du butadiène (M_2^+). Les énergies de transition calculées sont en accord avec les données expérimentales. La formation de M_2^+ et les efforts sans succès à prouver la présence de M_2^+ ont été interprétés par la méthode de CNDO et par les calculs étendus d'après Hückel. De ce point de vue le procès $M + M^+ \to M_2^+$ est énergétiquement favorable pendant que le procès $M + M^- \to M_2^-$ est accompagné d'une perte d'énergie. Les calculs d'après la méthode de CNDO soutiennent la structure supposée de M_2^+.

Introduction

A striking similarity in the electronic spectra of the positive and negative ions of alternant hydrocarbons has been successfully interpreted [1] by the pairing properties of Hückel molecular orbitals or molecular orbitals resulting from the calculations within the π-electron approach adopting the Pariser, Parr, and Pople's approximations. From the experimental material on alternant hydrocarbon radical ions benzene and butadiene appear to be the only exception since their radical cations [2, 3] exhibit a long-wave absorption, which is absent in the electronic spectra of the corresponding radical anions [3, 4]. The extended Hückel calculation [5] offered a tempting interpretation of this finding. The energy scheme of orbital levels yielded by that calculation for butadiene in Fig. 1

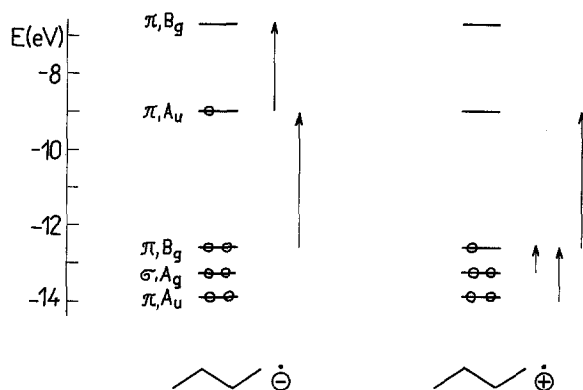* Part XI: Čársky, P., Hobza, P., Zahradník, R.: Collect. Czechoslov. Chem. Commun., in press.

Fig. 1. Part of the extended Hückel MO level scheme for butadiene. The lowest transition energies in the negative and positive ion are indicated by arrows

indicates a possible assignment of the first absorption band of the butadiene cation radical to a $\sigma \to \pi$ transition. However, Badger and Brocklehurst [6] concluded from the concentration dependence that the long-wave absorption is due to the dimeric radical cation. The species of that type consisting of one molecule of the neutral hydrocarbon and one molecule of the cation radical have been found also with benzenoid hydrocarbons [7]. The goal of the present paper is to confirm the assumed sandwich geometry of the butadiene dimer cation radical, to investigate a potential surface along a varying interplanar distance and to reproduce the transition energies of the monomeric cation and anion radicals and dimeric radical cation of butadiene by means of the CNDO calculations.

Calculations

The open shell PPP-like calculation within the π-electron approach combining the SCF procedure of Longuet-Higgins and Pople with the configuration interaction calculation has been reported previously [8] and need not be described here.

Extended Hückel (EHT) calculations were performed following all computational details suggested by Hoffmann [5].

For the interpretation of electronic spectra we selected the modified CNDO method reported by Del Bene and Jaffé [9], which appears to be so far the only version of the CNDO method capable of reproducing satisfactorily the observed transition energies. It differs from the original CNDO/2 method of Pople and Segal [10] in the evaluation of resonance integrals

$$\beta_{\mu\nu} = \tfrac{1}{2} (\beta_A^0 + \beta_B^0) S_{\mu\nu}, \tag{1}$$

where the π-type contributions of the overlap integrals are multiplied by an empirical parameter $\varkappa = 0.585$ and the new readjusted values for bonding parameters β^0 are used. Furthermore the electron-repulsion integrals are evaluated

semiempirically instead of calculating the analytic integrals for Slater's orbitals. Del Bene and Jaffé have used the approximation of Pariser and Parr, which by assuming the analogy with the PPP calculations appears to be a probable reason for the discrepancy found e.g. for the transition energy of the p-band of benzene. This was also pointed out by Jaffé in a later paper [11]. Therefore we employed a formula of Mataga and Nishimoto

$$\gamma_{AB} = \frac{14.3986}{R_{AB} + A}, \qquad A = \frac{14.3986}{\frac{1}{2}(\gamma_{AA} + \gamma_{BB})} \tag{2}$$

which proved to be more suitable in the PPP calculations for singlet-singlet transition energies. For the one-center integrals we used the values $\gamma_{HH} = 12.85$ eV and $\gamma_{CC} = 11.22$ eV. Other parameters used are same as in the paper of Del Bene and Jaffé [9].

The application of this computational method to open shell systems was carried out in the same way as reported in our earlier paper [8] for calculations in the π-electron approach. We used the open shell SCF method of Longuet-Higgins and Pople, which leaves the CNDO/2 matrix elements

$$F_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) + [(P_{AA} - Z_A) - \frac{1}{2}(P_{\mu\mu} - 1)]\,\gamma_{AA} \\ + \sum_{B(\neq A)} (P_{BB} - Z_B)\,\gamma_{AB}, \tag{3}$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB} \tag{4}$$

unchanged, except the new definition of the electron-density and bond-order matrix

$$P_{\mu\nu} = \sum_{i=1}^{m-1} 2c_{i\mu}c_{i\nu} + c_{m\mu}c_{m\nu}, \tag{5}$$

where m is an index of the singly occupied molecular orbital. Configuration interaction was incorporated into the computational scheme in the same way as in the procedure within a π-electron approach [8] and therefore its description need not be repeated here. For the monomeric ions we considered 40 excited configurations arising formally from one-electron transitions between the four highest doubly occupied orbitals, the singly occupied and the four lowest vacant orbitals. For the dimeric radical cation we used 31 configurations representing all one-electron transitions among the eight "perturbated π-molecular orbitals" of two butadiene units.

The geometry chosen for monomeric ions was derived from that experimentally found for butadiene [12] through the following equation

$$R_{\mu\nu} = 1.517 - 0.18\,P_{\mu\nu}, \tag{6}$$

where $P_{\mu\nu}$ stands for the C–C bond orders obtained from the open shell calculation within the π-electron approach. For the C–C bond lengths in the dimeric radical cation we used the intermediate values of the corresponding bond lengths in butadiene and its monomeric ion. Thus the $R(C_1 - C_2)$ and $R(C_2 - C_3)$ bond lengths were taken to be of 1.396 Å and 1.410 Å in the monomeric ion and

1.370 Å and 1.450 Å in the dimeric radical cation. The interplanar distance in the latter was fixed at 3.5 Å, which is predicted by EHT calculations (Fig. 2). Although the bond lengths estimated from the EHT calculation must be taken with some caution, we think the value yielded in this case is reasonable and chemically acceptable. According to the results of X-ray crystal structure analysis of several Würster's salts [13], the interplanar distances between the stacked radicals lie in the range of 3.1–3.7 Å and in the semiempirical calculation on the 1-alkyl-4-carbomethoxypyridinyl radical dimer Itoh and Nagakura [14] assumed the interplanar separation to be 3.4 Å. For the C–H bond lengths and valence angles we used the values of 1.08 Å and 120° in all three radicals under study. In the EHT calculations the butadiene geometry [12] was considered.

To our knowledge only one attempt has been reported [15], in which the electronic spectrum of a radical was interpreted by means of the restricted open shell CNDO calculations. In that paper the calculated $n \to \pi^*$ and $\pi \to \pi^*$ transition energies for the H_2NO radical were about of 1 eV in error with those observed. We think this is not due to the employment of the SCF procedure of Longuet-Higgins and Pople but rather to the adoption of the original CNDO/2 computational scheme.

As the procedure of Del Bene and Jaffé appears to be unreliable in estimation of bond lengths and structural predictions, the total energies of butadiene and its monomeric and dimeric ions were calculated by the original CNDO/2 method [10] adopting the parametrization suggested by Wiberg [16].

Interaction between Butadiene and Its Monomeric Ions

While with many conjugated systems the dimeric cation radicals have been detected, from the dimeric anion radicals to our knowledge only that of benzene was reported [17]. Attempts to detect the butadiene dimer anion radical were unsuccessful [6]. In order to obtain some insight into the different electronic nature of positive and negative dimers, we first employed the extended Hückel method. Fig. 2 shows the varying calculated total electron energy of the sandwich dimer as the two butadiene units come nearer to each other. In the case of two uncharged butadienes in their ground states only a repulsion occurs, as expected. With the positive and negative dimer radicals shallow minima are seen, which indicate the dimers are 0.068 eV and 0.048 eV more stable than the isolated monomeric species. The shape of these potential curves is, however, influenced by the choice of the simple model, in which all C–C bond lengths are taken to be the same as in the neutral butadiene at any interplanar distance. If a more realistic geometry for the monomeric ions, obtained through Eq. (6), is adopted, the energy change accompanying dissociation $M_2^+ \to M^+ + M$ is then nearly zero, while the isolated M and M^- are of 0.2 eV more stable than M_2^-. Thus one can conclude that the extended Hückel calculations indicate a possible formation of the positive dimer radical, which should be energetically more favourable than the negative dimer radical formation.

The situation with regard to the application of the CNDO method has been less clear-cut. We found the version of the CNDO method reported by Del Bene and Jaffé [9], which appears to be valuable in the interpretation of electronic
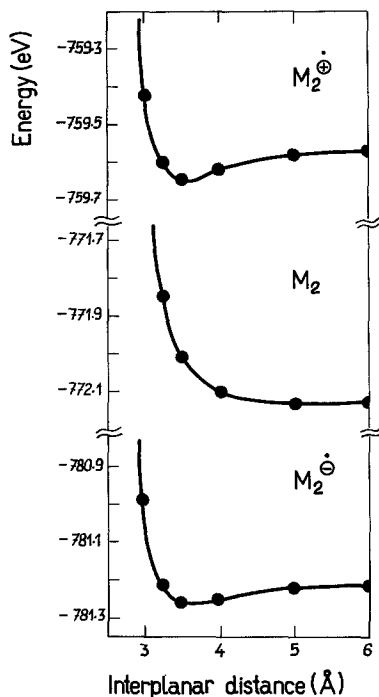
Fig. 2. Total energy calculated by the EHT method as a function of the interplanar distance of two butadienes in a sandwich complex for a positive (M_2^+), neutral (M_2), and negative (M_2^-) dimer

spectra, gives disappointing results for bond lengths and isomerization energies: the estimated C–C bond length in ethylene is unreasonably high if the core-core repulsions are calculated for point charges and unreasonably short if the core-core repulsions are set equal to integrals for electron-electron repulsions; *trans*-butadiene is favoured too much over *cis*-butadiene, the respective energy difference amounts to 20.2 eV and 9.2 eV depending on whether the core-core repulsions are calculated for point charges or set equal to electron-electron repulsions. Therefore we were forced to use the original CNDO/2 method [10] with the parametrization of Wiberg [16] which appears to be suitable for structural and energetic predictions [18]. Butadiene and its monomeric and dimeric ion radicals were calculated by this CNDO version assuming the reasonable geometry (see section Calculations). Dimer cation radical M_2^+ was found to be of 0.132 eV more stable than separated monomeric species M and M^+ while M and M^- are favoured over M_2^- of 0.116 eV, which is in qualitative agreement with the experimental finding.

Our theoretical treatment reflects shortcomings of the present state of the CNDO method, which is not capable of providing reasonable results simultaneously for ground and excited states properties. A creation of a new CNDO version, which would be successful in the interpretation of electronic spectra as the method of Del Bene and Jaffé [9] and could at the same time provide reasonable estimates of the potential surfaces, would be, therefore, very topical.

Electronic Spectra

Absorption curves of the negative and positive radical ions of butadiene are presented in Fig. 3. Badger and Brocklehurst [6] have reinterpreted the absorption curve of the butadiene cation radical recorded by Shida and Hamill [3], and assigned the maxima at 8300 cm^{-1} and 23500 cm^{-1} to the dimeric radical cation absorption and the maximum at 17400 cm^{-1} and a shoulder at about 26000 cm^{-1} to the monomeric cation radical absorption. The latter is seen to occur at the same wavelengths as the absorption bands of the butadiene anion radical, in agreement with the open shell PPP-like calculations, which owing to the pairing properties of MO's give identical results for the negative and positive ion. Both PPP-like and CNDO calculations (Figs. 4 and 5) indicate that none of the observed maxima of the monomeric ions is due to a $\sigma \to \pi$ transition. Two observed absorption maxima of butadiene monomeric ion radicals can be in both theoretical approaches assigned to the strongly mixed $m - 1 \to m$ and $m \to m + 1$ transitions ($\pi \to \pi$), where m denotes the singly occupied molecular orbital. For the second transition energy of the butadiene cation radical the CNDO calculation is in error of about 5000 cm^{-1}, which is a larger hypsochromic shift than that usually found in the open shell PPP-like calculations on the transition energies of short-wave bands of aromatic hydrocarbon radical ions [8, 19]. CNDO calculations for the dimeric cation radical is in a good agreement with the experimental results of Badger and Brocklehurst [6] (Fig. 5). Even a shoulder at 15500 cm^{-1}, which was not recorded by Shida and Hamill [3], is interpreted by the present calculation. The longest wavelength band is predicted to be polarized along the direction perpendicular to the planes of butadiene units. The nature of that band becomes more clear-cut if the wave functions of the lowest states are considered in a way, which was used by Ishitani and Nagakura [4] in the calculation for the paracyclophane anion. Let us assume the ground state wave functions of the butadiene dimer cation as constructed by removing one electron either from φ_2 or φ'_2 molecular orbital

$$\psi_1^G = |\varphi_1 \overline{\varphi}_1 \varphi'_1 \overline{\varphi}'_1 \varphi'_2 \overline{\varphi}'_2 \varphi_2|$$

$$\psi_2^G = |\varphi_1 \overline{\varphi}_1 \varphi_2 \overline{\varphi}_2 \varphi'_1 \overline{\varphi}'_1 \varphi'_2|,$$

where φ_n and φ'_n mean the molecular orbitals in two butadiene units. The degeneracy of ψ_1^G and ψ_2^G is removed through the interaction yielding the new states:

$$\psi_\pm^G = \frac{1}{\sqrt{2(1 \pm S_{12})}} (\psi_1^G \pm \psi_2^G) ; \quad E_\pm^G = \frac{H_{11} \pm H_{12}}{1 \pm S_{12}} .$$

Owing to that interaction the charge resonance occurs and as $\psi_+^G \to \psi_-^G$ represents the lowest electronic transition, the longest wavelength band of the dimer cation radical can be called a charge resonance band. From the point of view of symmetry considerations that transition can be classified as a $B_g \to B_u$ one and therefore it must be polarized along the direction perpendicular to planes of butadiene units.
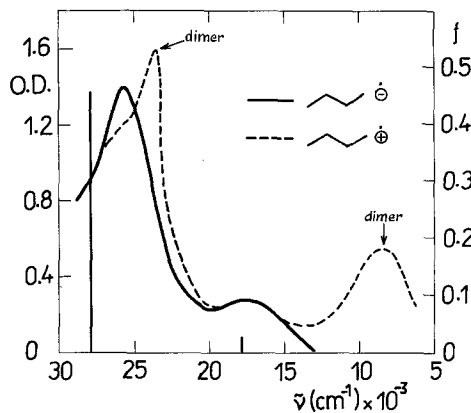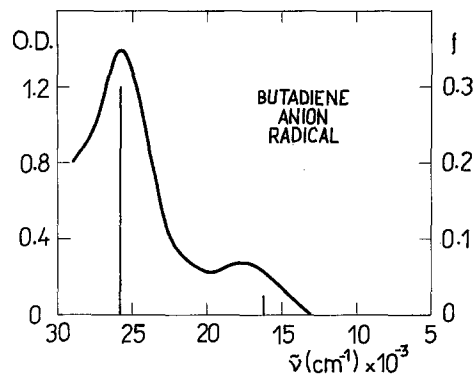
Fig. 3

Fig. 4

Fig. 3. Absorption curves of the butadiene anion and cation radicals [3]. Vertical lines represent the results of the open shell PPP-like calculation (for discussion see text and Table). The left side scale concerns the observed optical density, the right side scale the calculated intensity, where f stands for the theoretical oscillator strengths

Fig. 4. Absorption curve of the butadiene anion radical [3] and the results of the CNDO calculations indicated by vertical lines. The right side scale concerns the calculated spectral intensities, where f stands for the oscillator strength
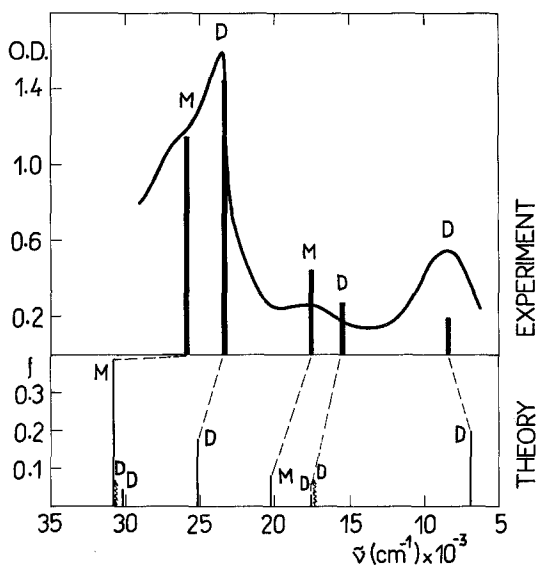

Fig. 5. Comparison of the experimental and calculated optical absorption of the monomeric (M) and dimeric (D) butadiene cation radicals. (For numerical values see table.) Absorption curve was recorded by Shida and Hamill [3], the thick vertical lines represent the positions and optical density of absorption maxima recorded by Badger and Brocklehurst [6]. Lower part of the figure contains the results of the CNDO calculations, where the allowed transitions are indicated by vertical lines and the forbidden ones by wavy lines with arrows. The calculated and observed spectral intensities cannot be compared directly, because the former are expressed in oscillator strengths while the latter in optical density. Dimer absorption at 15500 cm^{-1} was recorded as a shoulder [6]

Table. *The doublet-doublet electronic transitions in the butadiene anion (M⁻), butadiene cation (M⁺), and butadiene dimer cation (M₂⁺)*

Radical	Transition energy (cm⁻¹ × 10⁻³) and oscillator strength					Classi-fication	Symmetry[c]	Polari-zation[c,d]
	Exp[a]	CNDO		PPP[b]				
M^-	17.6	16.1	0.021	17.9	0.015	$\pi \to \pi$	$A_u \to B_g$	‖
	25.8	25.8	0.338	28.0	0.460	$\pi \to \pi$	$A_u \to B_g$	‖
		37.4	0.000			$\pi \to \sigma$	$A_u \to B_u$	
		41.1	0.000			$\pi \to \sigma$	$A_u \to A_g$	
		43.0	0.000	40.5	0.000	$\pi \to \pi$	$A_u \to A_u$	
M^+	17.4	21.4	0.057	17.9	0.015	$\pi \to \pi$	$B_g \to A_u$	‖
	26.0	31.0	0.396	28.0	0.460	$\pi \to \pi$	$B_g \to A_u$	‖
		36.9	0.000	40.5	0.000	$\pi \to \pi$	$B_g \to B_g$	
		37.2	0.000			$\sigma \to \pi$	$B_g \to A_g$	
		43.2	0.000			$\sigma \to \pi$	$B_g \to A_g$	
M_2^+	8.3	6.8	0.205				$B_g \to B_u$	⊥
		17.2	0.000				$B_g \to A_g$	
	15.5	17.6	0.015				$B_g \to A_u$	‖
	23.3	25.2	0.177				$B_g \to A_u$	‖
		30.2	0.049				$B_g \to B_u$	⊥
		30.7	0.000				$B_g \to B_g$	
		36.1	0.000				$B_g \to A_g$	
		45.8	1.533				$B_g \to A_u$	‖

[a] See Refs. [3] and [6].

[b] Open shell SCF CI calculations, see Ref. [8].

[c] Refers to CNDO calculations, in case of $\pi \to \pi$ transitions in monomeric ions the same results are also obtained with PPP-like calculations.

[d] Parallel (‖) or perpendicular (⊥) to the planes of butadienes.

The results obtained for monomeric butadiene ions and the dimeric cation radical are summarized in the Table.

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