62. Computation of the ESR. Coupling Constants of the [16]Annulene Radical Anion; Theoretical and Experimental Reinvestigation of the Excited States of [16]Annulene and its Mono- and Dinegative Ions

by **Harold Baumann** and **Jean F.M. Oth**

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule,
Universitätstrasse 16, CH-8092 Zürich

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Summary

The problem of assigning the two small ESR. coupling constants of the [16]annulene radical anion to the two sets of four equivalent outer and inner ring protons is treated by three different semiempirical MO methods. All three methods indicate that the smaller coupling constant (0.743 Gauss) should be assigned to the inner protons, and the larger one (0.963 Gauss) to the outer ones. The electronic spectra of [16]annulene, its radical anion, and its dianion have been remeasured. Especially interesting was the detection of a symmetry-forbidden band of the radical anion at 1473 nm (6789 cm^{-1}, logε 2.57). The spectra are discussed in terms of different MO models.

Introduction. - Preliminary results obtained by the variable *β-Hückel* method [1] indicated that only a D_{4h} symmetry was consistent with the ESR. spectrum of the [16]annulene radical anion. In order to reproduce the experimental coupling constants, the highest doubly occupied orbital must belong to the a_{2u} irreducible representation and the singly occupied orbital to a_{1u}. The assignment of the two small ESR. coupling constants to the two sets of four equivalent protons was not possible. The electronic spectra of the annulene and its ions could only be discussed in a very qualitative way.

In the meantime *Koning & Zandstra* [2] have described the MCD. and absorption spectra of the mononegative and dinegative ions of [16]annulene. Contrary to our prediction that the first excited state of [16]annulene radical anion should be about 11250 cm^{-1} (890 nm) above the A_{1u} state, these authors find from PPP calculations that the A_{2u} state is 15-450 cm^{-1} (670000-22000 nm) lower than A_{1u}. From the MCD. spectrum they could not decide which state is the ground state. *Concepcion & Vincow* [3] have prepared the [16]annulene radical anion from the *syn* [2+2] dimer of cyclooctatetraene and studied the disproportionation equilibrium of radical anion with dianion and neutral hydrocarbon. Finally, *Jones* [4] concluded from ESR. studies of temperature-dependent coupling constants that [16]annulene

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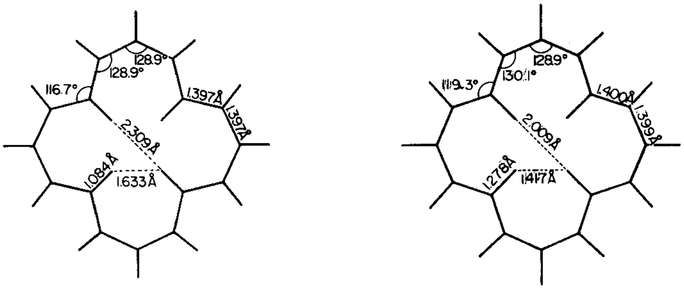
radical anion has a thermally accessible excited electronic state of symmetry A_{2u} lying 1140 cm^{-1} (8772 nm) above the A_{1u} ground state.

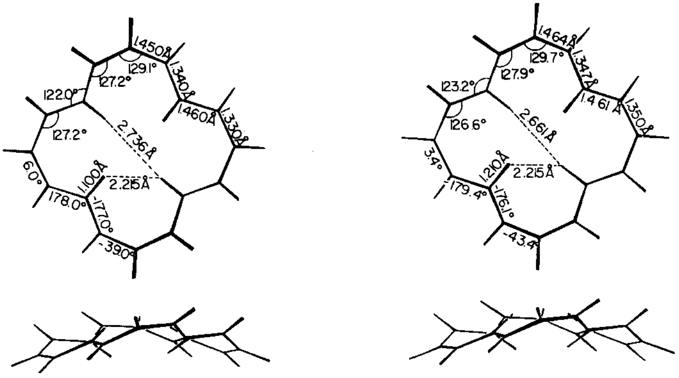
In order to assign the small ESR. coupling constants and to interpret the electronic spectra in a more quantitative way, properties of [16]annulene and its ions have now been recalculated with more elaborate methods than before. Moreover, the forbidden band of the radical anion at long wave length, predicted theoretically, has now been observed at 6789 cm^{-1} (1473 nm).

Structures. - The CNDO/CI calculations for [16]annulene are based on the X-ray structure **C** *(Fig. 1)*. For the radical anion and dianion the calculations are based on structure **B** obtained by the geometry-optimization procedure of *McIver & Komornicki* [5] using the MINDO/2 method.

The parameters of this method have been optimized by *Dewar et al.* [6] with respect to the structures and enthalpies of formation of a particular set of organic molecules. In the initial parametrization all carbon-hydrogen bonds were found to be systematically too long, and strain energies of small ring molecules were poorly reproduced. The structure **B** found by the procedure used [5] depends on the symmetry of the starting structure (**A** in *Fig. 1*), the parameter set of MINDO/2, and the limitations of the INDO approximation. This situation is illustrated by the



[16] Annulene Dianion **A** [16] Annulene Dianion **B**



[16] Annulene **C** [16] Annulene **D**

Fig. 1. *Structures used for the calculations.* **A** initial structure, **B** final structure of the optimization process of the dianion. **C** X-ray structure, **D** final structure of the optimization process of the neutral compound.

optimization of the X-ray structure **C**; the experimental structure lies 3.6 eV above the 'optimized' **D** which has a calculated ΔH_f° of 593 kJmol^{-1}. Indeed, it is possible to find a planar structure of [16]annulene by MINDO/2 which is most stable (ΔH_f°= 515 kJ mol^{-1}). A more detailed study of the MINDO/2 properties with inclusion of the correlation energy has been published elsewhere [7].

For the dianion we have optimized three structures belonging to different symmetry groups (S_4, C_{4h}, D_{4h}). The structure of symmetry C_{4h} immediately changed in direction of the higher symmetry D_{4h}. The S_4-geometry caused troubles by splitting off hydrogen, a result of the unrealistic H–H-parametrization of MINDO/2 and refused to converge. The C–C-bond lengths of the D_{4h}-structure (ΔH_f°=464 kJ mol^{-1}) are all equal (~ 1.400 Å) and do not point to one of the two situations given in *Figure 2* where in the righthand case the nonbonded hydrogen interactions are smaller.

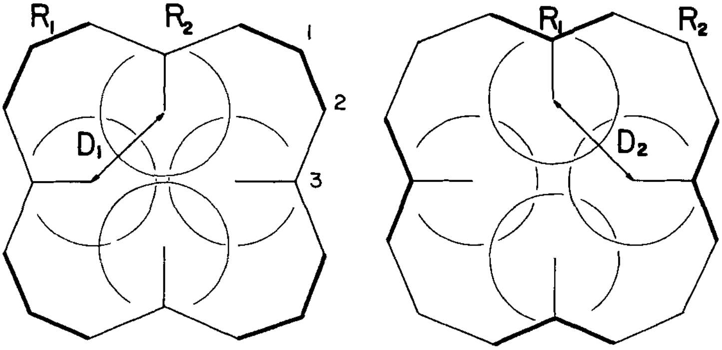


Fig. 2. *Distances of non-bonded inner ring protons in two planar structures differing in the bond length succession*

Results and discussion. - 1. *Spin densities.* The spin densities computed by three different semi-empirical MO methods are presented in *Tables 1, 2,* and *3*, and in *Table 4* are given the results of our calculations together with those of [1]. The values

Table 1. *Bond orders, charge densities, and spin densities calculated by the configuration interaction method of PPP.* The symmetry of the singly occupied orbital is a_{1u} (D_{4h}).

Center	Charge density	Spin density	Bond	Bond order
1	1.131	−0.0338	1-2	0.6284
2	1.007	0.1585	2-3	0.6281
3	1.105	−0.0331		

Table 2. *Bond orders, charge densities, and spin densities calculated by the a,β-spin orbital method of PPP.* The symmetry of the singly occupied orbital is a_{1u} (D_{4h}).

Center	Charge density	Spin density	Bond	Bond order
1	1.130	−0.064	1-2	0.599
2	1.007	0.187	2-3	0.602
3	1.105	−0.061		

are similar to those found by the variable *β-Hückel* calculation. In order to obtain good results by the *Hückel* calculation, however, we have to optimize the parameter λ of the *McLachlan* formula [8].

2. *Electronic transitions (Fig. 3).* The absorption spectrum of [16]annulene shows two bands (λ_{max} 293 (306), and 446 nm). The first one has a shoulder and

Table 3. *Bond orders, charge densities and spin densities calculated by the configuration interaction method of CNDO/2.* The symmetry of the singly occupied orbital is a_{1u} (D_{4h}).

Center	Charge density	Spin density	Bond	Bond order
1	4.078	−0.0436	1-2	0.5083
2	4.034	0.1588	2-3	0.5079
3	4.072	−0.0428		

Table 4. *Calculated and experimental coupling constants ($Q = -24.84$ Gauss).*

Center	*Hückel*	Variable β *Hückel McLachlan*a)	CI-method PPP	CI-method CNDO	α,β-spin orbital method	Experiment
1	0	0.840	0.836	1.084	1.594	0.963
2	−3.105	−3.910	−3.921	−3.946	−4.655	−3.958
3	0	0.768	0.795	1.062	1.505	0.743

a) $\beta_{12} = 0.9$, $\beta_{23} = 1$, $\lambda = 0.7$ for the *McLachlan* correction.

Table 5. *Comparison of the theoretical and experimental transition energies and extinctions*a).

	Experiment		Theory					
			CNDO CI			PPP		
	λ_{max}(nm)	$\log\varepsilon_{max}$	λ_{max} (nm)	Sym.	$\log\varepsilon_{max}$	λ_{max} (nm)	Sym.	$\log\varepsilon_{max}$
R	293	4.88	269	E	4.57	–	–	–
	306 sh.	4.66	290	E	3.95	–	–	–
	446	3.33	435	A	f	–	–	–
$R^{\dot{-}}$	319 sh. 330	4.20 4.58	288	E_g	4.79	292	E_g	5.08
	368 sh.	4.55	297	B_{1u}	f	–	–	–
			298	B_{2u}	f	–	–	–
	380	5.18	303	E_g	4.89	333	E_g	4.44
	444	3.80	362 364	B_{1u} B_{2u}	f f	342 349	B_{1u} B_{2u}	f f
	565	3.90	604	E_g	2.98	587	E_g	1.32
	617	3.95						
	675	3.95	726	E_g	2.91	729	E_g	1.50
	1473	2.57	1458	A_{2u}	f	8959	A_{2u}	f
$R^{=}$	412	5.20	333	E_u	4.94	318	E_u	4.90
	560 600	4.20 4.25	648	E_u	1.17	586	E_u	0.02

a) f = forbidden transition.

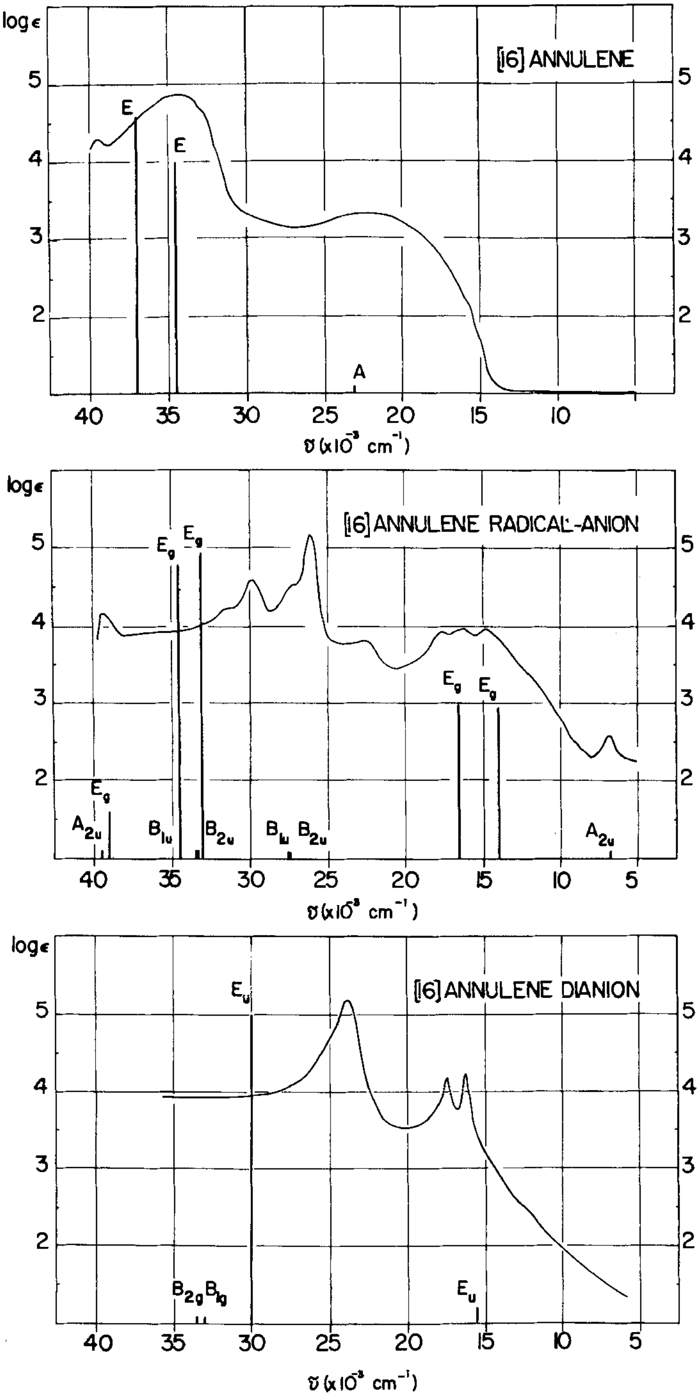


Fig. 3. *Measured and computed electronic transitions of [16]annulene, radical anion, and dianion*

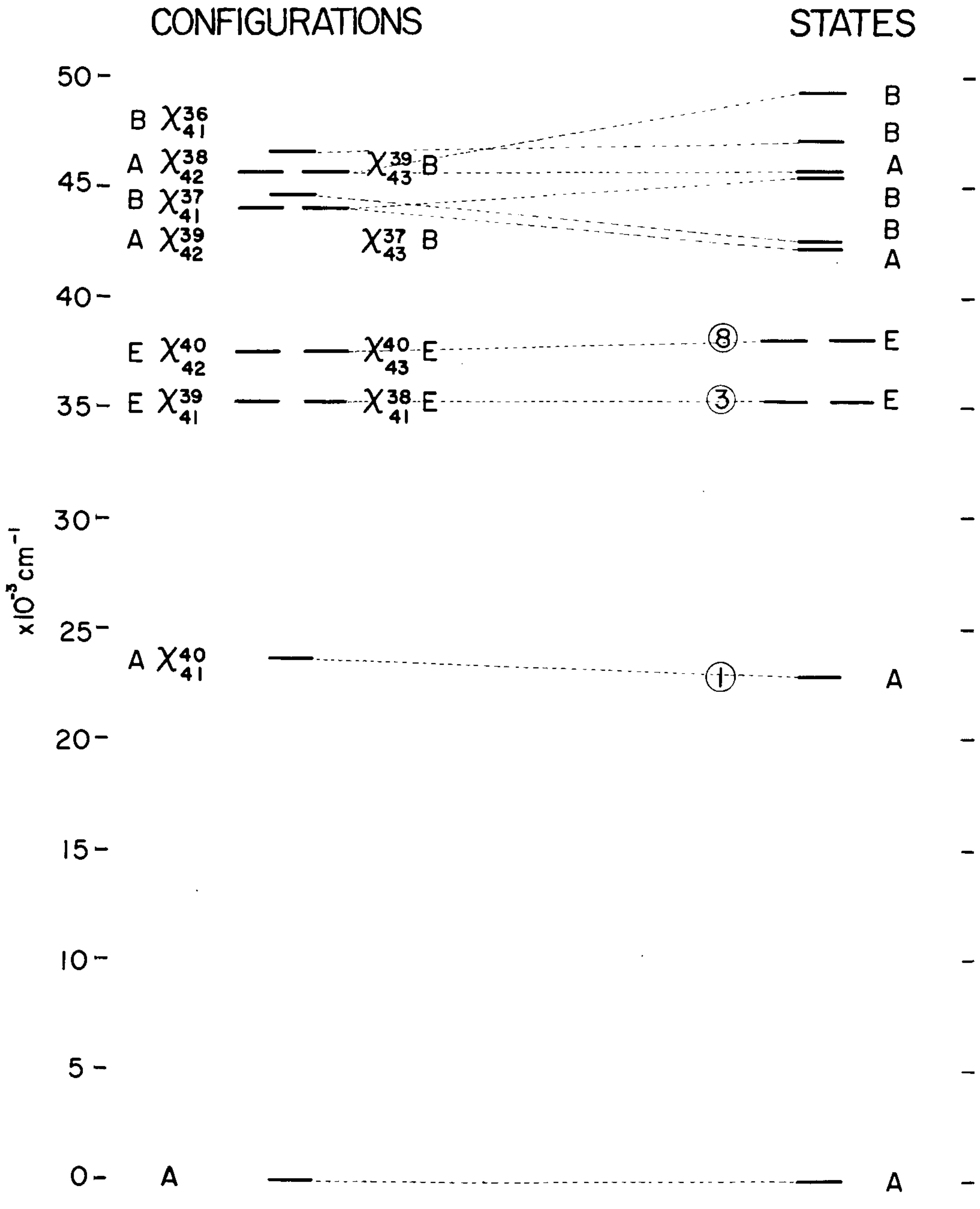


Fig. 4. *Correlation of electronic configurations and states of [16]annulene.* The correspondence of the orbital numeration to *Figure 12* in [1] is the following: 36, 4a; 37, 3a; 38, 39, 3e; 40, 3b; 41, 2b; 42, 43, 2e.

corresponds to the A→E transitions to the states 3 and 8, the second to the lowest forbidden A→A transition to state 1 *(Fig. 4)*.

The absorption spectrum of the radical anion shows narrower bands than the neutral molecule and is the most complicated of the three spectra. It consists of 7 bands with λ_{max} of 1473, 675, 617, 565, 444, 380 (368), and 330 (319) nm. Contrary to *Koning & Zandstra* [2] we found from PPP and CNDO/CI calculations the $^2A_{1u}$ state to be the ground state. According to our calculations the first forbidden band must be attributed to the $A_{1u} \rightarrow A_{2u}$ transition to state 1 in *Figure 5*. The maxima at

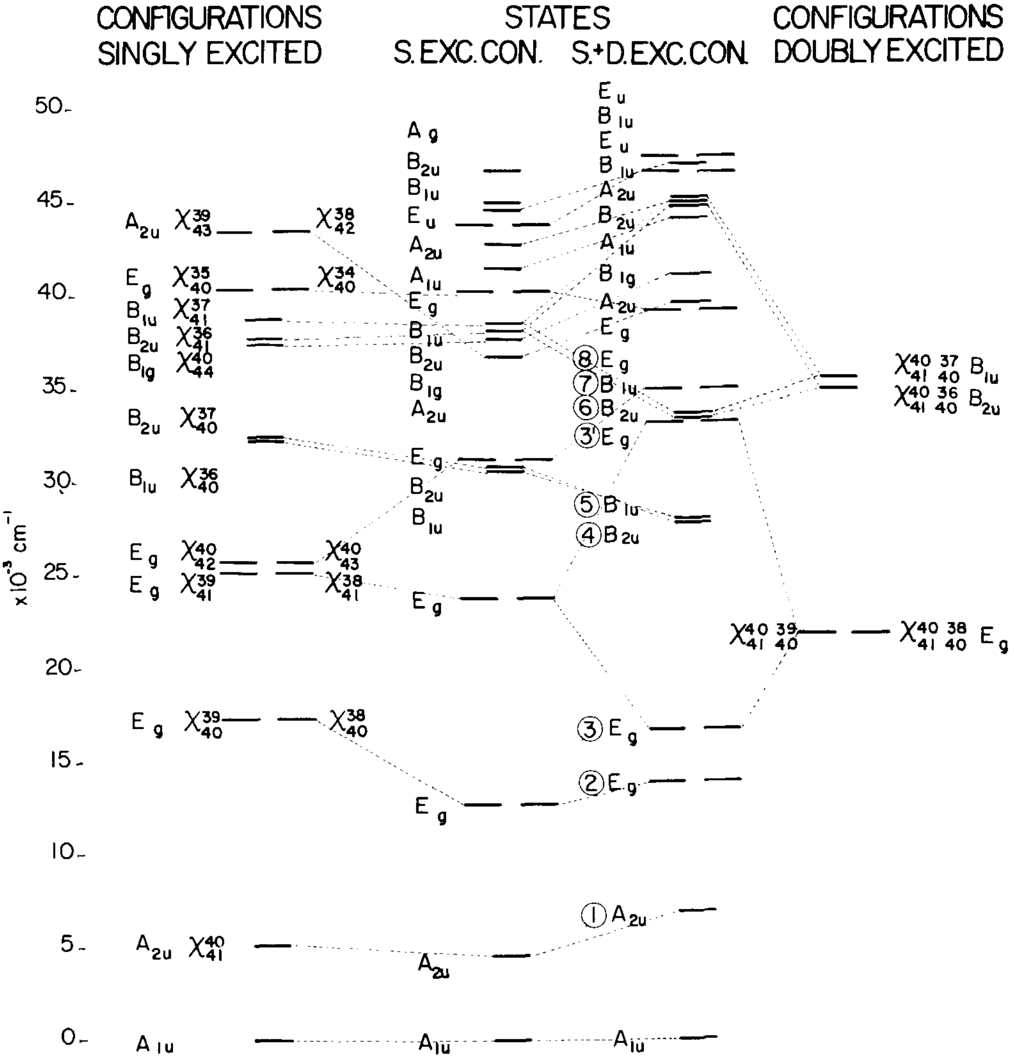


Fig. 5. *Correlation of electronic configurations and states of [16]annulene radical anion.* The correspondence of the orbital numeration to *Figure 12* in [1] is the following: 34, 35, $4e_g$; 36, $2b_{1u}$; 37, $2b_{2u}$; 38, 39, $3e_g$; 40, a_{1u}; 41, $2a_{2u}$; 42, 43, $2e_g$; 44 is a σ-orbital not present in [1].

675, 617, and 565 nm, a region not measured by [2], can best be related to the $A_{1u} \rightarrow E_g$ transitions to the states 2 and 3. The splittings of 1392 cm^{-1} and 1492 cm^{-1} in this band probably correspond to molecular skeleton vibrations. The weaker band at 444 nm was assumed by [2] to consist of two transitions to very close lying

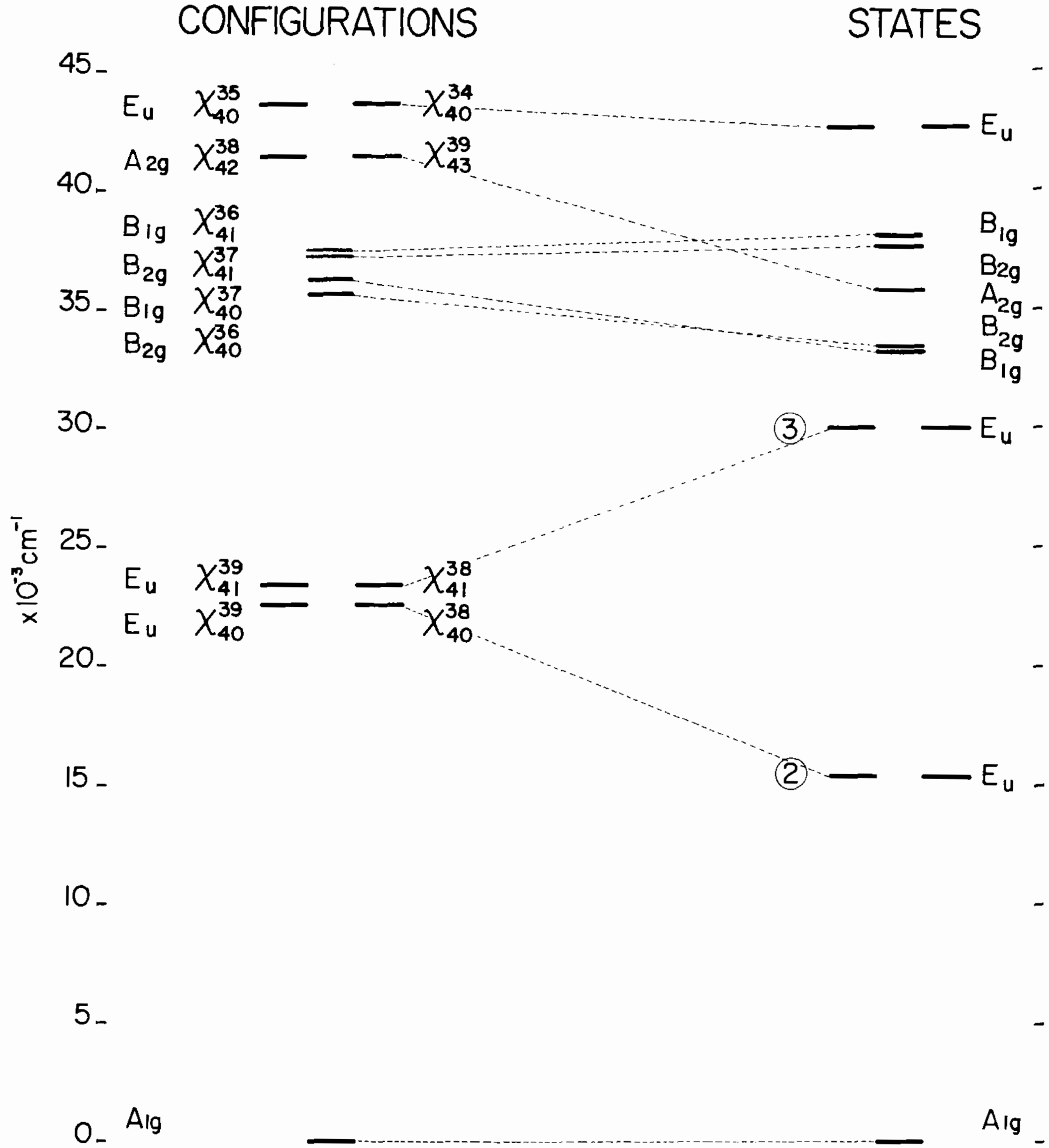


Fig. 6. *Correlation of electronic configurations and states of [16]annulene dianion.* The correspondence of the orbital numeration to *Figure 12* in [1] is the following: 34, 35, $4e_g$; 36, $2b_{1u}$; 37, $2b_{2u}$; 38, 39, $3e_g$; 40, $2a_{2u}$; 41, a_{1u}; 42, 43, $2e_g$.

excited states. The most probable candidates are the states 4 and 5 of symmetry B_{2u} and B_{1u}, respectively. The bands at 380 and 330 nm with shoulders at 368 and 319 nm should then be assigned to the $A_{1u} \rightarrow E_g$ transitions to the states 3′ and 8. The shoulders could again be explained by in-plane and out-of-plane deformation vibrations of the hydrogens with characteristic frequences of 858 and 1044 cm^{-1} or to perturbation of the forbidden $A_{1u} \rightarrow B_{2u}$ and $A_{1u} \rightarrow B_{1u}$ transitions to the states 6 and 7.

The spectrum of the dianion consists of three bands (600, 560, and 412 nm). The first and second correspond to the $A_{1g} \rightarrow E_u$ transition to state 2 *(Fig. 6)*, which is split by vibration of the molecule (1190 cm^{-1}); the third band is assigned to the $A_{1g} \rightarrow E_u$ transition to state 3.

A comparison of the experimental and the theoretical spectra of the three species is given in *Table 5*.

Formally it is possible to relate the calculated state-transitions to the orbital-transitions given in *Figure 1* of [1]. For the [16]annulene only two orbital-transitions were given, namely $2b \rightarrow 3b$ and $2b \rightarrow 3e$ which may be related to the transitions to state 1 and 3, respectively. *Figure 4* reveals that the state-transition to 8 corresponds to $2e \rightarrow 3b$. This transition could be responsible for the shoulder.

For the [16]annulene radical anion four transitions were given in [1], namely $2a_{2u} \rightarrow a_{1u}$, $a_{1u} \rightarrow 3e_g$, $a_{2u} \rightarrow 3e_g$, and $2e_g \rightarrow a_{1u}$. They correspond in *Figure 5* to the transitions to the states 1, 2, 3′, and 8, respectively. State 3 has a large contribution of a doubly excited configuration. The band with $\lambda_{max} \sim 444$ nm would correspond to the symmetry-forbidden transitions to the states 4 and 5, which would appear in Diagram 1 of [1] as $a_{1u} \rightarrow 2b_{1u}$, and $a_{1u} \rightarrow 2b_{1u}$. Two other forbidden transitions to states 6 and 7 correspond to $2a_{2u} \rightarrow 2b_{1u}$ and $2a_{2u} \rightarrow 2b_{2u}$.

Finally, the [16]annulene dianion is characterized completely by the transitions $2a_{2u} \rightarrow 3e_g$ and $a_{1u} \rightarrow 3e_g$ which correspond to the transitions to the states 2 and 3 of *Figure 6*.

Conclusion. - The essential agreement between the calculated and observed values indicates that, as for the neutral [16]annulene *(Fig. 1)*, the molecular geometries used in the computation for the corresponding mono- and dianion should not be too far from the true ones. With three different methods we found that the smallest coupling constant of 0.743 Gauss should be assigned to the inner proton set. The symmetry of the ground state is A_{1u} (D_{4h}) according to all our calculations. This state is much closer to the A_{2u}-state in PPP (1116 cm^{-1}) than in CNDO (6859 cm^{-1}) using the same molecular geometry. The smaller energy gap found in the PPP-approximation agrees better than the CNDO-value with the result of *Koning et al.* [2] who found the A_{2u} state to be 15-450 cm^{-1} more stable than the A_{1u} state.

The temperature dependence of the coupling constants measured in diethyleneglycol dimethyl ether (diglyme) by *Jones* [4] (−68− +80°) has not been observed in hexamethylphosphoramide (HMPA) a solvent used by *Concepcion & Vincow* [3] (0-60°). No temperature dependence of the coupling constants could be detected in dimethylformamide (DMF) [1]. If the A_{2u} state was thermally accessible the effect should be independent of the solvent. Since we have found the A_{2u} state to lie

82 kJ mol^{-1} above the ground state we must exclude a thermal accessibility of this state.

Acknowledgment is made to the computing center of the Eidg. Tech. Hochschule for the computing time.

Appendix. - *Computational methods.* - **1.** The PPP programs. The closed shell calculations were performed with a modified version of a program written by *Straub* [9]. The open shell calculations were performed with two modified programs written by *Bloor & Gilson* [10] and *Janiszewski* [11]. In all three programs parameters proposed by *Nishimoto & Mataga* [12] and *Kon* [13] were used.

2. The CNDO/2 programs. The calculations were performed with two programs called CNDUV99 [14] and ONDUV80 [15], optimized with respect to computer space and calculation time. On the CDC6500 computer with 140000_8 core memory it is possible to treat molecules with up to 120 orbitals. Overlay and buffer technique are used.

3. The geometry optimization program [7]. The program of *Komornicki & McIver* [16] was modified by buffer technique in order to treat larger molecules. Instead of 100000_8 core memory for 50 orbitals it needs now 120000_8 for 90 orbitals. The Extended *Hückel* part of the program has been deleted.

Spin density calculations. - **1.** Configuration interaction method. The ground state of a radical is approximated by the expression (1)

$$^2\Gamma_0 = {^2\chi_0} + \sum_i \lambda_i {^2\chi_i} \tag{1}$$

$^2\chi_0$ and $^2\chi_i$ are given by *Slater* determinants and represent the lowest configuration and the excited configurations. They are given by

$$\begin{aligned} {^2\chi_0} &= |\psi_1\bar{\psi}_1 \dots \psi_{m-1}\bar{\psi}_{m-1}\psi_m| \\ {^2\chi_i} &= 1/\sqrt{6}\,\{2|\psi_1\bar{\psi}_1 \dots \psi_i\bar{\psi}_m \dots \psi_p| + |\psi_1\bar{\psi}_1 \dots \psi_i\bar{\psi}_p \dots \psi_m| - |\psi_1\bar{\psi}_1 \dots \psi_p\bar{\psi}_i \dots \psi_m|\} \end{aligned} \tag{2}$$

The molecular orbitals ψ_i are calculated by the SCF method proposed by *Longuet-Higgins & Pople* [17] and improved by *Roothaan* [18]. Since the orbitals are self-consistent, the *Brillouin* theorem excludes the mixture of singly excited configurations with the ground configuration. The spin density at the nuclear position of atom N, is defined by (3)

$$\hat{\rho}_s(r_N) = \sum_\mu 2\hat{S}_{z\mu}\delta(r_N - r_\mu) \tag{3}$$

r_μ = position vector of the μ^{th} electron
$\hat{S}_{z\mu}$ = component of the electron spin angular momentum operator
$\delta(r)$ = *Dirac* delta function

Applying (3) on (1) we obtain (4):

$$\langle {^2\Gamma_0}|\hat{\rho}_s|{^2\Gamma_0}\rangle = \lambda_0^2\langle {^2\chi_0}|\hat{\rho}_s|{^2\chi_0}\rangle + 2\lambda_0\sum_l \lambda_l\langle {^2\chi_0}|\hat{\rho}_s|{^2\chi_l}\rangle \tag{4}$$

In equation (4) the quadratic term is neglected and λ_l is determined by a perturbation method proposed by *Hobey* [19]

$$\lambda_l = -\frac{\langle {^2\chi_0}|\hat{H}|{^2\chi_l}\rangle}{E_l - E_0} \tag{5}$$

The spin density is now given by expression (6)

$$\langle {^2\Gamma_0}|\hat{\rho}_s|{^2\Gamma_0}\rangle = \lambda_0^2\psi_m^2 + \lambda_0\sum_{i,k}\frac{2(im|mk)}{\varepsilon_k - \varepsilon_i - (ii|kk) + (im|mi) + (mk|km)}\,\psi_k\psi_i \tag{6}$$

$\varepsilon_k, \varepsilon_i$: SCF eigenvalues k and i
(im|mk), (ii|kk), (im|mi) and (mk|km): two electron repulsion integrals

2. *α,β-spin orbital method.* The ground state of the radical anion is approximated by the expression (7)

$$^2\Gamma_0 = {}^2\chi_0 \tag{7}$$

For the function $^2\chi_0$ *Pople & Nesbet* [20] and *Brickstock & Pople* [21] proposed the determinant (8)

$$|\psi_1^\alpha \cdots \psi_i^\alpha \psi_{i+1}^\beta \cdots \psi_m^\beta| \tag{8}$$

Applying the operator (3) on this function we find

$$\langle {}^2\chi_0 | \hat{\rho}_s | {}^2\chi_0 \rangle = \sum_{j=1}^{i} \psi_j^2 - \sum_{j=i+1}^{m} \psi_j^2 \tag{9}$$

Replacing molecular orbitals by expansions of atomic orbitals it is possible to write for the spin density at center k the expression (10)

$$\rho_k = P_{kk}^\alpha - P_{kk}^\beta \tag{10}$$

Because of the fact that $^2\chi_0$ is only an eigenfunction of $\hat{S}_z$ with eigenvalue $1/2\,\hbar$ but not an eigenfunction of $\hat{S}^2$ the above spin densities have to be corrected. *Amos & Snyder* [22] derived approximate formulas by applying a single annihilator which removed the major contaminating spin multiplet from the wave function (11).

$$\rho_k = P_{kk}^\alpha - P_{kk}^\beta - \frac{2}{x(\mathbf{P}^\alpha \mathbf{P}^\beta \mathbf{P}^\alpha - \mathbf{P}^\beta \mathbf{P}^\alpha \mathbf{P}^\beta)_{kk}} \tag{11}$$

x $= (s'+1)(s'+2) - 1/4(n_\alpha - n_\beta)^2 - 1/2(n_\alpha + n_\beta) + \mathrm{Tr}\,\mathbf{P}^\alpha \mathbf{P}^\beta$
n_α = number of α-orbitals
n_β = number of β-orbitals
$\mathbf{P}^\alpha, \mathbf{P}^\beta$ = α-,β-spin density
s' $= \frac{1}{2} \sum_{i=1}^{n} |\mathrm{occ}_i^\alpha - \mathrm{occ}_i^\beta|$

CI theory. For the open-shell case the following configurations are considered:

Type 0: ground configuration

$$^2\chi_0 = |\psi_1 \bar{\psi}_1 \cdots \psi_{m-1} \bar{\psi}_{m-1}\ \psi_m|$$

Type 1: singly excited configurations

$$^2\chi_i^m = |\psi_1 \bar{\psi}_1 \cdots \psi_i \bar{\psi}_m \cdots \psi_{m-1} \bar{\psi}_{m-1} \psi_m| \qquad i < m$$

Type 2: singly excited configurations

$$^2\chi_m^k = |\psi_1 \bar{\psi}_1 \cdots \psi_{m-1} \bar{\psi}_{m-1} \psi_k| \qquad k > m$$

Type 3: singly excited configurations

$$^2\chi_i^k = 1/\sqrt{2}\,\{|\psi_1 \bar{\psi}_1 \cdots \psi_i \bar{\psi}_k \cdots \psi_{m-1} \bar{\psi}_{m-1} \psi_m| + |\psi_1 \bar{\psi}_1 \cdots \psi_k \bar{\psi}_i \cdots \psi_{m-1} \bar{\psi}_{m-1} \psi_m|\} \quad i < m, \quad k > m$$

Type 4: doubly excited configurations

$$\begin{aligned} {}^2\chi_i^k = {} & \sqrt{2}/\sqrt{3}\,|\psi_1 \bar{\psi}_1 \cdots \psi_i \bar{\psi}_m \cdots \psi_{m-1} \bar{\psi}_{m-1} \psi_k| + 1/\sqrt{6}\,|\psi_1 \bar{\psi}_1 \cdots \psi_i \bar{\psi}_k \cdots \psi_{m-1} \bar{\psi}_{m-1} \psi_m| \\ & - 1/\sqrt{6}\,|\psi_1 \bar{\psi}_1 \cdots \psi_k \bar{\psi}_i \cdots \psi_{m-1} \bar{\psi}_{m-1} \psi_m| \qquad i < m, \quad k > m \end{aligned}$$

The 5 configuration energies and 24 interaction types among them have to be calculated.

For the closed-shell case the following configurations are considered:

Type 0: ground configuration

$$^1\chi_0 = |\psi_1\bar{\psi}_1 \cdots \psi_i\bar{\psi}_i \cdots \psi_m\bar{\psi}_m|$$

Type 1: singly excited configurations

$$^1\chi_i^k = 1/\sqrt{2}\,\{|\psi_1\bar{\psi}_1 \cdots \psi_i\bar{\psi}_k \cdots \psi_m\bar{\psi}_m| + |\psi_1\bar{\psi}_1 \cdots \psi_k\bar{\psi}_i \cdots \psi_m\bar{\psi}_m|\}$$

The 2 configuration energies and 4 interaction types among them have to be calculated.

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