184. The Low-Temperature UV./VIS. Absorption Spectrum of [18]Annulene

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 UV./VIS. absorption spectrum of [18]annulene has been remeasured in 3-methylpentane at room and at liquid nitrogen (glass) temperature and interpreted by the CNDO/S-CI-method. The confrontation of the experimental electronic transitions with the CNDO/S-CI-calculated ones favors a structure with D_{6h}-symmetry, *i.e.* a structure with delocalized π-bonds.

Introduction. – The structure of [18]annulene has been a subject of controversy since many years (see *Table*). In 1969 *Van-Catledge & Allinger* [1] reviewed all important works already published on the subject; on the grounds of their own PPP-calculations and having at their disposal an incomplete experimental UV./VIS. spectrum they came to the conclusion that [18]annulene presents π-bonds fixation and belongs to the symmetry group D_{3h} and in a note added in proof they expressed their belief that the long-wavelength absorption band observed by *Blattmann et al.* [2] should correspond to an electronically allowed ($\pi \leftrightarrow \sigma$)-transition. *Blattmann et al.* [2] reported the complete electronic spectrum and proposed a molecular D_{6h}-symmetry to explain the general features of the spectrum, but postulated 'bond alternation (at least in the ground state)' to take into account the relative position of the B_{2u}, B_{1u} and E_{1u} ($\pi \rightarrow \pi^*$)-transitions.

In 1973, *Allinger & Sprague* [3] performed molecular-mechanics (MM) calculations on [18]annulene and computed the UV./VIS. spectrum using the PPP-method and assuming the MM-structure of symmetry D_3 to be most stable. In their contribution the long-wavelength band, considered as an electronically allowed ($\pi \leftrightarrow \sigma$)-transition (*cf.* [1]), was not mentioned.

In 1974, *Dewar et al.* [4] published their MINDO/3-study in which they found for [18]annulene a structure with localized π-bonds and D_{3h}-symmetry. In the same year *Oth et al.* [5] showed by a thermochemical investigation that [18]annulene is stabilized by 155 kJmol^{-1} relatively to a hypothetical planar *Kekulé* structure, a fact which supports a π-bonds-delocalized structure. *Kao & Allinger's* [6] MM-calculations and *Gutman et al.*'s [7] nonparametric resonance-energy computation of [18]annulene 'indicate a very small π-electron delocalization' (*sic!*) [7].

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Table. *Some contributions to the [18]annulene problem in chronological order*

Method	Ref.	Remarks	Year
1) HMO	[14]	[18]Annulene is predicted as an aromatic hydrocarbon by the (4n+2)-rule	1931
2) SCF-LCAO	[15]	Prediction of alternance for large rings	1957
3) Synthesis	[16]	UV./VIS. spectrum (200–500 nm)	1959
4) PPP	[17]	Interpretation of the UV./VIS. spectrum/Postulation of π-bonds alternance	1960
5) Vibronical analysis	[18]	Low-temperature UV./VIS. spectrum (200–500 nm)/Postulation of π-bonds delocalization	1962
6) X-Ray structure	[19]	C_i-symmetry (delocalization)	1965
7) PPP	[20]	Theoretical transition beyond 500 nm for X-ray structure	1965
8) UV./VIS. spectrum	[2]	Experimental confirmation of band at ~790 nm	1968
9) PPP	[1]	Transition at ~790 nm is considered to be a $(\sigma \leftrightarrow \pi)$-transition	1969
10) NMR.	[8]	The conformational mobility study supports X-ray structure	1972
11) Ring current	[21]	Favors a π-bonds-localized structure	1972
12) MM	[3]	π-Bonds-localized structure of D_3-symmetry	1973
13) MINDO/3	[4]	π-Bonds-localized structure of D_{3h}-symmetry	1974
14) Thermochemistry	[5]	Stabilization through delocalization	1974
15) Fluorescence spectrum of [18]annulene and of monofluoro-[18]-annulene	[22]	Fluorescence of the second excited state	1976
16) ^{13}C-NMR. and ^{1}H-NMR. spectra of [18]annulene at very low temperature	[23]	Only two chemical shifts are found, which is only compatible with a structure with D_{6h}-symmetry	1976
17) ^{13}C-NMR. and ^{19}F-NMR. spectra of monofluoro-[18]annulene at different temperature	[24]	Supports a structure with π-bonds delocalization	1976
18) MM	[6]	π-Bonds-localized structure of D_3-symmetry	1977
19) Topological resonance energy	[7]	Very small delocalization energy	1977
20) Electron correlation	[13]	Correlation energy favors delocalization	1978
21) Unified theory of resonance and ring current	[9]	Resonance energy very small, favors a π-bonds-localized structure	1979
22) Ring current	[12]	Inclusion of local anisotropic effects favors structure of D_{6h}-symmetry	1979
23) STO-3G-SCF-LCAO-MO	[10]	π-Bonds-localized structure of D_{3h}-symmetry	1980
24) MNDOC	[25]	Inclusion of all doubly excited configurations favors π-bonds-delocalized structure	1981
25) PE. spectrum	[26]	Cation with localized π-bonds	1982

In 1971, *Gilles et al.* [8] made a NMR. study of the conformational mobility of [18]annulene; they showed that a structure with delocalized π-bonds and with D_{6h}-symmetry is best compatible with the NMR. observations. On the grounds of a unified theory for resonance energies, ring currents and aromatic character [9] and of a SCF-STO-3G *ab initio* calculation [10] using a suitably modified version of the HONDO-program [11] *Haddon* suggested for [18]annulene a molecular structure with D_{3h}-symmetry, *i.e.* with π-bonds localized. *Vogler* [12] computed the ring current and the local anisotropy contributions of the π-electrons and of the σ-core to the proton chemical shifts of [18]annulene and showed that the calculated

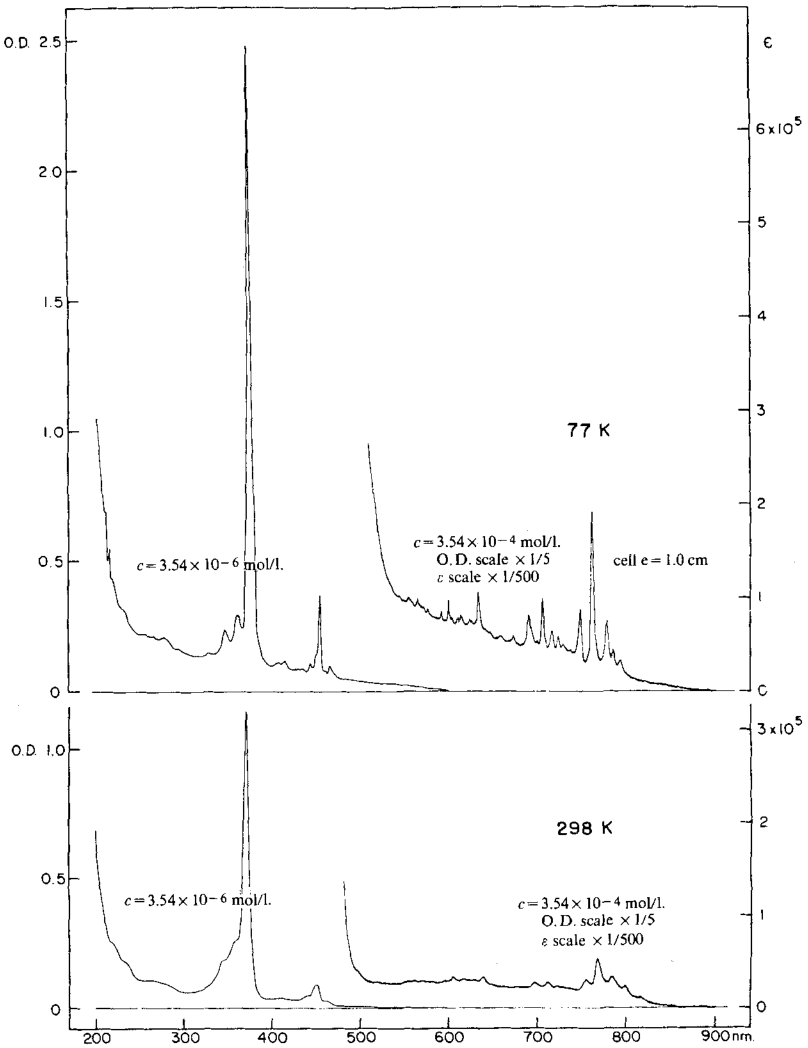

Fig. 1. *UV./VIS. spectrum of [18]annulene at 298K and 77K*

shifts can be matched with the observed ones only if a nearly planar structure with no appreciable bond-length alternation is assumed.

An investigation of the importance of electron correlation in computations of molecular energies and geometries of large annulenes has been published in 1978 by *Baumann* [13]. This study indicates that for cyclic $(4n+2)\pi$-systems a twofold axis or a symmetry plane passing through π-centers brings extra stabilization due to electron correlation and, therefore, that a π-bond-delocalized structure with D_{6h}-symmetry is very probable for [18]annulene in spite of the SCF-results mentioned above.

This contribution deals with the interpretation of the UV./VIS. spectrum of [18]annulene recorded at 77 K in organic glass. We compare the experimental spectrum with the transitions calculated (CNDO/S-CI) for different geometries; more precisely we discuss the relative values of the energy gaps between the first and second and between the second and third spectral bands. As already mentioned, these energy gaps could not be interpreted satisfactorily with PPP-calculations as reported by *Blattmann et al.* [2].

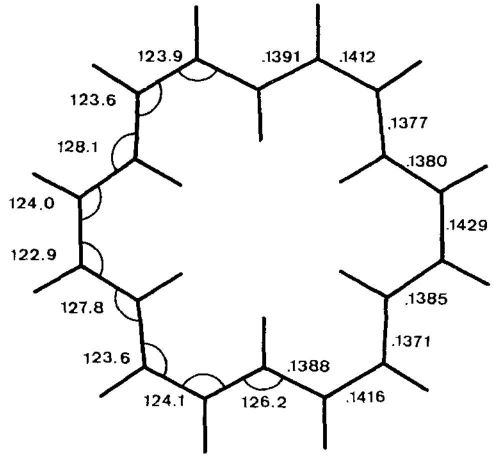

Fig. 2. *Idealized X-ray structure of [18]annulene* (C_{2h} very close to D_{6h}; bond length in nm, angles in degrees)

Experimental results. – *The UV./VIS. spectra. Figure 1* shows the UV./VIS. spectrum of [18]-annulene recorded in 3-methylpentane at r.t. and liquid N_2 temp. using a *Cary-17* spectrometer and a home-made cryostat equipped with a 1-cm-cell. The first weak absorption band in the region of 790 nm was measured in a 3.54×10^{-4} molar solution while the second and third bands were recorded in a 3.54×10^{-6} molar solution. As it can be seen on *Figure 1*, the spectrum consists of many sharp peaks which correspond to vibrational fine structures of several main transitions: the very weak $(0 \rightarrow 0)$-component at 795.2 nm ($\log\varepsilon = 1.97$) of the first absorption band implies a high symmetry for the molecule.

Theoretical results. – *The molecular structures. Bregman et al.* [19] have determined by X-ray diffraction the crystal structure of [18]annulene. According to this study the molecule is nearly planar, has π-bonds delocalized but is slightly distorted

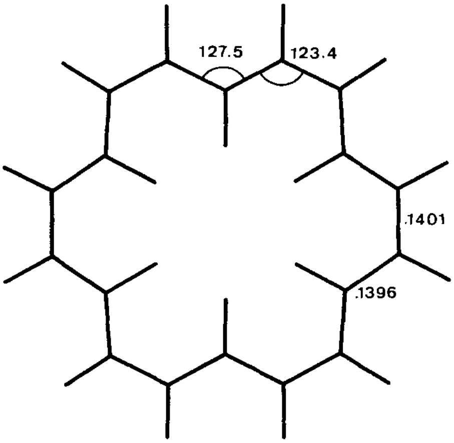

Fig. 3. *MINDO/2-optimized structure of [18]annulene* (D_{6h})

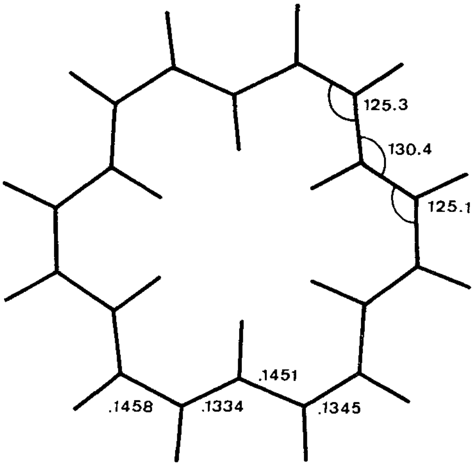

Fig. 4. *MINDO/2-optimized structure of [18]annulene* (D_{3h})

from D_{6h}-symmetry; strictly it belongs to the point group C_i. Neglecting small deviations, a structure belonging to point group C_{2h} *(Fig. 2)* is obtained.

We have performed a geometry optimization using a modified version of the program[1] of *Komornicki & McIver* [27]. *Figures 3* and *4* reproduce these MINDO/2-optimized structures which belong to the symmetry group D_{6h} and D_{3h} and which are very similar to the structures found by *Allinger & Sprague* [3] and by *Dewar et al.* [4].

The CNDO/S-CI-calculations [28]. With the three geometries represented in *Figures 2, 3* and *4* we have computed the transitions $S_1 \leftarrow S_0$, $S_2 \leftarrow S_0$ and $S_3 \leftarrow S_0$

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[1] OPTMO 90 is a modified version of the original program suitable for the computation of large molecules.

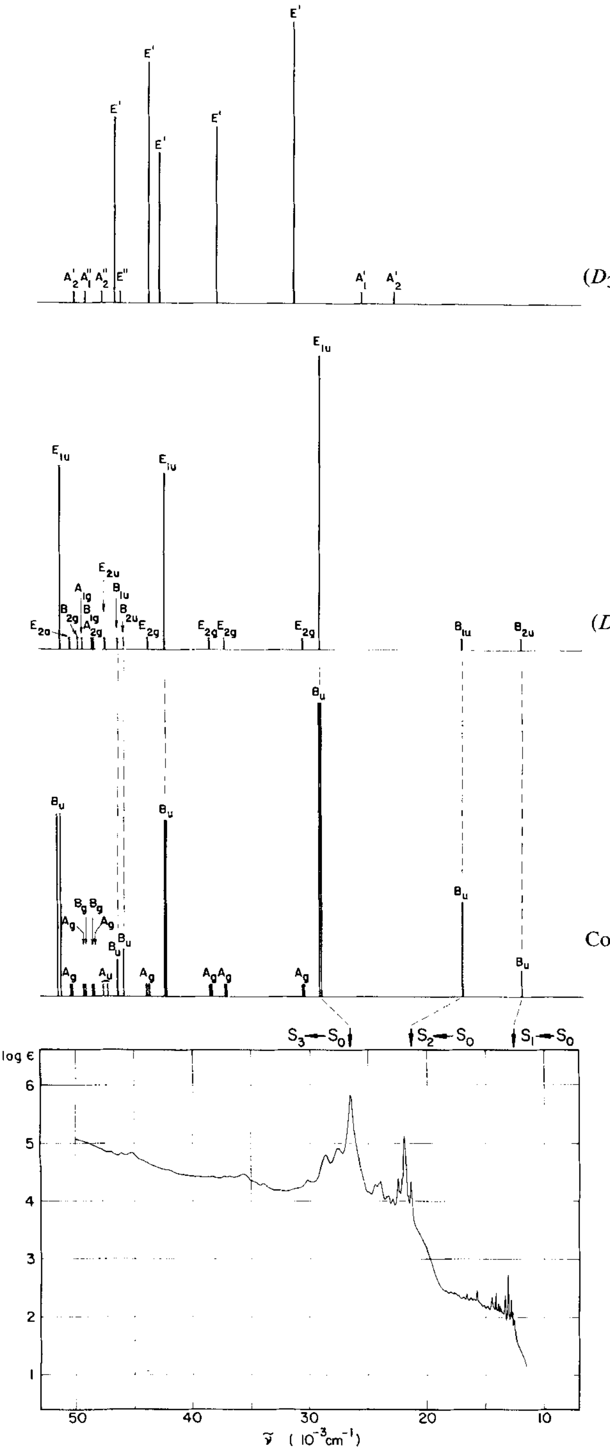

Fig. 5. *Comparison of the experimental spectrum with the CNDO/CI-calculated transitions considering the geometries indicated* (the doubly excited configurations are not considered)

using the CNDO/S-CI-method [28] [29], taking into consideration 50 singly excited configurations. With the geometry reproduced in *Figure 2* (X-ray structure with symmetry C_{2h}) we have further considered 45 doubly excited configurations. The transition moments were computed as dipole vectors with all the simplifications following from the ZDO-assumption.

The results of all these calculations are compared in *Figures 5* and *6* with the experimental spectrum. As it can be seen, only the structures with delocalized π-bonds (D_{6h}, C_{2h}) lead to theoretical transitions which are compatible with the experimental spectrum; this was already pointed out by *Blattmann et al.* [2]. However, the positions of the three characteristic transitions $S_1 \leftarrow S_0$, $S_2 \leftarrow S_0$ and $S_3 \leftarrow S_0$ are not appropriately reproduced; the ratio of the energy gaps ($S_2 - S_1$) to ($S_3 - S_2$) is 0.41 while a value of 2.0 is found experimentally. Only by introducing doubly excited configurations in the CI-calculations (and not by going to symmetry D_{3h}) is this ratio noticeably improved (0.90) (see *Fig. 6*). It is obvious that the doubly excited configurations are of importance for the relative positions of the states *(Fig. 7)*. The fact that S_2 is depressed by about only one third of the amount by which S_1 and S_3 are depressed leads to a ratio of the relative gaps between the three states $(S_2 - S_1)/(S_3 - S_2)$ which is in better agreement with the experiment.

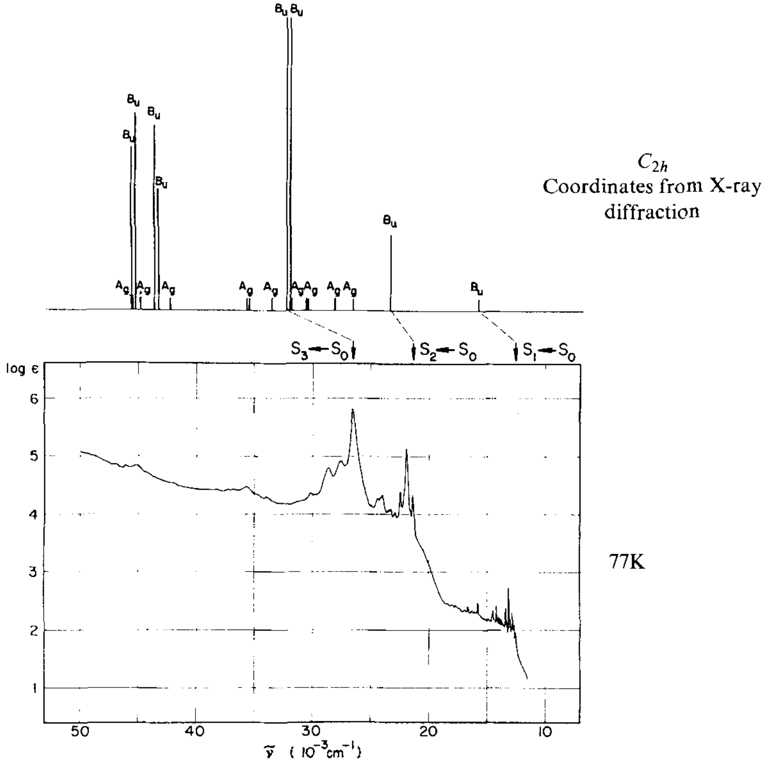

Fig. 6. *Comparison of the experimental spectrum with the CNDO/CI-calculated transitions considering the X-ray geometry and including the doubly excited configurations*

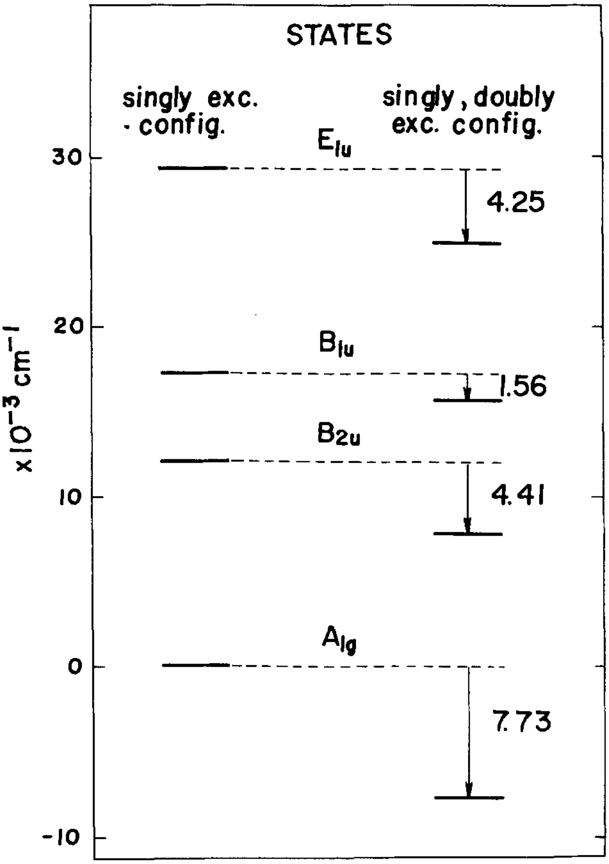

Fig. 7. *Influence of the doubly excited configurations on the energies of the* S_1-, S_2- *and* S_3-*states of [18]-annulene with* D_{6h}-*symmetry*

Furthermore when considering the doubly excited configurations, six forbidden states of symmetry A_g appear around state S_3; transitions ending to these states could well be responsible for some of the fine structure observed in the experimental main band. Because we have used the parametrization of *Ellis et al.* [28] developed for calculations in which the doubly excited configurations are not taken into consideration, our theoretical spectrum appears at too short wavelengths. As we are interested in the relative position of the states and not so much in their absolute energy, we did not reparametrize the method.

Conclusions. - Recently, we have demonstrated that CNDO/S-CI-methods allow to calculate quite correctly the positions of the electronic transitions observed with the dianion of [16]annulene [30]. There is no reason to have doubts about the ($\pi \rightarrow \pi^*$)-nature of the transitions observed with [18]annulene at ~450 nm (B_{1u}) and ~790 nm (B_{2u}); these transitions are also found at 560 and 600 nm with the iso-electronic [16]annulene dianion as transitions ending to a vibronically split E_u

state (the [16]annulene dianion has D_{4h}-symmetry). Calculations do not indicate the existence of $(\pi \leftrightarrow \sigma)$-transitions in the spectral regions investigated with the two isoelectronic systems. We have great confidence in these CNDO/S-CI-results because the method also excellently reproduces the experimental spectrum of neutral [16]annulene, a non planar molecule with localized π-bonds for which the X-ray analysis indicates a S_4-symmetry. Our conviction that for such large annulenes the failure of the simple SCF-methods could be a general phenomenon is confirmed by the fact that the SCF-STO-3 G-geometry optimization [11] leads to a [18]annulene structure with π-bond fixation which we consider to be inadequate. Further arguments in favor of a π-bond delocalization in [18]annulene result from low-temperature ^{1}H-, ^{13}C- and ^{19}F-NMR. studies [23] [24] and from fluorescence spectroscopy studies [22] on [18]annulene and on monofluoro-[18]annulene.

REFERENCES

[1] *F.A. Van-Catledge & N.L. Allinger,* J. Am. Chem. Soc. *91,* 2582 (1969).
[2] *H.-R. Blattmann, E. Heilbronner & G. Wagnière,* J. Am. Chem. Soc. *90,* 4786 (1968).
[3] *N.L. Allinger & J.T. Sprague,* J. Am. Chem. Soc. *95,* 3893 (1973). See also: *N.L. Allinger,* "Advances in Physical Organic Chemistry", Vol. 13, p.57, 1976.
[4] *M.J.S. Dewar, R.C. Haddon & P.J. Student,* Chem. Commun. *1974,* 569.
[5] *J.F.M. Oth, J.-C. Bünzli & Y. de Julien de Zélicourt,* Helv. Chim. Acta *57,* 2276 (1974).
[6] *J. Kao & N.L. Allinger,* J. Am. Chem. Soc. *99,* 975 (1977).
[7] *I. Gutman, M. Milun & N. Trinajstić,* J. Am. Chem. Soc. *99,* 1692 (1977).
[8] *J.-M. Gilles, J.F.M. Oth, F. Sondheimer & E.P. Woo,* J. Chem. Soc. (B) *1971,* 2177.
[9] *R.C. Haddon,* J. Am. Chem. Soc. *101,* 1722 (1979).
[10] *R.C. Haddon,* Chem. Phys. Lett. *70,* 210 (1980).
[11] *M. Dupuis, J. Rys & H. King,* QCPE 11, 338 (1977).
[12] *H. Vogler,* J. Mol. Struct. *51,* 289 (1979).
[13] *H. Baumann,* J. Am. Chem. Soc. *100,* 7196 (1978).
[14] *E. Hückel,* Z. Physik, *70,* 204 (1931).
[15] *Y. Ooshika,* J. Phys. Soc. Jpn. *12,* 1238, 1246 (1957).
[16] *F. Sondheimer & R. Wolovsky,* Tetrahedron Lett. *1959,* 3.
[17] *H.C. Longuet-Higgins, F.R.S. & L. Salem,* Proc. Roy. Soc. A*257,* 445 (1960).
[18] *M. Gouterman & G. Wagnière,* J. Chem. Phys. *36,* 1188 (1962).
[19] *J. Bregman, F.L. Hirshfeld, D. Rabinovich & G.M.J. Schmidt,* Acta Crystallogr. *19,* 227, 235 (1965).
[20] *C. Weiss jr. & M. Gouterman,* J. Chem. Phys. *43,* 1838 (1965).
[21] *R.C. Haddon,* Tetrahedron *28,* 3613, 3635 (1972).
[22] *U.P. Wild, H.J. Griesser, Vo Dinh Tuan & J.F.M. Oth,* Chem. Phys. Lett. *41,* 450 (1976).
[23] *J.F.M. Oth,* unpublished results
[24] *J.F.M. Oth & Y. de Julien de Zélicourt,* unpublished results, see: *Y. de Julien de Zélicourt,* «Contribution à l'Etude de la Dynamique de quelques Annulènes», Thesis ETH Zürich Nr. 5679, Juris Druck + Verlag, Zürich 1976.
[25] *W. Thiel,* J. Am. Chem. Soc. *103,* 1420 (1981).
[26] *H. Baumann, J.-C. Bünzli & J.F.M. Oth,* Helv. Chem. Acta *65,* 582 (1982).
[27] *A. Komornicki & J.W. McIver jr.,* QCPE *11,* 217 (1972).
[28] *R.L. Ellis, G. Kühnlenz & H.H. Jaffé,* Theoret. Chim. Acta *26,* 131 (1972).
[29] *H. Baumann* QCPE *11,* 333 (1977).
[30] *H. Baumann & J.F.M. Oth,* Helv. Chim. Acta *63,* 618 (1980).