65. Tris(methylidene)-cyclopropane ("[3]Radialene").
Part 2. Electronic States of the Molecular Cation
and Revised UV.-Absorption Spectrum of the Parent Neutral[1])

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Summary

The photoelectron spectrum of *tris*(methylidene)-cyclopropane **1** ("[3]radialene") is reported and the electronic states of **1**$^+$ assigned. *Jahn-Teller* activity in the degenerate states of **1**$^+$ is discussed. Differences in the *Franck-Condon* profile of the first PE band and the *Rydberg* series in the Vacuum-UV./UV. absorption spectrum indicate for the *Rydberg* series (n = 3) a $^1A_2''$-species, which supports earlier tentative proposals. The high intensity absorption in the 5.5 eV-6 eV energy range of the latter spectrum recorded earlier are definitely due to impurities. The vibrational fine structure of a weak band system around 5.5 eV in our spectrum suggests for this transition $S_0 \rightarrow S_2 (^1A_1')$, which is dipole forbidden but borrows intensity from $S_1 (^1E')$ trough vibronic coupling *via* an e'-mode. From vapor pressure measurements ε (λ_{max} = 289 nm) = 9390 ± 1170 for gaseous **1** was found.

Photoelectron Spectrum of Tris(methylidene)-cyclopropane ("[3]Radialene") (1). – *Figure 1* displays the HeIα-PE spectrum of **1**. Indicated are the different ionization energies together with their assignments which have been extensively discussed in [2] for the hexamethyl derivative **2**.

Since the PE spectra of **1** and **2** prove to be qualitatively similar for the relevant bands, the underlying arguments shall not be repeated here. Instead, the reader is requested to consult [2].

$^2E''(\pi)$-*state.* The MINDO/3 calculations discussed in [2] have shown that the ground state of **1**$^+$ of symmetry $^2E''$ suffers from a moderate *JT*-distortion leading to two species $^2A_2$ and $^2B_1$ of comparable energy, separated by very flat saddles.

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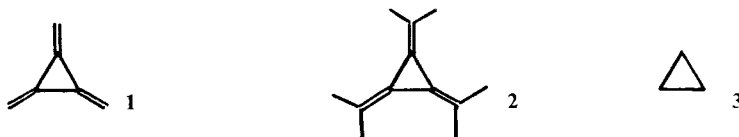
[1])   Part 1: [1].
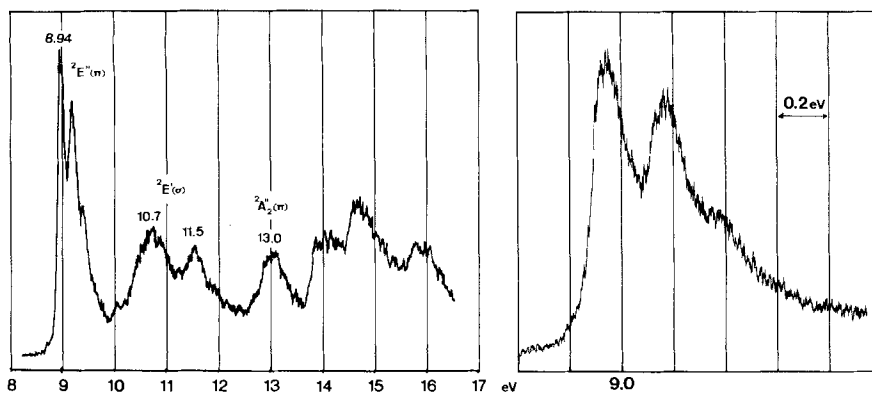[2])   Author to whom correspondence should be addressed.

Fig. 1. *Photoelectron spectrum of* **1** (First band expanded to right)

Indeed, the general appearance of the first PE band of **1** (or **2**) gives no indication of a large *JT*-effect operating in the $^2E''$-ion. We find $I_1^v = 8.94$ eV, in excellent agreement with the value 9.00 ± 0.1 eV deduced by *Rice et al.* from the *Rydberg* series observed in the UV spectrum of **1** [3]. The spacings between the first three members of the vibrational progression are 1810 cm^{-1} and 1610 cm^{-1}, respectively (expanded scale), hence, not equal. This feature was also (though less clearly) exhibited by **2** and was rationalized by us assuming the e'-(C=C)-stretching mode v_{13} [4] to be responsible for this band structure. The band shape could nicely be simulated using $v_{13} \cong 1300$ cm^{-1} for $2^+(^2E'')$. We have repeated the calculations for $1^+(^2E'')$; the results show clearly that $v_{13} \cong 1450$ cm^{-1} will lead to a satisfactory agreement with experiment. As expected this frequency is reduced with respect to $v_{13} \cong 1620$ cm^{-1} for **1** [4] as the process $1(^1A_1') \rightarrow 1^+(^2E'')$ involves removal of a π-electron, thus weakening the double bonds. Note also that the first spacing of 1810 cm^{-1} found for $1^+(^2E'')$ is larger than any of the frequencies involving C-C-motions for neutral **1**. Hence, the above spacing cannot be directly related to a normal frequency of 1^+ but must arise through vibronic coupling.

In [2] we have already pointed out the discrepancy between our choice v_{13} for the PE spectrum of **2** and the choice $v_2 \cong 1670$ cm^{-1} (symmetrical a_1'-(C=C)-stretching mode) made in [3] for the fine structure of the *Rydberg* transitions observed for **1**. We are now able to comment on this on much safer grounds as the present paper deals also with **1**. Comparison of the vibrational fine structures, in particular the spacing between the first two members of the progression (1810 cm^{-1} in the PE spectrum, 1644 cm^{-1} in the *Rydberg* series (n = 3) [3]) clearly shows them to originate from different modes. Hence, the hypothesis put forward by us in [2] seems to be verified: the *Rydberg* transitions of **1** terminate in a $^1A_2''$-state with the totally symmetric mode v_2 being excited, whereas direct ionization leads to a $^2E''$-state of the ion whose degeneracy is broken by the degenerate v_{13}-mode. Thus, **1** provides an example for which the *Franck-Condon* profile of photoelectron and *Rydberg* bands are not identical since two different fundamentals are excited in the two experiments.

$^2E'(\sigma)$-*state*. – The general appearance of the second PE band of **1** (clearly developed double-humped structure) indicates that the $^2E'$-state of **1** is strongly JT-distorted to two states of $^2A_1$ and $^2B_2$-symmetry, in analogy to the analysis given in [2] for **2** which was supported by MINDO/3 calculations of the JT-stabilization energies for this ionic state. An estimate of $I_2^v(1)$ can be obtained using the semiclassical equations of *Schwarz* [5].

$$I^{\max,1} = I^v - \sqrt{n \cdot v}$$
$$I^{\max,2} = I^v + \sqrt[3]{20n \cdot v}$$

$$\tag{1}$$

$I^{\max,1}$, $I^{\max,2}$ position of first and second maximum in the double humped structure.

v frequency of the degenerate e′-vibration breaking the degeneracy (in eV).

n   number of v quanta equal to JT-stabilization.

For **2** the $^2E'$ band shape could well be simulated with $\tilde{v}$ around 1000 cm^{-1}. This wave number is about the same as that for v_{15} ($\cong 1108$ cm^{-1}), the e′-ring stretching mode of **1** which is able to break the degeneracy of the $^2E'(\sigma)$-state of **1**$^+$. Taking $v_{15} \cong 1000$ cm^{-1} for the present **1**$^+$ and $I^{\max,2}-I^{\max,1} = 0.81$ eV *(Fig. 1)* affords with (1) n = 5, a value also proposed by *Schwarz* for the $^2E'(\sigma)$-state of cyclopropane cation **3**$^+$. Hence, from (1) $I_2^v(1) \sim 11$ eV is estimated, which is in good agreement with the value predicted from SPINDO calculations [2]. For $I_2^a(1)$ a value of 10.4 eV follows.
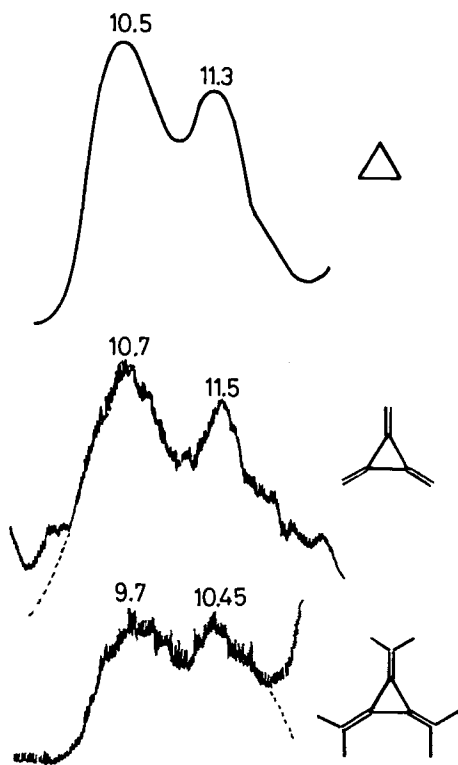

Fig. 2. JT *splittings in the PE bands corresponding to* $^1A_1' \rightarrow {}^2E'(\sigma)$ *of* **1**, **2** *and* **3** (values in eV)
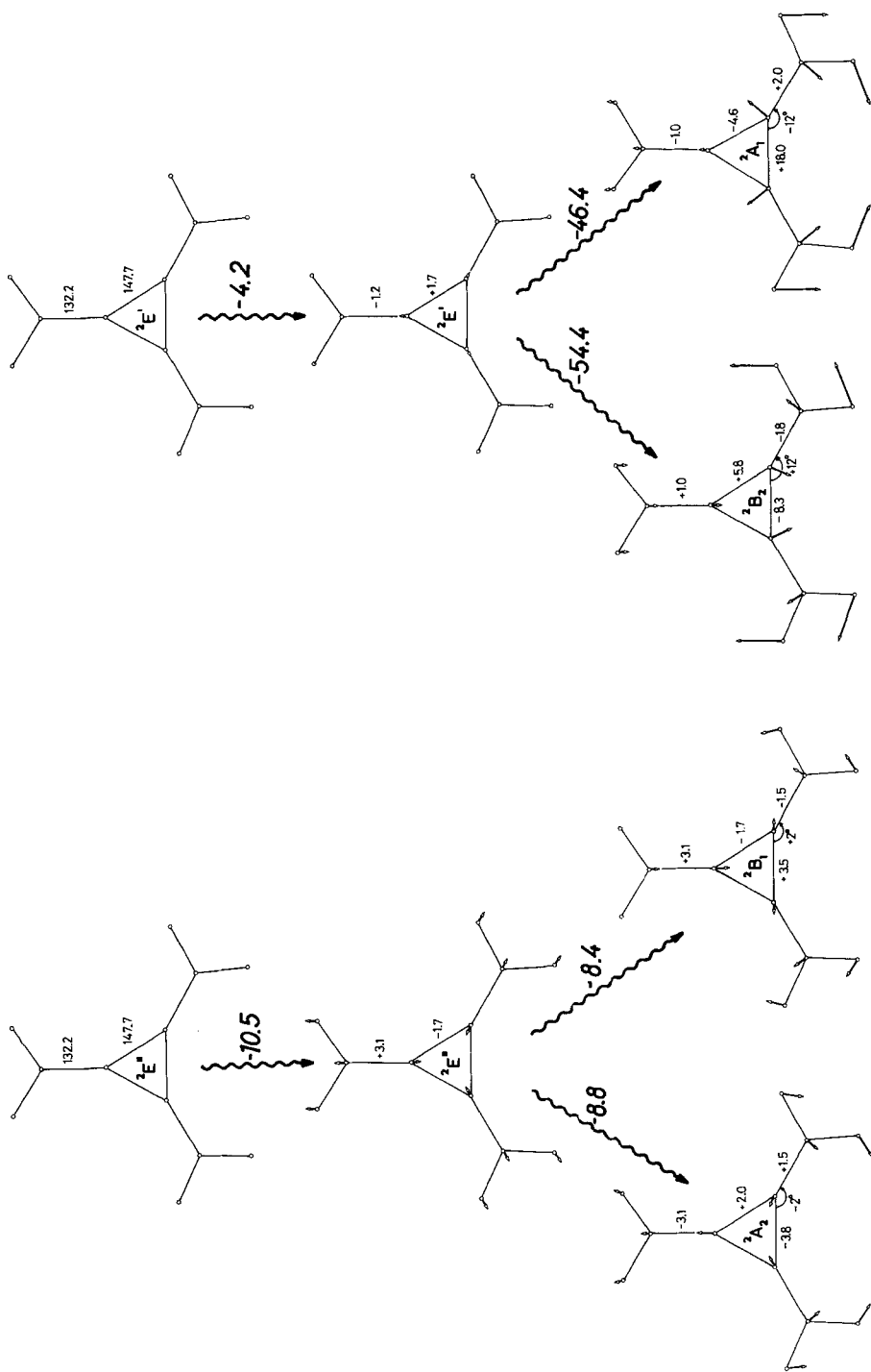
Fig. 3. *Structural relaxations of vertically produced* **1**+, $^2E''(\pi)$-*state* (left) *and* $^2E'(\sigma)$-*state* (right) *from MINDO/3-calculations*

Upper part: totally symmetric relaxation. Lower part: *JT* distortions. Energy changes in kJ mol^{-1}, changes in bondlengths in pm.

Schwarz has predicted that increasing *JT*-coupling should lead to a further splitting of the band shape due to additional resonances in the upper *JT* well. We are tempted to assign the shoulder at 12 eV to such a second transition. Indeed, the similarity between the present experimental band shape and the one calculated for a somewhat larger *JT* effect in [5] is striking, in particular with respect to the two resonances in the upper *JT* well. Note also the nice similarity in *JT* splittings in the $^2E'(\sigma)$-band shapes for **1, 2** and **3**, shown in *Figure 2*.

The *JT* effects occurring in the two degenerate states of **1**$^+$ just discussed are represented in *Figure 3* on the basis of MINDO/3 results for the nuclear displacement vectors and the associated stabilization energies. The results show that *JT* distortion of the (vertically produced) $^2E''(\pi)$-state involves mainly C=C-motions whereas for the $^2E'(\sigma)$-state the ring bonds are strongly affected. The results thus agree with the choice of fundamentals made above, which were used to simulate the band profiles.

$^2A_2''(\pi)$-*state.* – For **2**$^+$ the position of the band corresponding to the $^2A_2''(\pi)$ state could not be given with great accuracy due to overlap with bands originating from further σ-ionizations. The present example is clear in this respect: We assign the well separated band peaking at $I_3^v = 13.0$ eV to $^1A_1' \rightarrow {}^2A_2''$. This value, however, provides a puzzle as it is significantly higher than any of the orbital energy predictions (assuming *Koopmans'* theorem to hold) from procedures which generally yield reliable results for this quantity (see below). Note that the accuracy of prediction for $\varepsilon(\pi, e'') = -I_1^v$ is on the average much greater. Only the modified HMO approach calibrated earlier with compounds closely related to **1** [10] yields a satisfactory estimate for $\varepsilon(\pi, a_2'')$.

	π-SCF[6]	π-SCF[7]	SPINDO[8]	mod. HMO[9]	mod. HMO[10]	exp.
$\varepsilon(\pi, e'')$	− 9.14	− 9.10	− 9.37	− 8.78	− 8.88	− 8.94
$\varepsilon(\pi, a_2'')$	− 12.49	− 12.49	− 12.30	− 12.47	− 13.32	− 13.0

Further support to our assignment comes from the fact that all [n]radialenes have a HMO energy for the lowest occupied MO of $a + 2.414\beta$. Hence the energies for ejection of an electron from this orbital should be rather independent from n. For [4]radialene we found recently [11] $\varepsilon(\pi, a_{2u}) = -13.1$ eV which indeed is very close to $\varepsilon(\pi, a_2'')$ for **1**.

Concerning the optical absorption spectrum of 1 in the gas phase. – *Spurious transitions in the 5.5–6 eV region. Figure 4* shows the gas phase UV. absorption spectrum of **1** measured by us, in comparison with that reported by *Rice et al.* [3]. Disagreement exists with respect to the 5.5 eV and 6.0 eV band systems which appear in the cited spectrum with appreciable intensity and were attributed to $S_2(^1A_2')$ and $S_3(^1A_1')$ of **1**[3]. Our spectrum shows definitely that these band systems are essentially due to an impurity in the sample, supporting thus the doubts already expressed [13].

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[3]) The Vacuum-UV.-region of our spectrum agrees with that reported in [3] and is therefore not drawn in *Figure 4*.
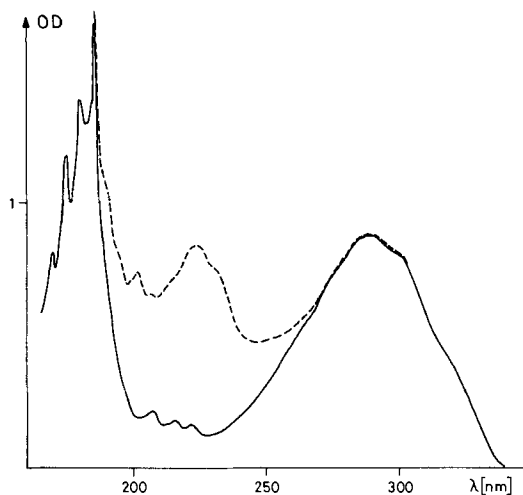
Fig. 4. *UV.-Absorption spectrum of* **1** *in the gas phase*
Solid line: present work
Dotted line: ref. [3]

Recent high quality calculations predict the $^1A_1'$- and $^1A_2'$-states at 6.5 eV and 7.76 eV, respectively [12], transitions to both of them being dipole forbidden. They may, however, borrow intensity through vibronic coupling to the E'-states. Consideration of the energetics suggests that our 5.5 eV system most likely corresponds to $S_0 \rightarrow S_2(^1A_1')$, the excited state being coupled to $^1E'$ through an e'-motion. As the dominant configuration in S_2 is $\pi_1 \rightarrow \pi_4^*$ of **1** [12] the transition is predominantly associated with changes in bond orders at the exocyclic double bonds. We note that the vibrational quanta in the 5.5 eV system correspond roughly to the e'-(C=C)-stretching motion $v_{13} \cong 1620$ cm^{-1} reported in [4] for ground state **1**. This finding further supports our assignment.

Determination of the Molar Extinction Coefficient of the Longest Wave Length Transition of Gaseous **1**. *Dorko* [14] has reported an extinction coefficient $\varepsilon = 3750$ for the longest wavelength band ($^1A_1 \rightarrow {}^1E'$) of gaseous **1** peaking at 289 nm. This value has also been subject of earlier debate as it contrasts unreasonably with $\varepsilon = 18200$ found for the analogous transition in the hexamethyl derivative **2** (in solution) [16]. In addition *Heilbronner* predicted that the longest wavelength transition is strongly allowed for the n=3 member but forbidden for all other members of the [n]radialene family, as long as D_{nh}-symmetry is retained and vibronic coupling neglected [17]. However, [4]radialene (in solution) exhibits $\varepsilon = 8000$ for this 'forbidden' transition [18].

We measured the optical density D (path length d = 10 cm) at $\lambda_{max} = 289$ nm for various pressures P, or assuming ideal behaviour, for various molar concentrations c of gaseous **1** at 293 K.

P (Pa)	3.199	6.399	9.866	13.332	18.932	24.131
$c \cdot 10^6$ (mol · l^{-1})	1.313	2.623	4.050	5.473	7.772	9.906
D	0.132	0.247	0.384	0.502	0.880	0.857

Linear regression yields the following least squares line with standard errors for slope and intercept ($\Phi = 6$):

$$D = (0.0131 \pm 0.0682) + (0.0939 \pm 0.0114)\, 10^6 \cdot c$$

A statistical test shows that, even on a security level as low as 70%, the intercept $D(c = 0) = 0.0131$ does not differ significantly from zero. Hence, for all practical purposes, the regression line passes through the origin as required by *Lambert-Beer's* law. Extrapolation to $c = 1$ mol $\cdot$ l^{-1} yields with d = 10 cm for gaseous **1**

$$\varepsilon\,(\lambda_{max} = 289 \text{ nm}) = 9390$$

with a standard error range of ± 1170. This value is significantly larger than that stated in [14], though still clearly much smaller than the one for **2** reported in [16]. We feel confident about the significance of our result as a similar determination for gaseous cycloheptatriene gave $\varepsilon_{max} = 2540$ in comparison with the value determined in heptane solution $\varepsilon_{max} = 3100$ [19].

In part 3 of this series we shall compare the PE spectrum of **1** with the optical absorption spectrum of **1**$^+$ prepared in an electron scavenging matrix by γ-irradiation. This comparison will allow us to comment on the structure of **1**$^+$ in condensed phase.

Experimental Part. – *Preparation and handling of* **1**. **1** was synthesized from tris(bromomethyl)-cyclopropane by a new modification of the procedure first described by *Dorko* [14].
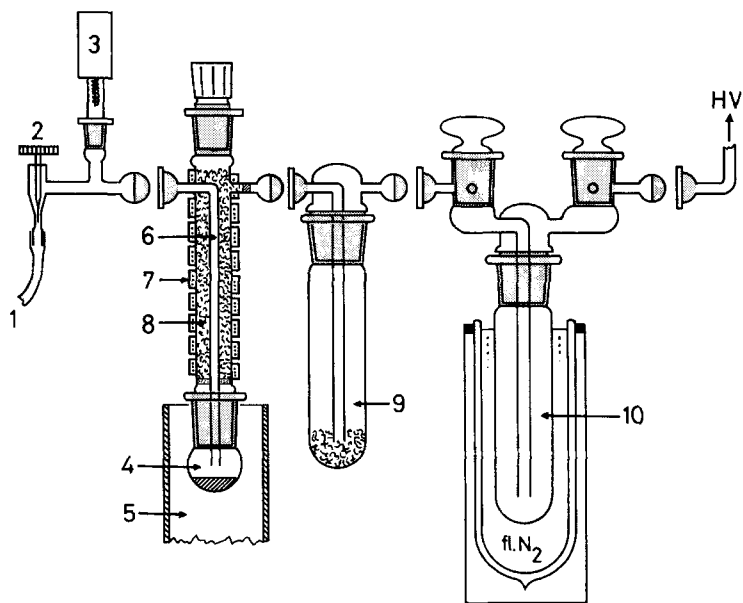
KOH was dried at 300 °C under high vacuum until the pressure in the system remained constant. In a dry-box the solid was powdered and three parts of it mixed with one part of CaO. The latter material served to trap water produced during the dehydrobromination reaction, thus preventing KOH from turning clammy. Glasswool was sprinkled with the powder mixture and inserted into the heatable tube (8) (heating band (7), 150 °C) as well as into the cooling trap (9). The bromo-precursor was inserted into vessel (4) which was heated to 70°–80 °C by oven (5). A stream of oxygenfree N_2 was flowed from (1) through (6), the flow being regulated by value (2) to yield a pressure of 1 Torr as measured at the *Pirani* gauge (3). This swept the precursor through (8). Trap (9), held at − 15 °C, kept back less volatile substances including H_2O. Raw **1** was collected at (10) kept at 77 K. Purification of **1** was accomplished as described in part 1 of this series [1]. All manipulations with pure **1** were carried out under high vacuum in allglass apparata. Solutions can be handled at low temperature under a blanket of N_2. For further details consult [20].

Measurements. The Heια-photoelectron spectrum was measured on *Perkin Elmer* PE 16 based on the *Turner* design. The Vacuum-UV./UV.-spectrum was recorded with a *McPherson* 225 1m-monochromator with normal incidence. Vapor pressures were measured at 20 °C with a *BURDON* capsule of *Texas Instruments.* The precision is ± 10^{-3} Torr in the pressure range covered by us. We thank Dr. *G. Bieri* and Mr. *R. Bär* for help during these measurements.

REFERENCES

[1] *T. Bally, H. Baumgärtel, V. Büchler, E. Haselbach, W. Lohr, J. P. Maier & J. Vogt*, Helv. *61*, 741 (1978).

[2] *T. Bally & E. Haselbach*, Helv. *58*, 321 (1975).

[3] *E.A. Dorko, A. Scheps & S.A. Rice*, J. phys. Chemistry *78*, 568 (1974).

[4] *K.H. Rhee & F.A. Miller*, Spectrochim. Acta *27A*, 1 (1971).

[5] *D. Habitz & W.H.E. Schwarz*, Theor. chim. Acta *28*, 267 (1973); *W.H.E. Schwarz*, J. Electron Spectrosc. *6*, 377 (1975).

[6] *M.J.S. Dewar & C. de Llano*, J. Amer. chem. Soc. *91*, 789 (1969).

[7] *M.J.S. Dewar & A. Harget*, Proc. Roy. Soc. *A 315*, 443, 457 (1970).

[8] *L. Åsbrink, C. Fridh & E. Lindholm*, J. Amer. chem. Soc. *91*, 5501 (1972).

[9] *F. Brogli & E. Heilbronner*, Theoret. chim. Acta *26*, 389 (1976).

[10] *E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung & A. de Meijere*, Helv. *57*, 783 (1971).

[11] *T. Bally & E. Haselbach*, Helv. *61*, 741 (1978).

[12] *P. Pancard, B. Huron, L. Praud, J. P. Malrieu & G. Berthier*, J. mol. Spectrosc. *60*, 259 (1976).

[13] *P.A. Waitkus, E.B. Sanders, L.I. Petersen & G. W. Griffin*, J. Amer. chem. Soc. *89*, 6318 (1967).

[14] *E.A. Dorko*, J. Amer. chem. Soc. *87*, 5518 (1965).

[15] *J.L. Laseter, A. Manmade, P.A. Waitkus & G. W. Griffin*, Spectrochim. Acta *27A*, 741 (1971).

[16] *G. Köbrich & H. Heinemann*, Angew. Chemie Int. Ed. *4*, 594 (1965).

[17] *E. Heilbronner*, Theoret. chim. Acta *4*, 64 (1966).

[18] *G. W. Griffin & L.I. Peterson*, J. Amer. chem. Soc. *84*, 3398 (1962).

[19] *K. Hirayama*, 'Handbook of UV/VIS-Absorption Spectra of Organic Compounds', Plenum Press, New York 1968.

[20] *T. Bally*, Ph.D. Dissertation, University of Basel 1977.