40. The Photoelectron Spectrum of Triisopropylidenecyclopropane ('Hexamethyl-3-radialene')[1])

In memoriam *Gert Köbrich*

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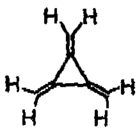
Summary. The photoelectron spectrum of the title compound **2** is discussed and compared with the results of MO-calculations for the parent unsubstituted hydrocarbon **1**. The ground-state of 2^+ is $^2E''$ which is *Jahn-Teller* (*JT*) active. Assuming the e' C=C-stretch to be responsible for breaking its degeneracy, satisfactory agreement between experimental and theoretical band shape is obtained. The latter is calculated from the diabatic two-state approximation using MINDO/3-SCF results for the *JT*-stabilization energies. Comparison with *Rydberg* studies on **1**, performed by other authors, yields further evidence for the A_2'' – (not E' –) symmetry of the *Rydberg* states. The next two observed higher lying states of 2^+ are $^2E'$ and $^2A_2'$, the former also being *JT*-active. Theoretical calculations of the corresponding band shape point toward the e'-ring stretching mode causing instability, an outcome reminiscent of the $^2E'$-groundstate of cyclopropane-ion. The energetic difference between the latter state and the $^2E'$-state of 2^+ is discussed using a simple MO-model with methylidene and ethylidene carbene as interacting units. The results suggest that the unsaturated carbene is strongly stabilized by hyperconjugation. The chemistry of the two carbenes is compared on this basis.

Introduction. – Trimethylidenecyclopropane **1** [2–4] is the simplest member of the family of 'n-radialenes' (n = 3,4,5...). It is isomeric with benzene but possesses three essential single and double bonds, that latter being completely cross-conjugated. This intriguing feature, also present in its hexamethyl-derivative **2** [5], has initiated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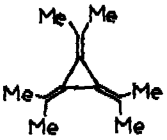
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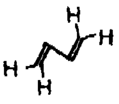
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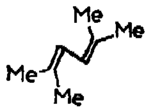
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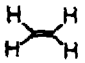
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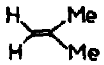
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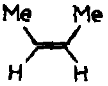
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10

$|C{=}CH_2$

11

$|CH_2$

12

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[1]) Part 80 of 'Applications of Photoelectron Spectroscopy'. Part 79: [1].

several studies of structural [6] [7], spectroscopic [8–12] and theoretical [13–16] type. In order to get some insight into the orbital electronic structure of this system we have studied the photoelectron (PE) spectrum of **2** which is easier to handle than the extremely unstable parent **1**.

Results and Discussion. – In Fig. 1 the He-I PE-spectrum of **2** is shown. The proposed correspondence between the observed ionisation potentials (IP) and transitions of **2** ($^1A_1'$-ground state) to various electronic states of $\mathbf{2}^+$ is based on the following arguments:

I. $^2E''$-state of $\mathbf{2}^+$. Simple HMO- as well as the more sophisticated calculations presented in Tab. 1 yield for the highest occupied orbital (HOMO) of **1** a degenerate π-orbital of symmetry species e″, being depicted in Fig. 2. The mean of the e″-orbital energies $\bar{\varepsilon}(e'') = -9.2$ eV, calculated with the semiempirical procedures, is in excellent agreement with $IP_1 = 9.0 \pm 0.1$ eV, found for **1** from *Rydberg* studies [11]. Further-

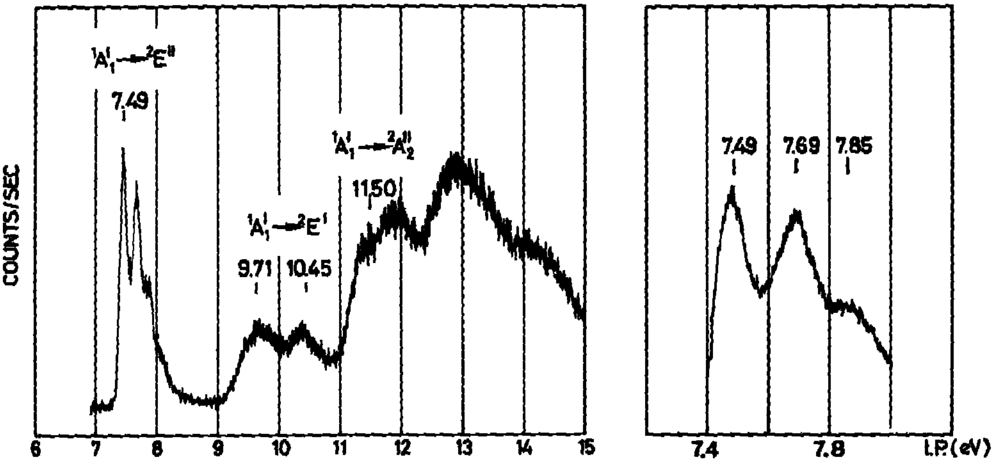

Fig. 1 *He-I PE-spectrum of* **2**. First band expanded at right

Table 1. *Calculated orbital energies* (eV) *for* **1**

Symmetry species	SCF-π [a]	SCF-π [b]	SPINDO [c]	*ab initio* [d]
$e''(\pi)$	9.14	9.10	9.37	5.48
e′('outer *Walsh*')			10.88	7.44
$a_2''(\pi)$	12.49	12.49	12.30	9.76
$a_2'(\sigma C{-}H)$			13.85	12.64
$e'(\sigma)$			14.62	12.83
a_1'('inner *Walsh*')			15.43	14.36

[a] Resonance integrals *via* thermocycle method [17].

[b] Resonance integrals *via* overlap method [18].

[c] SPINDO-procedure *cf.* [19].

[d] Taken from [14].

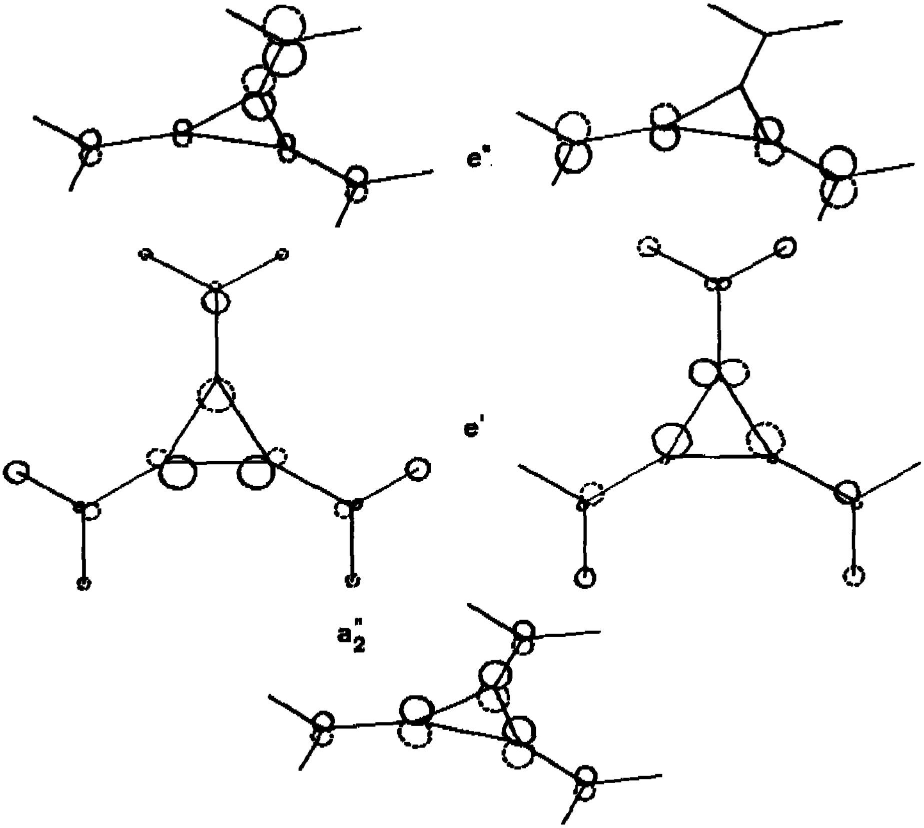

Fig. 2. *Pictorial representation of the highest three occupied orbitals of* **1**. MINDO/3-SCF wavefunctions, MOPLOT-program [54]

more this value agrees closely with $IP_1 = 9.03$ eV, found for *t*-butadiene (**3**) [20] as would be expected in view of the nodal characteristics of the e''-HOMO of **1**. Indeed in a HMO-calculation the HOMO-energies of **1** and **3** are identical.

For **2**, the above might suggest that $IP_1 = 7.49$ eV (Fig. 1) bears close resemblance to IP_1 (= 7.83 eV [20]) found for *t*-1,1′,4,4′-tetramethylbutadiene (**4**)- an expectation obviously not satisfied. Though it has been noted that steric congestion by methyl groups leads to lower IP's [21] this argument does not apply to **2** after inspection of its structural parameters [7]2). It seems as if the amplitude of the HOMO-wave-

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2) The nearest distance between the methyl group C-atoms at different isopropylidene units in **2** amounts to 3.92 Å, which is significantly larger than the corresponding distance within one isopropylidene group (2.56 Å [7]). Hence steric contact between the methyl groups will be larger for the latter case, which therefore determines their ground-state minimum energy conformation. In analogy to isopropylidene [55] or even more significantly to 1,8-dimethylnaphthalene [56] this conformation exhibits local C_{2v}-symmetry with the distance between the in-plane H-atoms being maximal. As a result the nearest distance between basis functions of π-symmetry centered at methyl groups of different isopropylidene units is 3.92 Å; *i.e.* there are no pseudo-π-basis functions from the out-of-plane H-atoms in close contact.
The 'abnormally' low value for IP_1 (**2**) can therefore not be rationalized on the basis of a destabilizing 1,6-'throughspace'-interaction.
We thank the referee for having suggested this possibility.

function at the external C-atoms is slightly larger in **1** than in **3**, giving rise to a larger first-order destabilization of this orbital upon alkyl substitution in **1** with respect to **3**.

Within the framework of HMO-perturbation theory the partial atom-bond polarizability $\pi^{\mathrm{HOMO}}_{1,23}$ for **3** is positive. Thus the HOMO-density at the external C-atoms of **1** will be larger than in **3** if the resonance integral across the essential single bond in **1** is decreased with respect to **3**. Indeed this is suggested by the relative lengths of those bonds, *i.e.* 1.467 Å in **1** [22] and 1.451 Å in **3** [7]. However since the observation

$$\mathrm{IP}_1\,(\mathbf{1}) \approx \mathrm{IP}_1\,(\mathbf{3}) \approx 9\ \mathrm{eV} \tag{1}$$

has to be satisfied the above requires the C-*Coulomb* integrals in **3** to be smaller than in **1**. Transforming these ideas into LCBO-language and denoting the C=C-basis energies (A) and the coupling parameters (B) across the essential single bonds in **1** and **3** by A_1, B_1 and A_3, B_3 resp., we obtain:

$$A_1 - A_3 = B_1 - B_3 < 0. \tag{2}$$

To obtain A_1, $A_5 = -10.51$ eV [23] for ethylene (**5**) is corrected by the additional influence of two adjacent double bonds. Taking for this twice the difference found between A_5 and A_3 ($\Delta A = 0.26$ eV [20]) yields:

$$A_1 = A_5 + 2 \times 0.26\ \mathrm{eV} = -9.99\ \mathrm{eV}. \tag{3}$$

The change in hybridisation of the internal C-atoms between the two similarly 'alkylated' systems isobutene **6** and methylidenecyclopropane **7** apparently produces a shift from $A_6 = -9.23$ eV [20] to $A_7 = -9.6$ eV [23].

It is interesting to note that the π-IP of a double bond associated with 'abnormal' valence angles – regardless of the 'direction of the anomaly' – is always larger than that of the formally hydrogenated unstrained analogue, *i.e.*

$$\mathbf{8}\ (\mathrm{IP}_1 = 9.43\ \mathrm{eV}\ [25],\ \alpha = 97°\ [24]) \xrightarrow{\mathrm{H}_2} \mathbf{9}\ (\mathrm{IP}_1 = 9.12\ \mathrm{eV}\ [20],\ \alpha = 125°\ [26])$$

$$\mathbf{7}\ (\mathrm{IP}_1 = 9.60\ \mathrm{eV}\ [23],\ \alpha = 148°\ [27]) \xrightarrow{\mathrm{H}_2} \mathbf{6}\ (\mathrm{IP}_1 = 9.23\ \mathrm{eV}\ [23],\ \alpha = 124°\ [28])$$

α: C–C=C angle

This is not found for similar systems without I-strain such as cyclohexene or methylidenecyclohexane (*cf.* [29]). As *Walsh* has pointed out [30] a $C_{sp^m} - C_{sp^n}$ bond is polarized toward the atom carrying more s-character in the hybrid. In extension to this one expects that polarization not only increases with increasing difference $d = m - n$ but also, for a given d, with decreasing value of n, *i.e.*, the polarity of a $C_{sp^2} - C_{sp}$ bond being larger than that of a $C_{sp^3} - C_{sp^2}$ bond. While the latter bond type is found in non-strained unsaturated hydrocarbons, maximum overlap considerations [31] yield $m = 3.52$, $n = 2.54$ for **8** and $m = 4.26$, $n = 3.13$ for **7**, suggesting thus decreased polarity of those bonds. Consequently the destabilizing inductive effect of the saturated ring-centers on the π-orbital energy is decreased, resulting in an increased π-IP.

Taking into account the above feature also present in **1** yields:

$$A_1 = -10.36\ \mathrm{eV}. \tag{4}$$

Finally in view of (1), $B_1 = -1.36$ eV is obtained. Comparing these values with $A_3 = -10.25$ eV, $B_3 = -1.24$ eV [20] indicates that (2) is satisfied, though not very significantly. Therefore the explanation for the exalted alkyl effect on the HOMO of **1** with respect to **3** proposed above ought to be taken *cum grano salis*. At any rate ours as well as other [32] theoretical calculations show a pronounced tendency for the π-electrons to migrate towards the external C-atoms in strained *exo*-methylidene compounds.

II. *Jahn-Teller* effect in the $^2E''$-state. – Further support to our assignment of a $^2E''$-ground state for $\mathbf{2}^+$ is obtained by considering the vibrational fine structure of the 7.5 eV band, the spacing between the first two members of the progression being 0.2 eV ($\tilde{\nu} = 1610$ cm^{-1}). In **1**, the dominant vibrational structure of the *Rydberg* series of symmetry A_2'' with $\tilde{\nu} = 1670$ cm^{-1} for the n = 3 members has been attributed to excitation of the totally symmetric a_1' (C=C-stretching vibration) ($\tilde{\nu}_2$ in [11]). This value, compared with $\tilde{\nu}_2 = 1800$ cm^{-1} for the ground state of **1** [12] suggests – in unison with the character of the e″-HOMO (Fig. 2) – a weakening of these bonds in the *Rydberg* states. It is reasonable to predict the same to happen in the final ionic $^2E''$-state of $\mathbf{1}^+$.

The additional alkyl substituents present in **2** will increase the a_1' (C=C-stretching) frequency $\tilde{\nu}_2$ by some 20 to 50 cm^{-1} [32] with respect to **1**, this being presumably true also for $\tilde{\nu}_2$ in $\mathbf{2}^+$ compared with $\mathbf{1}^+$. Since however $\tilde{\nu} = 1610$ cm^{-1} observed in the PE-spectrum of $\mathbf{2}^+$ is smaller than $\tilde{\nu}_2 = 1670$ cm^{-1} for the *Rydberg* states of **1**, one is encouraged to seek some other species with lower frequency than $\tilde{\nu}_2$ also involving C=C-weakening. A likely candidate is the degenerate e′ (C=C-stretching) frequency $\tilde{\nu}_{13} = 1620$ cm^{-1} in **1** [12], presumably somewhat higher in **2** and reduced to $\tilde{\nu}_{13} = 1610$ cm^{-1} in $\mathbf{2}^+$.

Clearly the above arguments suffer from the uncertainties in the determination of vibrational frequencies. Hence they are not sufficient to exclude the possibility that we also observe the symmetrical a_1' (C=C-stretching) mode $\tilde{\nu}_2$ in the $^2E''$-state of $\mathbf{2}^+$. This matter will therefore be further elaborated below.

According to the selection rules for electronic transitions between non-degenerate states, vibrational fine structure due to excitation of a non-totally symmetrical vibration $\tilde{\nu}_K$ in the upper state appears only at energies of $E_0 + (2n + 2) \cdot \tilde{\nu}_K$, n = 0,1,2... ($E_0$ = adiabatic transition energy). Contrary to this, for transitions involving a non-degenerate and a degenerate state, members at $E_0 + n \cdot \tilde{\nu}_K$ may be discernible *if* there is weak vibronic interaction in the degenerate state, *i.e.* if this state is subject to a weak *JT*-effect [34]. For stronger vibronic interaction however, the spacing between the individual members of a progression need not be $\tilde{\nu}_K$ [34].

Inspection of the expanded 7.5 eV-band (Fig. 1) suggests that the spacings between the three discernible peaks are 0.2 eV and 0.16 eV, resp., providing thus a further argument that vertically produced $\mathbf{2}^+$ possesses a $^2E''$-ground state which suffers a moderate *JT*-effect, induced by the e′ (C=C-stretching) mode $\tilde{\nu}_{13}$.

On the basis of this proposal we have calculated the shape of the 7.5 eV band, assuming for the active mode $\tilde{\nu}_{13} = 1610$ cm^{-1}, *e.g.* the splitting between the first two members of the progression in Fig. 1. Using the MINDO/3-semiempirical SCF-procedure [35] – which gives improved results for strained systems when compared with earlier MINDO-versions – we have calculated the geometries and the energies of three points on the lower sheet of the *JT*-potential surface:

(i) a D_{3h} – 2^+ ion of electronic state-symmetry $^2E''$ where the energy is a minimum with respect to all totally symmetrical coordinates. It corresponds to the 'centre' of the *JT*-cone;

(ii) two sets of three equivalent C_{2v} – 2^+ ions, one of symmetry $^2A_2$ (saddle point) and the other of symmetry $^2B_1$ (minimum).

The results given in Fig. 3a show indeed that the *JT*-distortion suffered by the $^2E''$-ion involves predominantly a C=C deformation associated with an energy gain (with respect to the relaxed D_{3h}-ion) of –1.67 kcal/mol (saddle point) and –1.92 kcal/mol (minimum). The smallness of these figures is of course entirely compatible with the rather 'normal' appearance of the corresponding PE-band. A weak *JT*-effect is also suggested by the MINDO/3 – vertical transition energy for $^2A_2 \rightarrow {}^2B_1$ (6.2 kcal/mol) and $^2B_1 \rightarrow {}^2A_2$ (5.6 kcal/mol), which indicates a small separation between outer and inner surface of the *JT*-cone at the saddle points and at the minima.[3]

In view of the small energy difference (0.25 kcal/mol) between minimum and saddle point we have neglected the presence of separate minima on the lower sheet, considering its potential function as pure through-like. This is justified on the basis of the pioneering work in [36] for cyclopropane **10** where it was found, that – apart from an increased complexity of the problem – the main effect of introducing weak

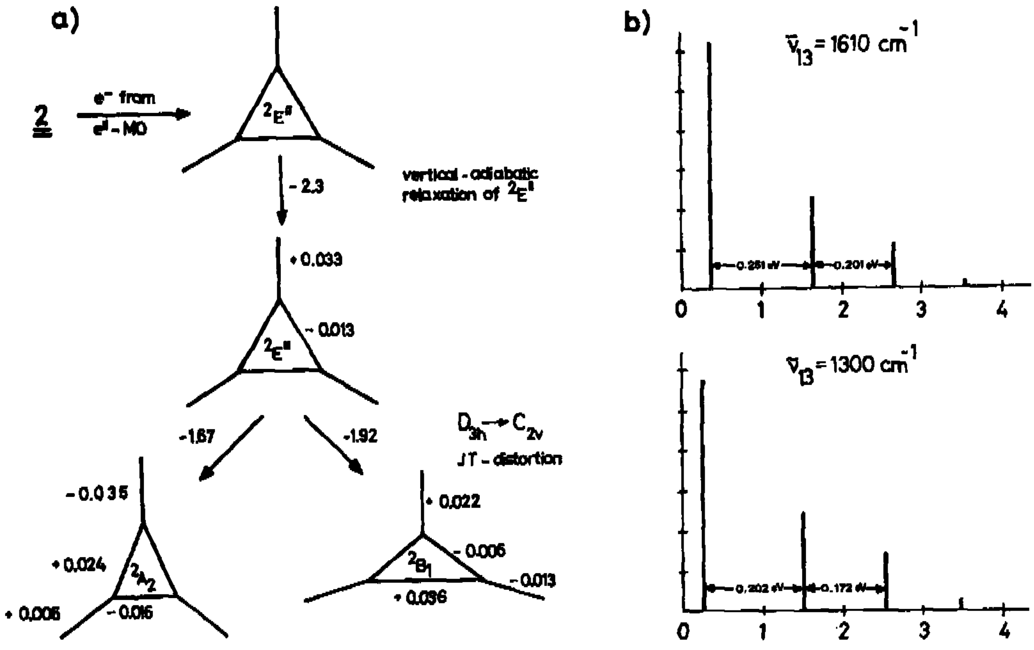

Fig. 3. a) *Calculated* JT-*effect in the* $^2E''$-*state of* 1^+. Changes in bondlengths (Å) and energies (kcal/mol) are with respect to next species above. The drawings are not in scale. b) *Calculated shape of the 7.49 eV band in the PE-spectrum of* **2**. Dependance from e'-frequency which induces *JT*-instability (see text). (The mean value of the *JT*-stabilization energies of saddle point and minimum was used.) The 0–0 transition is at the left of each diagram

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[3] The energies of the excited radical cations were calculated by forcing the radical electron into the appropriate orbital after the diagonalization step of each SCF-cycle.

second-order coupling between the vibronic levels of that magnitude required by our calculated difference of 0.25 kcal/mol, is to increase the number of allowed transitions in the spectrum, but not to alter the shape of the bands in general. Applying the diabatic two-state approximation [37]4) to first-order interactions between the vibronic levels of the $^2E''$-state yields the theoretical band shape displayed in Fig. 3b, which compares favorably with the general appearance of the experimental band.

The results predict further that the three progression-members of decreasing intensity have different energy spacings of $1.26\tilde{\nu}_{13}$ and of $1.0\tilde{\nu}_{13}$. While this sequence coincides with that found in the experimental spectrum, the absolute figures suggest that our choice $\tilde{\nu}_{13} = 1610$ cm^{-1} was too large. Additional calculations showed that $\nu_{13} = 1300$ cm^{-1} gave spacings of $1.25\tilde{\nu}_{13} = 0.2$ eV and $1.07\,\tilde{\nu}_{13} = 0.17$ eV which agree nicely with those observed. Note the large reduction of $\tilde{\nu}_{13}$ in going from **2** ($\tilde{\nu}_{13} >$ 1620 cm^{-1}, *vide supra*) to **2**$^+$, indicating a significant weakening of the C=C-bonds. For ethylene **5** the corresponding fundamental is $\tilde{\nu}_2 = 1623$ cm^{-1}, for **5**$^+$ $\tilde{\nu}_2 = 1230 \pm$ 50 cm^{-1} [23].

The agreement between theoretical and experimental intensity ratio is less satisfactory, presumably because of the rather simplifying model used. In any case the observed intensity distribution will include a contribution due to the a_1' (C=C-stretching) frequency $\tilde{\nu}_2$. This is suggested by the change in geometry associated with the calculated vertical-adiabatic energy difference of −2.3 kcal/mol for the $^2E''$-state (*cf.* Fig. 3a). Taking for **2**$^+$ $\tilde{\nu}_2 \approx 1700$ cm^{-1} (*vide supra*), in the semiclassical *Franck-Condon* approximation [38] the corresponding band would have the appreciable half-width of 0.34 eV.

The selfconsistency in the above discussion supports our basic assumption5) that the progressions in the 7.5 eV band are due to the e′(C=C-stretching) vibration which breaks the degeneracy of the $^2E''$-ground state of **2**$^+$. We note however the discrepancy between our result and the interpretation of the *Rydberg* state fine structure of **1** given in [11] as being due to the a_1' totally symmetrical C=C-stretching. As pointed out in [39] there is sufficient evidence that the *Franck-Condon* factors for photoelectron and optical spectroscopy are very similar. Hence the band profile of a PE-band should look very much like that of the members of *Rydberg* series leading up to that ionization. This is nicely confirmed in the case of cyclopropane **10** where both spectra show a 490 cm^{-1} progression of e′-species associated with the *JT*-active $^2E'$-ground state of **10**$^+$ [39].

In **10** the *Rydberg* transitions conceivably originate in the 'outer *Walsh*'-HOMO of e′-symmetry. In order then to be allowed, a *Rydberg* state of **10** can only be of E′-symmetry *i.e.* is also *JT*-active like the final $^2E'$-state of **10**$^+$. On the other hand in **1**, the allowed *Rydberg* transitions originate from the HOMO of e″-symmetry, yielding two possibilities for the symmetry of the *Rydberg* states: E′ and A_2''. The discrepancy pointed out above can be resolved if the A_2''-choice is realized in **1**. In fact this state designation was also favoured in [11] on other grounds; it is apparently supported by our considerations.

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4) Thirty-two two-dimensional harmonic oscillator functions were used as basis functions.

5) We are currently attempting to prepare the parent hydrocarbon **1** in order to be able to check the underlying arguments.

In conclusion we wish to emphasize that the cited rule about the similarity between the band shape of a PE-band and the *Rydberg*-bands converging to that IP is only applicable in a straight-forward manner to non-linear molecules if both the *Rydberg* states and the ionic state are non-degenerate, or if both are degenerate and the molecule belongs to the point groups:

$$C_n,\ D_n,\ C_{nh},\ D_{nh},\ C_{nv}\ (n = 3,4,6);\ D_{nd}\ (n = 2,3);\ S_4,\ S_6.$$

In the latter case the vibrational species producing *JT*-instability are the same for each possible degenerate electronic state within one of these point groups (for the underlying group theoretical considerations consult [34], p. 50).

III. $^2A_2''$-state of 2$^+$. – The quantity B_1 derived for **1** in section I enables us to predict that the $^2A_2''$-state of **1**$^+$ will lie 4.08 eV above its ground state. Carried over to **2**$^+$, the corresponding IP is expected at 11.57 eV. On this basis we have assigned the 11.5 eV peak in the PE of Fig. 1 to the transition $^1A_1' \rightarrow {}^2A_2''$. This assignment however should be taken as tentative in view of the procedure used for the derivation of B_1. The *ab initio* work cited in Tab. 1 predicts a $^2E'' - {}^2A_2''$-splitting of 4.28 eV. With this the above transition may well be hidden under the 12 eV band system. On the other hand, from the semiempirical π-calculations for **1** the predicted splitting is 3.4 eV, supporting again our 11.5 eV assignment. From the SPINDO-value for this splitting (2.93 eV) one might assign the band at 10.45 eV to $^1A_1' \rightarrow {}^2A_2''$. This, however, would conflict with the interpretation for the $^2E'$-state of **2**$^+$, given below.

IV. $^2E'$-state of 2$^+$. – Theoretical calculations of Tab. 1 predict the $^2E'$-state of **1**, generated by removal of an electron from the 'outer *Walsh*' e'-MO of **1**, to lie about 1.5 to 2 eV above its $^2E''$-ground state. Alkyl substitution of **1** leading to **2** will definitely affect the e″- more than the e'-MO; this in view of their relative amplitude at the site of substitution (Fig. 2). Hence the above difference will be larger in **2**$^+$ than in **1**$^+$ and we expect the corresponding PE-band in an energy region where one indeed observes a double humped structure with maxima at 9.71 eV and 10.45 eV (splitting 0.74 eV), the mean between these being 10.08 eV. The presence of two peaks suggests – in analogy to the $^2E'$-ground state of **10** [36] [39] [40] – a strong *JT*-effect operating in the ion. Indeed the two respective PE-bands of **2** and **10** are practically equal in shape, the latter also showing a splitting between the maxima of 0.77 eV [39]. It is interesting however to note that their mean energy is shifted by 0.84 eV towards higher IP with respect to **2**, in qualitative accord with the SPINDO-eigenvalues: $\varepsilon(e'(\mathbf{10})) = -11.18$ eV, $\varepsilon(e'(\mathbf{1})) = -10.88$ eV and the reasonable expectation: $\varepsilon(e'(\mathbf{2})) > \varepsilon(e'(\mathbf{1}))$ because of the alkyl effect in **2**. This feature is quite contrary to what one would expect on the basis of:

(i) a $=C(CH_3)_2$-substituent being more electronegative than two H-atoms, and

(ii) the C–C-bond length in **2** (1.451 Å [7]) being much shorter than in **10** (1.51 Å [41])[6]).

For a possible explanation of this observation consider the following interaction diagram:

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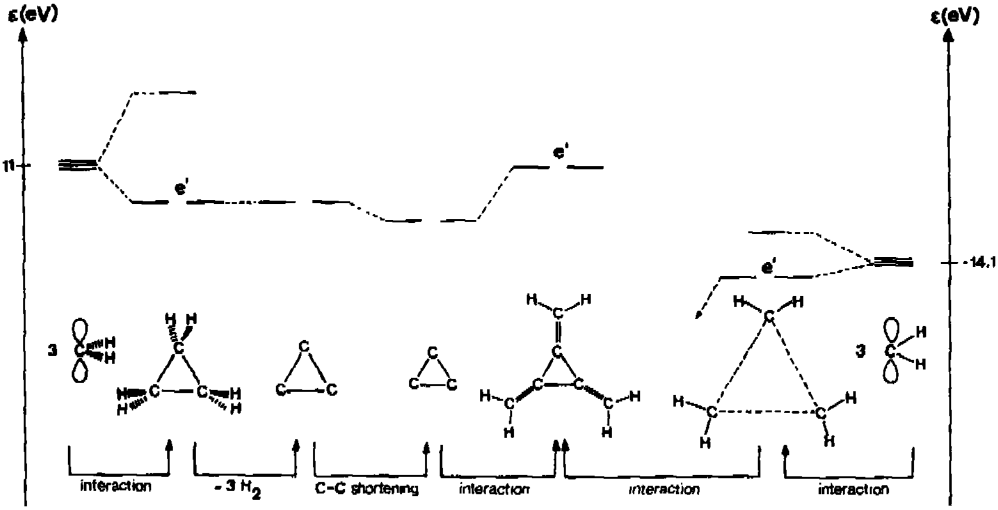
[6] Following *Walsh* [42], the *Moebius*-type interaction of the p-AO's of three CH_2-units leading to **10** yields as the lower root the e'-MO which is occupied. Hence decreasing distance between the C-atoms leads to a decreasing energy of this e'-level.



Interaction of three CH_2-units leads to **10** with $\varepsilon(e') \approx -11$ eV. Formal dehydrogenation, yielding hypothetical triangular C_3 [43] will not affect the e'-levels, since the 1s-basisfunctions of the H-atoms are not involved in these. Shortening of the C–C-bonds decreases $\varepsilon(e')$ due to larger interaction between the 2p-AO's[6]). Finally these e'-orbitals mix with an e'-level formed by three equivalent CH_2-bonding orbitals, their basis energy being at –14.1 eV [44]. Since interaction between the CH_2-groups is negligible this e'-level will also lie around –14.1 eV; hence $\Delta\varepsilon = \varepsilon(e'(C_3)) - \varepsilon(e'(CH_2)_3) < 3$ eV. Given the short C–C bond length in the final product **1** interaction between these two e'-orbitals is expected to be rather large, the upper out-of-phase combination being presumably displaced towards higher energy than –11 eV. Consequently it should also exhibit a significant amplitude at the external CH_2-groups, in agreement with the pictorial representation of the corresponding SCF-orbital in Fig. 2.

Since **1** could also be built up by union of three ethylidene carbenes **11** the above ideas suggest that **11** is strongly stabilized by hyperconjugation of its empty p-AO with the CH_2-group. The following points are in favour of this prediction:

(i) MINDO/2 [45] calculations give for the $^1S_0$-ground state of **11** a rather short C–C-bond length of 1.265 Å [46], being much shorter than the ordinary C_{sp}-C_{sp^2} bond length of 1.308 Å found for allene [41].

(ii) The above mentioned calculations yield for the heat of formation of **11** ΔH_f^0 (**11**) = 104.1 kcal/mol. If the bonds in **11** were localized this quantity could be estimated from the following process:

$$\underset{\mathbf{12}}{H{-}\bar{C}H} \xrightarrow{\Delta H_1} CH_3{-}\bar{C}H \xrightarrow{\Delta H_2} \underset{\mathbf{11}}{CH_2=C|}$$

ΔH_f^0 (**12**, $^1S_0$) = 101 kcal/mol [47]

$\Delta H_1 = \Delta H_f^0(CH_2{=}CH_2) - \Delta H_f^0(CH_3{-}CH{=}CH_2) = -7.9$ kcal/mol [48]

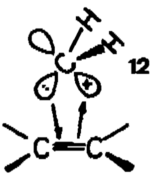
$\Delta H_2 = \Delta H_f^0(CH_3{-}CH{=}CH_2) - \Delta H_f^0(CH_2{=}C{=}CH_2) = 41.3$ kcal/mol [48].

ΔH_f^0(**11**) = 134.4 kcal/mol

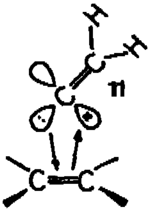
A 30 kcal/mol difference between calculated and estimated heat of formation is obtained, indicating strong delocalization in **11**.

The discussion above might imply that $^1S_0$-methylidene **12** is more electrophilic than ethylidene carbene **11**. This is not borne out experimentally. Additions of *e.g.* dichlorocarbene to substituted styrenes proceeds with a *Hammett*-ϱ-value of -0.6 [49], whereas for additions of **11** to the same substrate, $\varrho = -3.4$ was found [50].

To explain this outcome: **12** and presumably also **11** add to olefinic double bonds in a concerted manner [51], a possible mode of approach being depicted below (see *e.g.* [46] and references cited therein).



12



11

It has been pointed out [52] that **12** is isoelectronic with methyl cation, the same relationship existing between **11** and vinyl cation. In analogy then to the ionic species the dominant interaction will occur between the empty carbene p-AO with the filled π-level of the olefin, the concomitant charge donation (↑) being opposed by back-donation (↓) from the filled sp^2- and sp-hybrids resp., into the empty olefin π^*-level. Apparently the two effects cancel each other to a greater extent in **12** than in **11**, rendering the latter more electrophilic. Since according to the previous discussion donation to the empty p-AO of **11** is expected to be less effective than for **12**, back-donation from **11** must be even less effective than from **12**. This however is not surprising in view of the greater s-character of the donor hybrid orbital in **11**.

At any rate these arguments lead to the prediction that **11** is inherently less reactive than **12** with respect to insertions. Unfortunately this can not be verified on the basis of the experiments performed in [49] and [50]. It is interesting to note however that methylcarbene for which also a strong hyperconjugative stabilization has been postulated [53] shows indeed less carbenoid activity than carbene **12** itself [51].

V. *Jahn-Teller* effect in the $^2E'$-state. – As mentioned above the double-humped structure of the 10 eV band in the PE-spectrum of **2** signals *JT*-activity in the ionic $^2E'$-state of $\mathbf{2}^+$ which must be induced by a vibration of e'-species. MINDO/3-calculations of the stabilization gained by $\mathbf{1}^+$ upon $D_{3h} \rightarrow C_{2v}$ distortion indicate a $^2A_1$-saddle point and a $^2B_2$-minimum on the lower *JT*-surface with energies relative to the relaxed $^2E'$-ion of –9.4 and –10.4 kcal/mol (Fig. 4a). Note that these energies are close to those calculated for the lowest $^2E'$-state of $\mathbf{10}^+$ [36] [40] and much larger than those for $\mathbf{1}^+$ in its lowest $^2E''$-state (*vide* II).

For the expected large separation between outer and inner *JT*-surface at the $^2B_2$-minima and the $^2A_1$-saddle points we attempted to calculate the energies of the upper (vertically produced) $^2A_1$- and $^2B_2$-states resp., but the SCF-procedure failed to converge. An estimate of this separation is obtained from the orbital energy difference between the split 'outer *Walsh*'-components in the correspondingly distorted singlet species $^1B_2$ and $^1A_1$, which amounts to 1.2 eV and 1.64 eV, resp.

Though the above results indicate clearly that the *JT*-cone has not $C_{\infty v}$- but C_{2v}-symmetry, the smallness of the energy difference between minima and saddle points (1 kcal/mol) with respect to the absolute magnitude of the achieved stabilization

($\sim$ 10 kcal/mol) leads us again – armed with the experience provided in [36] – to neglect second-order interaction between the vibronic levels. The calculated C_{2v}-geometries depicted in Fig. 4a involve predominantly changes in the internal coordinates of the ring system. Lacking a better choice we assumed the e'(ring-stretch) vibration with $\tilde{\nu}_{15} = 1108$ cm^{-1} in **1** [12] to be responsible for the *JT*-effect. The theoretical PE-band shape displayed in Fig. 4b was then calculated along the lines already mentioned in II.

Comparison with the experimental spectrum shows that with respect to the separation of the peaks as well as to their relative intensity the agreement is as good as can conceivably be expected, supporting our $\tilde{\nu}_{15}$-choice. (In fact using this frequency a semiclassical *Franck-Condon* calculation [38] requires already a splitting of 0.49 eV).

In analogy to II $\tilde{\nu}_{15}$ in $\mathbf{2}^+$ might be smaller than $\tilde{\nu}_{15}$ in **1**. We have repeated the calculation with $\tilde{\nu}_{15} = 900$ cm^{-1}; the result is again displayed in Fig. 4b. Obviously, there is a close similarity between the plots though with the smaller frequency the splitting between the maxima as well as their intensity ratio (1.37 *vs.* 1.47 before) has slightly improved when compared with the experimental spectrum. Further decrease of $\tilde{\nu}_{15}$ however worsens the agreement.

Perfect agreement may not be achieved because the observed intensity distribution includes also a progression from the totally symmetric a_1' (ring-stretching) mode with

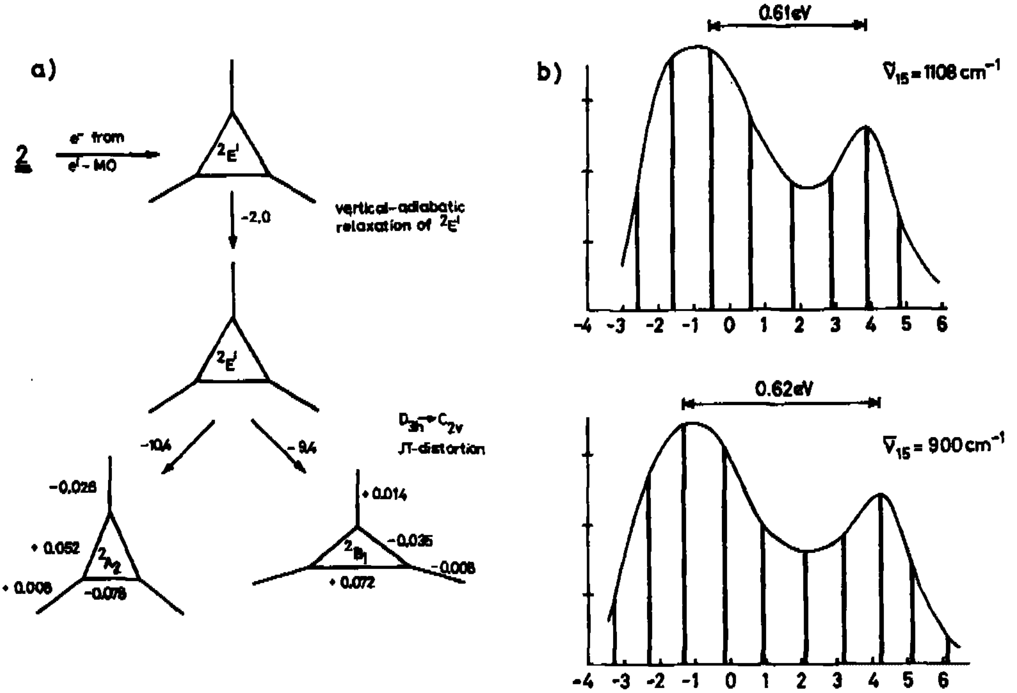


Fig. 4. a) *Calculated JT-effect in the $^2E'$-state of* $\mathbf{1}^+$. Changes in bondlengths (Å) and energies (kcal/mol) are with respect to next species above. The drawings are not in scale. b) *Calculated shape of the 10 eV band in the PE-spectrum of* **2**. Dependance from e'-frequency which induces *JT*-instability (see text). (The mean value of the *JT*-stabilization energies of saddle point and minimum was used.) The 0–0 transition is at the left of each diagram

$\tilde{\nu}_4 = 779$ cm^{-1} in **1** [12] and presumably $\tilde{\nu}_4 < 779$ cm^{-1} in **2**$^+$. This is suggested in view of the vertical-adiabatic energy difference of the D_{3h}-ions of 2 kcal/mol, accompanied by a lengthening (*e.g.* weakening) of the C–C-bonds by 0.03 Å (Fig. 4a). Near the onset of the 10 eV PE-band there is scanty evidence of a progression with average spacings of $\sim$ 400 cm^{-1} which could be due to this vibration, smoothing out the above discussed vibronic fine structure.

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Erratum

Helv. 57 (1974) Contribution Nr. 225 by *A. F. Thomas* and *R. Dubini*, p. 2084: In the summary, and on lines 1, 5 and 17 of the text, in place of "[2] [3] sigmatropic,,, read "[2,3] sigmatropic,,.

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