236. Studies on Radical Cations I. Molecular and Electronic Structure of [3]Radialene Cation Produced by γ-Irradiation in Condensed Phase[1])

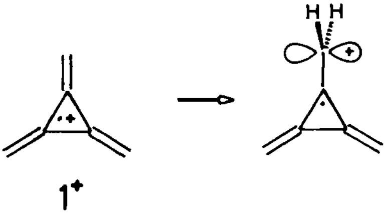
by **Thomas Bally, Edwin Haselbach**[2]) and **Zuzana Lanyiova**
Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80,
CH-4056 Basel

and **Peter Baertschi**
Eidg. Institut für Reaktorforschung (EIR),
CH-5303 Würenlingen

(17.VIII.78)

Summary

γ-Irradiation of tris(methylidene)-cyclopropane ('[3]radialene') **1** in a rigid electron scavenging matrix (butylchloride/i-pentane, 1:1) at 77 K leads to formation of its molecular cation $\mathbf{1}^+$. Slight softening of the matrix by a temperature increase of 3-5 K results in formation of a newly absorbing species, tentatively assigned as arising from structural relaxation of $\mathbf{1}^+$ by π-bond rotation:



Introduction. - A UV.-photoelectron (PE.) spectrum of a neutral closed shell molecule **M** can be considered as the state diagram of its radical cation $\mathbf{M}^+$ in which the difference between $I_n (n>1)$ and I_1 (I = ionization energy) corresponds to the energy of an electronically excited state of $\mathbf{M}^+$ relative to its ground state. Another way to obtain such a state diagram consists in recording the electronic spectrum of $\mathbf{M}^+$, or, in principle, the emission spectrum of excited $\mathbf{M}^+$. At first sight one might suspect that such studies would yield only redundant information, but a closer

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[1]) This paper also constitutes part 3 of the series: Tris(methylidene)cyclopropane('[3]radialene'). Parts 1 and 2: [4] and [5].

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

inspection reveals that this is not generally the case as often one or more of the following points may apply:

a) Some of the excited states of M^+ observed in its electronic spectrum are dominated by 'Non-*Koopmans*'-configurations[3]). Such states are usually not observed in UV./PES;

b) Some electronic transitions between the ground state of M^+ and the various '*Koopmans*-type' excited states are forbidden;

c) The ground state equilibrium geometry of M^+ differs significantly from that of neutral **M**.

A large class of molecules for which c) does not play a role are condensed aromatic systems whose radical cations have been studied extensively [1]. For such systems a very good correlation can be obtained for a plot of $\tilde{\nu}^{v}_{1,\mathrm{max}}$ of M^+ against $\Delta I^v = I^v_2 - I^v_1$ of **M** [2] [3]. A three-dimensional example to that class is provided by barrelene (=bicyclo[2.2.2]octatriene) as shown in *Figure 1* by the

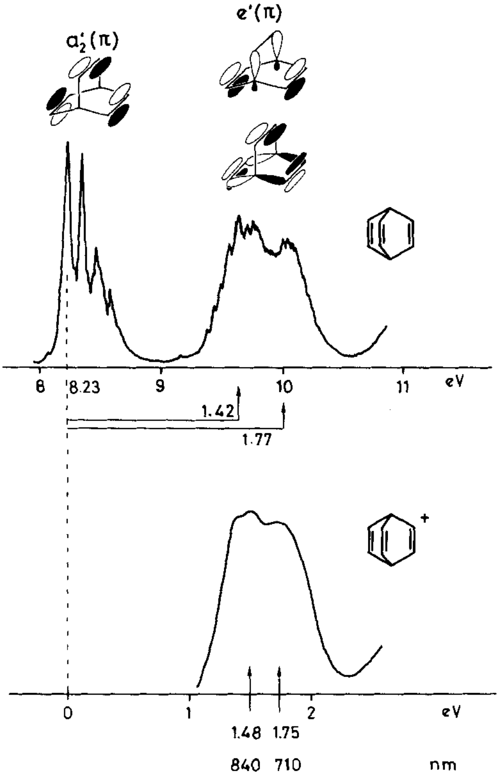

Fig. 1. *PE. spectrum of barrelene and electronic absorption spectrum of its cation, produced by γ-irradiation in butylchloride/2-methylbutane* 1:1 at 77 K

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[3]) '*Koopmans*'-configurations of M^+ are obtained by removing an electron from a doubly occupied molecular orbital of **M**. 'Non-*Koopmans*'-configurations arise through additional promotion of an electron into a virtual molecular orbital.

strong resemblance of the band profiles for the ionization process $^1A'_1 \rightarrow {}^2E'$ of the neutral and the excitation process $^2A'_2 \rightarrow {}^2E'$ of the parent ion.

Similar correlations for systems where c) is likely to play a role are lacking. Such work, however, could be particularly revealing as any noncongruency between the PE. spectrum of **M** and the electronic spectrum of $\mathbf{M}^{+}$ would provide insight into the structural changes suffered by **M** upon ionization.

In the course of our investigations on [3]radialene (**1**) and its radical cation $\mathbf{1}^{+}$ [4] [5] it occurred to us that this substrate might just be a particularly interesting candidate in this respect as a distortion *must* occur in the radical cation $\mathbf{1}^{+}$ due to the *Jahn-Teller (JT)* effect operating in its degenerate ground state $^2E''(\pi)$. The *Franck-Condon (FC)* envelope of the first PE. band of **1** suggests - in agreement with MINDO/3-calculations - a rather weak *JT*-effect for $\mathbf{1}^{+}$, *i.e.* small $D_{3h} \rightarrow C_{2v}$-distortions accompanied by feeble energy gains [4]. Hence, the shape of the band corresponding to the first (dipole allowed) electronic transition in $\mathbf{1}^{+}$ is likely to show some similarity to that of the second PE. band. Experimental verification of this expectation would add to our concepts regarding the nature of $\mathbf{1}^{+}$ [4]. Possible disagreements would shed some light on the vibronic selection rules operating for $^1A_1(\mathbf{1}) \rightarrow {}^2E'(\mathbf{1}^{+})$ in comparison with $^2E''(\mathbf{1}^{+}) \rightarrow {}^2E'(\mathbf{1}^{+})$, the latter type of transition incidentally being rarely observed in organic substrates.

Results and Discussion. - *Spectra of γ-irradiated* **1**. γ-Irradiation [6] of a butylchloride/2-methylbutane (nBuCl/2MB, 1:1) matrix [7-10] at 77 K produces spectrum S in *Figure 2.* Addition of **1** (0.03 M)[4] yields, after γ-irradiation with the same dose (~500 krad), spectrum 1 in *Figure 2.* The difference between the absorbances in the two spectra at low energies is due to the different and for successive experiments non-reproducible optical qualities of the matrix. There are, however, marked differences in absorbance around 650 nm and 420 nm, indicating the presence of at least one new species for spectrum 1.

On slight warming of the matrix ($\Delta T = 3$-5 K) a reaction sets in, yielding an increase of the 650 nm band system with concomitant decrease of absorption at 420 nm (curves 2-9 in *Fig. 2*). An isosbestic point at 523 nm is developed after about 10' from the beginning (t=0) of the warm-up period. Spectra taken at $0 < t < 10'$ (not shown except for curve 1) do not perfectly pass through this point as slight changes in the overall transparency of the matrix occur as a result of softening during this time interval.

The nature of the observed reaction. Neglecting coincidences in reactant absorptivities the presence of an isosbestic point leaves, in view of the present knowledge about experiments of this kind, four possible mechanisms that account for the observed process which takes place on slight softening of the matrix induced by ΔT:

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[4]) Based on previous experience [8-10], this concentration appears sufficiently low to prevent molecular aggregation on freezing the solution, which would result in dimer cation formation upon γ-irradiation.

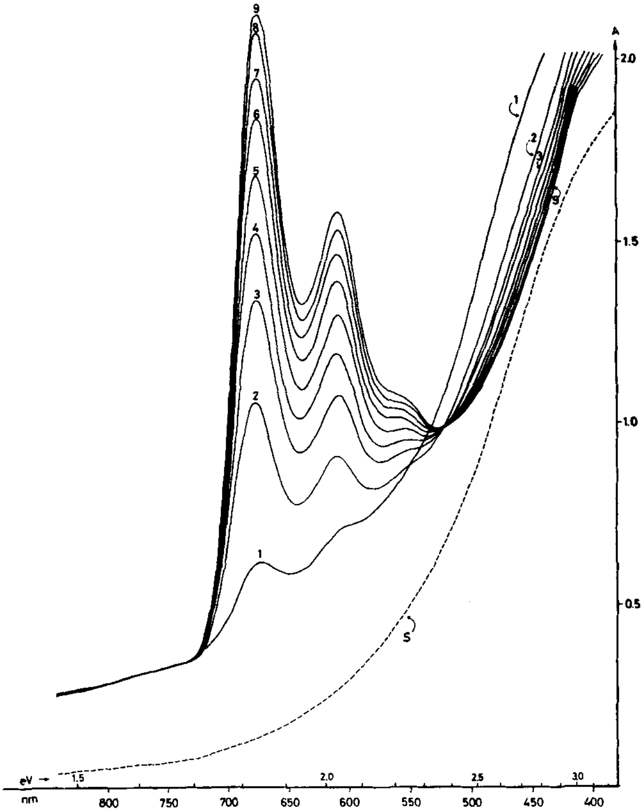

Fig. 2. *Electronic spectra obtained after γ-irradiation.*
S matrix BuCl/2 MB 1:1 at 77 K
1 0.03 M solution of **1** at 77 K
2-9 sample **1** after warming to 80-82 K

A) Thermally activated hole transfer from solvent to solute: $\mathbf{S}^+ + \mathbf{1} \rightarrow \mathbf{S} + \mathbf{1}^+$[5]).

γ-Irradiation of a matrix **S** containing alkyl chlorides (RCl) leads to creation of positive holes ($\mathbf{S}^+$), whereby the electrons are dissociatively attached to RCl yielding R· and Cl^-. Due to their initial excess energy, primarily formed $\mathbf{S}^+$ migrate within the matrix *via* resonance transfer ($\mathbf{S}^+ + \mathbf{S} \rightarrow \mathbf{S} + \mathbf{S}^+$). They may eventually exchange charge with near-by substrate molecules **M** present at low concentration ($\mathbf{S}^+ + \mathbf{M} \rightarrow \mathbf{S} + \mathbf{M}^+$) if $I^a(\mathbf{M}) < I^a(\mathbf{S})$ is satisfied. At thermal equilibrium, therefore, holes may be attached to **M** (*i.e.* $\mathbf{M}^+$) as well as to **S** (*i.e.* $\mathbf{S}^+$), the latter not being anymore able to overcome the *FC.*-barrier for resonance migration. This process may, however, be subsequently activated thermally by raising T which leads to a further increase of $[\mathbf{M}^+]$ at the expense of $[\mathbf{S}^+]$ (see [6]). It has been reported in a number of cases, unfortunately without specifying the rise in temperature needed to induce the reaction [6]. As $I_1^a(\mathbf{1}) = 8.94$ eV is smaller than $I_1^a(\mathrm{nBuCl}) = 10.67$ eV or $I_1^a(2\ \mathrm{MB}) = 10.32$ eV, this process is also here thermodynamically feasible and must therefore be considered. We have performed control experiments with benzene, using the same conditions as for **1** (*i.e.* same concentration, dose, ΔT). No hole transfer was found to occur, which speaks against *A* operating in this experiment.

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[5]) Neither the unirradiated solvent nor **1** [4] absorb in the region specified in *Figure 2.*

Further support for this conclusion is obtained from the fact that the rising band system at 650 nm can hardly be attributed to **1**$^+$, but must be due to some other species henceforth designated **X**$^+$. *Figure 3* shows this band system superimposed on the low energy part of the PES. of **1**. The energy scale has its origin coinciding with the 0-0-transition of the first photoionization process. The *FC.* profile of the absorption band is dominated by a clearly discernible progression of 1600 cm^{-1}, strikingly similar to that in the *first* PE. band but bearing no resemblance to that of the *second.* While this finding, if need be, could be attributed to strongly different vibronic selection rules for the two transitions in question (*cf.* introduction), the difference between $I_2^a - I_1^a = 1.46$ eV of **1**$^+$ [4] and the adiabatic (= vertical) transition energy of 1.83 eV for **X**$^+$, as well as the intensity of the latter transition speak against **X**$^+$ ≡ **1**$^+$:

(i) Several authors have compared gas with condensed phase transition energies of charged species with closed [11] or open shells [12] [13]. For systems where excitation is not accompanied by significant intramolecular charge migration, the same solvation effects seem to operate on both the ground and the excited states, as transition energies are virtually independent of the nature of the molecular invironment. As excitation of **1**$^+$ also does not result in charge migration the significant difference of 0.36 eV noted above is hardly compatible with **X**$^+$ ≡ **1**$^+$.

(ii) A further argument against **X**$^+$ ≡ **1**$^+$ rests on the molar extinction coefficient $\varepsilon = 2500$ of the 678 nm peak of **X**$^+$, calculated for G = 1.6 [2]. This medium to strong intensity is incompatible with the 'forbidden' character *(vide infra)* of the $^2E''(\pi) \rightarrow {}^2E'(\sigma)$ transition in **1**$^+$.

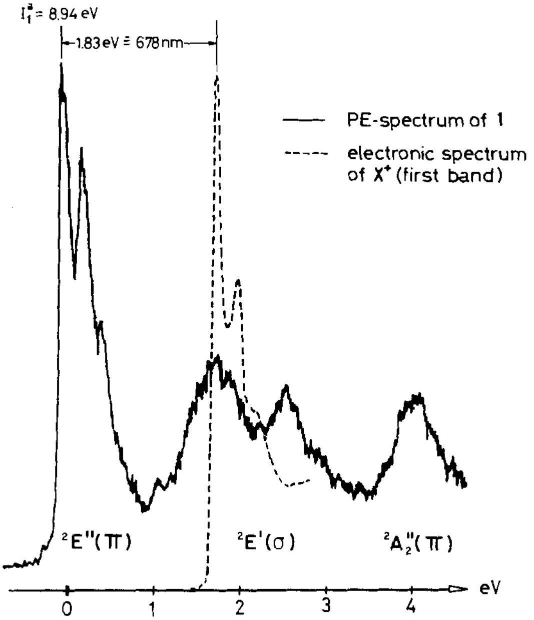

Fig. 3. *PE. spectrum of* **1** *in comparison with electronic spectrum of* **X**$^+$ (the origin of the energy scale is set at $I_1^a(\mathbf{1}) = 8.94$ eV)

B) Dimer cation formation $\mathbf{1}+\mathbf{1}^{+} \rightarrow \mathbf{1}_2^{+}$ 5)6).

This process is well documented for several solutes [6-10] [14] [15]. The ΔT-conditions reported, however, indicate that it requires considerable softening of the matrix (*e.g.* $\Delta T = 13$ K in [7-10]). Indeed, from our control experiments quoted under *A*, no (benzene)$_2^{+}$-formation was observed. Additional spectral features speaking against $\mathbf{X}^{+} \equiv \mathbf{1}_2^{+}$ are:

(i) Dimer cations $\mathbf{M}_2^{+}$ exhibit particularly low energy charge resonance (CR.) transitions $\psi(\mathbf{R}_{-}) \rightarrow \psi(\mathbf{R}_{+})$, the two states arising from CR. between the two components:

$$\psi(\mathbf{R}_{\pm}) = \psi(\mathbf{M}_a^{+}\mathbf{M}_b) \pm \psi(\mathbf{M}_a\mathbf{M}_b^{+}).$$

The transition energies are remarkably similar for the few cases known, *e.g.* (benzene)$_2^{+}$, 1.34 eV [9, 15]; (naphthalene)$_2^{+}$, 1.20 eV [7] [10] [14]; (butadiene)$_2^{+}$, 1.03 eV [8].

Inspection of the *Hückel*-HOMO's of **1** [4] and butadiene suggests, that we ought to expect a CR. transition for $\mathbf{1}_2^{+}$ at around 1 eV. *Figure 4* shows only solvent absorption in this region or anywhere near it (the IR. part of the spectrum has been recorded at the final stage of the reaction in order to prevent IR. light induced bleaching of $\mathbf{X}^{+}$).

(ii) Higher excited states of $\mathbf{M}_2^{+}$ are described by:

$$\psi(\mathbf{C}_{\pm}) = \psi(\mathbf{M}_a^{+*}\mathbf{M}_b) \pm \psi(\mathbf{M}_a\mathbf{M}_b^{+*}),$$

$\mathbf{M}_a^{+*}$ and $\mathbf{M}_b^{+*}$ being excited states of the monomeric ions. It has been shown that the energies for an allowed monomer transition in $\mathbf{M}^{+}$ and the corresponding allowed dimer transition $\psi(\mathbf{R}_{-}) \rightarrow \psi(\mathbf{C}_{-})$ are very close, the difference between them being *inter alia* dependent on the geometry of the dimer cation [16].

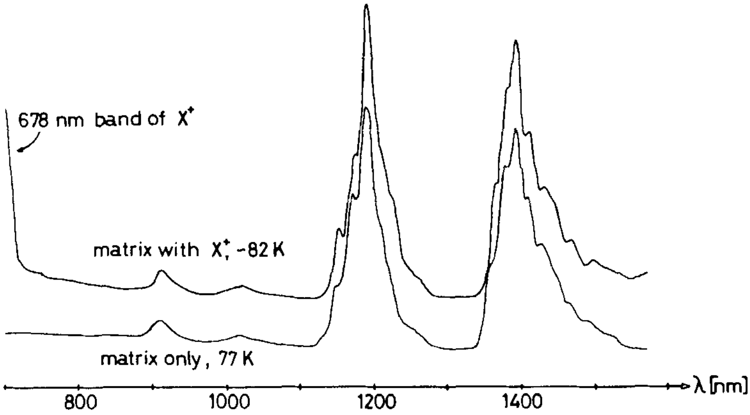

Fig. 4. *Near IR. spectra of γ-irradiated matrix and sample containing* $\mathbf{X}^{+}$

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6) **1** is present in great excess. Hence, this reaction would exhibit pseudo first-order behaviour.

Experimental differences of the above type for the cited substrates benzene, naphthalene and butadiene are -0.4, -0.41 and $+0.27$ eV, respectively [7-10] [14] [15]. In addition, recent work [17] has provided evidence that such corresponding transitions in $\mathbf{M}^+$ and $\mathbf{M}_2^+$ exhibit similar oscillator strength. This also rules out dimer formation as being responsible for the process shown in *Figure 2:* There are no bands of comparable intensity situated ± 0.5 eV from the 650 nm band system, which vanish on its formation.

C) Complex formation of $\mathbf{1}^+$ (or **1**) with some other substance formed upon radiolysis of solvent molecules.

Though two such processes have been recently reported [15] [17] to occur at rather low temperatures (even at 77 K [15]), the solvents used in these studies were of highly halogenated type, possessing in both cases a labile C-Br bond. For solvents of the present kind, no reaction of type *C* has yet been observed.

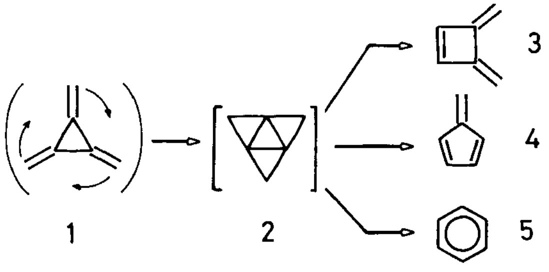
Having excluded mechanisms *A-C*, we suggest reaction *D* as being the source of the present observation.

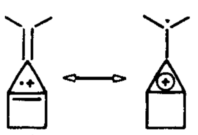
D) Monomolecular reaction $\mathbf{1}^+ \rightarrow \mathbf{X}^+$.

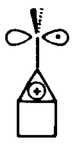
Evidence for the initial presence of $\mathbf{1}^+$ *at 77 K.* The PE. spectrum of **1** *(Fig. 3)* suggests at first sight for $\mathbf{1}^+$ a lowest energy allowed transition $^2\mathrm{E}''(\pi) \rightarrow {}^2\mathrm{E}'(\sigma)$ with adiabatic onset at 1.46 eV [4], but spectrum 1 *(Fig. 2)* shows no significant absorption there except for the 650 nm band system due to an already present small concentration of $\mathbf{X}^+$ *(vide infra).* A small oscillator strength is associated with the expected transition which involves a $\sigma \rightarrow \pi$ electron promotion with the transition density being confined to overlap regions of orthogonal basis functions. Indeed, the resulting transition moment would vanish within the ZDO. framework.

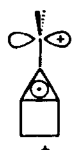
For the next allowed transition the PE. spectrum suggests $^2\mathrm{E}''(\pi) \rightarrow {}^2\mathrm{A}_2''(\pi)$ at ~4 eV. CNDO/S- [18] as well as single determinant 'half-electron' MINDO/3-calculations yield, however, an excited state at 3 eV and 3.27 eV, respectively, above ground state $\mathbf{1}^+$. As the CI. calculations indicate it to be of rather pure 'non-*Koopmans*' nature³) it would not give rise to a PE. band. The energy of this state, however, matches well with the position of the short wavelength absorption around 420 nm, which vanishes in the course of the reaction documented in *Figure 2.*

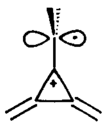
The nature of $\mathbf{X}^+$. Earlier work had shown that slight softening of the matrix may lead to conformational relaxation of the solute cation [1]. We have observed valence isomerization of *Dewar* benzene to benzene cation [2] or, more recently, of quadricyclane to norbornadiene cation [19] to occur even at 77 K. Additionally, light induced valence isomerization of 1,3-cyclohexadiene to 1,3,5-hexatriene cation has been found at 77 K [13]. All the above processes have in common that the change of internal coordinates accompanying the reaction is modest and no great reshuffling of matrix molecules is required. Apart from this matrix effect, only such processes are expected to occur that proceed, for the isolated system, without activation (conformational relaxation) or with a barrier low enough to be surmountable even at 77 K (ionic valence isomerization, *cf.* discussion in [19]). Accordingly we consider for $\mathbf{X}^+$ the following isomers or conformers of $\mathbf{1}^+$:

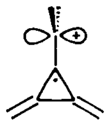



6$^+$ **6a**$^+$


7$^+$


8$^+$


9$^+$


10$^+$

All candidates except **10**$^+$ were ruled out as follows:

3$^+$–**5**$^+$: *Rice et al.* [20] have speculated about the origin of the low fluorescence quantum yield of **1**. They suggested that its excited state is effectively depopulated *via* a photochemical path involving **2** as an intermediate and rendering eventually **3**, **4** and **5**. Since molecules often behave similarly on ionization as on excitation [21] we felt obliged to include isomers **3**$^+$–**5**$^+$ in our evaluation procedure. As shown in *Table 1* they are indeed all more stable than **1**$^+$.

Nevertheless it is difficult to imagine, how **3**$^+$, **4**$^+$ or **5**$^+$ would be formed in a thermal process taking place at 80–82 K. In any case the large strain operating in **2**$^+$ rules it out as a thermal intermediate for all practical purposes.

Stronger arguments against **3**$^+$, **4**$^+$ and **5**$^+$ rest on spectral grounds. The first electronic transition in **5**$^+$ gives rise to a broad, unstructured band peaking at 555 nm [9]. The transition energies of **3**$^+$ and **4**$^+$ can be estimated from the PE. spectra [23] and PPP-CI-calculations [26]. While the former yield energy differences between the ground states of the ions and those excited states dominated by '*Koopmans*'-configurations, the PPP-CI-calculations provide us with reliable predictions about the position of $\pi \rightarrow \pi^*$ excited states not observed in PES [18] [26]. Since $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ promotions (available from neither of the above

Table 1. *Experimental and estimated enthalpies of formation* (ΔH_f°) *for* **1** *and its* 6π*-electron isomers* **3**–**5**, *as well as for the corresponding radical cations* **1**$^+$, **3**$^+$–**5**$^+$

M	ΔH_f°(M) [kJmol^{-1}]	I_1^v(M) [eV]	ΔH_f°(M$^+$) [kJmol^{-1}]
1	398 [5]	8.94 [4]	1260
3	311 [22][a])	8.80 [23]	1160
4	226 [22][a])	8.36 [23]	1032
5	83 [24]	9.25 [25]	975

[a]) Estimated from *Benson*'s group increments [22]. For the increment $C_d(C_d)_2$ we have interpolated a value of 31 kJmol^{-1} (see [5]). The values above are lower bounds as for **3** and **4** only the reported strain increments of cyclobutene and cyclopentadiene, respectively, were included.

considerations) are not likely to play a role presently, we declined to perform further calculations (using for example the CNDO/S procedure). As shown in *Table 2* neither $\mathbf{3}^+$ nor $\mathbf{4}^+$ are predicted to absorb as observed for $\mathbf{X}^+$. The presence of $\mathbf{4}^+$ can even be excluded rigorously since the IR. portion of the spectrum accessible to us *(Fig. 4)* shows no absorption apart from that attributed to the matrix. Though we do not claim that these figures constitute a proof, they provide strong evidence against all 5 π-electron isomers of $\mathbf{1}^+$ as being $\mathbf{X}^+$.

Table 2. *Experimental* (PES) *and calculated* (PPP-CI) *transition wave lengths for* $\mathbf{3}^+$ *and* $\mathbf{4}^+$ (in nm)[a])

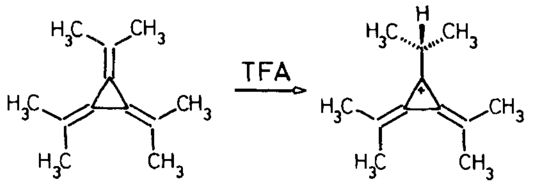
		λ_1(nm)	λ_2(nm)	λ_3(nm)	λ_4(nm)
4^+	PPP	1000 ($\pi \rightarrow \pi^\circ$)	544 ($\pi^\circ \rightarrow \pi^*$)	481 ($\pi^\circ \rightarrow \pi^*$)	-
	PES	1050 ($\pi \rightarrow \pi^\circ$)	-	-	330 ($\sigma \rightarrow \pi^\circ$)
3^+	PPP	1887 ($\pi \rightarrow \pi^\circ$)	574 ($\pi^\circ \rightarrow \pi^*$)	495 ($\pi^\circ \rightarrow \pi^*$)	-
	PES	1940 ($\pi \rightarrow \pi^\circ$)	-	-	460 ($\sigma \rightarrow \pi^\circ$)

[a]) See also [26].

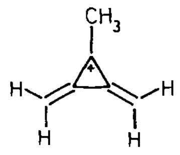
$\mathbf{6}^+$-$\mathbf{8}^+$: Though $\mathbf{6}^+$ is stabilized conjugatively by a cyclopropenium system (*cf.* valence structure $\mathbf{6a}^+$) it possesses considerable strain. From MINDO/3 calculations $\Delta H_f^\circ(\mathbf{1}^+ \rightarrow \mathbf{6}^+) = 81.2$ kJmol^{-1}. For the neutral species (both completely optimized within C_{2v}) the same quantity amounts to 215.5 kJmol^{-1}. As MINDO/3 notoriously underestimates strain in four-membered rings, this value is to be considered as a lower bound. Other thermochemical estimates also show the reaction to be significantly endothermic. In addition excitation in $\mathbf{6}^+$ is accompanied by strong charge transfer from the three-membered ring to the exocyclic carbon atom with concomitant large changes of bond orders for the essential single bonds. One would not expect a single progression of such large frequency (1600 cm^{-1}) with the 0-0-transition most pronounced for the associated absorption band, as found for $\mathbf{X}^+$ *(Fig. 2)*.

System $\mathbf{7}^+$ can be ruled out because cyclopropenium ion itself does not absorb above 200 nm [27]. For the corresponding π-radical $\mathbf{8}^+$ (a $\sigma \rightarrow \pi$ excited state of $\mathbf{7}^+$), the lowest energy allowed transition $^2E''(\pi) \rightarrow {}^2E'(\sigma)$ is calculated to be at 335 nm [18]. Finally, there is no reason why the stability of $\mathbf{7}^+$ or $\mathbf{8}^+$ should exceed that of $\mathbf{6}^+$ (which was already excluded above for thermochemical reasons) by more than 80 kJmol^{-1} so as to compete with $\mathbf{1}^+$.

$\mathbf{9}^+$: Evidence against $\mathbf{9}^+$ is obtained from the electronic spectrum of the iso-π-electronic system $\mathbf{11}H^+$, prepared by protonation of $\mathbf{11}$, the hexamethyl derivative of $\mathbf{1}$, in trifluoroacetic acid.



11 11H$^+$



1H$^+$

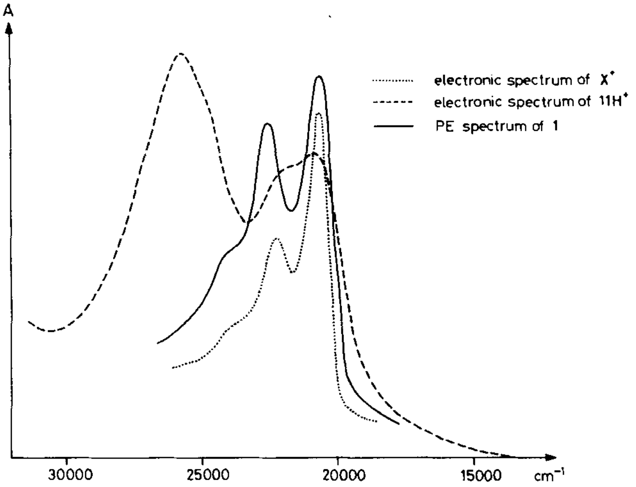


Fig. 5. *Comparison of vibrational fine structure in the first band of the electronic spectra of* $\mathbf{X}^+$ *and* $\mathbf{11H}^+$, *and of the PE. spectrum of* **1**. The wave number scale corresponds to the spectrum of $\mathbf{11H}^+$, the other two spectra being drawn with matching 0-0-transitions (for their correct energy scale see *Fig. 3*)

The first band *(Fig. 5)* of $\mathbf{11H}^+$ peaks at 480 nm (=2.58 eV). It exhibits two members of a progression of 1300 cm^{-1}. Preliminary studies indicate that $\mathbf{1H}^+$ absorbs similarly, but its spectrum is difficult to confirm due to the extreme tendency of **1** to undergo cationic polymerization. PPP-CI-calculations for $\mathbf{1H}^+$ (*i.e.* neglecting the effect of the methyl groups in $\mathbf{11H}^+$) place the first transition $^1A_1 \rightarrow {}^1B_2$ at 480 nm in agreement with the observation for $\mathbf{11H}^+$. Apparently, the shift induced by the alkyl groups and by the medium, and the error in the calculated figure cancel.

In the following we list positive evidence for $\mathbf{X}^+ \equiv \mathbf{10}^+$:

(i) PPP-CI-calculations for $\mathbf{10}^+$ considering only its 5 π-electron system predict a lowest energy allowed transition $^2B_1(\pi) \rightarrow {}^2A_2(\pi)$ at 734 nm (= 1.69 eV), in good agreement with the observed spectrum ($\lambda_{\max} = 678$ nm $\widehat{=}$ 1.83 eV). The same is true for the molar extinction coefficients of the corresponding band: ε (PPP-CI) = 2400, ε (exp) = 2500.

(ii) Consideration of the HMO-diagram displayed in *Figure 6* shows that there are some striking similarities between the orbitals involved in π-ionization of **1** and $\pi \rightarrow \pi$ excitation of $\mathbf{10}^+$ or $\mathbf{1H}^+$ (where the nonbonding b_1 π-orbital (NBMO) bears no electron in the ground configuration)[7]. If we consider, for simplicity, ionization of **1** to occur from the a_2-component of the e″-HOMO, it follows that the change in bond orders for this process is *identical* to that experienced by excitation of $\mathbf{10}^+$ or $\mathbf{1H}^+$, as here the electron is raised to a NBMO! Indeed, the first band in the electronic spectra of $\mathbf{X}^+ \equiv \mathbf{10}^+$ and $\mathbf{11H}^+$ and in the PE. spectrum of **1** show a remarkably similar shape *(Fig. 5)*. Note that the vibrational frequency displayed by $\mathbf{11H}^+$ is slightly smaller than that found in the PE. spectrum of **1** or the electronic

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[7] All MO's, including the two components of the e″-HOMO of **1**, are classified in C_{2v}.

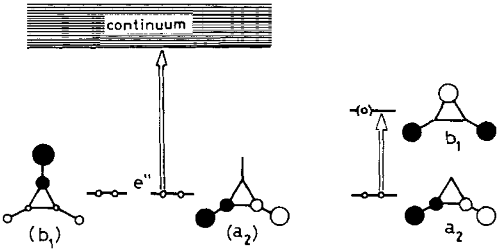

Fig. 6. *π-MO's involved in the first ionization process of* **1** (left) *and the first excitation process of* $X^+ = \mathbf{10}^+$ *or* $\mathbf{1}H^+$ (right)

spectrum of $\mathbf{10}^+$. This alkyl group effect exactly parallels the one found in the PE. spectrum of **11** as compared to that of **1** [4].

Why does $\mathbf{1}^+ \rightarrow \mathbf{10}^+$ *occur?* MINDO/3 calculations show twisting of a CH_2-group of isolated $\mathbf{1}^+$ ($^2B_1$)^7) to be free of activation, the potential minimum being attained for a torsional angle $\varphi = 43°$ with $\Delta H^{\circ}_{rot} = -26$ kJmol^{-1} *(Fig. 7)*^{8}). (Torsion in the other *JT*-component $\mathbf{1}^+$ ($^2A_2$)^7) leads to a steady increase in energy.) How can the calculated spontaneous twisting of the C(1)–C(6) π-bond, exhibiting a sizeable π-bond order, be rationalized?

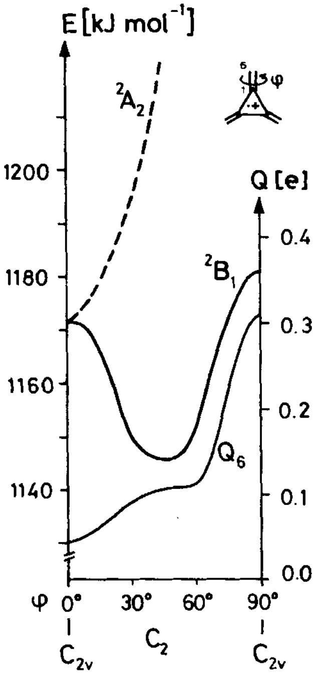

Fig. 7. *MINDO/3 calculations: Potential energy* (E) *for double bond rotation of* $\mathbf{1}^+$ ($^2A_2$- and $^2B_1$-states); *charge density* (Q) *at* C(6) *of* $\mathbf{1}^+$ *for the* $^2B_1$ *process*

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[8] The torsional angle between the CH_2-groups in ethylene cation is experimentally found to be 25° [28]. Theoretical calculations support this finding [29] or yield a planar minimum [30], though associated with an extremely flat torsional potential.

For φ departing from 0° the p_z-lobe at C(6) of $\mathbf{1}^+$ starts interacting with the antisymmetric component of the e′(σ) *Walsh*-orbital associated with the three-membered ring. This interaction is well established for alkyl derivatives of cyclopropyl-methylcation and amounts to ~60 $kJmol^{-1}$ [31]. As the orbital energies ε (e′, cyclopropane) and ε (e′, **1**) are about equal [4], this stabilization may well be of the same magnitude in $\mathbf{10}^+$ ($\varphi = 90°$), too.

For progressive distortions from planarity, however, the π-energy of $\mathbf{1}^+$ increases. A balance between these two opposing effects is established at $\varphi = 43°$ (MINDO/3). But attention is drawn to the fact, that strong charge localization at the exocyclic carbon atom C(6) is predicted on passing from $\varphi = 60°$ to $\varphi = 90°$ as shown by curve Q_6 in *Figure 7*. Hence, solvent-solute interaction improves drastically for higher torsional angles, thus displacing the calculated minimum to the range of $\varphi \sim 90°$ for the condensed phase. In addition to this solvation effect, covalent bond formation between the empty p-AO at C(6) and a Cl-atom of the BuCl matrix component may yield a chloronium ion of the type discussed by *Olah et al.* [32], which additionally favours a conformation with $\varphi \sim 90°$ such as implied by our structure $\mathbf{10}^+$.

Final comments. Three last comments seem in order regarding our interpretation $\mathbf{X}^+ \equiv \mathbf{10}^+$:

(i) At first sight, the theoretical finding that rotation around C(1)–C(6) for $\mathbf{1}^+ \rightarrow \mathbf{10}^+$ proceeds free of activation contrasts with the experimental observation that $\mathbf{10}^+$ appears only after warming of the matrix by $\Delta T = 3$-5 K. We ascribe this phenomenon to an intrinsic matrix effect. On forming the rigid matrix the S-molecules will essentially be randomly oriented around apolar **1**. This situation will pertain also to $\mathbf{1}^+$ after γ-irradiation as long as $T = 77$ K is maintained. Hence, only few ions will find themself in a solvent shell arranged so not to energetically inhibit bond rotation. Spectrum 1 in *Figure 2* shows that, indeed, some small concentration of $\mathbf{10}^+$ is present immediately after γ-irradiation. The temperature increase $\Delta T = 3$-5 K, though not allowing free diffusion, apparently softens the matrix enough to allow readjustment of the solvent shell around $\mathbf{1}^+$ in the course of intrinsically spontaneous $\mathbf{1}^+ \rightarrow \mathbf{10}^+$, and twisting occurs even beyond the predicted gas phase conformation[9]). (For a recent discussion of matrix effects on molecular potentials see [33].)

In line with this interpretation is the extreme temperature sensitivity of the reaction. While spectrum 1 *(Fig. 2)* at 77 K remains unchanged with time, a temperature rise $\Delta T = 10$ K speeds up the ensuing reaction $\mathbf{1}^+ \rightarrow \mathbf{10}^+$ beyond detectability of intermediate stages. This delicate temperature dependence follows equally from *Figure 8* where a *Guggenheim*-plot [34] is shown for those spectra passing through the isosbestic point, assuming first or pseudo-first order behaviour of $\mathbf{1}^+ \rightarrow \mathbf{10}^+$. The plot deviates from linearity, the rate of reaction decreasing less than expected for the assumed kinetics. This feature may be ascribed to the presence of a small temperature gradient, decreasing with time, between walls and interior of

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[9]) *Shida & Iwata* have observed that dibenzo-cyclooctatetraene cation, prepared by γ-irradiation of the tub-shaped parent neutral in a s-BuCl matrix at 77 K, relaxes to its planar equilibrium conformation only after slight warming of the matrix [1].

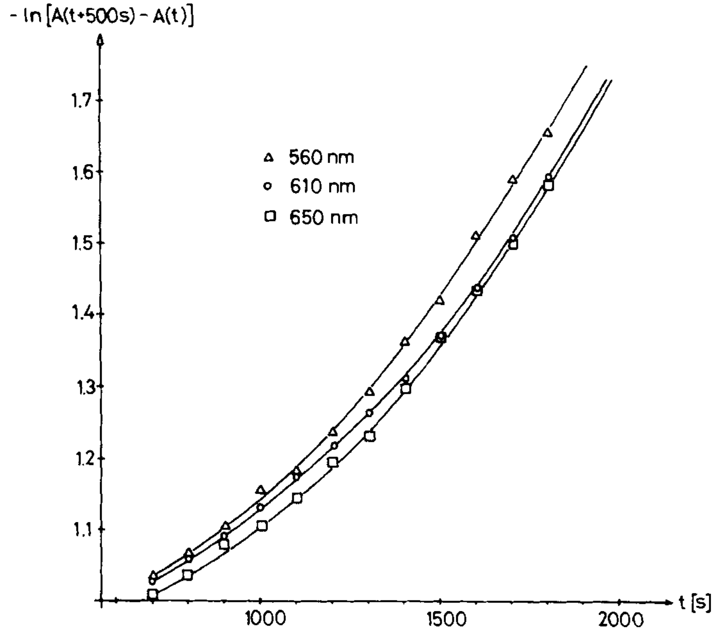

Fig. 8. Guggenheim-*plot for* $\mathbf{1}^+ \rightarrow \mathbf{10}^+$ *at 80-82 K in BuCl/2MB* 1:1. (Values given are calculated from spectra 2-9 *(Fig. 2)* with the absorbances at 560, 610 and 650 nm)

the sample where the light beam of the spectrophotometer passes. Alternatively some sort of 'phase transition' may occur extending isothermally from the walls and progressively conditioning the matrix for successful bond rotation of $\mathbf{1}^+$.

(ii) From sole inspection of the isolated systems $\mathbf{9}^+$ and $\mathbf{10}^+$ our preference for $\mathbf{10}^+$ is not obvious: there is no clear-cut *prima facie* argument for the relative energy of the respective singly occupied MO's, both being non-bonding in a zeroth approximation. As expected, therefore, ionization energies of appropriate reference systems do not clarify this picture: I(cyclopropyl-$CH_2^{\cdot}$) ~ 7.5 eV [35], I(divinyl-$CH^{\cdot}$) ~ 7.8 eV [36]. Finally, from MINDO/3-calculations for the C_{2v}-optimized species we obtain: $\Delta H_f^\circ(\mathbf{9}^+, {}^2B_1(\pi)) = 1180$ kJmol^{-1} and $\Delta H_f^\circ(\mathbf{10}^+, {}^2B_2(\sigma)) = 1192$ kJmol^{-1}. Hence, there are no good thermochemical reasons to exclude one of the 'electronic isomers', in particular as formation of both from $\mathbf{1}^+ ({}^2B_1(\pi))^7$) proceeds adiabatically along the C_2-symmetry reaction coordinate.

The situation is reminiscent of that encountered for the radical cation of 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane, for which a D_{2d}-isomer (electronic symmetry $^2B_2$) competes with a C_{2v}-isomer (electronic symmetry $^2B_1$ or $^2B_2$) [37]. Experimentally, however, the C_{2v}-isomer is favoured in condensed phase as it exhibits stronger charge localization, allowing greater solvent-solute interaction [37] [38]. On this basis $\mathbf{10}^+$ is clearly favoured over $\mathbf{9}^+$ in condensed media, in line with our spectral assignment given above.

(iii) On further increase of T the matrix becomes fluid, and $\mathbf{10}^+$ is readily bleached out, but no indications of sandwich dimer cation formation (*i.e.*

appearance of new bands attributable to $\psi(\mathbf{R}_-) \rightarrow \psi(\mathbf{R}_+)$ or $\psi(\mathbf{R}_-) \rightarrow \psi(\mathbf{C}_-)$ mentioned in *B*) are obtained. This contrasts with observations made earlier for related hydrocarbons, in particular with butadiene, as cited in *B*. It must be realized, however, that the present system itself is also rather exceptional. Unlike for the cited substrates, dimer cation $\mathbf{M}_2^+$ formation would not occur between **M** and its structurally related molecular ion $\mathbf{M}^+$ (where $\mathbf{M}^+$ exhibits a well delocalized positive charge), but between the two essentially different substrates **1** and $\mathbf{10}^+$. The former exhibits a low HMO cation localization-energy for C(6), $L_6^+ = 1.46\ \beta$ as exemplified by the fact that protonation occurs readily in TFE. On the other hand, $\mathbf{10}^+$ bears a strongly electrophylic C(6)-atom. Hence, while the reference systems, at low T, combine to a sandwich π-complex and covalent bonding appearantly occurs only at significantly higher T (*cf.* [39]), the present substrates **1** and $\mathbf{10}^+$ engage covalently already at low T.

Conclusions. – Radical cation intermediates are becoming increasingly important in all branches of chemistry. Studies of their molecular and electronic structure as well as of their reactivity are therefore highly desirable, though more difficult to perform than for ordinary compounds due to the high reactivity of the open shell ions. The PE. spectrum of the parent neutral provides a first source of information for the isolated species, but the insight obtained therefrom is limited due to the vertical nature of the experiment. Combining it, however, with spectral results gained on the ion as described in this paper, gives information on relaxation processes accompanying ionization in the condensed phase. These link the features of the ion formed with those of the known molecular properties of the precursor.

This work is part of project Nr. 2.544–0.76 of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. Financial support by the *Fond zur Förderung von Lehre und Forschung, Ciba-Geigy SA, F. Hoffmann-La Roche SA, Sandoz SA* and the *Ciba-Geigy-Foundation* are gratefully acknowledged. We thank Dr. *P. Carsky* (Prague) for performing the CNDO/S-calculations and Prof. *T. Shida* (Kyoto) for constructive criticism of this work.

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