

41. The Molecular Ion of 5-Methylene-1,3-cyclohexadiene: Electronic Absorption Spectrum and Revised Enthalpy of Formation

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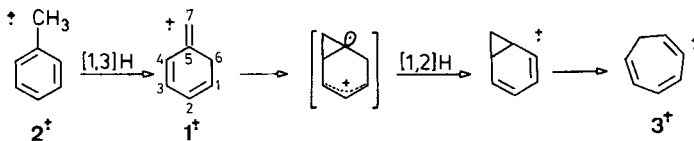
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The title compound (**1**) is prepared *in situ* from 5-methylenebicyclo[2.2.0]hex-2-ene by pyrolysis and subsequent photoionization in a photoelectron spectrometer or by X-ray irradiation in an Ar matrix where its electronic absorption spectrum is obtained. The results confirm earlier conjectures that the title cation exists as a distinct entity on the $C_7H_8^+$ hypersurface and can be obtained photochemically from other isomeric ions or by a *McLafferty* rearrangement. The enthalpies of formation of **1**, its precursor and the corresponding radical ions are compared to the most recent data available for other C_7H_8 isomers and their ions. It is shown that the thermodynamic stability of 1^+ is closer to that of toluene cation than concluded on the basis of earlier results.

Introduction. – Although the gas-phase interconversion of toluene and cycloheptatriene molecular ions, which is often accompanied by extensive C- and/or H-scrambling, has attracted continuing interest over the last two decades [1], its reaction mechanism has not been fully elucidated. It was, however, recognized that the molecular ion of 5-methylene-1,3-cyclohexadiene (1^+) may play a key role in this process [2]. It is, for example, almost certainly involved in the H_a/H_r exchange in toluene radical cations, and is probably an intermediate in the toluene radical cation (2^+) → cycloheptatriene radical cation (3^+) interconversion (*Scheme 1*) [3].

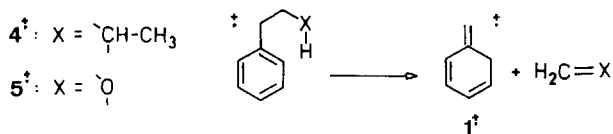
Scheme 1



Furthermore its formation by a *McLafferty* rearrangement of the butylbenzene radical cation (4^+) or 2-phenylethanol radical cation (5^+) (*Scheme 2*) can be inferred by analogy with many other examples [4], although it remained unclear until recently whether the structure of 1^+ was indeed retained after fragmentation of 4^+ or 5^+ .

For these reasons, recent investigations have centered on the identification of 1^+ in the gas [5–8] or solid phase [9]. Thus, *Dunbar* and *Klein* investigated the *McLafferty* rearrangement product (*Scheme 2*) by gas-phase photodissociation (PD) spectroscopy [5]. They obtained a spectrum which differed substantially from those of 2^+ or 3^+ but

Scheme 2



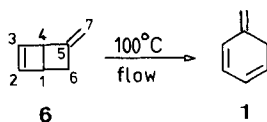
agreed qualitatively with the spectrum expected for planar 1^+ [10]. On the other hand, the Collisional Activation (CA) technique yielded almost identical spectra for this product and for 3^+ [6], which suggested (but did not prove!) that the two species have identical structures. These investigations were, however, recently repeated with more refined equipment [7], yielding clear-cut CA-spectral differences between the ions originating from 4^+ or 5^+ , and 3^+ . The high intensity of the $M^+ - \text{CH}_2$ peak supported a structure with intact CH_2 moieties such as 1^+ .

Bartmess generated for the first time 1^+ directly from **1** and compared its appearance potential, gas-phase basicity and ion-molecule reactivity to that of 2^+ [8]. He concluded that 1^+ is a distinct entity which differs markedly in its chemical behavior and heat of formation from 2^+ .

Recently, *Kelsall* and *Andrews* [9] reported that various C_7H_8 isomers, as well as butylbenzene (**4**) and 2-phenylethanol (**5**) subjected to VUV photoionization during Ar matrix isolation, formed species which could all be photolyzed to give products with a common electronic absorption spectrum (EAS) showing the same general features as the above mentioned PD spectrum [5]. On the basis of the arguments given in [5], they concluded that the observed spectrum corresponded to that of 1^+ .

In view of this wealth of information on indirectly formed 1^+ we deemed it worthwhile to reexamine some of the above mentioned findings on samples of 1^+ obtained *via* a more direct pathway. Although **1** seems to be the most obvious precursor, we decided against this compound because of its high propensity to undergo easily catalyzed H-shift, yielding toluene which would have seriously perturbed our measurements. Thus, we elected to start with 5-methylenebicyclo[2.2.0]hex-2-ene (**6**), a reasonably persistent compound which can be transformed cleanly and quantitatively into **1** by flow pyrolysis at 100°C [11] [12] (Scheme 3).

Scheme 3



Furthermore, it has recently been shown that a derivative of **6** undergoes spontaneous ring opening upon electron transfer to excited chloranil at room temperature in solution [13]. Also, strained polycyclic olefins generally show a high propensity for ring-opening upon radiolytic ionization in cryogenic matrices [14]. These observations led us to expect that 1^+ would be the sole observable product after ionization of **6** under our experimental conditions.

Results and Discussion. – *Electronic Absorption Spectrum (EAS) of 1^+ .* Fig. 1 shows the EAS of matrix-isolated **6** after X-ray irradiation. The same spectrum was also obtained if **6** was heated to 150°C during sample deposition (as evidenced by the formation of a new absorption band at 303 nm, typical of neutral **1** [15]), or if matrix-isolated **6** was photolyzed at 200 nm prior to ionization (with concomitant formation of the same UV-absorption spectrum). Our expectation of ring-opening during ionization, therefore, seems to be confirmed, as no optical absorption traceable to 6^+ was ever detected. We note that the spectrum in Fig. 1 is almost identical to that published in [9], which makes it very likely that its assignment to 1^+ was (and is) indeed correct.

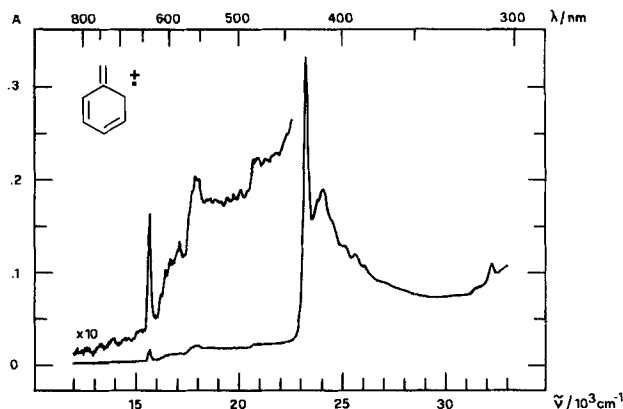


Fig. 1. *Electronic absorption spectrum of 1^+* (see text) in Ar at 20 K

Apart from the main band at 430 nm and the small sharp peak at 638 nm, the spectrum shows some additional (reproducible) features between 500 and 600 nm which could not be removed by prolonged photolysis in this spectral range, but vanished in concert with the other bands upon bleaching with 430 nm radiation. Since 1^+ – essentially a linear conjugated polyene cation – is not expected to have any additional electronic states in the visible region [10], we conclude that the 500–600-nm peaks are vibrational progressions of the electronic transition originating at 638 nm. As noted in [5], the spectrum compares very well with that of 1,3,5-hexatriene cations, *i.e.* the first band is close to the corresponding transition in several hexatriene-radical-cation ‘rotamers’ ($\lambda_{\max} = 670; 655; 643$ nm [16]). Furthermore, its position matches closely the ionization-energy difference between the onset of the first and second PE band (~ 1.95 eV, see below). The second intense band is known to be more strongly affected by conformational changes in polyene cations [16] [17], and the +58 nm shift relative to that of (all-*E*)-hexatriene radical cation is in line with similar shifts for some of the (*Z*)-configured ‘rotamers’ of this open-chain cation. Apparently, the bridging CH_2 group does not affect the *relative* energies of the electronic states, whereas their *absolute* energies are lowered by about 0.4 eV (see below).

*Photoelectron (PE) Spectra of **1** and **6**.* Fig. 2 shows the PE spectra of **6** at room temperature (top trace) and after pyrolysis at 200°C (lower two traces). Between 100 and 150°C the spectrum undergoes a complete change without the appearance of any inter-

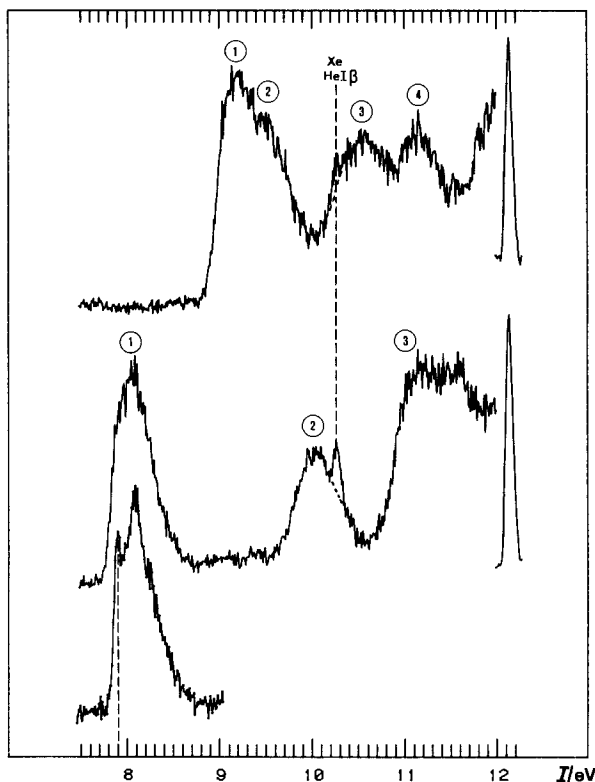


Fig. 2. PE spectrum of **6** at room temperature (top trace) and after pyrolysis at 200°C (giving **1**, see text). The bottom trace shows the first PE-band of **1** at higher resolution.

mediate bands. Based on previous experience with **6** [11][12] and on the discussion given below, we assign this spectrum to **1**. The bottom trace shows a scan of the first band of **1** at higher resolution (fwhm = 45 meV) using variable preretardation of the photoelectrons passing subsequently at constant energy (3.8 eV) through the analyzer [18]. This allows to discern some vibrational structure and the thermochemically important assignment of the adiabatic ionization energy of **1**. The Table sums up the positions of the observed peaks and compares them to MNDO orbital energies.

The PE spectrum of **1** in the illustrated energy region can be discussed on the basis of the principles pertaining to linear conjugated polyenes outlined recently in [10]. Thus, the first band is due to ionization from the triene π -HOMO whereas the second, noticeably less intense band is due to a π -excited state which must be described as the negative combination of ionization from the second π -orbital and HOMO-LUMO (π - π^*) excitation. The band system originating at 10.7 eV comprises the positive counterpart of the first excited state which gives rise to the intense 430 nm absorption on the EA spectrum of **1**⁺ (see above) and should therefore occur 2.88 eV above the ionic ground state, i.e. at 10.8 eV. Due to its predominant non-Koopmans' nature it will, however, only give rise to a weak feature in the PE spectrum which is in accord with observations. Furthermore, ionization from the lowest π -orbital (mixed with higher excitations into virtual π -orbitals

Table. Observed Ionization Energies and MNDO Orbital Energies for **1** and **6**

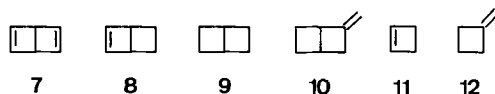
Compound	Band i	I_i (exp)/eV	$-\varepsilon_i$ (MNDO)/eV	Orbital Character ^{a)}
1	①	8.1 (7.9) ^{b)}	8.17	95% π_3 – 5%CH ₂
	②	10.05	10.23	π_2
	③	11.1	11.28	87% π_1 – 13%CH ₂
6	①	9.2	9.47	85% $\pi_{2,3}$ – 4% $\pi_{5,7}$
	②	9.5	9.64	85% $\pi_{5,7}$ + 4% $\pi_{2,3}$
	③	10.55	11.02	55% $\sigma_{1,4}$
	④	11.15	11.62	σ_{C-C} mixed

^{a)} The single-digit π -subscripts for **1** refer to the usual hexatriene π -MO numbering. The double-digit π -subscripts for **6** designate C–C bonds on which the corresponding π -bonding basis orbitals are localized (for atom numbering, see structural formula).

^{b)} The value in parentheses refers to the adiabatic ionization energy.

[10]) occurs in this range (at 11.28 eV according to MNDO) and finally, σ (C–C) orbitals of the ring also start to contribute above 11 eV.

An unambiguous assignment of the PE spectrum of **6** is less straightforward. For assistance, we make use of reference compounds **7–12** listed below:



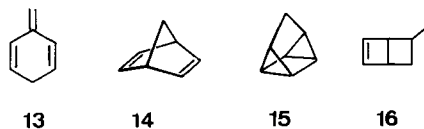
The first band system certainly comprises ionizations from orbitals associated with the C(2)–C(3) and the exocyclic π -bonds. The example of *Dewar* benzene **7** shows that the splitting of the two ionic states described by singly occupied π -orbitals in a bicyclo[2.2.0]hexane frame is very small [19], a feature which will also prevail in **6**⁺. Furthermore, symmetry in the latter case does not require any mixing on the level of canonical orbitals between the two π -orbitals. In fact the two highest occupied MNDO orbitals of **1** are localized to more than 85% in one of the two π -bonds with less than 4% admixture from the other. Thus, we expect two ionizations to occur near I_1 (**8**) and I_1 (**10**). While the PE spectrum of **8** is published ($I_1 = 9.4$ eV [19]), that of compound **10** [11] [12] is unknown. However, the close agreement between I_1 (**8**) and I_1 of related cyclobutene **11** (9.43 eV [20]) allows us to infer that methylenecyclobutane **12** ($I_1 = 9.19$ eV [20]) is a valid reference compound. Thus, we expect two ionizations to occur around 9.2 (exocyclic double bond) and 9.4 eV (endocyclic double bond), in excellent agreement with the observed spectrum. Note from the *Table* that MNDO predicts an inverse ordering of states which we can trace back to the fact that MNDO overestimates I_1 of **12** (calculated: 9.90 eV) more than I_1 of **11** (calculated: 9.77 eV).

Band ③ at 10.55 eV can be assigned to ionization from an orbital localized predominantly in the weak central C–C σ -bond. Indeed, MNDO predicts orbitals of this character (> 55% σ (C–C)) to occur in **6** (–11.02 eV), **7** ($7a_1$; –11.43 eV), **8** ($12a'$; –11.14 eV), and **9** ($8a_1$; –11.02 eV). According to the assignment of the PE spectra of **7–9** on the basis of SPINDO calculations given in [19], it is in all cases the *third* ionization which occurs from the central σ (C–C) orbital.

Thermochemistry of 1⁺. – Comparison with Other C₇H₈⁺ Isomers. In order to properly assess the role of **1**⁺ in the interconversion of other C₇H₈⁺ isomers, it is of crucial

importance to know its thermodynamic stability relative to those related ions. There have been two recent attempts at establishing $\Delta H_f^\ominus(\mathbf{1}^+)$: One made use of gas-phase deprotonation to bracket $\Delta H_f^\ominus(\mathbf{1})$ at 96 ± 12 kJ/mol above that of toluene (assuming that a common ion was formed from both isomers in the process), i.e. $\Delta H_f^\ominus(\mathbf{1}) = 146 \pm 12$ kJ/mol [8]. This value can be compared with the estimate obtained from *Benson's* group increment scheme [21] ($\Delta H_f^\ominus(\mathbf{1}) = 166.5$ kJ/mol) which in this case would be expected to give a reliable estimate because $\mathbf{1}$ is nearly strain free (see below), and all necessary group increments are based on firmly established experimental data. Furthermore, calculations using a version of the MM2 force field program [22] whose parameters were modified for conjugated polyenes [23] yielded $\Delta H_f^\ominus(\mathbf{1}) = 172.0$ kJ/mol. Compared to the above strain-free group-increment value this implies a 5.5 kJ/mol strain energy for $\mathbf{1}$. Therefore, the value for $\Delta H_f^\ominus(\mathbf{1})$ obtained in [8] is probably too low by some 25 kJ/mol.

To arrive at $\Delta H_f^\ominus(\mathbf{1}^+)$, we now have to add the adiabatic ionization energy ($I_{a,1}$) of $\mathbf{1}$. This quantity was indirectly estimated to be 8.6 ± 0.1 eV from the appearance potential of tautomeric 3-methylene-1,4-cyclohexadiene ($\mathbf{13}$) and the MNDO prediction of $I_1(\mathbf{1}) = I_1(\mathbf{13}) = 8.67$ eV. Since our own MNDO calculations gave $I_1(\mathbf{1}) = 8.17$ eV (see the *Table*), we repeated the calculations on $\mathbf{13}$ (with two different program packages to exclude accidental errors in the software) and found $I_1(\mathbf{13}) = 8.67$ eV as quoted in [8]. The two ionization energies are therefore *not* equal (as opposed to the heats of formation which are both 152.1 kJ/mol by MNDO, in reasonable accord with $\Delta H_f^\ominus(\mathbf{13} \rightarrow \mathbf{1}) = -4.0$ kJ/mol predicted by MM2). Actually, $I_1(\mathbf{1})$ according to MNDO agrees very well with the measured *vertical* ionization energy of $\mathbf{1}$ (8.1 eV) but the quantity to be employed in assessing the ionic heat of formation is $I_{a,1} = 7.9$ eV which adds to $\Delta H_f^\ominus(\mathbf{1}) = 172.0$ kJ/mol to give $\Delta H_f^\ominus(\mathbf{1}^+) = 934.3$ kJ/mol.



The second attempt was aimed directly at $\Delta H_f^\ominus(\mathbf{1}^+)$ by means of the appearance potential of $C_7H_8^+$ resulting from $\mathbf{4}$ or $\mathbf{5}$ [7] (see *Scheme 1*). The absence of evidence for kinetic shifts and/or barriers allowed a direct calculation of $\Delta H_f^\ominus(\mathbf{1}^+) = 959.0 \pm 1.0$ kJ/mol using the well-established heats of formation of the precursors and neutral cofragments. Combined with the electron affinity of $\mathbf{1}^+$ ($I_{a,1}(\mathbf{1}) = 7.9$ eV according to our PE spectrum), this value would give $\Delta H_f^\ominus(\mathbf{1}) = 196.6$ kJ/mol or about 25 kJ/mol more than the above MM2 value. We can offer no explanation for this discrepancy which is beyond the error range of MM2 or the *Benson* scheme for such compounds but maintain our preference for $\Delta H_f^\ominus(\mathbf{1}) = 172.0$ kJ/mol and $\Delta H_f^\ominus(\mathbf{1}^+) = 934.3$ kJ/mol.

This new value can now be used to examine the relative thermodynamic stability of the $C_7H_8^+$ isomers. $\Delta H_f^\ominus(\mathbf{2}^+) = 900.0$ kJ/mol can be calculated very reliably from the enthalpy of formation of $\mathbf{2}$ [24] and from $I_{a,1} = 8.81$ eV [25]. On the other hand, $\Delta H_f^\ominus(\mathbf{3}^+)$ is more difficult to assess. Due to the strong relaxation of the vertically formed ion $\mathbf{3}^+$, $I_{a,1}$ cannot easily be determined by spectroscopic means. *Traeger* and *McLoughlin* have established an upper limit of 8.29 eV by variable energy photoionization and they also give a value of 8.03 eV as obtained from a PE spectrum [26]. Combining these values with

the enthalpy of formation of the neutral (183.7 kJ/mol [24]), one arrives at $\Delta H_f^\ominus(3^+) \leq 983$ or $= 958$ kJ/mol, respectively. Both values lie significantly higher than ΔH_f^\ominus of 1^+ which is, therefore, certainly accessible in the course of the $2^+ \rightarrow 3^+$ interconversion. Of the other investigated C_7H_8 cations, those of norbornadiene **14** ($\Delta H_f^\ominus(14^+) \leq 1046$ kJ/mol from $\Delta H_f^\ominus(14) = 240.2$ kJ/mol [27] and $I_{a,1}(14) \leq 8.35$ eV [26]) or quadricyclane **15** ($\Delta H_f^\ominus(15^+) \geq 1084$ kJ/mol from $\Delta H_f^\ominus(14^+ \rightarrow 15) = -37.4$ kJ/mol¹⁾) lie considerably higher in energy. ΔH_f^\ominus of the even more unstable isomer 6^+ can be obtained as follows: from the *Benson*-group increments, we can calculate the enthalpy of formation of a strain-free reference compound $\Delta H_f^\ominus(6, \text{strain-free}) = 111.0$ kJ/mol²⁾. To this, we have to add the strain energy $E_s(6)$ which can be equalled to that of related **16**³⁾ plus the difference in strain energies of **12** and similarly related methylcyclobutane (**17**) which we take to be zero⁴⁾. This leads to $\Delta H_f^\ominus(6) = 356.8$ kJ/mol⁵⁾, to which we add $I_{a,1}(6) = 9.0$ eV from the PE spectrum to finally arrive at $\Delta H_f^\ominus(6^+) = 1225.0$ kJ/mol. Hence, the reaction $6^+ \rightarrow 1^+$ is exothermic by almost 300 kJ/mol! Considering the fact that even slightly exothermic electrocyclic ring openings occur with very small activation barriers in radical cations as compared to neutrals [31], this can serve as a rationale for our failure to detect 6^+ .

Finally, we wish to compare the thermochemical data obtained above with the corresponding figures predicted by MNDO/UHF as presented in *Fig. 3*. MNDO gives $\Delta H_f^\ominus(2^+) = 891.0$ kJ/mol, a slight improvement over MINDO/3 (887.8 kJ/mol [3]). 1^+ is less than half as much destabilized relative to 2^+ than in MINDO/3 [3] and lies now even closer in energy to the latter than we propose on the basis of the available experimental evidence. As for 3^+ , the obviously wrong MINDO/3 prediction (3^+ being 23.4 kJ/mol *more* stable than 2^+ [3]) is corrected by MNDO to stand in better accord with experiment although the stability of 3^+ is still overestimated by ≥ 42 kJ/mol. This may be partly due to the fact that contamination with higher spin states in the UHF wave-function is more pronounced in 3^+ ($\langle S^2 \rangle = 1.02$) than in any of the other calculated $C_7H_8^+$ isomers ($\langle S^2 \rangle = 0.75 \pm 0.05$), which may account for some extra stabilization⁶⁾. The exothermicity of the reaction $6^+ \rightarrow 1^+$ is about 42 kJ/mol less in MNDO than on the basis of the estimate given above but the tendency of MNDO to severely overestimate the stability of four-membered ring compounds [33] can easily account for this. Finally, the relative stability of **14**⁺ *vs.* **15**⁺ is in accord with available experimental [28] and theoretical [34]

¹⁾ Value quoted in [28] corrected for the recent reassessment of $\Delta H_f^\ominus(14)$ [27].

²⁾ To obtain this figure, we need the unlisted fragment $C(C_d)_2(C)(H)$ whose energy we derive from that of $C(C_d)(C)_2(H) = -6.19$ kJ/mol plus the difference between $C(C_d)(C)(H)_2 = -19.92$ kJ/mol and $C(C_d)_2(H)_2 = -17.95$ kJ/mol which gives -4.22 kJ/mol for the needed fragment.

³⁾ $\Delta H_f^\ominus(16) = 234$ kJ/mol (derived from the measured enthalpy of hydrogenation of **16** to methylcyclohexane, $\Delta H_{H_2} = -388.7 \pm 0.8$ kJ/mol, [12]) minus ΔH_f^\ominus of strain-free **16** according to *Benson* (-11.8 kJ/mol) gives $E_s(16) = 245.8$ kJ/mol.

⁴⁾ $\Delta H_f^\ominus(12) = 121.5$ kJ/mol [29] minus ΔH_f^\ominus of strain-free **12** according to *Benson* (9.0 kJ/mol) gives $E_s(12) = 112.5$ kJ/mol. $E_s(17)$ cannot be evaluated similarly due to the lack of reliable experimental data for this compound. We, therefore, take the value of 113 kJ/mol obtained by *Schleyer et al.* from force-field calculations [30] which is almost identical to the above $E_s(12)$.

⁵⁾ This value is in good accord with $\Delta H_f^\ominus(6) = 368$ kJ/mol derived from the approximate enthalpy of hydrogenation of **6** to methylcyclohexane ($\Delta H_{H_2} \cong -525$ kJ/mol [12]).

⁶⁾ In fact, RHF calculations (using the half-electron method [32]) at the UHF-optimized geometries gave $\Delta H_f^\ominus(1^+) - \Delta H_f^\ominus(2^+) = 22.3$ kJ/mol as opposed to 12.3 kJ/mol in UHF (the absolute energies of all $C_7H_8^+$ isomers are some 17 kJ/mol lower in UHF than in RHF, a typical value for systems of this size). Hence, the extra stabilization of 2^+ due to admixture of higher spin states in UHF amounts to about 10 kJ/mol.

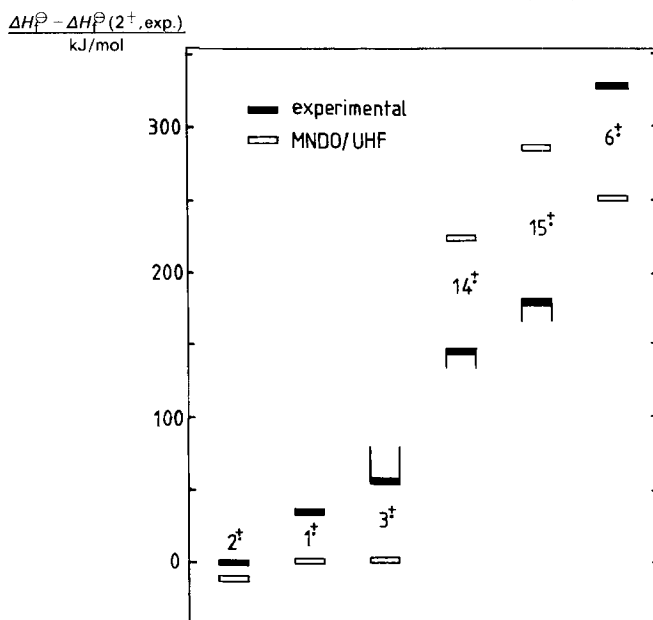


Fig. 3. Relative enthalpies of formation in kJ/mol of different $C_7H_8^+$ isomers as obtained on the basis of experimental data (see text) and calculated by MNDO/UHF

evidence (as opposed to MINDO/3 which had predicted 15^+ to be more stable than 14^+ ! [28]) although the absolute energies are still off by > 80 kJ/mol. Note, however, that $\Delta H_f^\ominus(15^+)$ may be rather meaningless because 15^+ does not represent a minimum but only a slightly inclined terrace on the MNDO- $C_7H_8^+$ hypersurface. Upon complete geometry optimization, 15^+ undergoes spontaneous distortion away from C_{2v} symmetry and moves eventually towards 14^+ . The open bar in Fig. 3 represents the enthalpy of formation of a geometry-optimized within C_{2v} symmetry.

Conclusions. – Compound 1^+ represents a stable minimum on the $C_7H_8^+$ hypersurface. Earlier assignments of PD spectra [5] or optical spectra [9] to this species were correct and, hence, its implied thermal or photochemical formation in various processes is now definitively established. Although 1^+ can be formed photochemically from almost any $C_7H_8^+$ precursor [9], it is most probably *not* the most stable such isomer. By reassessing its enthalpy of formation we have, however, shown that its thermodynamic stability is much closer to that of 2^+ than concluded on the basis of previous experiments [7] [8]. Semiempirical calculations have proven to be of little help in predicting the relative stabilities of various $C_7H_8^+$ isomers although the recently introduced MNDO method shows some definitive improvements.

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Experimental. *Syntheses.* Compound **6** was synthesized according to the procedure in [11] [12]. The final hydrocarbon mixture was separated by prep. GC on β,β' -oxydipropionitrile (ODP) at r.t. Samples of **6** obtained in this way contained less than 1% impurities according to 270-MHz $^1\text{H-NMR}$.

Preparation of Ions and Electronic Absorption Spectroscopy. The techniques for preparing matrix-isolated radical cations described in [10] were followed. Spectra were recorded on a *Perkin-Elmer Lambda 9 UV/VIS/NIR* instrument and worked up digitally. Background spectra taken prior to X-ray irradiation were subtracted from the ionic spectra to compensate for sample scattering and neutral absorption (in the case of **1**). After ionization, the sample was first illuminated at 340 nm (8 nm fwhm) until all absorptions due to CH_2Cl_2 cations had vanished. After that, even prolonged photolysis outside the range of 380–430 nm had no effect on the absorptions ascribed to $\mathbf{1}^+$ whereas bleaching in the latter region led to the concerted disappearance of all bands visible in *Fig. 1* except the few wiggles around 400 nm.

PE Spectra. PE spectra were recorded on a modified *PE 16* instrument [18] equipped with a heatable inlet system [35]. Spectra were calibrated using the Xe(He I β) line at 10.26 eV. Resolution was 80 meV at 12.13 eV (Xe, He I α) and probably above 100 meV at 8 eV. In the preretardation run (lowest trace of *Fig. 2*), resolution was at 45 meV throughout the spectrum. Pyrolysis temps. were deduced from the heating current using a calibration curve established earlier.

Calculations. MNDO [36] calculations were done with a version of the MOPAC program package [37] for *IBM* computers. In case of **13**, where some disagreement with previously published results occurred, calculations were repeated using the MNDOC series of programs [38] without invoking the correlation treatment and identical results were obtained. All reported figures refer to fully optimized geometries whose corresponding potential minima were identified as such by diagonalization of the force constant matrix. Radical ions were calculated with the UHF procedure unless noted otherwise. Although we would have liked to present some information on reaction paths and activation energies, this was impossible because in spite of claims to the contrary, the 'SADDLE' option provided in our version of MOPAC does not permit location of transition states except in the most trivial of cases. More detailed calculations on the C_7H_8^+ hypersurface will be presented once this problem has been solved.

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