64. Tris(methylidene)-cyclopropane ("[3]Radialene") Part 1. Enthalpy of Formation and Strain Energy

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Dedicated to Prof. *C.A. Grob* on the occasion of his sixtieth birthday

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Summary

The enthalpy of formation of *tris*(methylidene)-cyclopropane ("[3]radialene", **1**) has been determined as $\Delta H_f^0 = 396 \pm 12$ kJ mol^{-1} from three fragmentation reactions of its molecular ion $\mathbf{1}^+$ formed from **1** by photoionisation using synchrotron radiation. Comparative electron impact measurements using conventional mass spectrometry were also performed. A treatment of the latter data is described which leads to satisfactory agreement with the photoionization data. The experimental value of $\Delta H_f^0(\mathbf{1})$ is compared with various theoretical estimates. The strain energy of **1** is calculated to be 226.3 kJ mol^{-1}. Linear extrapolation of this quantity from the increase of strain in passing from cyclopropane to methylidenecyclopropane yields 282.4 kJ mol^{-1}. The discrepancy between these values, already predicted by *Dewar* and *Baird* ten years ago from theoretical calculations, is discussed on the basis of maximum overlap considerations. The enthalpy of formation of *bis*(methylidene)cyclopropane is predicted to be $\Delta H_f^0 = 309$ kJ mol^{-1}.

Introduction. - There are two distinct ways in which N double bonds can be arranged in a regular cyclic fashion. While the compounds representing one of these classes - the [*n*]*annulenes* (n = 2 N) - have received wide attention both from experimentalists and theoreticians, the high reactivity of the other class - the [*n*]*radialenes* (n = N) - has prevented comparable experimental efforts. Even though highly sophisticated techniques of gas phase synthesis have become available, only the members with n = 3 and n = 4 have been isolated and subjected to some

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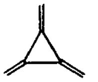
spectroscopic studies so far [1-3]. Recently [6]radialene has been postulated as an intermediate during the formation of *tris*-cyclobutenobenzene [4]. On the other hand these systems have been the object of several theoretical papers dealing with electronic structure [5], resonance- [6-9] and strain-energy [10] [11].

On various occasions [10] [12] it has been pointed out that a knowledge of the enthalpy of formation (ΔH_f^0) of the [n]radialenes would be highly desirable. Since radialenes are very sensitive to polymerization, and contact with oxygen must be carefully avoided (see experimental part), these compounds cannot be subjected to the usual calorimetric techniques. In the course of our studies on the properties of [3]radialene radical cation **1**$^+$ [13], we found that we could take advantage of some dissociation processes exhibited by **1**$^+$ to encircle the desired value ΔH_f^0(**1**). We therefore determined the appearance potentials for various fragment ions using photon or electron impact (PI and EI, respectively) on **1**.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Technique and Results. - The PI data were obtained using the experimental set-up at the DESY (*Deutsches Elektronen-Synchrotron*, Hamburg), where synchrotron radiation provides the continuous photon source. A detailed description of the apparatus and the procedures has been given previously [14]. The sample of **1** was led directly into the ionisation chamber *via* a regulating inlet valve from a glass vessel held at – 60 °C.

The following four processes were studied:

	X^+	AP(X^+) [eV] PI	EI
$1 \xrightarrow{A}$	$C_6H_5^+ + H$	10.36±0.05	10.6±0.2
$1 \xrightarrow{B}$	$C_3H_3^+ + C_3H_3$	10.60±0.05	10.6±0.1
$1 \xrightarrow{C}$	$C_4H_4^+ + C_2H_2$	10.71±0.05	10.6±0.1
$1 \xrightarrow{D}$	$C_2H_2^+ + C_4H_4$	15.26±0.05	11.6±0.2

The associated experimental threshold curves leading to the four PI-AP-values are shown in *Fig. 1.*

Although AP data obtained by PI are considered the most reliable ones, such measurements are not readily available. We therefore undertook a comparative study using conventional mass spectrometry where molecular and fragment ions are generated by electron impact (EI). The main experimental drawback of this method, apart from the less favourable threshold behaviour, lies in the temperature broadened energy distribution of the electrons obtained by thermal emission. In addition, potentials drop across an electrically heated filament, as well as surface potentials in the ion source often distort this energy distribution. Empirical methods for the evaluation of AP data from EI ionization-efficiency (IE) curves usually do not give very reliable results [15]. To account for the electron energy distribution, mathematical deconvolution procedures have been used in a few cases [16-18], but they need highly noise-free IE curves [18].

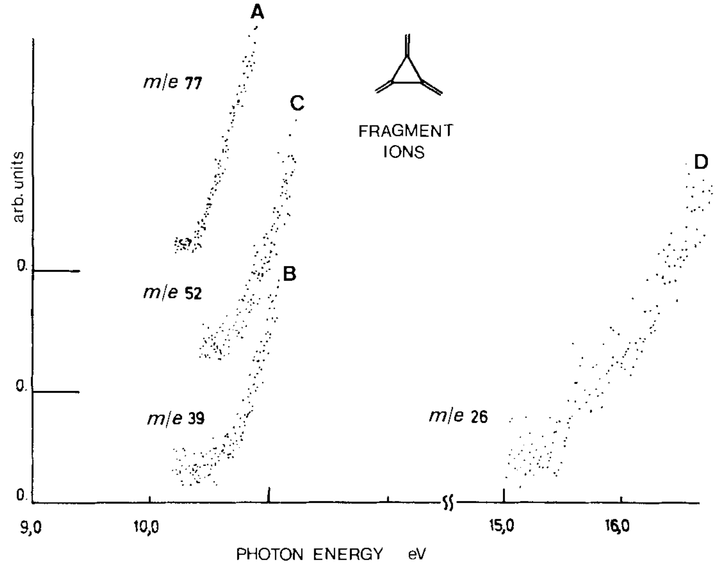


Fig. 1. *Ion efficiency curves for processes A, B, C and D from photoionization of* **1** *using synchrotron radiation* (see text)

The EI data of this study were based on the second derivative of the experimental IE curves, which, in principle, is very similar to a deconvolution with the actual apparatus function. If the ionization cross section is linearly dependent on the excess energy above the threshold, the second derivative of the IE curve directly reflects the (energetically reversed) electron distribution [16]. The actual AP of an ion is obtained by fitting the second derivatives of the IE curves of the substrate and of a reference. The resulting difference in energy scales is taken as the difference in AP's.

Figure 2 shows the experimental IE curves from EI, their second derivatives and the best fit with the electron-distribution curve as obtained by fitting a modified *Maxwell* function with the second derivative of the IE curve of He^+. Comparison of the AP values (shown in the scheme above) with those from PI reveals agreement within ±0.2 eV for the processes A, B and C. This indicates that for both methods we are probably dealing with the same mechanisms of fragmentation. Furthermore, the AP's are presumably near the threshold as in these energy regions (and below) states of $\mathbf{1}^+$ are *Franck-Condon* accessible on photoionization. This is revealed by the He(Iα)-photoelectron spectrum of **1** [13], which shows a continuous sequence of populated states of $\mathbf{1}^+$ from 8.8 to 12 eV.

There is, however, a considerable discrepancy (3.66 eV) between the two values for process D. The IE curve for this reaction exhibits a small slope above 11.6 eV with a sharp increase above 15.2 eV (the PI-AP). We attribute the ions produced below 15.2 eV to either a process not accessible by PI or to an impurity in the sample gas. Alternatively, the PI curve for this process being quite noisy below the assigned AP, a low intensity ion production at lower energies would

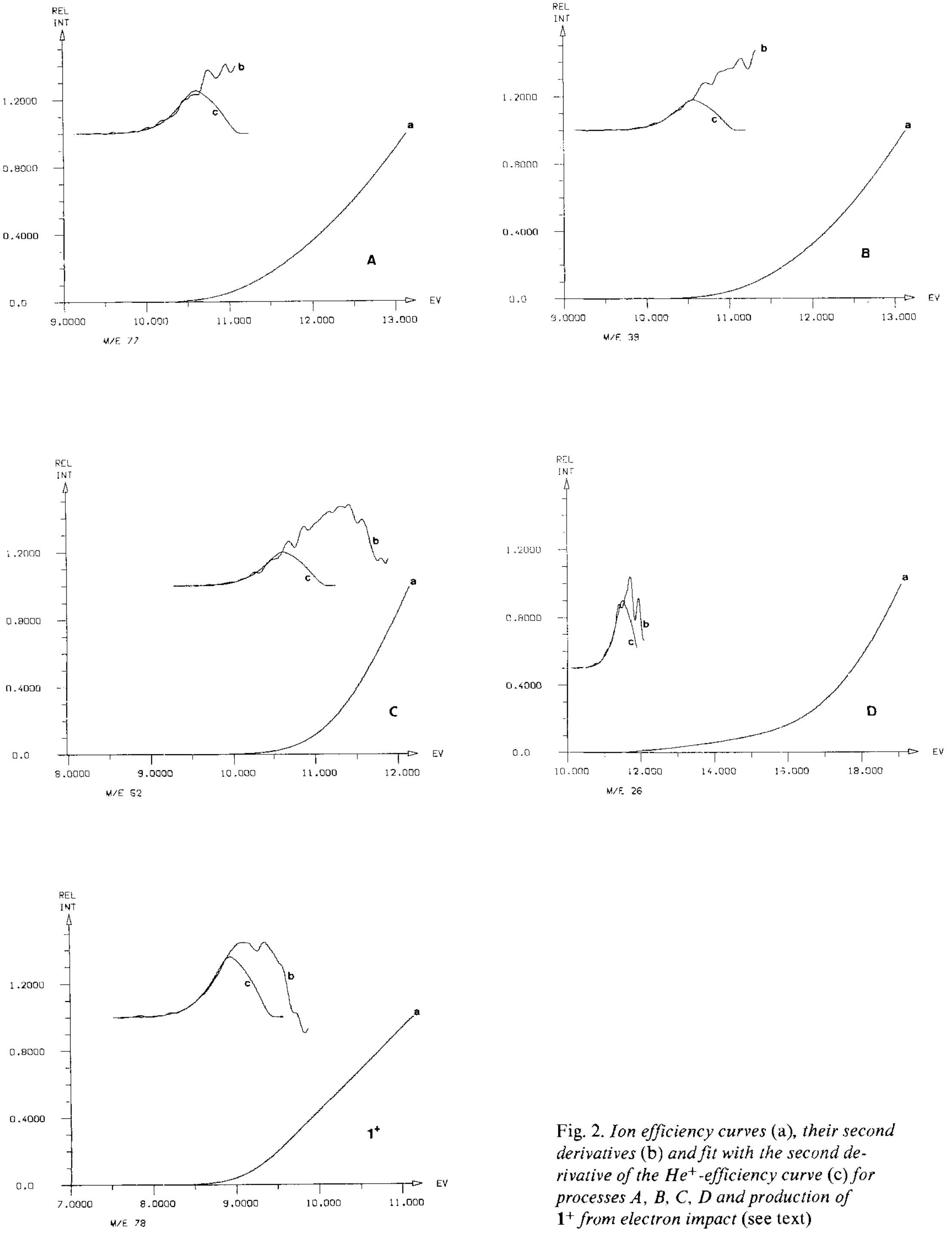


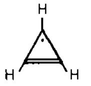
Fig. 2. *Ion efficiency curves* (a), *their second derivatives* (b) *and fit with the second derivative of the He$^+$-efficiency curve* (c) *for processes A, B, C, D and production of* **1**$^+$ *from electron impact* (see text)

perhaps not have been detected. In view of these questions we shall disregard process D in the evaluation of ΔH_f^0 (**1**)[4].

Discussion. - *Elaboration of ΔH_f^0*(**1**). The ensuing discussion makes use of the inherently more accurate AP values from PI. For processes A-C the following points are pertinent:

Ad A. - *Borchers & Levsen* [21] have shown that $C_6H_5^+$-fragments originating from various types of precursors (benzene derivatives and open chain hydrocarbons) show nearly identical collisional activation spectra and hence are likely to have a common structure. *Rosenstock* arrived at the same conclusion, since the enthalpies of formation of $C_6H_5^+$-fragments generated from different C_6H_6-isomers turned out to be nearly equal regardless of the structure of the precursor [22]. Although the structure of this ubiquitous species is not clearly decided we can see no reason why $\mathbf{1}^+$ should yield a different $C_6H_5^+$-fragment, being also a $C_6H_6^+$-isomer. We therefore assume $\Delta H_f^0(C_6H_5^+) = 1180$ kJ mol^{-1} as proposed in [22]. With $\Delta H_f^0(H) = 217.9$ kJ mol^{-1} [23] we arrive at $\Delta H_f^0(\mathbf{1}) = 398.3$ kJ mol^{-1}.

Ad B. - Although it is difficult to imagine what kind of process would yield cyclic $C_3H_3^+$ ($\mathbf{2}^+$) from $\mathbf{1}^+$, the fact that this structure represents by far the most stable species on its hypersurface [24] [25] leads us to assume that cyclopropenium cation $\mathbf{2}^+$ is formed during fragmentation B. $\Delta H_f^0(\mathbf{2}^+)$ has been determined as 1071.6 kJ mol^{-1} [25]. Turning now to the neutral C_3H_3-fragment, $\Delta H_f^0 = 343.3$ kJ mol^{-1} for the propargyl radical **3** has recently been established [26]. Another isomer of this formula is cyclopropenyl radical **2**, for which unfortunately no reliable value is reported. We are, however, able to provide a lower bound for ΔH_f^0(**2**). The C−H bond-dissociation energy (BDE) of a methylene C−H bond in cyclopropene (neglecting for the moment any special stabilizing effects operating in **2**) is clearly larger than BDE (C−H) for an alkane due to the higher s-character of the C-hybrids in the cyclic system. For the latter quantity we take BDE $= \Delta H^0 = 392.2$ kJ mol^{-1} from $C_3H_8 \rightarrow CH(CH_3)_2 + H$ [27]. *Baird* has conclusively shown [28] that the conjugative interaction between the double bond and the unpaired electron in **2** (minimum energy symmetry C_s) amounts to about 28 kJ mol^{-1}. Combining these arguments we arrive at:



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$HC{\equiv}C{-}\dot{C}H_2$

3

$$\Delta H_f^0(\mathbf{2}) \geqslant \Delta H_f^0(\text{cyclopropene}) + (392.2 - 28) - \Delta H_f^0(H)$$
$$\geqslant 421.6 \text{ kJ mol}^{-1}.$$

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[4] Analysis of process D suggests that it cannot be discussed in a straightforward manner. In a forthcoming paper [19] we shall deal in detail with the question of the structure of the $C_2H_2^+$-fragment encountered there and generated also from other sources. This fragment probably does not have an acetylenic structure but may correspond to vinylidene cation. Using calculated values for $\Delta H_f^0(:C{=}CH_2)$ and $I(:C{=}CH_2)$ [20], together with AP(D) = 15.26 eV from PI yields an estimate for $\Delta H_f^0(\mathbf{1})$ which is not in contradiction to that elaborated presently on the basis of processes A−C.

Hence the open chain species **3** is at least 78.3 kJ mol^{-1} more stable than **2**. On the basis of C_3H_3=**3** we arrive at ΔH_f^0 (**1**)=392.1 kJ mol^{-1} which is in satisfactory agreement with the corresponding value from A.

Ad C. - There are again two candidates of comparable energy for the charged fragment $C_4H_4^+$, **4**$^+$ and **5**$^+$. Their enthalpies of formation can be obtained from ΔH_f^0 of the uncharged species (ΔH_f^0 (**4**)=322 kJ mol^{-1} [29], ΔH_f^0 (**5**)=304.5 kJ mol^{-1} [30]) and the respective ionization energies (I_a(**4**)=9.15 eV [31], I_a(**5**)=9.58 eV [32]), which sum up to 1205 kJ mol^{-1} for **4**$^+$ and 1228.9 kJ mol^{-1} for

$$H_2C{=}C{=}C{=}CH_2 \qquad HC{\equiv}C{-}CH{=}CH_2$$

4 **5**

5$^+$, hence **4**$^+$ being favoured on energetic grounds. In addition it is obtained directly (*i.e.* without rearrangement) by breaking two endocyclic C–C-bonds in **1**$^+$. On the other hand the uncharged C_2H_2-fragment is likely to rearrange to the energetically favoured acetylenic structure [19]. With ΔH_f^0(acetylene)=227.1 kJ mol^{-1} [30] and ΔH_f^0 (**4**$^+$)=1205.1 kJ mol^{-1} we end up with ΔH_f^0 (**1**)=398.8 kJ mol^{-1} supporting the values derived from A and B.

When discussing the reliability of the three estimates for ΔH_f^0(**1**) obtained above one has to keep in mind that the measured AP's in principle could well be distorted by considerable amounts of excess energy stored in various degrees of freedom of the products. The near equality of the three estimates, however, would imply that these contributions were equal for A, B and C, a coincidence which seems unlikely. We therefore propose ΔH_f^0(**1**)=396 kJ mol^{-1}. The errors quoted for ΔH_f^0 of some of the fragments imply that the above figure is correct within ± 12 kJ mol^{-1}.

*Comparison with theoretically calculated values for ΔH_f^0(**1**).* Below we list the available theoretical estimates for ΔH_f^0 (**1**) in kJ mol^{-1}.

exp.	*ab-initio* [33]	PNDO [10]	MINDO/1 [34]	MINDO/2 [35]	MINDO/3 [36]	MOA [37]
396±12	974.6	390.3	328.4	304.5	347.6	412.4

One immediately notes that the *ab-initio* value (obtained from a simple *Hartree-Fock* calculation using a floating spherical *Gaussian* basis set) is very much off from the observed one and reflects once more the tendency of correlation errors to increase with decreasing ring size. The same calculation predicts *Dewar*-benzene to be less stable than **1** by 602 kJ mol^{-1}. Thermal rearrangement of the former to benzene liberates some 251 kJ mol^{-1} [38] which places ΔH_f^0(*Dewar*-benzene) at about 335 kJ mol^{-1}. Hence *Dewar*-benzene is significantly more stable than **1**.

The PNDO procedure [39] was the first semiempirical all-valence SCF method aiming at theoretical estimates for enthalpies of formation of "chemical accuracy". Unfortunately, the method gave unreasonable molecular geometries upon minimization of the total energy and was therefore abandoned. The calculations were actually performed using a set of standard bond lengths and bond angles. Apart from this limitation the method's prediction of strain energies was on the average superior to those obtained from its successors such as MINDO/i (i = 1 [34], 2 [40], 3 [41]) or even the recently presented MNDO method [42]. The present example provides further support to this conclusion. While PNDO predicts ΔH_f^0(**1**) within the experimental error limits, MINDO/1, MINDO/2 and MINDO/3 are off by some 67.6, 91.5 or 48.4 kJ mol^{-1} resp., reflecting again their notorious underestimation of *I*-strain.

The "Maximum Overlap Approach" (MOA) [43] has recently been shown to yield good estimates of total energies [44] [46] as well as strain energies [45] [47] if properly parametrized. At first sight there is indeed almost perfect agreement between the experimental and the theoretical MOA-value for ΔH_f^0(**1**). Since, however, the method at its present stage of development does not include π-delocalization energies the predicted value has to be considered as an upper bound. *Dewar* has conclusively demonstrated that the extent of π-bonding across single bonds in classical polyenes is essentially constant [6]. Moreover he found [6] [7] that the polyenic bond increments are also applicable to the radialenes, a conclusion supported by the work of *Hess & Schaad* [8] and emerging also from the somewhat more sophisticated approach of *Aihara* [9]. Taking the rotational barrier in *trans*-butadiene as a measure of π-delocalization energy across an essential single bond ($\sim$21 kJ mol^{-1} [48]) the corresponding contribution in **1** amounts to about 63 kJ mol^{-1}. This reduces the MOA value to 349.4 kJ mol^{-1} which is significantly less than the experimental one. As ΔH_f^0 of unstrained conjugated systems (corrected for π-delocalization in the above manner) are rather accurately represented by MOA [46] we conclude that the strain present in **1** is presumably underestimated. We note from [45] that saturated 3-membered rings required special parametrization. As **1** embodies a slightly different bonding situation with respect to overlap (see following section) the parameters found for the saturated systems may not be appropriate to it. This however does not imply that the hybrids and overlaps emerging from MOA calculations are useless in discussing trends. In the following section we shall in fact make heavy use of such data.

The strain energy of **1** (E_s(**1**)). The quantity E_s(**1**) shall be established using the following three different procedures (ΔH_f^0 for the reference molecules are taken from [30]):

1) The homodesmotic bond separation process [49] **1** + 3 $CH_2{=}CH{-}CH_3 \rightarrow 3\ CH_2{=}CH{-}C(CH_3){=}CH_2$ is accompanied by a change in enthalpy of 230 kJ mol^{-1}, a figure which reflects directly E_s(**1**).

2) *Benson*'s group-additivity scheme [50][5] gives $\Delta H_f^0 = 171.7$ kJ mol^{-1} for the hypothetical strain-free reference system, hence $E_s(\mathbf{1}) = 224.3$ kJ mol^{-1}.

3) ΔH_f^0 for the same system using *Baird*'s bond increments [51] is 171.5 kJ mol^{-1} which yields $E_s(\mathbf{1}) = 224.5$ kJ mol^{-1}.

Note that all the above ways of estimation account for the stabilization of **1** due to π-delocalization. Hence $E_s(\mathbf{1}) = 226.3$ kJ mol^{-1} is an appropriate mean estimate

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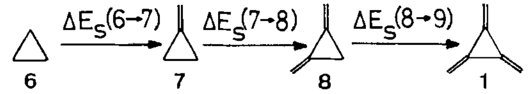
[5] As experimental data for cross-conjugated olefins are lacking we estimated the group contribution of the fragment $C_d(C_d)_2$ by making the reasonable assumption $E[C_d(C_d)_2] = 2\ E[C_d(C_d)(C)] - E[C_d(C)_2] = 31.05$ kJ mol^{-1}.

for the angular strain operating in **1** (non-bonded repulsions are virtually absent in this species).

Ten years ago, *Dewar & Baird* noted [10] that $E_s(\mathbf{1})$ (as calculated using the PNDO procedure) is actually smaller than expected on the basis of the following "chemically reasonable" extrapolation:



$$E_s(\mathbf{1}) = E_s(\mathbf{6}) + 3\,\Delta E_s(\mathbf{6}\rightarrow\mathbf{7}) \tag{1}$$

As $E_s(\mathbf{6}) = 115.5$ kJ mol^{-1} and $E_s(\mathbf{7}) = 171.1$ kJ mol^{-1} [50], equation (1) yields the extrapolated estimate $E_s(\mathbf{1}) = 282.3$ kJ mol^{-1}. This figure is, however, about 56 kJ mol^{-1} higher than our experimental value[6]. Our findings therefore support fully what we might term "*Dewar*'s strain-puzzle".

In the following we shall try to rationalize this peculiar feature on the basis of the hybrids and overlaps obtained from the MOA procedure for the above series of molecules and for some appropriate reference systems. The principal reason for angular strain is that the hybrid orbitals forming the bonds in small rings are unable to follow the internuclear angles if they are forced to stay orthogonal[7]. This results in the formation of "bent bonds" [52] which are characterized by a smaller overlap than the correponding bonds in unstrained systems. Bond overlaps are linearly related to the one-electron core resonance integral *via* the *Mulliken* approximation. As the latter quantity is responsible for chemical bonding [53] one might expect a linear correlation between a sum of properly weighted bond overlaps and the enthalpies of atomization. This indeed has been shown to be the case [54]. *Figure 3* displays the bond overlaps (S_b), the hybridization parameters sp^n and the deviation angles δ for the hybrids forming the single bonds in the presently relevant systems **1**, **6**, **7**, **8** as well as in the unstrained reference systems ethane (**9**)[8], propene (**10**) and butadiene (**11**) as published in [11] (**1**, **6**, **7**, **8**) and [46] (**9**, **10**, **11**).

As pointed out by *Walsh* some time ago [55], increasing polarity of a bond increases its strength. This is the reason why

$$E(C_s - C_d) > \frac{1}{2}\,[E(C_s - C_s) + E(C_d - C_d)] \tag{2}$$

(C_s and C_d designate carbon atoms attached to single or double bonds respectively). This prediction is reflected in the change of S_b for $\mathbf{9}\rightarrow\mathbf{10}\rightarrow\mathbf{11}$, where ΔS_b ($\mathbf{9}\rightarrow\mathbf{10}$) is about twice as large as $\Delta S_b(\mathbf{10}\rightarrow\mathbf{11})$ (0.0395 and 0.0193, respectively). A similar discontinuity can, however, not be found for the series of the strained molecules.

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[6] This discrepancy becomes even more pronounced when it is taken into account that for $\mathbf{6}\rightarrow\mathbf{7}$ four nonbonded eclipsed H–H-interactions are relieved, which are twice as many as for $\mathbf{7}\rightarrow\mathbf{8}$ and $\mathbf{8}\rightarrow\mathbf{1}$ together.

[7] For a discussion concerning the "chemical reasonability" of this constraint see [45].

[8] Since ethane itself is not treated in [46] we have taken the relevant figures from 3-methyl-2-pentene.

Here, the corresponding values $\Delta S_b(\mathbf{6}\rightarrow\mathbf{7})$ and $\Delta S_b(\mathbf{7}\rightarrow\mathbf{8})$ are roughly equal (0.0102 and 0.0119, respectively). Note also that $\Delta S_b(\mathbf{9}\rightarrow\mathbf{10})\approx 4\cdot\Delta S_b(\mathbf{6}\rightarrow\mathbf{7})$. Hence, although $E(C_s-C_d)$ in **7** is larger than in **6** due to enhanced s-character of the bond forming hybrids (as properly noted in [11]) it has increased much less than in the unstrained reference systems (*i.e.* **9**→**10**). This feature reflects the experimental observation that angular strain grows considerably on passing from **6** to **7**. If we consider the difference ΔS between the sum of bond overlaps in the ring (S_{tot}) and the equivalent sum of overlaps for the unstrained reference systems (S_{ref}) as a quantitative measure of strain in the framework of the MOA formalism, we note that this quantity increases by 0.0586 for **6**→**7**, but by only 0.0331 for **7**→**8** and 0.0127 for **8**→**1**. This tendency nicely parallels the one predicted by *Dewar & Baird* and confirmed by our observations.

We found that the above figures may even be used quantitatively. The increase of strain in passing from **6** to **7** is $\Delta E_s(\mathbf{6}\rightarrow\mathbf{7})=55.6$ kJ mol^{-1} [50]. This process involves loss of four eclipsing H-contacts which, in view of the ethane rotational barrier (12.25 kJ mol^{-1}, six eclipsing H-contacts in transition state), liberates ~8 kJ mol^{-1}. Hence, for the increase in pure angular strain (*I*-strain) we obtain $\Delta E_s^I(\mathbf{6}\rightarrow\mathbf{7})=63.6$ kJ mol^{-1} which is associated with $\Delta S(\mathbf{6}\rightarrow\mathbf{7})=0.0586$. This calibration allows us to calculate ΔE_s^I for **6**→**8** and **6**→**1**, (or ΔE_s after accounting

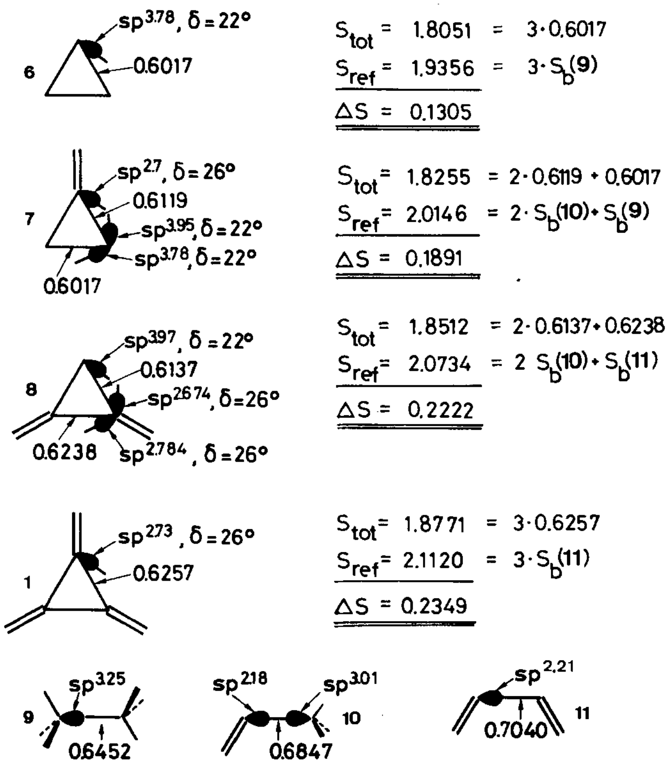


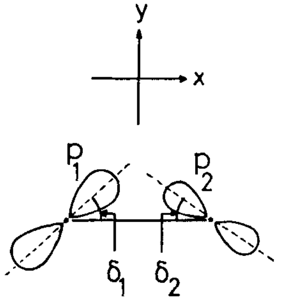
Fig. 3. *Relevant MOA figures for* **1** *and some reference systems*

properly for changes in H-contacts in the above manner). One finally arrives at $E_s(\mathbf{8})=203$ kJ mol^{-1} and $E_s(\mathbf{1})=216.6$ kJ mol^{-1}. As the latter estimate is in fair agreement with the value deduced above, we wish to predict $\Delta H_f^0(\mathbf{8})=309$ kJ mol^{-1} from $E_s(\mathbf{8})$ and the strain free estimate $\Delta H_f^0(\mathbf{8})=106$ kJ mol^{-1} from *Benson*'s group increments [50]. Note the excellent agreement with the PNDO quantum chemical prediction $\Delta H_f^0(\mathbf{8})=302.5$ kJ mol^{-1} [10].

Chemical thinking is heavily based on additivity principles. Additivity of substituent effects on many physical and chemical properties of molecular systems are well established, additivity of bond energies or bond moments holds for a huge number of them. Significant deviations from such schemes indeed initiated creation of new chemical concepts, the most famous among them being the notion of aromaticity.

Although we are able to relate the above discussed breakdown of the reasonable additivity principle (1) to some theoretical figures we are not surprised if this reasoning does not satisfy part of the chemical audience. It is based on numerical calculations and cannot be appreciated using traditional chemical arguments. We admit that we are unable to provide such type of rationalization, but we are at least able to give a straightforward qualitative mathematical explanation:

As pointed out above $[E(C_d-C_s)-E(C_s-C_s)]-[E(C_d-C_d)-E(C_d-C_s)]$ is considerably larger for the unstrained reference systems than for those embodying a three-membered ring. As in both series the bonding hybrids exhibit the same monotonic increase in s-character *(Fig. 3)* this contribution is presumably not decisive for the above feature. For the p-contributions, however, there is a notable difference between the two series. While the single-bond overlaps S_p are of pure p_σ-type in the unstrained species, we must take into account p_σ- and p_π-type overlaps9) (S_p^σ and S_p^π, respectively) in the strained systems where the hybrids deviate from the internuclear axes. Importantly, the ratio S_p^σ/S_p^π varies as the hybrid angles change along the series. Consider now the overlap S_p between two p-AO's (neglecting presently s-contributions) lying off-axis in a strained system (δ_1, δ_2 = deviation angles of AO's).



$S_p^\sigma = \langle p_{1x} | p_{2x} \rangle$
$S_p^\pi = \langle p_{1y} | p_{2y} \rangle$

$$S_p = S_p^\sigma \cdot \cos\delta_1 \cdot \cos\delta_2 + S_p^\pi \cdot \sin\delta_1 \cdot \sin\delta_2 \qquad (3)$$

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9) Note that by p_π-type interaction we do not refer to interference of hybrids above or below the molecular plane, but to those interactions which derive from the in-plane hybrid components perpendicular to the internuclear axes.

Substitution of $\delta+\Delta\delta$ for δ_1 and $\delta-\Delta\delta$ for δ_2 (where $\delta_1-\delta_2=2\Delta\delta$) yields

$$S_p=\cos^2\Delta\delta\,(\sin^2\delta\cdot S_p^\pi+\cos^2\delta\cdot S_p^\sigma)-\sin^2\Delta\delta\,(\sin^2\delta\cdot S_p^\sigma+\cos^2\delta\cdot S_p^\pi)$$

$$\frac{\mathrm{d}S_p}{\mathrm{d}\Delta\delta}=-\sin^2\Delta\delta\,(S_p^\sigma+S_p^\pi),$$
$$\frac{\mathrm{d}^2S_p}{\mathrm{d}\Delta\delta^2}=-\cos 2\Delta\delta\,(S_p^\sigma+S_p^\pi). \tag{4}$$

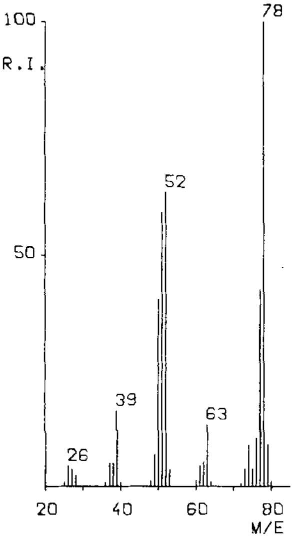
It follows that S_p is maximal for $\Delta\delta=0$, independent of the magnitude of δ itself! Thus, **7** and **8** - due to the nonequivalence of the hybrids forming two of the three ring bonds (*i.e.* $\Delta\delta\neq0$) - experience an "extra" destabilizing contribution to the total energy with respect to reference systems where $\Delta\delta=0$.

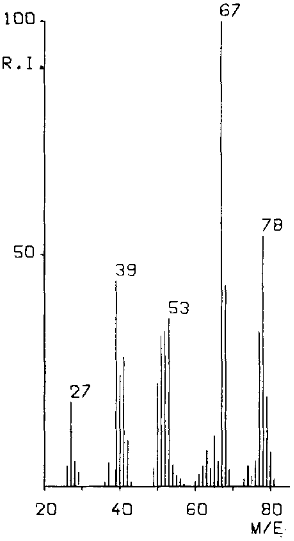
Experimental Part. - Syntheses of **1** were previously reported in [1]. In a forthcoming paper we shall give detailed information about modifications of these procedures designed by us [13]. Purification of the raw product was achieved via two routes:

a) Gas chromatography: **1** was inserted into a GC. *Varian* 712 *via* a specially designed inlet system for oxygen sensitive volatile substances [56]. Conditions were: Column SE-30 (5m), furnace temperature 150°, carrier gas flow 100 ml/min. By-products occurring in our synthesis had retention times of 15 min and 21 min, **1** has 30 min.

b) Fractional condensation: An apparatus consisting of three successive cold traps held at temperatures of 230 K(A), 210 K(B) and 77 K(C), respectively, was evacuated to 10^{-4} Torr. **1** stored at 77 K was sublimed into the system by warming the recipient to room temperature. While unwanted by-products were held back in A or passed down to C, essentially pure **1** condensed in trap B. As solid **1** polymerizes markedly at 210 K the procedure has to be carried out quickly in order to prevent loss of **1** (polymers of **1** are not volatile under the conditions employed in the transfer of **1** from B into the ionization chamber). Repetitive execution of this procedure leads eventually to equal purity of **1** as the more elaborate GC.-method.

The purity of **1** was monitored by mass spectrometry. The sample was considered to be pure after all signals not attributable to fragments of **1** had essentially vanished. Below we depict





the mass spectra of raw (right) and purified (left) **1**. Before each EI- or PI-run the purity of **1** was rechecked.

All manipulations with pure **1** have to be carried out under high vacuum or at low temperatures under dry, oxygen-free nitrogen.

The electron impact data were obtained on a *Hitachi/Perkin Elmer* RMU7 with a modified ionization chamber linked on line to a PDP-9 computer.

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