249. The Stabilization Energy of [18]Annulene. A Thermochemical Determination

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Summary. The thermal rearrangement of [18]annulene in solution gives benzene and 1,2-benzo-1,3,7-cyclooctatriene. This reaction has been investigated using a differential scanning calorimeter and the associated enthalpy change has been measured. The enthalpy of the reaction (in the gas phase at 298 °K) is

$$\Delta H_r(g, 298°) = -50.7 \pm 5 \text{ kcal mol}^{-1}.$$

From this value and the enthalpies of formation of the reaction products, the enthalpy of formation of [18]annulene is obtained:

$$\Delta H_f°(\mathbf{1}, g, 298°) = 124 \pm 5.5 \text{ kcal mol}^{-1}.$$

The stabilization energy of [18]annulene, defined as the difference between the enthalpy of formation of the hypothetical Kékulé [18]annulene (with single and double bonds of normal lengths) and the heat of formation of the real molecule is then

$$\Delta H_{stab.}(\mathbf{1}) = 37 \pm 6 \text{ kcal mol}^{-1},$$

a value close to the corresponding quantity found for benzene.

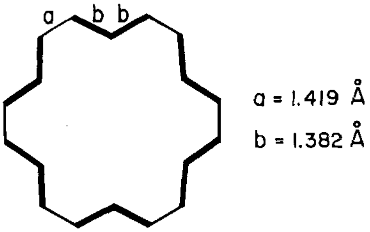
The very large stabilization energy of [18]annulene (100 ± 6 kcal mol^{-1}) previously reported in the literature, based on measurements of the heat of combustion, is not correct since the annulene is certainly oxidized in the bomb prior to combustion.

The isodynamic conformational mobility of [18]annulene is not incompatible with a stabilization energy of 37 kcal mol^{-1}; the activation enthalpy observed for this process ($\Delta H^{\neq} = 16.1$ kcal mol^{-1}) indicates that the stabilization is not completely destroyed in the transition state.

The mechanism of the thermolysis of [18]annulene, investigated by kinetic measurements and by analysis of the shape of the thermograms, is discussed.

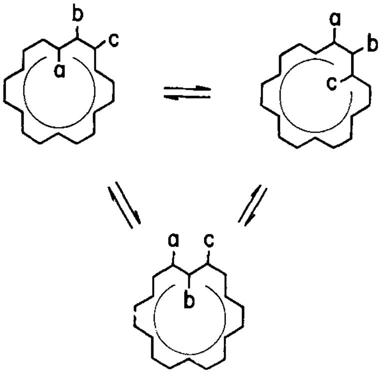
1. Introduction. – [18]annulene **1** [1] is a $(4n+2)\,\pi$ system and thus, according to *Hückel*'s rule, a potential aromatic hydrocarbon. The question whether **1** is stabilized with respect to its *Kékulé* structure or not has long been debated and has not yet received a definitive answer. The same year that *Dewar & Gleicher* predicted, on the basis of semi-empirical SCF-MO calculations, this stabilization energy to be as small as 6–9 kcal mol^{-1} [2] an X-ray structure of **1** was published [3]: [18]annulene was shown to be very nearly planar and its carbon skeleton to conform to the D_{6h} symmetry. This high symmetry implies that the π-bonds are delocalized; two slightly different C–C bond lengths are observed, both different from the normal single and double bond lengths, and are distributed in the molecule as shown in *Scheme 1*. Other data concerning this molecule such as the diamagnetic ring current observed by ^{1}H-NMR. spectroscopy [4], its thermal stability, which is greater than that of the known [4n]annulenes of comparable size ([16]-, [20]-, [24]annulenes), suggest that a substantial stabilization energy must be associated with the π-bond delocalization.

Scheme 1. *Bond lengths in [18]annulene [3]*



Two attempts to obtain a quantitative evaluation of this stabilization energy $\Delta H_{stab}(\mathbf{1})$ have been published so far. One determination is based on measurements of the heat of combustion [5]. The reported value is $\Delta H_{stab}(\mathbf{1}) = 100 \pm 6$ kcal mol^{-1}, a value almost three times that found for benzene (36 kcal mol^{-1}). The other estimation was published by one of us [4]. It results from the interpretation of the activation enthalpy of the conformational mobility that takes place in [18]annulene and by which the 6 protons pointing inside the ring exchange their environment with protons pointing outside the ring. Three isodynamic [6] conformers are implied in this process as indicated in *Scheme 2.*

Scheme 2. *The three isodynamic conformers of [18]annulene*



With the assumption that the π-bond delocalization does not persist and that all the stabilization is lost in the transition state it was concluded that the stabilization energy should be at most 19 kcal mol^{-1}.

The drastic discrepancy between these two determinations prompted us to reconsider the problem and to try to obtain a value based on reliable thermochemical measurements. The heat of combustion data [5] are, in fact, questionable: the [18]-annulene is so sensitive to oxygen that it could well be oxidized in the bomb prior to combustion. It is also difficult to understand why [18]annulene possesses the above-mentioned conformational mobility if its stabilization energy is as high as 100 kcal mol^{-1}!

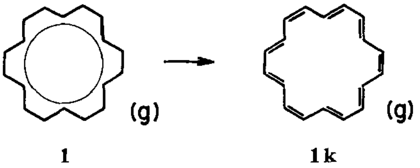
2. Specification of the thermochemical quantities we are looking for. – When discussing energy effects such as those associated with π-bond delocalization a fundamental question arises: in respect to what structure is the molecule considered to be stabilized?

As has been done in the case of benzene, we shall consider the stabilization energy in [18]annulene as the difference between the enthalpy of formation (in the gas phase at 298°K) of the hypothetical planar *Kékulé* structure **1k** with alternating single and double bonds of normal lengths and the enthalpy of formation (gas, 298°K) of [18]annulene **1**:

$$\Delta H_{\text{stab}}(\mathbf{1}) = \Delta H_f^\circ(\mathbf{1k}, \text{g}, 298^\circ) - \Delta H_f^\circ(\mathbf{1}, \text{g}, 298^\circ).$$

It is thus the heat of the following reaction (*scheme 3*):

Scheme 3

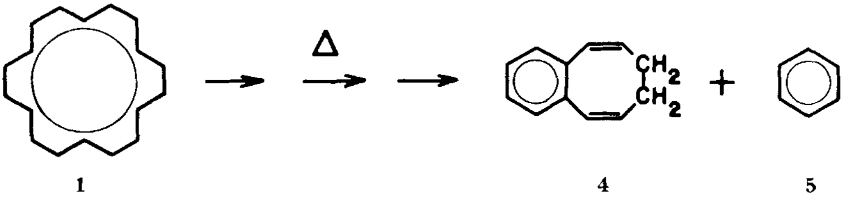


We have to find an appropriate sequence of reactions leading from [18]annulene to molecules whose enthalpies of formation are known or can be calculated with confidence. The heat of these reactions has then to be measured and the enthalpy of formation of the hypothetical planar *Kékulé* structure has to be calculated from thermochemical tables. Apart from the combustion of [18]annulene, two other reactions sequences are appropriate for thermochemical investigations:

a) the catalytic hydrogenation of [18]annulene and the combustion of the saturated $C_{18}H_{36}$ macrocyclic compound;

b) the thermal rearrangement of [18]annulene which takes place above 90°C and gives benzene **5** (whose heat of formation is known) and 1,2-benzo-1,3,7-cyclooctatriene **4** [7].

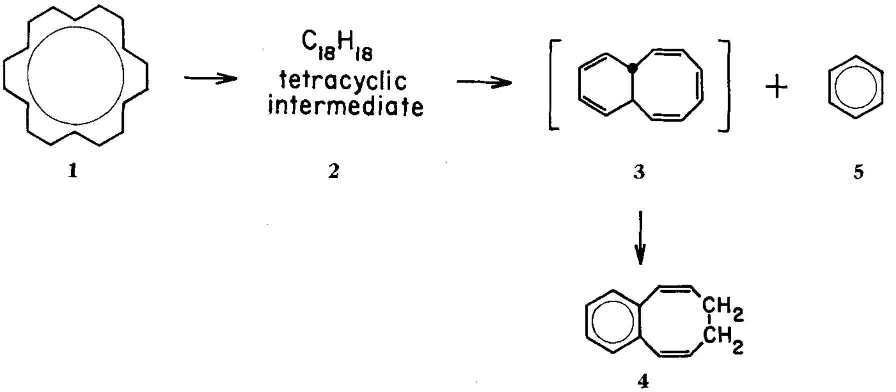
Scheme 4



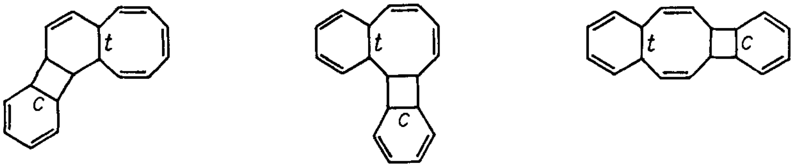
We have decided to investigate the thermolysis of [18]annulene (alternative b) above) using our differential scanning calorimeter. From the heat of this thermal rearrangement we should be able to deduce the enthalpy of formation of this molecule and to estimate its stabilization energy as defined above. Furthermore, the kinetic information extracted from the thermograms, combined with classical kinetic measurements (using ^{1}H-NMR. spectroscopy), should allow us to deduce mechanistic details and even enthalpies of activation of different reaction steps.

3. The thermal rearrangement of [18]annulene. – In a previous communication [7], we have briefly mentioned that an intermediate compound **2**, isomeric with [18]annulene, can be isolated when the thermolysis is stopped at *ca.* 30% of conversion of **1** (see Section 8 below and also Fig. 4). This intermediate compound **2** is tetracyclic and has one of the three possible structures **2a**, **2b** or **2c**. These structures are the only ones compatible with the following observations:

Scheme 5. *Mechanism of the thermal rearrangement of [18]annulene*



The possible structures of **2** (*c* = *cis* ring fusion; *t* = *trans*)



2a **2b** **2c**

a) ¹H-NMR. spectrum (see Fig. 1) and decoupling experiments, IR. and MS. (molecular peak at *m/e* = 234);

b) the photochemical rearrangement of **2** carried out at –100° in THF-d_8 gives benzene and [12]annulene;

c) the catalytic hydrogenation of **2** indicates the presence of 6 double bonds in the molecule; the MS. of the fully hydrogenated derivative (molecular peaks at *m/e* = 246) indicates a tetracyclic saturated C_{18}-hydrocarbon. The ¹H-NMR. spectra of **2** and of its fully hydrogenated derivative are reproduced in Fig. 1.

The formation of 1,2-benzo-1,3,7-cyclooctatriene is best understood if one assumes that the intermediate **3** (*trans*-bicyclo[6.4.0]dodeca-2,4,6,9,11-pentaene) is formed when benzene is split off **2**; **3** would then rearrange thermally into **4** *via* two symmetry-allowed 1,5 suprafacial sigmatropic migrations of hydrogen. The *cis*-isomer corresponding to **3** is known to give only benzene on thermolysis [8].

4. Calorimetric investigation of the thermal rearrangement of [18]annulene. – We have measured the enthalpy of thermolysis of **1** in a temperature

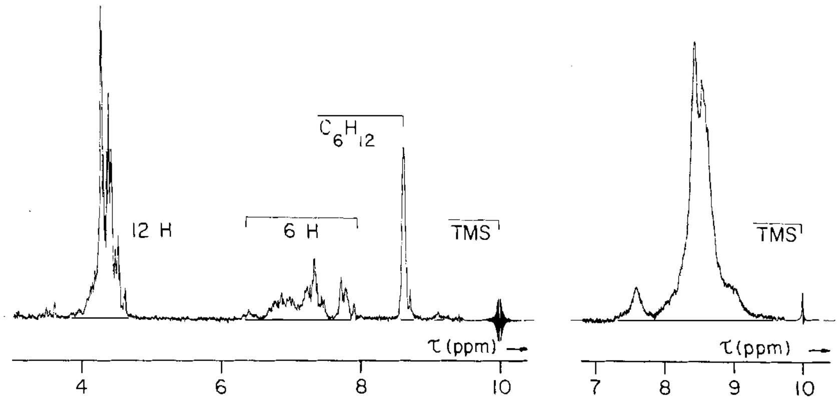


Fig. 1. *^{1}H-NMR. spectra of the intermediate $C_{18}H_{18}$ tetracyclic compound* **2** *(in cyclohexane-d_{12}, 100 MHz, 30°C) and of its fully hydrogenated derivative (in benzene-d_6, 100 MHz, 30°C).*

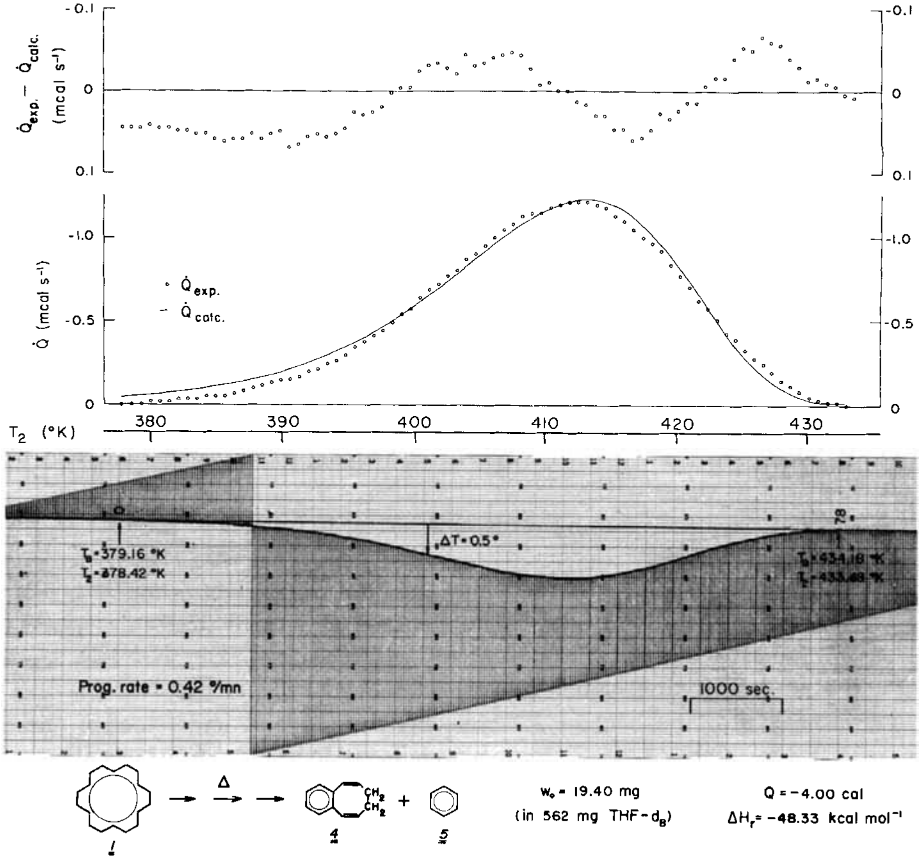


Fig. 2. *Experimental and calculated thermograms for the thermolysis of [18]annulene.* The experimental recording displays both the linearly increasing block temperature (T_B) and the temperature difference (T_1–T_2) between the reference and the sample cells as a function of time.

programmed calorimeter in which the heat flow due to a reaction is evaluated from the recorded temperature difference between a sample and a reference cell. Integration of the heat flow curve yields the heat of the reaction; analysis of the shape of the curve also provides kinetic information [9]. The solution of the compound to be investigated is contained in a small sealed Pyrex ampulla. A typical thermogram for the thermolysis of **1** is shown in Fig. 2.

Three runs have been made using toluene-d_8 or tetrahydrofuran-d_8 as solvent. Table 1 summarizes the thermochemical results obtained.

Table 1. *Experimental heat of the thermal rearrangement* **1** → **4** + **5**

Run no.	w_0(mg) [18]annulene	w(mg) solvent	Progr. rate deg. min^{-1}	$-Q_r$ cal	$-\Delta H_r$(sol., 415°) kcal mol^{-1}
101	22.65	550 a)	0.532	4.59	47.45
104	18.57 c)	441 b)	0.532	3.87	48.79
105	19.40 c)	582 b)	0.423	4.00	48.33

a) Toluene-d_8.
b) Tetrahydrofuran-d_8.
c) Freshly recrystallized sample.

The ^{1}H-NMR.-spectrum of the solution has been recorded after each run (see Fig. 3). No signals other than those arising from **4** and **5** can be seen; however, the integration of the different signals indicates that the molar ratio of benzene to cyclooctatriene is always slightly larger than unity. This is likely due to a partial polymerization of **4** (a suspension of insoluble material can be seen in the solution). The extent of polymerization, estimated from the NMR. signal intensities, is fortunately small (see Table 2).

5. Corrections to apply to the observed enthalpy of reaction. – In order to evaluate the enthalpy of the rearrangement **1** → **4** + **5** in the gas phase and at 298 °K, we have to apply the following corrections to the ΔH_r listed in Table 1:

a) a correction for the partial polymerization of **4**;

b) a correction for differences in the heats of solution and for differences in the heats of vaporization or sublimation;

c) a correction to reduce the results to the standard temperature of 298 °K.

The thermograms indicate that the thermolysis of **1** occurs in the temperature range of *ca.* 378 °K to *ca.* 438 °K; in order to simplify the calculations of the different corrections we shall, however, take 415 °K (the temperature at which the maximum heat flux due to the reaction is observed) as the experimental temperature.

5a. *Correction for the polymerization of* **4**. Each *cis* double bond involved in the polymerization of **4** is transformed into a $>$CH–CH$<$ single bond. The enthalpy change associated with the polymerization of one mole of **4** is thus simply the difference between the heat of formation of one $>$CH–CH$<$ group (or of two $-\overset{|}{\underset{|}{C}}H$ groups) and the heat of formation of one –CH=CH–(*cis*) group. With thermochemical tables

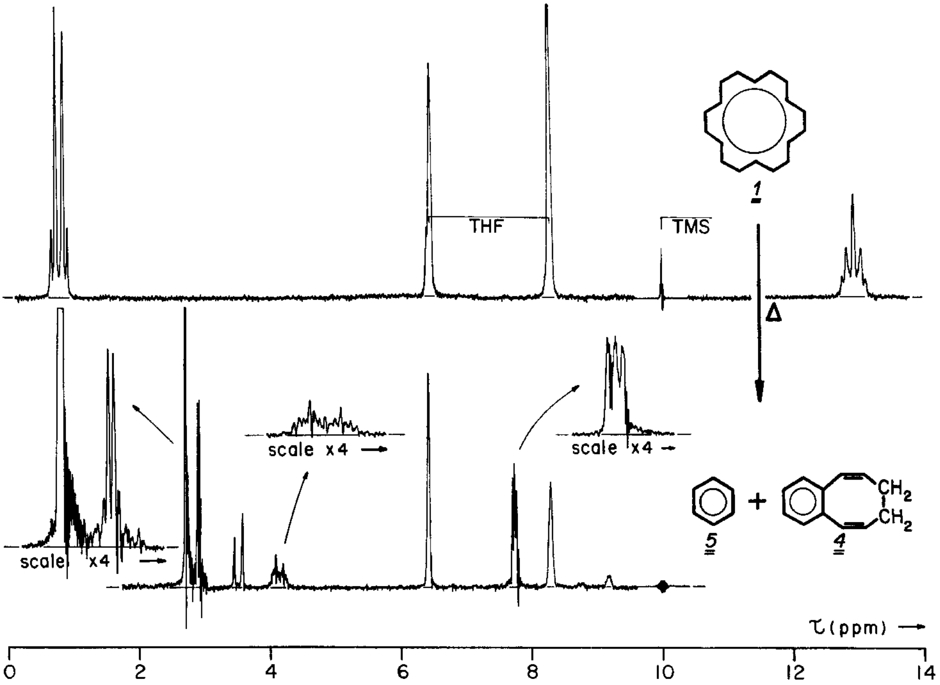


Fig. 3. *^{1}H-NMR. spectra of a solution of [18]annulene in tetrahydrofuran-d_8 before and after thermolysis (100 MHz, at –30°C and +30°C, respectively)* (run no. 105)

giving the enthalpy of formation of such groups (tables of *Franklin* [10] [11] or of *Franklin* revised by *Wiberg* [12]) one estimates the enthalpy of polymerization of **4** at 415°K to be – 20.72 kcal mol^{-1}. We have assumed, as it is reasonable, that only one of the two ethylenic double bonds of **4** is involved in the polymerization. The corrections to be applied are reported in Table 2.

Table 2. *Corrections to ΔH_r for the partial polymerization of* **4**[a])

Run no.	$-\Delta H_r$(sol., 415°) kcal mol^{-1}	% of **4** polymerized[b])	$-\Delta H_{polym.}$ (correction) kcal mol^{-1}	$-\Delta H_r$(sol., 415°) (corrected) kcal mol^{-1}
101	47.45	13	2.69	44.8
104	48.79	14	2.90	45.9
105	48.33	5	1.04	47.3
Average				46.0
Error		± 2[c])	± 0.41[c])	± 1.5[d])

[a]) The corrections are based on an enthalpy of polymerization of – 20.72 kcal mol^{-1}; see Section 5.

[b]) From ^{1}H-NMR.-spectra, see Section 4 and Fig. 3.

[c]) Estimated.

[d]) Calculated as $2\bar{s} = 2[(n^2 - n)^{-1} \sum_i (\bar{x} - x_i)^2]^{1/2}$, according to ref. [13].

From now on, we will adopt for the experimental enthalpy of thermolysis of **1** the value

$$\Delta H_r(\text{solution}, 415°) = -46 \pm 1.5 \text{ kcal mol}^{-1}.$$

5b. *Correction for differences in the heats of solution and for differences in the heats of vaporization or sublimation.* The enthalpies of solution of **1**, **4** and **5** are not known but can be considered as negligible with respect to the other heat effects involved. The following values have been adopted for the different heats of vaporization or sublimation (kcal mol^{-1})

$$\Delta H_{\text{vap.}}(\mathbf{5}) = 8.09 \pm 0.01 \qquad [13]$$

$$\Delta H_{\text{vap.}}(\mathbf{4}) = 14 \pm 1.5$$

$$\Delta H_{\text{subl.}}(\mathbf{1}) = 28 \pm 1.5.$$

The heat of vaporization of **4** is chosen from a comparison of values reported for other liquid hydrocarbons of analogous size (C_{11}, C_{12} and C_{13} hydrocarbons [13]). The heat of sublimation of [18]annulene is chosen on the same basis, *i.e.* from a comparison of values reported for other C_{18} solid hydrocarbons [13]. The correction to apply is thus equal to

$$\Delta H_{\text{vap.}}(\mathbf{4}) + \Delta H_{\text{vap.}}(\mathbf{5}) - \Delta H_{\text{subl.}}(\mathbf{1}) = -5.9 \pm 3 \text{ kcal mol}^{-1}$$

and the enthalpy of thermolysis of **1** in the gas phase at 415 °K is then

$$\Delta H_r(g, 415°) = -51.9 \pm 4.5 \text{ kcal mol}^{-1}.$$

5c. *Correction required to reduce the enthalpy of thermolysis to 298 °K.* The enthalpy of thermolysis of **1** in the gas phase and at 298 °K can now be calculated using *Kirchhoff*'s equation under one of the two following forms:

a) $\Delta H_r(g, T_0) = \Delta H_r(g, T) + \Sigma[(H^\circ_{T_0}-H^\circ_0) - (H^\circ_{T_0}-H^\circ_0)]$ (reactants) $-\Sigma[(H^\circ_T-H^\circ_0) - (H^\circ_{T_0}-H^\circ_0)]$ (products)

The heat contents $(H^\circ_{T_0}-H^\circ_0)$ and $(H^\circ_T-H^\circ_0)$ for each compound can be calculated using the group increments given by *Franklin* [10] [11].

b) $\Delta H_r(g, T_0) = \Delta H_r(g, T) - (T-T_0)\,\Delta C_P$

where $\Delta C_P = \Sigma C_P(\text{products}) - \Sigma C_P(\text{reactants})$, the specific heats being taken at the mean temperature $(T-T_0)/2$; ΔC_P can be calculated with the group-increment method using *Benson*'s tables [14].

Depending on how the different molecules are dissected into groups one finds, with each of the two methods, corrections between + 1.8 and + 0.7 kcal mol^{-1}. We have applied a correction of 1.2 ± 0.5 kcal mol^{-1}; the enthalpy of thermolysis of **1** in the gas phase at 298 °K is then

$$\Delta H_r(g, 298°) = -50.7 \pm 5 \text{ kcal mol}^{-1}.$$

6. The enthalpy of formation of [18]annulene in the gas phase at 298 °K. – The enthalpy of formation of [18]annulene in the gas phase at 298 °K, $\Delta H^\circ_f(\mathbf{1}, g, 298°)$, can now be derived as

$$\Delta H^\circ_f(\mathbf{1}, g, 298°) = \Delta H^\circ_f(\mathbf{4}, g, 298°) + \Delta H^\circ_f(\mathbf{5}, g, 298°) - \Delta H_r(g, 298°).$$

The heat of formation of benzene is known; the recommended value is

$$\Delta H_f^\circ(\mathbf{5}, g, 298^\circ) = 19.81 \pm 0.13 \text{ kcal mol}^{-1}. \quad [13]$$

The heat of formation of 1,2-benzo-1,3,7-cyclooctatriene can be estimated with confidence using the group-increment methods. As indication of the type of agreement one obtains with such methods we compare, in Table 3, the calculated and observed heats of formation of compounds of structures related to that of **4**. As can be seen, the agreement between calculated and experimental enthalpies of formation is very good in the case of styrene and *cis*-stilbene. The agreement is not so good for *trans*-stilbene; in this case we have to bear in mind that conjugation between the two benzene rings through the *trans* double bond is possible since the molecule can adopt a planar conformation (this is not possible in the case of *cis*-stilbene). The discrepancy Δ between calculated and observed heats of formation (Δ = 5 to 6 kcal mol^{-1}) must represent the stabilization energy associated with this effect. The question whether a correction for conjugation has to be applied to the calculated enthalpy of formation of **4** then arises. We believe that no such correction should be applied since **4** can not be planar as a model indicates. However, a correction of + 2 kcal mol^{-1} has to be applied to take into account the strain energy associated with the two eclipsing $>CH_2$ groups. We will thus take for the enthalpy of formation of **4** (see Table 3)

Table 3. *Comparison of experimental and calculated enthalpies of formation, $\Delta H_f^\circ(g, 298^\circ)$, of some molecules and calculated enthalpy of formation of* **4**

	Experimental value [13] kcal mol^{-1}	Calculated values					
		Franklin [10] [11] kcal mol^{-1}	Δ[a]	*Franklin-Wiberg* [12] kcal mol^{-1}	Δ[a]	*Benson* [14] kcal mol^{-1}	Δ[a]
Styrene	35.30 ± 0.25	35.78	+ 0.48	35.68	+ 0.38	35.22	– 0.08
cis-stilbene	61.31 ± 0.42	60.44	– 0.87	60.16	– 1.15	61.54	+ 0.23
trans-stilbene	54.22 ± 0.8[b]	59.39	+ 5.17	59.19	+ 4.97	60.54	+ 6.32
1,2-benzo-1,3,7-cyclooctatriene		51.07		50.51		51.99	

[a] $\Delta = \Delta H_f^\circ(\text{calculated}) - \Delta H_f^\circ(\text{experimental})$.

[b] The enthalpy of vaporization of *trans*-stilbene is not known but was considered to be the same as that of *cis*-stilbene.

$$\Delta H_f^\circ(\mathbf{4}, g, 298^\circ) = 53.5 \pm 0.5 \text{ kcal mol}^{-1}.$$

The enthalpy of formation of [18]annulene is then

$$\Delta H^\circ(\mathbf{1}, g, 298^\circ) = 50.7 + 19.81 + 53.5 = 124 \pm 5.5 \text{ kcal mol}^{-1}.$$

This value is much larger than that deduced from heat of combustion measurements and reported by *Beezer et al.* [5]

$$\Delta H_f^\circ(\mathbf{1}, g, 298^\circ) = 67 \pm 6.0 \text{ kcal mol}^{-1}$$

but, as mentioned in the introduction, this value is certainly incorrect (and much too small) since oxidation of [18]annulene in the bomb prior to combustion is unavoidable. Oxidation product would of course have a lower enthalpy of formation than [18]annulene itself and the heat of combustion would be much smaller than the correct value.

7. The stabilization energy in [18]annulene. – The stabilization energy associated with the delocalization of the π-bonds as defined above (see section 2) can now be calculated. The heat of formation of the hypothetical *Kékulé* [18]annulene (**1k**) with normal double and single bonds is readily calculated from different thermochemical tables giving enthalpies of formation of groups. The values found are reported in Table 4.

Table 4. *Enthalpy of formation (in kcal mol⁻¹) of the hypothetical* Kékulé *[18]annulene* **1k**, *$\Delta H_f°$(**1k**, g, 298°), calculated with different thermochemical tables*[a])

	Tables used		
	Franklin [10] [11]	*Franklin-Wiberg* [12]	*Benson* [14]
Kékulé [18]annulene **1k**	(163.62)	161.4	160.62
		value adopted: 161 ± 0.5	

[a]) Calculated as strain-free.

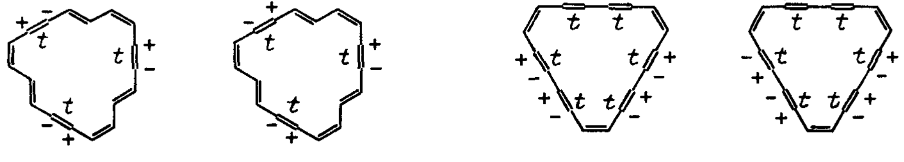
We finaly find for the stabilization energy of [18]annulene with respect to its *Kékulé* structure

$$\Delta H_{stab.}(\mathbf{1}) = 161 - 124 = 37 \pm 6 \text{ kcal mol}^{-1}$$

i.e. a value very close to the corresponding quantity found for benzene.

It remains to explain why the value $\Delta H_{stab.}(\mathbf{1}) \leqslant 19$ kcal mol^{-1} that we had deduced from the activation enthalpy of the conformational mobility occurring in [18]annulene ($\Delta H^{\neq} = 16.1$ kcal mol^{-1}) [4] is much smaller than the value reported above. Our argument was that, in the transition state of the conformational process, some *trans* double bonds must be perpendicular to the 'mean' plane of the molecule and consequently that the cyclic delocalization of the π-bonds must be destroyed, *i.e.* that the stabilization energy must be completely overcome. In fact this argu-

Scheme 6. *Possible structures (with their symmetry) of the transition state implied in the conformational mobility of* **1**. The *trans* double bonds perpendicular to the 'mean' plane of the molecule are indicated by *t*; + and – indicate H atoms above and under the 'mean' plane of the molecule, respectively.



$\mathcal{C}_3$ $\mathcal{C}_1$ $\mathcal{D}_3$ $\mathcal{C}_2$

ment is not strictly correct. The transition state of the conformational process can be one of the structures represented in *Scheme 6*. Each of these structures consists of three planar butadiene residues (with a *transoid* conformation) connected by 'isolated' *cis* double bonds. They can thus still be stabilized by an amount of energy equal to three times the stabilization energy of 1,3-butadiene (in its planar *transoid* conformation). This stabilization energy was estimated by different authors and lies between 8.2 and 3.1 kcal mol^{-1} [15] [16], the most realistic value being 3.5 kcal mol^{-1} (deduced from a comparison of the heats of hydrogenation of 1,3-butadiene and of 1-butene [16]).

If we add $3 \times 3.5 = 10.5$ kcal mol^{-1} to the stabilization energy that we had deduced from the activation enthalpy of the conformational mobility of **1** we obtain

$$\Delta H_{\mathrm{stab.}}(\mathbf{1}) = 19 + 10.5 = 29.5 \text{ kcal mol}^{-1}$$

i.e. a value now in better agreement with that derived from the heat of thermolysis. We can thus conclude that the conformational mobility exhibited by the [18]annulene molecule is not incompatible with a stabilization energy of this molecule of 37 ± 6 kcal mol^{-1}; the transition state of the dynamic process is stabilized with respect to the hypothetical planar *Kékulé* structure by *ca.* 21 ($\pm$ 6) kcal mol^{-1}, thus indicating that a certain conjugation between the π-bonds always persists.

8. Some kinetic information concerning the thermolysis of [18]annulene.

– In an attempt to elucidate the mechanism of the thermolysis $\mathbf{1} \rightarrow \mathbf{4} + \mathbf{5}$ we have followed this reaction at 92°C and 111°C by ^{1}H-NMR. spectroscopy. The concentrations of the different species present in solution have been calculated from the intensities of their NMR. signals (one peak of THF-d_8 being taken as intensity standard). The time dependance at 92°C of the concentrations of **1**, **2**, **4** and **5** (normalized with respect to the initial concentration of **1**) is shown in Fig. 4. One sees that after *ca.*

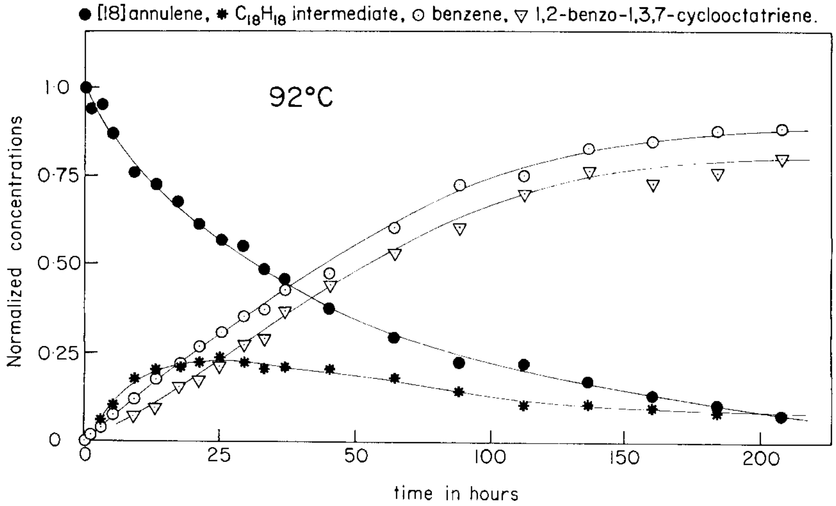


Fig. 4. *Concentration of the different compounds* **1**, **2**, **4** *and* **5** *present in a solution as function of the time of thermolysis at 92°C*

25 hours the concentration of the intermediate compound **2** goes through a maximum and amounts to 24% of the initial concentration of **1**. The analysis of the concentration curves allows us to deduce the kinetic parameters listed in Table 5.

Table 5. *Kinetic parameters of the different consecutive reactions implied in the thermolysis of* **1**

Reaction	Rate constant	at 92°C s^{-1}	at 111°C s^{-1}	E_a kcal mol^{-1}	$\log_{10}A$
1 → **2**	k_1	$5.3\ 10^{-6}$	$64\ 10^{-6}$	36.5	16.6
2 → **3** + **5**	k_2	$\sim 10\ 10^{-6}$	$93\ 10^{-6}$	~33	~14.5
3 → **4**	k_3	$k_3 > k_2$			

Since no signals arising from the intermediate **3** can be detected in the NMR.-spectra, we conclude that the concentration of this species is always very small and that k_3 is at least five times larger than k_2.

Kinetic information can also be extracted from the shape of the thermograms. Fig. 2 shows that the experimental thermogram cannot be perfectly fitted to a theoretical first order curve. Indeed the thermogram should be analysed as arising from two (or even three) consecutive first order reactions. However these reactions have their rate constants so similar that a complete determination of all the parameters on the basis of the shape of the heat flux curve alone is impracticable. We should however point out that the kinetic parameters extracted from the tentative first order fit of the thermogram (k at 92°C $= 6.4\ 10^{-6}\ s^{-1}$, $E_a = 36.8$ kcal mol^{-1} and $\log_{10}A = 16.4$) are in good agreement with the data given in Table 5 for the reaction **1** → **2**. Additional information can only be obtained by the investigation of the thermolysis of pure **2** and of pure **3**. Such investigations are in progress.

Note added in proof. – The enthalpy of formation of [18]annulene has been recently calculated by *Dewar et al.* (J.C.S. Chem. Commun., *1974*, 569) using a semiempirical SCF-MO method (namely the new version MINDO-3).

These authors have found, with an iterative procedure, that the lowest enthalpy of formation is obtained for an [18]annulene with π-bonds localized (D_{3h}symmetry):

$$\Delta H_f(\mathbf{1}, D_{3h}) = 129.3 \text{ kcal mol}^{-1}$$

The enthalpy of formation of the [18]annulene having the geometry deduced from X-ray data (π-bonds delocalized, D_{6h}symmetry) is 25.7 kcal mol^{-1} greater:

$$\Delta H_f(\mathbf{1}, D_{6h}) = 155.0 \text{ kcal mol}^{-1}$$

The first value is in good agreement with our experimental enthalpy of formation of [18]annulene [$\Delta H°$ (**1**, g, 298°) $= 124 \pm 5.5$ kcal mol^{-1}]. This agreement is probably a pure coincidence and can not be regarded as an experimental support of the calculations.

We can not agree with *Dewar et al.* when they conclude that π-bonds alternate in lenght in [18]annulene; in fact the NMR., UV. and PE. spectra of [18]annulene are best quantitatively interpreted with a π-bonds delocalized structure of D_{6h}symmetry.

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250. The Ionization Energies of Bridged [14]Annulenes and of Dicyclohepta[*cd*, *gh*]pentalene¹)

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Dedicated to Prof. Dr. *Hermann Hartmann* on the occasion of his sixtieth birthday

(2. IX. 74)

Summary. The ionization energies I_J of 1,6;8,13-alkanediylidene-[14]annulenes (**2** to **5**) and of dicyclohepta[*cd,gh*]pentalene (**1**) have been determined by photoelectron spectroscopy, using HeI radiation. The data are interpreted in terms of *Koopmans'* theorem ($I_J = -\varepsilon_J$) on the basis of correlation diagrams and with the help of simple molecular orbital models.

If the bridge is an ethane-, propane- or butane-diylidene group, the π-orbital sequence, in descending order of orbital energies, is (in C_{2v}): b_1, b_2, a_2, a_1. The sequence is due to a complicated

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¹) On occasion of the 2nd International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds in Lindau (September 23–27, 1974) it was found that the PE. spectra of the compounds **3**, **4** and **5** had been investigated independently and unknown to us by *J. F. M. Oth, J.-C. Bünzli, H. Baumann & J.-C. Gfeller* (Organisch-chemisches Laboratorium, ETH-Z, Zürich) as part of the thesis of *J.-C. Gfeller*. The results obtained by both groups were presented in plenary lectures at the Symposium mentioned above and are referred to in the corresponding manuscripts submitted for the Symposium Volume to the Journal of Pure an Applied Chemistry. Therefore the present publication does ndt involve and priority claim.