Tetrahedron. Vol. 26, pp. 5225–5234. Pergamon Press 1970. Printed in Great Britain

QUANTUM-CHEMICAL STUDIES ON THE AROMATICITY OF CONJUGATED SYSTEMS—II

AROMATIC AND ANTI-AROMATIC ANNULENES: THE (4n + 2)-π ELECTRON RULE*

H. P. FIGEYS
Service de Chimie Organique, Faculté des Sciences, Université Libre de Bruxelles,
50, Av. F. D. Roosevelt, Bruxelles, Belgique

(*Received in the UK* 4 *April* 1970; *Accepted for publication* 15 *July* 1970)

Abstract—The LCAO-BETA method described in Part I of this series[21] has been applied to the calculation of the heats of atomization of annulenes up to $C_{30}H_{30}$ and to a number of even linear polyenes. It is shown that, in the compounds of the second type, the heats of atomization are additive functions of "single" and "double" C—C bond energies. The results obtained were used to investigate the aromaticity of the annulenes according to Breslow's and Dewar's definition. Hückel's rule is verified, the (4n + 2)-π electron systems showing increased stability with respect to the "localised" model compound; the (4n)-π electron annulenes on the other hand are anti-aromatic.

INTRODUCTION

SEVERAL decades ago, Hückel formulated his famous (4n + 2)-rule, which states that "Those monocyclic coplanar systems of trigonally hybridized atoms which contain (4n + 2)-π electrons will possess relative electronic stability".[1,2] Experimental verification of this rule includes, for example, the great stability shown by benzene, the cyclopentadienide anion and the cycloheptatrienium (tropylium) cation. Hückel's argument is based on the assumption that, if a molecule has occupied antibonding or non-bonding π-orbitals, its stability should be considerably reduced; on the other hand, if the electrons can be put into bonding orbitals, stability should be gained.

In the field of the neutral cyclic polymethines with equal C—C bonds, only the (4n + 2)-π electron annulenes show a closed-shell system of *bonding* orbitals and should thus be aromatic.[2–5]

However, if the delocalisation energy (DE) of different 4n- and (4n + 2)π electron annulenes is calculated with respect to the hypothetical structures made up of alternating pure single and pure double bonds, it emerges that no sound theoretical reason can be given why the [4n]-annulenes, except cyclobutadiene (n = 1), should not be aromatic.[5–6] Furthermore, the [4n]-annulenes have an orbitally degenerate ground-state and should thus, according to the Jahn–Teller rule,[5,7–10] be unstable with respect to a displacement of atoms which removes that degeneracy; the distorted hydrocarbon has a closed-shell bonding singlet ground-state[8–11] and should thus, according to Hückel's argument, show normal "aromatic" properties, but none would claim it to be true.

Recently, Breslow[12] and Dewar[6] proposed a thermodynamic criterion to define aromaticity, namely "cyclic conjugated systems are considered aromatic if cyclic delocalisation of electrons makes a negative contribution to their heat of formation". By this definition, an opposite phenomenon can be imagined in which cyclic delocali-

---

* Part I: see Ref. 21.

sation of electrons is destabilising; such a phenomenon is called *anti-aromaticity*. As a result, *non-aromaticity* should be a simple lack of stabilisation energy in the cyclic compound as compared with the linear one.

The problem which rises is to define the contribution of a formal "double" bond and of a formal "single" bond of an open chain polyene to the heat of formation of such molecules from atoms in the gas phase. Indeed, cyclic polyenes have one formal "single" bond more than the corresponding open-chain derivatives. This in turn raises the fundamental question of bond-fixation in the linear polyenes. As has been pointed out by Dewar *et al.*[6, 13, 14] valence-electrons must, according to current quantum theory, be completely delocalised; however, a molecule may behave *almost as if* the electrons were localised in certain bonds, provided the collective molecular properties can be represented as additive functions of bond properties. So, for example, heats of atomization of paraffins can be given in terms of localised bond energies, even if the interactions between the individual bonds are not negligible, for it may be possible to include a correction for these interactions into the "empirical" bond energies.

Recently, Dewer *et al.* have shown by the Pople-SCF-MO-theory that the classical linear even polyenes might be represented in terms of localised "single" and "double" bonds, provided the variation of the core resonance integrals β^c_{ij} with bond length are taken into account by an iterative procedure;[6, 13, 14] they were also able to show that the lower members of the [4n + 2]-annulenes series should be aromatic and those of the [4n]-series anti-aromatic (n $\leqslant$ 2), the higher members in each case tending to non-aromaticity.[6*] These results are however in rather severe disagreement with the recent determination of the heat of combustion of [18]-annulene,[19] showing important resonance energy for this molecule,[14] and with the results of NMR investigations concerning the aromaticity or anti-aromaticity of the larger [N]-annulenes (with N $\geqslant$ 14)[22–29] by the magnetic criterion.[5, 12]

The aim of this paper is to reinvestigate the bond localisation in the linear polyenes and the aromaticity of the annulenes by the improved iterative Hückel method (called LCAO-BETA)[20] by which promising accurate results have been obtained in the calculation of the ΔH°_f-values for a series of open-chain as well as cyclic, alternant and non-alternant, fully conjugated hydrocarbons.[21]

RESULTS AND DISCUSSION

(a) *The linear polyenes.* Previous theoretical work on the linear polyenes has been concerned mainly with the problem of bond alternation in these molecules.[10, 30–37] The fundamental experimental fact which suggests the existence of such a phenomenon is the slow decrease of the frequency of maximum absorption in the UV spectra of α,ω-dimethylpolyenes as a function of n toward a *finite* limit for the λ_{max} of an "infinite" polyene. Relatively few authors however have been interested in the total energy of such polyenes as a function of the number of formal "single" and "double" bonds.[5, 6, 13, 14] The theoretical analysis which follows is essentially based on Dewar's ideas,[6, 13, 14] using the LCAO-BETA method instead of the iterative Pople theory.

---

[*] Earlier S.C.F.-M.O. calculations made by Dewar *et al.*(15, 16) for the (4n)-π electron annulenes were carried out by an open-shell-theory for the lowest triplet states and are not considered here.

Adopting the notation introduced in Part I,[21] we can write for the total σ-bonding energy of a polyene:

$$E_{\sigma b} = \sum_{i} E^{\sigma}_{cc}(i) + n_{CH} \cdot E_{CH} \tag{1}$$

where $E^{\sigma}_{cc}(i)$ is the σ-energy of a C_{sp_2}—C_{sp_2} bond length r_i, E_{CH} that of a C_{sp}—H bond and n_{CH} the number of the latter bonds. If σ-compression energy is taken into account, we have :

$$E^{\sigma}_{cc}(i) = E^{\sigma}_{cc} - 1/2 \,.\, k_{cc}(r_i - 1{\cdot}517)^2 \tag{2}$$

where E^{σ}_{cc} is the σ-energy of a C_{sp_2}—C_{sp_2} bond at its "natural" length of 1·517 Å and k_{cc} the appropriate force constant.[21] Substitution in eq. 2 yields finally:

$$E_{\sigma b} = n_{cc} \,.\, E^{\sigma}_{cc} + n_{CH} \cdot E_{CH} - V \tag{3}$$

where V is the total molecular compression energy and is given by:

$$V = \sum_{i} 1/2 \,.\, k_{cc} \,.\, (r_i - 1{\cdot}517)^2 \tag{4}$$

It appears that since $n_{cc} = n_s + n_d$, $E_{\sigma b}$ will be an additive function of the number of formal "single" (n_s) and "double" (n_d) carbon–carbon bonds if, and only if, V is an additive function of n_s and n_d:

$$V = n_s \,.\, V_s + n_d \cdot V_d \tag{5}$$

V_s and V_d are respectively the compression energies of a formal "single" and of a formal "double" CC bond.

V was calculated for a series of linear polyenes up to C_{30} by the iterative computer programme described earlier[20] (the values of r_i are those obtained at self-consistency of the procedure*); the results are gatered in Table 1. It is easy to see from Fig 1 that, in this type of molecule, we always have $n_d = n_s + 1$, so that eq. 5 can be written:

$$V = n_s(V_s + V_d) + V_d \tag{6}$$

and a plot of V against n_s should be a straight line of slope ($V_s + V_d$) and intercept V_d. Fig II shows that this is effectively the case; this gives us the following results:

$$\begin{aligned} V_s &= 0{\cdot}0404 \text{ eV.} \\ V_d &= 0{\cdot}4293 \text{ eV.} \end{aligned} \tag{7}$$

The same computer programme yielded also the total π-bonding energy of these polyenes (Eq. 12 of Part I) $E_{\pi b}$; the results are given in Table 1. The simplest way to show that $E_{\pi b}$ is an additive function of n_s and n_d, is to show that eq. 8 is verified:

$$E_{\pi b} = n_s(E^{\pi}_s + E^{\pi}_d) + E^{\pi}_d \tag{8}$$

This relation is demonstrated by Fig III; the calculated values are:

$$\begin{aligned} E^{\pi}_s &= 0{\cdot}5209\,\beta = 0{\cdot}6731 \text{ eV} \\ E^{\pi}_d &= 2{\cdot}0127\,\beta = 2{\cdot}6006 \text{ eV} \end{aligned} \tag{9}$$

Accordingly, even linear polyenes can be represented in terms of localised "single"

---

* Similar calculations have also been carried out by A. Y. Meyer[37]: our conclusions concerning bond alteration in the polyenes are in good agreement with those reported by this author.

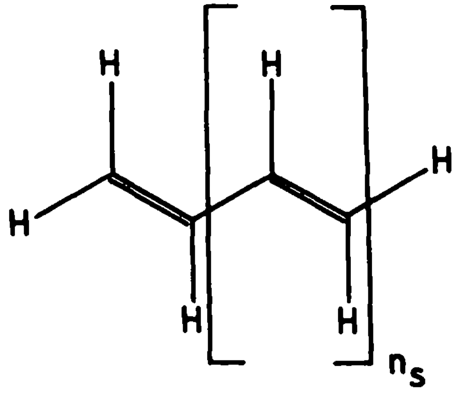

FIG. 1. General formula of the linear polyenes.

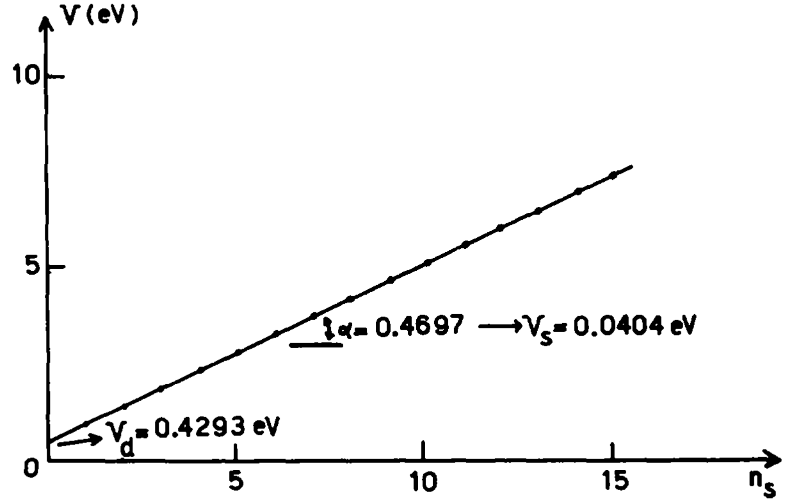

FIG. 2. Total σ-compression energy in the linear polyenes.

and "double" bonds, in agreement with Dewar's findings. The heat of atomization of a "localised" hydrocarbon is then given by the following relation:[21]

$$\Delta H_f^\circ(\text{loc}) = n_{cc} . E_{cc}^{\sigma} - (n_d . V_d + n_s . V_s) + (n_d . E_d^{\pi} + n_s . E_s^{\pi}) + n_{CH} . E_{CH} \tag{10}$$

Defining

$$V(\text{loc}) = n_d . V_d + n_s . V_s \tag{11}$$

and

$$E_{\pi b}(\text{loc}) = n_d . E_d^{\pi} + n_s . E_s^{\pi} , \tag{12}$$

Eq. 10 can be written in a form which will be useful in the following section of this paper:

$$\Delta H_f^\circ(\text{loc}) = n_{cc} . E_{cc}^{\sigma} - V(\text{loc}) + E_{\pi b}(\text{loc}) + n_{CH} . E_{CH} \tag{13}$$

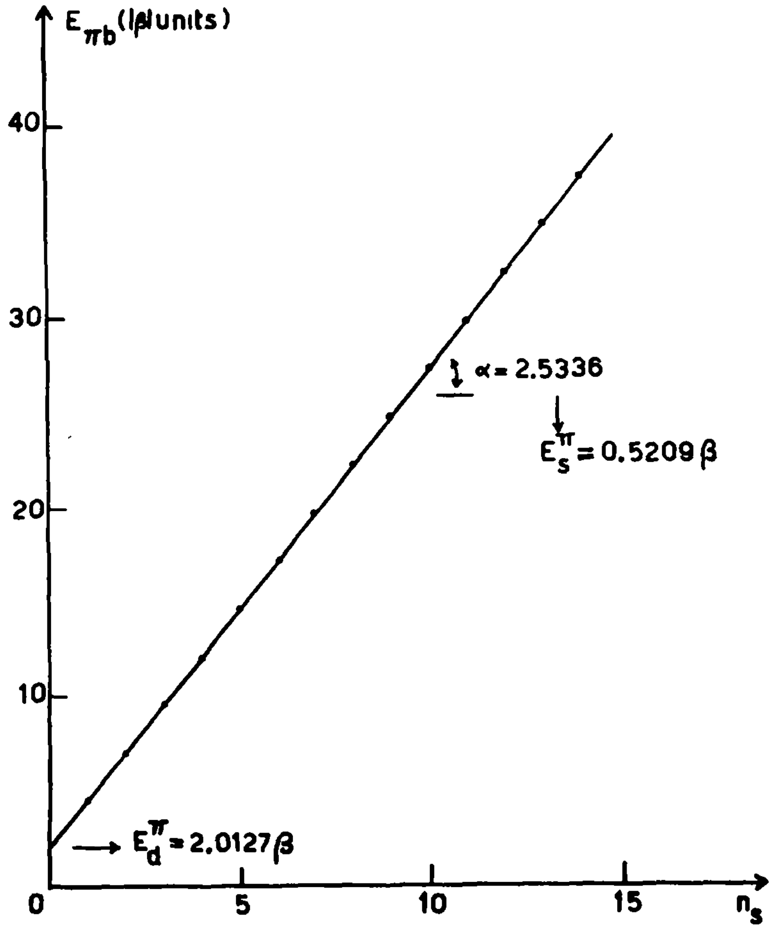

FIG. 3. Total π-binding energy of linear polyenes.

Using the previously determined value of E_{cc}^{σ} (3·726 eV),[21] and Eqs 7 and 9, the contributions of a "localised single" and of a "localised double" C—C bond to the heat of atomization of a conjugated hydrocarbon are given by:

$$\begin{aligned} E_s^{cc} &= E_{cc}^{\sigma} - V_s + E_s^{\pi} = 4{\cdot}3589\,\text{eV} \\ E_d^{cc} &= E_{cc}^{\sigma} - V_d + E_d^{\pi} = 5{\cdot}8975\,\text{eV} \end{aligned} \qquad (14)$$

These values compare favourably with the results obtained by Dewar and de Llano[14] for the heats of atomization of linear polyenes by the β-iterative Pople-method; they found 4·3499 eV and 5·5378 eV respectively for E_s^{cc} and E_d^{cc}.

Taking into account that $n_{cc} = n_s + n_{d'}$, Eq. 10 can be written in its final form:

$$\Delta H_f^{\circ}(\text{loc}) = n_s . E_s^{cc} + n_d . E_d^{cc} + n_{CH} \cdot E_{CH} \qquad (15)$$

with

$$E_{CH} = 4{\cdot}314\,\text{eV}^{21}$$

TABLE 1. TOTAL σ-COMPRESSION ENERGY (V) AND π-BONDING ENERGY ($E_{\pi b}$) IN THE LINEAR POLYENES

n (see Fig 1)	V(eV)	$E_{\pi b}$ in $\lvert\beta\rvert$ units
1	0·9013	4·5762
2	1·3678	7·0864
3	1·8356	9·6092
4	2·3042	12·1378
5	2·7930	14·6696
6	3·2436	17·2032
7	3·7130	19·7378
8	4·1830	22·2736
9	4·6547	24·8096
10	5·1247	27·3458
11	5,5939	29·8834
12	6·0655	32·4206
13	6·5352	34·9580
14	7·0084	37·4952

$\lvert\beta\rvert = 1{\cdot}2921$ eV[21]

TABLE 2. π-CONTRIBUTION (ΔE_{π}), σ-CONTRIBUTION (ΔE_{σ}) AND TOTAL RESONANCE ENERGY (E_{R}) OF THE [N]-ANNULENES

Annulenes			E_R	
[N]	ΔE_{π}(eV)	ΔE_{σ}(eV)	eV	Kcal/M
4	−1·1097	0·0534	−1·0563	−24·34
6	0·5375	−0·1030	0·4345	10·01
8	−0·5360	0·0680	−0·4680	−10·78
10	0·3370	−0·0637	0·2733	6·30
12	−0·3295	0·0438	−0·2857	− 6·58
14	0·2615	−0·0493	0·2122	4·89
16	−0·2202	0·0262	−0·1940	− 4·47
18	0·2264	−0·0414	0·1850	4·26
20	−0·1499	0·0149	−0·1350	− 3·11
22	0·2088	−0·0413	0·1675	3·86
24	−0·0982	0·0099	−0·0883	− 2·03
26	0·2011	−0·0379	0·1632	3·76
28	−0·0584	0·0006	−0·0578	− 1·33
30	0·1987	−0·0438	0·1549	3·57

(b) *The annulenes.* The results of the previous section were applied to the calculation of the resonance energy according to Breslow's and Dewar's definition for the different members of the annulene series up to $C_{30}H_{30}$. It has been shown in Part I[21] that the heat of atomization of any neutral unsaturated hydrocarbon is given by:

$$\Delta H_f^\circ = n_{cc}\,.\,E_{cc}^{\sigma} - V + n_{CH}\,.\,E_{CH} + E_{\pi b} \tag{16}$$

V and $E_{\pi b}$ being calculated by the L.C.A.O.-BETA method. For the corresponding "localised" hydrocarbon, $\Delta H_f^\circ(\text{loc})$ is given by Eq. 13. The resonance energy of our hydrocarbon is, by definition:

$$\begin{aligned} E_R &= \Delta H_f^\circ - \Delta H_f^\circ(\text{loc}) \\ &= \{E_{\pi b} - E_{\pi b}(\text{loc})\} + \{V(\text{loc}) - V\}. \end{aligned} \tag{17}$$

and putting,

$$\begin{aligned} \Delta E_\pi &= E_{\pi b} - E_{\pi b}(\text{loc}) \\ \Delta E_\sigma &= V(\text{loc}) - V, \end{aligned}$$

we obtain finally:

$$E_R = \Delta E_\pi + \Delta E_\sigma \tag{18}$$

Table 2 lists resonance energies calculated in this way for the series of compounds investigated; Fig IV shows the plot obtained for E_R as a function of the dimension of the ring [N].

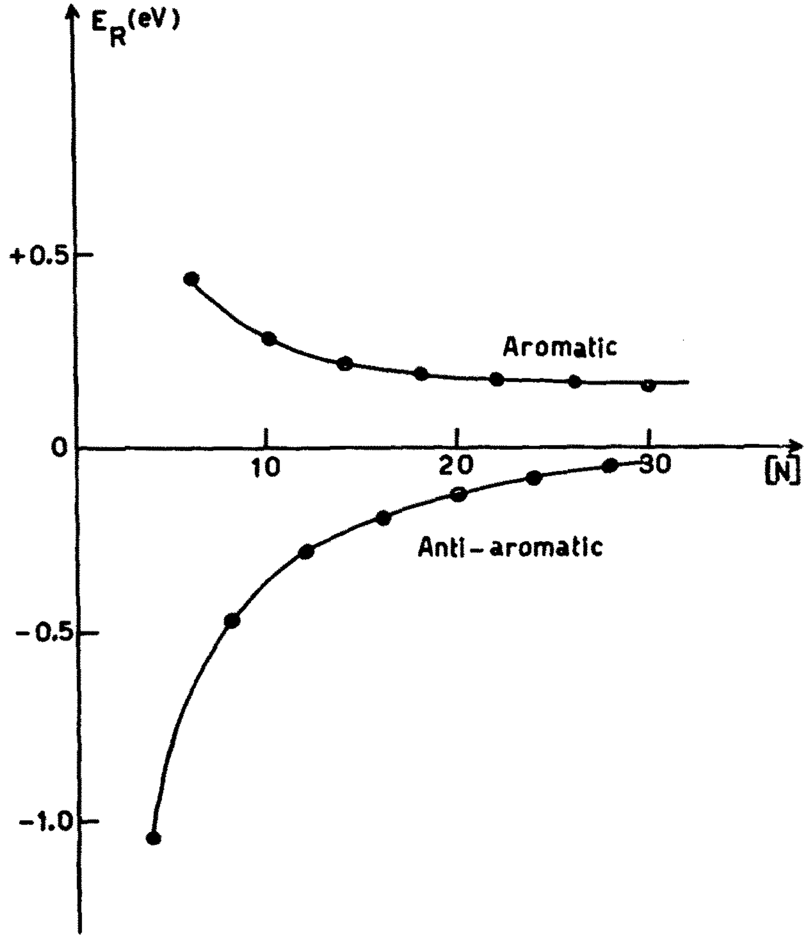

FIG. 4. Total resonance energy of the [N]-annulenes.

Obviously, the thermodynamic criterion divides the annulenes into two well separated series: the $(4n + 2)\pi$ electron ring-systems with stabilising resonance energy (positive values of E_R) and the $(4n)\pi$ electron ring-systems showing decreased stabilisation as compared with the "localised" model compounds. Thus, the first should be called *aromatic*, the latter *anti-aromatic*. The higher members in each case seem to converge to *non-aromaticity* ($E_R = 0$). The same results can also be obtained in a more qualitative way by simple MO-perturbation theory.[6,17,18] It is interesting to note (Table 2) that the general trend shown by the E_R-values is imposed by the π-contribution to the resonance energy ΔE_π, the σ-contribution being relatively small and *opposite in sign* to ΔE_π.

As shown by Eq. 18, resonance energies include the difference in σ-bond compression energy between the "localised" and delocalised structures. It must be pointed out, however, that the distortion energy and the steric effects which should be present in the planar geometries of the annulenes,[5,38] are not taken into account for calculating resonance-energies. In fact, electron diffraction measurements[39] and X-ray studies[40–42] show that at least up to [18]-annulene, the molecules are not planar, σ-orbital bending, due to relatively large deviations of the bond angles from 120°, being important even in [18]-annulene.[43,44] These interactions and deformations will perturb not only the π-electronic structure and π-energy of the molecule, but may alter to an even greater extent its σ-structure and σ-energy. Accordingly, it appears that experimentally, except for the very large annulenes ($N > 30$), the thermodynamic criterion of aromaticity will hardly be applicable to this type of molecules.

The only molecules listed in Table 2 for which experimental data are available are benzene,[14] cyclooctatetraene[45] and [18]-annulene.[19] As was shown in Part I, the heat of atomization of the first of them is accurately calculated by the LCAO-BETA method,[21] however, the resonance energy we obtain ($\sim$ 10 Kcal/M) is substantially lower than that given in modern textbooks (36 Kcal/M)[2,3] and more recently by Dewar (20 Kcal/M).[14]

From the experimental heats of combustion and evaporation of cyclooctatetraene[45] (COT), a heat of atomization of 1714·3 Kcal/M may be calculated for the observed tub-form. Using our localised bond energy values (Eq. 15), a *negative* experimental resonance energy (thus destabilizing) of −26·2 Kcal/M is obtained. Since the strain-energy in the tub-form has been estimated to be only 3·5 to 8·2 Kcal/M,[46,47] it looks as if these thermochemical data verify the predicted anti-aromaticity of COT. However, whether this negative resonance energy is due either to simple lack of "polyenic conjugation" or to a considerable tridimensional π-interaction is not yet known. This second assumption seems however to be in agreement with a recent magneto-optical study[48] showing an exceptionally large Faraday effect.

For planar "delocalised" cyclooctatetraene, a ΔH_f°-value of 1729·6 Kcal/M may be calculated; taking into account that a strain-energy of 25·5 to 43·6 Kcal/M has been advanced for the planar form,[46,47] the stable form of the molecule should indeed be the tub-form. An energy barrier for ring-inversion of 10·8 to 28·3 Kcal/M may be calculated,* in good agreement with the observed values: $\Delta G^\ddagger = 14{\cdot}8$ Kcal/M at −2°[49] and 12·7 Kcal/M at 0°.[50]

---

* In this calculation, it is assumed that inversion in C_8H_8 goes via the planar state; this problem has been discussed in detail recently by Dewar *et al.*(52)

The observed heat of combustion for [18]-annulene in the crystalline form is 2346·8 ± 4·0 Kcal/M.[19] The latent heat of sublimation for this compound has not yet been measured, but by comparison with other aromatic compounds of about the same molecular weight, a value of 28 ± 2 Kcal/M can be estimated.[19] From these values, a heat of formation of 3946·67 Kcal/M (171·30 eV) is obtained; this result is in severe disagreement with the theoretical value of 3·920,18 Kcal/M (170·25 eV) calculated in this work. The discrepancy lies however in the opposite direction from what would be expected if non-bonded intramolecular interactions were important.[51] It seems likely therefore that a definite answer to this puzzling problem will only be obtained by a complete a-priori calculation of the ($\sigma + \pi$) energy content of the molecule; an error of the order of 20 Kcal/M in the estimation of the latent heat of sublimation of the molecule seems indeed improbable.

In forthcoming publications, the Jahn–Teller deformations and energy barriers will be investigated by the LCAO-BETA method for the series of annulenes under study.

Acknowledgement—We are grateful to Professors R. H. Martin and M. J. S. Dewar for stimulating discussions and kind interest in our work. Financial support from the "Fonds Belge de la Recherche Fondamentale Collective" to the laboratory is gratefully acknowledged.

REFERENCES

[1] E. Hückel, *Z. Physik.* **70**, 204; **72** 310 (1931)

[2] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* Chapt. 10. Wiley, New York (1967)

[3] L. Salem, *The Molecular Orbital Theory of Conjugated Systems* pp. 110–126. Benjamin, New York (1966)

[4] D. M. G. Lloyd, *Carbocyclic Non-Benzenoid Aromatic Compounds* Chapt. 1. Elsevier, Amsterdam (1966)

[5] H. P. Figeys, in D. Lloyd, *Topics in Carbocyclic Chemistry* Vol. I, Chapt. 5. Logos Press, London (1969)

[6] M. J. S. Dewar, in *Aromaticity* Special Publication no 21 of the *Chemical Society* pp. 177–198. London (1967)

[7] H. A. Jahn and E. Teller, *Proc. Roy. Soc.* **161A**, 220 (1937)

[8] L. C. Snyder, *J. Phys. Chem.* **66**, 2299 (1962)

[9] M. Gouterman and G. Wagnière, *Ibid.* **36**, 1188 (1962)

[10] Ref. 3, Chapt. 8

[11] H. P. Figeys, to be published

[12] R. Breslow, J. Brown and J. J. Gajewski, *J. Am. Chem. Soc.* **89**, 4383 (1967)

[13] M. J. S. Dewar and G. J. Gleicher, *Ibid.* **87**, 692 (1965)

[14] M. J. S. Dewar and C. de Llano, *Ibid.* **91**, 789 (1969)

[15] A. L. H. Chung and M. J. S. Dewar, *J. Chem Phys.* **42**, 756 (1965)

[16] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.* **87**, 685 (1965)

[17] M. J. S. Dewar, in Y. Prigogine, *Advances in Chemical Physics* Vol. 8, p. 120. Interscience, London (1965)

[18] K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, *Bull. Chem. Soc. Japan* **33**, 1591 (1960)

[19] A. E. Beezer, C. T. Mortimer, D. H. Springall, F. Sondheimer and R. Wolovsky, *J. Chem. Soc.* 216 (1965)

[20] H. P. Figeys and P. Dedieu, *Theor. Chim Acta* **9**, 82 (1967)

[21] H. P. Figeys, *Tetrahedron* **26**, 4615 (1970)

[22] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* **257A**, 445 (1960)

[23] L. Salem, *Proc. Cambridge Phil. Soc.* **57**, 353 (1961)

[24] T. Nakajima and S. Kohda, *Bull. Chem. Soc. Japan* **39**, 804 (1966)

[25] J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.* **88**, 4811 (1966)

[26] F. Baer H. Kuhn and W. Regel, *Z. Naturforsch.* **22A**, 103 (1967)

[27] L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky and A. A. Bothner-By, *J. Am. Chem. Soc.* **84**, 4307 (1962)

[28] F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohman, G. Di Mayo, J. Mayer, M. V. Sargent and R. Wolovsky, in *Aromaticity* Special Publication no 21 of the *Chemical Society* p. 75. London (1967)

[29] F. Sondheimer, *Proc. Roy. Soc.* **297A**, 173 (1967)

[30] H. Kuhn, *J. Chem. Phys.* **16**, 840 (1948)

[31] M. J. S. Dewar, *J. Chem. Soc.* 3544 (1952)

[32] H. Labhart, *J. Chem. Phys.* **27**, 957 (1957)

[33] Y. Ooshika, *J. Phys. Soc. Japan* **12**, 1238, 1246 (1957)

[34] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* **251A**, 172 (1959)

[35] W. T. Dixon, *Tetrahedron* **18**, 875 (1962)

[36] J. M. Andre and G. Leroy, *Theor. Chim. Acta* **9**, 123 (1967)

[37] A. Y. Meyer, *Tetrahedron* **25**, 4449 (1969)

[38] K. Mislow, *J. Chem. Phys.* **20**, 1489 (1952)

[39] O. Bastiansen, L. Hedberg and K. Hedberg, *Ibid.* **27**, 1311 (1957)

[40] J. Bregman, *Nature, Lond.* **194**, 679 (1962)

[41] S. M. Johnson and I. C. Paul, *J. Am. Chem. Soc.* **90**, 6555 (1968)

[42] J. Bregman, F. L. Hirshfeld, D. Rabinovich and G. M. J. Schmidt, *Acta Cryst.* **19**, 227 (1965)

[43] F. L. Hirshfeld and D. Rabinovich, *Ibid.* **19**, 235 (1965)

[44] J. N. Murrell and A. Hinchliffe, *Trans Farad. Soc.* **62**, 2011 (1966)

[45] H. D. Springall, T. R. White and R. C. Cass, *Ibid.* **50**, 815 (1954)

[46] N. L. Allinger, *J. Org. Chem.* **27**, 443 (1962)

[47] N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford and J. C. Graham, *J. Am. Chem. Soc.* **87**, 3430 (1965)

[48] J. F. Labarre and O. Chalvet, *Tetrahedron Letters* 5053 (1967)

[49] F. A. L. Anet, A. J. R. Bourn and Y. S. Lin, *J. Am. Chem. Soc.* **86**, 3576 (1964)

[50] J. F. M. Oth, Personal communication quoted in Ref. 5

[51] C. A. Coulson and A. Golebiewski, *Tetrahedron* **11**, 125 (1960)

[52] M. J. S. Dewar, A. Harget and E. Haselbach, *J. Am. Chem. Soc.* **91**, 7521 (1969)