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QUANTUM CHEMISTRY STUDIES EQUILIBRIA IN SOME ACENE DERIVATIVES

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Abstract— Semi-empirical SCF-pi-molecular-orbital studies are presented for (I) tautomeric equilibria between methylacenes and methylene-dihydroacenes and (II) equilibria between isomers of dihydroacenes. The results are in excellent agreement with experiment.

I. *Methylacenes and methylene-dihydroacenes*

A remarkable study of the rather surprising equilibria existing between some methylacenes and their methylene-dihydroacene counterparts was published by Clar and Wright in 1949.[1] These reactions are hydrocarbon analogues of the keto-enol type of prototropic tautomerism found widely in heteroatomic systems. Despite the fact that these results have important consequences for the concepts of resonance energy and aromaticity, they have not gained the familiarity they deserve. In the hope of renewing interest in these reactions and of shedding more light on the chemistry involved, we made a theoretical investigation of the following equilibria between "aromatic" methylacenes and "less-aromatic" methylene-dihydroacenes.

In their study, Clar and Wright examined reactions 4, 6, and 9. They concluded from UV studies, that the equilibrium in reaction 4 was almost completely to the side of 9-methyl anthracene but they could not exclude the possible presence of a small percentage of the methylene form. The equilibrium in reaction 6 was also in favor of the methyl compound, but "an appreciable proportion of a weakly absorbing methylene form" was postulated. In the case of reaction 9, however, the equilibrium was well over to the side of the "less-aromatic" 6,13-dihydro-6-methylene isomer. Furthermore, when this pale yellow equilibrium mixture was heated to 200°, the solution became violet-red and the UV bands expected for the methylpentacene system appeared. On cooling, the spectrum returned to that seen previously. Thus the reversible character of this tautomerism was demonstrated.

Several groups have presented theoretical studies of these reactions,[2] all based on the Hückel Molecular Orbital (HMO) method. These correctly demonstrated the relative decrease in resonance energy with increased annelation. However, none were able to conclude that the equilibrium would fall on the side of the methylene derivative in the case of reaction 9. On the basis of the HMO method, it is predicted that as the number of annelated rings is increased to infinity, the difference in resonance energies between the methyl-form and the methylene-form will approach zero, but the energy of the methylene-form will never become lower than that of the methyl-form.

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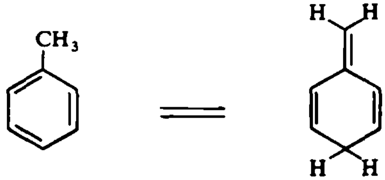
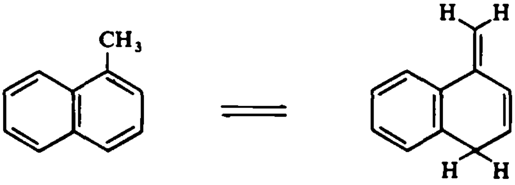


I A I B

(1)



II A II B

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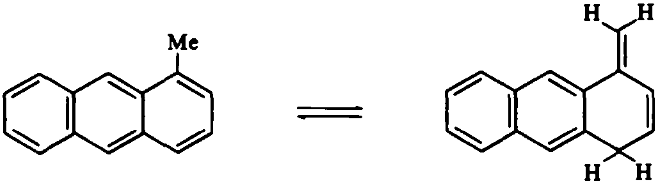
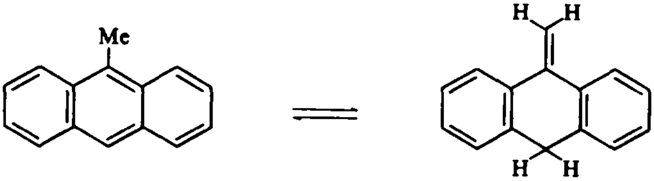


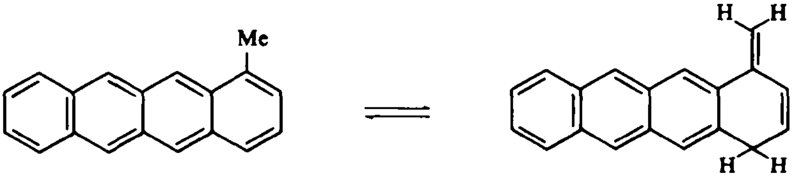
III A III B

(3)



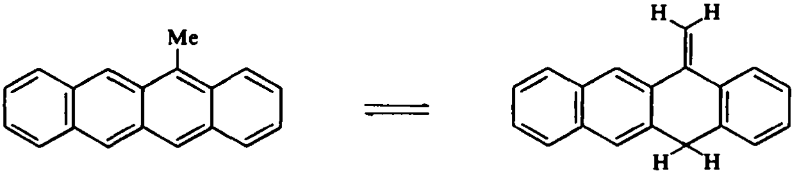
IV A IV B

(4)



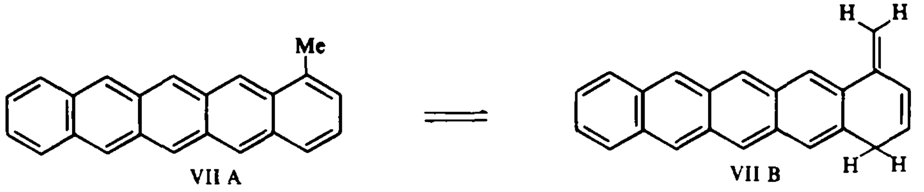
V A V B

(5)

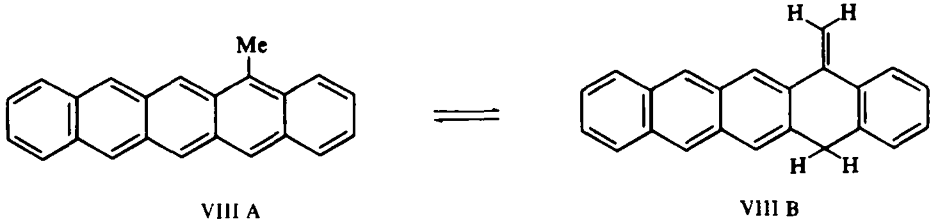


VI A VI B

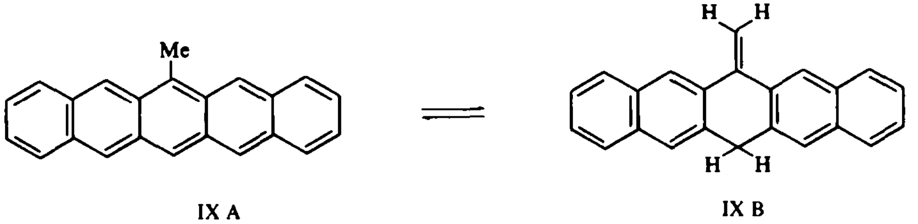
(6)



VII A VII B (7)



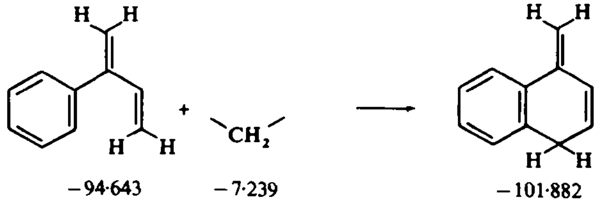
VIII A VIII B (8)



IX A IX B (9)

We undertook a reinvestigation of this problem in terms of the semi-empirical SCF-MO treatment of conjugated molecules developed by Dewar *et al.*.[3] This method has been shown to be at least equal to laboratory methods for determining ground state properties of π-systems lacking substantial ring strain and non-bonded interactions.

Since this method calculates only unsaturated molecules, it was necessary to make adjustments for the saturated portions of the compounds in these equilibria. Thus, for example in the case of 1,4-dihydro-1-methylene-naphthalene, II B, the SCF-method was used to calculate the heat of atomization of the analogous 2-phenyl-1,3-butadiene having the same π-system. This was then converted to the molecule of interest by adding a factor for the methylene bridge of −7·239 eV found by Dewar *et al.*[4] by comparing the heats of atomization of cyclopentadiene and *cis*-1,3-butadiene.



That this factor should not differ from that in our 6-membered ring system was inferred from the calculations on strain energies of analogous 5- and 6- membered rings made by Cox.[5]

The heats of atomization of the methyl compounds were treated similarly by calculating the unsubstituted acenes*[, 3] and then adding a factor for the methyl group of −12·270 eV found by comparing the heats of atomization of benzene and toluene (−57·16 eV and −69·43 eV, respectively). The results of these calculations are listed in Table 1.†

TABLE 1. CALCULATED ENERGIES OF METHYLACENES AND METHYLENE-DIHYDROACENES

	Compound	$-\Delta H_a$(eV)[a]	$\Delta H_a(A) - \Delta H_a(B)$	Resonance energies (eV)	$\lvert\delta E\rvert$[b]
IA	Toluene	69·427	−1·400	0·869	$4a\beta$
IB	3-Methylene-1,4-cyclohexadiene	68·027		−0·025	$2a\beta$
IIA	1-Methyl-naphthalene	102·880	−0·998	1·322	$6a\beta$
IIB	1,4-Dihydro-1-methylene-naphthalene	101·882		0·830	$4a\beta$
IIIA	1-Methyl-anthracene	136·168	−0·821	1·609	$8a\beta$
IIIB	1,4-Dihydro-1-methylene-anthracene	135·347		1·294	$6a\beta$
IVA	9-Methyl-anthracene	136·168	−0·428	1·609	$4a\beta$
IVB	9,10-Dihydro-9-methylene-anthracene	135·740		1·687	$4a\beta$
VA	1-Methyl-tetracene	169·385	−0·745	1·826	$10a\beta$
VB	1,4-Dihydro-1-methylene-tetracene	168·640		1·587	$8a\beta$
VIA	5-Methyl-tetracene	169·385	−0·179	1·826	$5a\beta$
VIB	5,12-Dihydro-5-methylene-tetracene	169·206		2·153	$6a\beta$
VIIA	1-Methyl-pentacene	202·562	−0·702	2·003	$12a\beta$
VIIB	1,4-Dihydro-1-methylene-pentacene	201·860		1·807	$10a\beta$
VIIIA	5-Methyl-pentacene	202·562	−0·061	2·003	$6a\beta$
VIIIB	5,14-Dihydro-5-methylene-pentacene	202·501		2·442	$8a\beta$
IXA	6-Methyl-pentacene	202·562	+0·111	2·003	$4a\beta$
IXB	6,13-Dihydro-6-methylene-pentacene	202·673		2·620	$6a\beta$

[a] Heat of atomization.
[b] Energy of union.

An examination of these results reveals that the equilibria of the first members of this series lie heavily on the side of the methylacenes. Certainly in the case of toluene and methylnaphthalene this is in line with common experience.‡ As the number of annelated rings increases, however, the energy differences between the two possible tautomers decreases, until, in the case of the 6-substituted pentacene, there is a reversal. The difference in heats of atomization between these two isomers is +0·111 eV and the equilibrium favors the methylene-dihydro-tautomer. The energy difference found for the 5-methyltetracene pair, −0·061 eV, is seen to be small and favoring the

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* The quantum chemical data for the compounds calculated in this study are being published.[6]

† Constants used in calculation of heats of atomization are:

$C_{(graphite)} \rightarrow C_{(gas)}$ 120·89 kcal/mole
$1/2\ H_{2(gas)} \rightarrow H_{(gas)}$ 52·102 kcal/mole
$CO_{2(gas)} \rightarrow C_{(graphite)} + O_{2(gas)}$ 94·0518 kcal/mole
$H_2O \rightarrow H_{2(gas)} + 1/2\ O_{2(gas)}$ 68·3154 kcal/mole
1 eV = 23·0609 kcal/mole

‡ The methylene isomer of toluene has been synthesized, and it converts smoothly to toluene at room temperature.[7]

methyl tautomer. Thus our results are in excellent agreement with those found experimentally.*

The as yet unknown 5-methylpentacene is also predicted to exist as a mixture with its 5,12-dihydro-5-methylene tautomer at equilibrium since the ΔH_a difference is a relatively low $-0{\cdot}061$ eV.

The resonance energy of a molecule is the difference between its true energy and the energy that it could have if its bonds were localized in pure single and double bonds. The hypothetical heat of atomization thus becomes a summation of the energies of the various types of bonds found in a classical (i.e. Kekulé) structure of a molecule:

$$\Delta H_a = a\,E_{\mathrm{C—H}} + b\,E_{\mathrm{C—C}} + c\,E_{\mathrm{C=C}},$$

where a, b, and c are the numbers of C—H, C—C, and C═C bonds respectively. The energies of these bonds are given by the following expressions:

$$E_{\mathrm{C—H}} = -4{\cdot}4375\,\mathrm{eV}$$
$$E_{\mathrm{C—C}} = -4{\cdot}3499\,\mathrm{eV}$$
$$E_{\mathrm{C=C}} = -5{\cdot}5378\,\mathrm{eV}$$

which are energies for these pure bond types which come out of this SCF treatment.†, [3] As an example, the equation for benzene becomes $\Delta Ha = 6(-4{\cdot}4375) + 3(-4{\cdot}3499) + 3(-5{\cdot}5378) = -56{\cdot}288$ eV. The resonance energy then is the difference between this hypothetical heat of atomization and that found experimentally or calculated by the SCF procedure. Thus the resonance energy for benzene becomes $57{\cdot}157 - 56{\cdot}288 = 0{\cdot}869$ eV. The results of these calculations are also found in Table 1.

It can be seen that in those cases where the difference in heats of atomization is greater than about $-0{\cdot}5$ eV (i.e. reactions 4, 6, 8 and 9) the resonance energies of the methylene isomers are *greater* than those of the methyl derivatives. Thus, based on these considerations, it is not at all surprising that the methylene tautomers should become more stable in the more highly annelated systems.

It is interesting to note that the perturbational molecular orbital (PMO) treatment of Dewar[9] yields results that are in better agreement with experiment and with the full calculations than those of HMO treatments[2] and in agreement with those that result from consideration of resonance energies alone.

Application of the PMO treatment will be illustrated by the example of reaction 2. The coefficients of the non-bonding molecular orbital (NBMO) of the phenyl allyl radical are shown in Fig. 1a.

The conjugated system for compound II A, naphthalene, is formed by union with a methyl radical as shown in Fig. 1b. The energy of union in this case is

$$\delta E = 2\,\Sigma\,|a_{or}|\beta = 2|-a - 2a|\beta = 6a\,\beta.$$

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* These calculations refer to the idealized case of gaseous molecules in their vibrational and rotational ground states and do not reflect the altered circumstances found in solution. Also, the small differences in entropy that will exist between tautomeric pairs is ignored.

† This measure of resonance energy has recently been reviewed.[8]

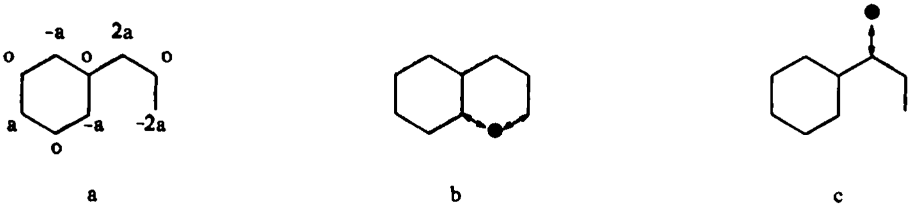
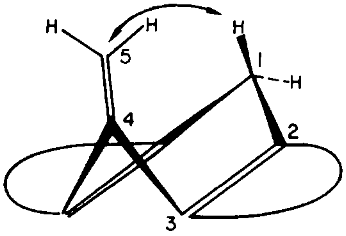


Fig. 1. Application of PMO method

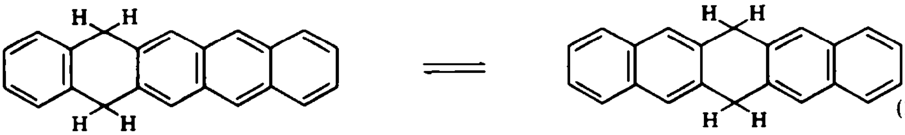
(Absolute values are used because the choice of signs of the coefficients is initially arbitrary). Similarly, the conjugated system of compound II B, 2-phenyl-butadiene, is formed by union with a methyl radical as in Fig. 1c. In this case, the energy of union is $\delta E = 2|2a|\beta = 4a\beta$. The values of these δE's are found in the final column of Table 1. It can be seen that compounds A are more stable than compounds B except in the cases of reactions 4, 6, 8, and 9 in conformity with the resonance energies.

One other point should be discussed briefly. In order to have the equilibria found here, not only must there be the energy differences we have been discussing, but also there should be a low energy pathway between the two forms. Such a pathway was suggested by Dreiding *et al.*[10] for the reaction I A → I B, i.e. a suprafacial 1,5 sigmatropic shift, as illustrated below for a generalized methylene tautomer.



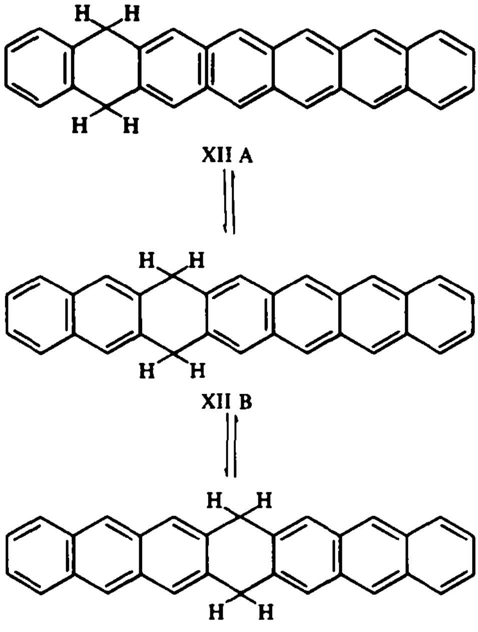
II. *Dihydroacenes*

Shown below is a series of reactions which can be similarly studied:



X A X B (10)

XI A XI B (11)

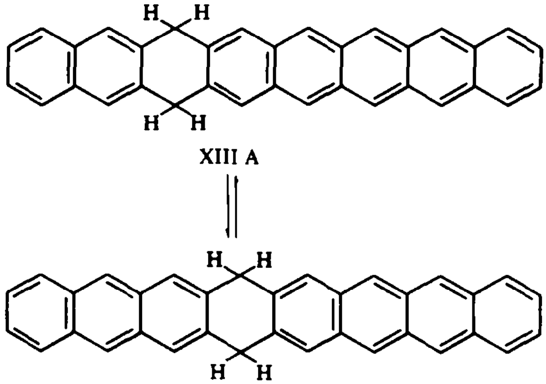


XII A

XII B

XII C

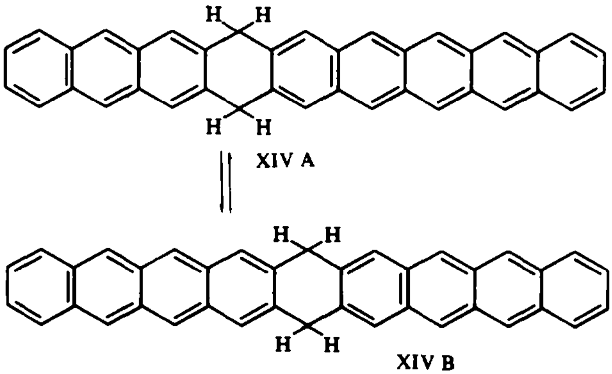
(12)



XIII A

XIII B

(13)



XIV A

XIV B

(14)

In all these equilibria, a pair of hydrogens migrate about the opposite apices of the rings making up large partially hydrogenated acenes. The first three of these reactions 10, 11, and 12, have been discussed by Clar.[1b]

When 6,13-dihydropentacene, X B, was heated to 250°C, in vacuum, about 5% of it was converted to its 5,14-dihydro isomer, X A. Similarly, at 300°C, 98% of 5,16-dihydrohexacene, XI A, was converted to its 6,15-dihydro-isomer, XI B. On refluxing in nitrobenzene, 5,18-dihydroheptacene, XII A, was completely and irreversibly converted to an approximately equimolar mixture of the 6,17- and 7,16-dihydro isomers, XII B and XII C. The compounds in reactions 13 and 14 are not yet known.

The heats of atomization of the compounds in this set of equilibria can be calculated by the following method, illustrated for the case of 5,14-dihydropentacene, X A. Using the calculated heats of atomization[3, 6] of benzene and anthracene, and twice the previously determined adjustment for —CH_2—, we calculate $-57{\cdot}157 - 123{\cdot}898 - 7{\cdot}239 - 7{\cdot}239 = -195{\cdot}533$ eV, reflecting the notion that X A is made up of a benzene, an anthracene, and two CH_2 bridges.

In Table 2 are found the calculated heats of formation.

TABLE 2. CALCULATED ENERGIES OF DIHYDROACENES

	Compound	$-\Delta H_a$(eV)[a]	ΔH_a(A) $-$ ΔH_a(B)	Resonance energy	Paralocalization energy
XA	5,14-Dihydropentacene	195·533	0·165	2·478	1·77 β
XB	6,13-Dihydropentacene	195·698		2·644	1·60 β
XIA	5,16-Dihydrohexacene	228·750	0·237	2·695	1·58 β
XIB	6,15-Dihydrohexacene	228·987		2·931	1·34 β
XIIA	5,18-Dihydroheptacene	261·927	0·276	2·872	1·44 β
XIIB	6,17-Dihydroheptacene	262·203		3·148	1·18 β
XIIC	7,16-Dihydroheptacene	262·275	0·072	3·218	1·11 β
XIIIA	6,19-Dihydrooctacene	295·380	0·110	3·325	1·06 β
XIIIB	7,18-Dihydrooctacene	295·491		3·435	0·96 β
XIVA	7,20-Dihydrononacene	328·668	0·039	3·612	0·85 β
XIVB	8,19-Dihydrononacene	328·707		3·652	0·82 β

[a] Heat of atomization.

These results are in excellent quantitative agreement with those obtained experimentally. The equilibrium mixture of reaction 13 should consist mostly of compound XIII B. In reaction 14 we should expect an almost equimolar mixture of the two components.

The resonance energies, also found in Table 2, are found by summing the resonance energies of the component aromatic parts. For example, again illustrated by compound X A the resonance energy is found by adding the resonance energies[3] of benzene and anthracene—$0{\cdot}069 + 1{\cdot}609 = 2{\cdot}478$ eV. It can be seen that these are in agreement with the heat of atomization differences, which is to be expected due to the similarities in the geometries of these compounds.

These results also give experimental confirmation to the assertion by Dewar[3] that the calculated value for the heat of atomization of tetracene (157·112 eV) is more accurate than the experimental value[11] (157·56 eV). If the experimental value had been used, the results for reaction 11 would have been reversed and compound XII B would have been projected as the most stable compound in reaction 12 in contrast to experimental results.

The PMO method may also be successfully applied to this series of reactions. Each compound may be thought of as being formed by the 1,4 attack of a reducing agent on a completely conjugated parent molecule. Thus, the different members of each of these equilibria are the products of attack at different pairs of apices of a single polyacene. PMO estimate of the relative loss of energy in these reductions can be obtained by calculating the paralocalization energies.[12] The relative stabilities of the products will be determined by the smallness of this term. These energies are shown in the final column of Table 2. It may be seen that the agreement with experiment and the full calculations is good.

Acknowledgements—Calculations were made on an IBM 360–44 on time donated by the Centre de Calcul of the Université de Louvain. Thanks are due to Prof. M. J. S. Dewar for supplying a listing of the MO-program and to Prof. L. Ghosez for welcoming me into his laboratory.

REFERENCES

[1] [a] E. Clar and J. W. Wright, *Nature* **163**, 921 (1949);
[b] E. Clar, *Chem. Ber.* **82**, 495 (1949)
[2] [a] J. Syrkin and M. Dyatkina, *Acta Physicochim USSR* **21**, 641 (1948); B. Pullman and A. Pullman, *Les Théories Électroniques de la Chimie Organique*, p. 250. Masson and Cie, Paris (1952)
[b] E. Hückel and B. Krause, *Z. Naturforsch* **6a**, 112 (1951);
[c] G. Berthier and A. Pullman, *Compt. Rend.* **229**, 1334 (1949)
[3] M. J. S. Dewar and Carlos de Llano, *J. Am. Chem. Soc.* **91**, 789 (1969)
[4] N. Bodor, M. J. S. Dewar and A. J. Harget, *Ibid.* **92**, 2929 (1970)
[5] J. D. Cox, *Tetrahedron* **19**, 1175 (1963)
[6] [a] M. J. S. Dewar and N. Trinajstić, *Coll Czech Chem. Comm.* **35**, 3136 (1970);
[b] M. L. Herr, *Ibid.* (in press)
[7] [a] H. Pleninger and W. Maier-Bost, *Angew. Chem.* **75**, 1177 (1963): (Internat. Edit. 3, 62 (1964);
[b] *Idem. Chem. Ber.* **98**, 2504 (1965)
[8] N. C. Baird, *J. Chem. Educ.* **48**, 494 (1971)
[9] M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, Chapter 6. Mc-Graw-Hill Book Co., New York (1969)
[10] M. Rey, U. A. Huber, A. S. Dreiding, *Tetrahedron Letters* 3583 (1968)
[11] A. Magnus, H. Hartmann, F. Becker, *Z. Physik Chem.* (Leipzig) **197**, 75 (1951)
[12] [a] Ref. 9, pàge 323;
[b] M. J. S. Dewar, *J. Am. Chem. Soc.* **74**, 3357 (1952)