405. The Basicity of Hydrocarbons. Part IV.* A Theoretical Treatment of Conjugated Hydrocarbons.

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The difference in π-electron coupling energies of a hydrocarbon base and its conjugate acid, as calculated by Hückel's molecular-orbital method, is taken as a theoretical measure of basicity. The treatment enables one to make predictions of the position of proton attachment to a conjugated system and of the relative basicity of structurally similar conjugated hydrocarbons which are in agreement with experiment.

THE equilibrium constant (K) for a reaction of the type $H_2SO_4 + B \rightleftharpoons HB^+ + HSO_4^-$ may be expressed as the product of the equilibrium constants of the two fictitious stages

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$H^+ + B \rightleftharpoons HB^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and it may also be related to the standard free-energy changes associated with these stages :

$$-RT \ln K = \Delta G_1^\circ + \Delta G_2^\circ \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

ΔG_1° is obviously independent of the base used and it is probably also safe to assume that the entropy change accompanying the second stage ("entropy of protonation") is independent of the base, provided that the structure changes involved in the protonation reaction are similar. Thus it is plausible to assume that the entropy of protonation of aryl-substituted ethylenes will be constant. It may not be equally correct to assume that the entropy of protonation of anthracene would be the same, for a different amount of internal "loosening-up" would accompany the reaction in this case. Attention being restricted to an isentropic series, equation (3) becomes

$$-RT \ln K = \Delta H_2 + \text{constant}$$

It is well established that in many reactions of conjugated hydrocarbon systems the most important structure-sensitive contribution to the heat of reaction or activation comes from the changes in the total energy of the π-electrons, the contribution from σ-electrons being less influenced by structural changes. It has also been shown in several cases that a good relative assessment of the π-electron contribution to heats of reaction and activation may be calculated by Hückel's molecular-orbital method (*Z. Physik*, 1931, **70**, 204; **72**, 310; 1932, **76**, 628). We have used this method in its simplest form, as it has been shown that for energy calculations the neglect of overlap does not introduce a structure-sensitive error, the chief consequence being a change in the value of an empirical energy parameter (usually given the symbol β or γ) in terms of which the energy changes are expressed (Wheland, *J. Amer. Chem. Soc.*, 1941, **63**, 2025).

$$\Delta H_2 = H_{HB^+} - H_B - H_{H^+}$$
$$= \{(E_\sigma)_{HB^+} - (E_\sigma)_B\} + \{(E_\pi)_{HB^+} - (E_\pi)_B\} - H_{H^+}$$
$$\text{Therefore} \quad -RT \ln K = (E_\pi)_{HB^+} - (E_\pi)_B + \text{constant}$$
$$= \Delta E_\pi + \text{constant}$$

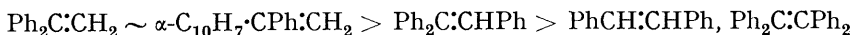where the terms E_σ and E_π represent the contributions from the energies of the σ- and π-electrons to the heat contents of the molecules referred to by the second subscript.

$(E_\pi)_{HB^+}$ and $(E_\pi)_B$ are obtained in terms of the energy parameter β from the molecular-orbital calculations. The approximations made in calculations of this type have been discussed by Coulson and Dewar (*Discuss. Faraday Soc.*, 1947, **2**, 54), who have stressed the greater uncertainty involved in applying molecular-orbital calculations to ions. However, it is probable that these difficulties are minimized in a comparison of structurally similar molecules. For instance, Wheland has successfully applied the method to positively and

* Part III, preceding paper.

negatively charged structures (*J. Amer. Chem. Soc.*, 1942, **64**, 900). We also assume that any errors in the calculation arising out of the non-coplanarity of the structures will cancel out in the difference ΔE_π.

There are several ways in which the results of the calculations (see Table) may be compared with experiment. First, by calculating $(E_\pi)_{HB^+}$ for the different possible carbonium ions which can be formed from the same hydrocarbon by proton addition at different carbon atoms, it is possible to predict the most stable carbonium ion and hence the position of the proton attachment. This may be compared with the experimental deductions of Part II (*J.*, 1952, 2172) with which there is complete agreement. Secondly, the order of basicity of the arylethylenes may be compared with the results reported in Part III (*loc. cit.*). The order derived from the calculations, *viz.*
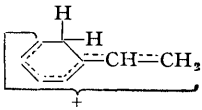
$$Ph_2C\!:\!CH_2 \sim \alpha\text{-}C_{10}H_7\!\cdot\!CPh\!:\!CH_2 > Ph_2C\!:\!CHPh > PhCH\!:\!CHPh, Ph_2C\!:\!CPh_2$$
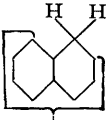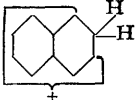
agrees with the sequence tentatively inferred from the partition experiments, the order of the first two compounds being less certain than that of the others. For addition reactions to conjugated systems which are thought to occur by a two-stage mechanism initiated by proton attack, such as the thermal addition of hydrogen halides, these calculations will predict the position of proton attachment (it being assumed that the thermodynamically most stable cation is formed in preference). For instance, it is seen that the addition of a proton should occur at the terminal position of buta-1 : 3-diene rather than in the middle. In agreement with this it is found that the products of the reaction between hydrogen chloride and butadiene are 3-chlorobut-1-ene and 1-chlorobut-1-ene. Of course, the physical principles underlying this conclusion (formation of the largest possible conjugated system) have been understood in a qualitative way for some time. In the aryl-substituted ethylenes these calculations lead to the conclusion that the two-stage heterolytic addition of a reagent HX should occur in such a way that the negative fragment X appears on the carbon atom carrying the smaller number of hydrogen atoms, which constitutes an *a priori* derivation of the equivalent of Markownikoff's rule for this particular class of compound.

In the case of proton addition to an aromatic ring, our calculations are analogous to those of Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900) on the position of aromatic substitution in benzene derivatives (see also Dewar, *J.*, 1949, 463.) In these calculations the transition state for aromatic substitution by a group X is supposed to have the structure (I), resulting in interruption of conjugation at the point of substitution, with the remaining

(I)   (II)

conjugated system sharing the electric charge of the reagent X. In the case of anthracene we concluded from our measurements of absorption spectra (Part II, *loc. cit.*) that a structure of this form is in fact stable (if X = H^+) and not just the transition state for a hydrogen-replacement reaction. It does seem likely, however, that the electronic arrangement in the transition state is more akin to this conjugate acid cation than to the ground state, which is a reason for the success of such calculations. For the case of aromatic substitution in polycyclic hydrocarbons it is difficult to compare the results of the calculations with experimental data. It appears that steric factors often assume a rôle of comparable importance to that of the π-electron energies. Already in anthracene the position of electrophilic substitution depends on the nature of the reagent employed. It may, however, be thought that the calculations should give the position of electrophilic replacement in the absence of structure-sensitive non-electronic contributions to the activation energy. The hydrogen-isotope replacement reaction may satisfy this requirement and it is hoped to report on this later.

The results for the calculation on polycyclic hydrocarbons are illustrated by the examples in the Table. Calculation for other molecules of this type leads to the generalization that proton addition is most likely in *meso*-positions, less so for α-positions in naphthalene structures, and least favourable for β-positions. Ions which contain the grouping (II) are par-

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B	$(E_\pi)_B$	HB+	$(E_\pi)_{HB^+}$	$-(\Delta E_\pi + 2a)\beta^{-1}$
$CH_2{:}CH_2$	$2a + 2\beta$	$CH_3{\cdot}CH_2^+$	0	$2{\cdot}00$
$CH_2{:}CH{\cdot}CH{:}CH_2$	$4a + 4{\cdot}47\beta$	$CH_3{\cdot}\overset{+}{CH}{=}CH{=}CH_2$	$2a + 2{\cdot}83\beta$	$1{\cdot}64$
		$\overset{+}{C}H_2{\cdot}CH_2{\cdot}CH{:}CH_2$	$2a + 2{\cdot}00\beta$	$2{\cdot}47$
$CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2$	$6a + 6{\cdot}96\beta$	$CH_3{\cdot}\overset{+}{CH}{=}CH{=}CH{=}CH{=}CH_2$	$4a + 5{\cdot}46\beta$	$1{\cdot}50$
		$CH_2{:}CH{\cdot}CH_2{\cdot}\overset{+}{CH}{=}CH{=}CH_2$	$4a + 4{\cdot}83\beta$	$2{\cdot}13$
		$\overset{+}{C}H_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH{:}CH_2$	$4a + 4{\cdot}47\beta$	$2{\cdot}49$
$Ph{\cdot}CH{:}CH_2$	$8a + 10{\cdot}42\beta$	$Ph{=}\overset{+}{CH}{\cdot}CH_3$	$6a + 8{\cdot}72\beta$	$1{\cdot}70$
		[ring structure with H, ${=}CH{=}CH_2$]	$6a + 8{\cdot}05\beta$	$2{\cdot}37$
		$Ph{\cdot}CH_2{\cdot}\overset{+}{C}H_2$	$6a + 8{\cdot}00\beta$	$2{\cdot}42$
$Ph{\cdot}CH{:}CHPh$	$14a + 18{\cdot}88\beta$	$Ph{=}\overset{+}{CH}{\cdot}CH_2{\cdot}Ph$	$12a + 16{\cdot}72\beta$	$2{\cdot}16$
$Ph_2C{:}CH_2$	$14a + 18{\cdot}81\beta$	$Ph_2\overset{+}{C}{\cdot}CH_3$	$12a + 17{\cdot}30\beta$	$1{\cdot}51$
		$Ph_2CH{\cdot}\overset{+}{C}H_2$	$12a + 16{\cdot}00\beta$	$2{\cdot}81$
$Ph_2C{:}CHPh$	$20a + 27{\cdot}26\beta$	$Ph_2\overset{+}{C}{\cdot}CH_2Ph$	$18a + 25{\cdot}30\beta$	$1{\cdot}96$
		$Ph_2CH{\cdot}\overset{+}{CH}{=}Ph$	$18a + 24{\cdot}72\beta$	$2{\cdot}54$
$Ph_2C{:}CPh_2$	$26a + 35{\cdot}72\beta$	$Ph_2\overset{+}{C}{\cdot}CHPh_2$	$24a + 33{\cdot}30\beta$	$2{\cdot}42$
$a{-}C_{10}H_7{\cdot}CPh{:}CH_2$	$18a + 24{\cdot}5_1\beta$ [1]	$a{-}C_{10}H_7{\cdot}\overset{+}{C}(Ph){\cdot}CH_3$	$16a + 23{\cdot}0_4\beta$ [2]	$1{\cdot}5$
		$a{-}C_{10}H_7{\cdot}CH(Ph){\cdot}\overset{+}{C}H_2$	$16a + 21{\cdot}68\beta$	$2{\cdot}8$
[benzene ring]	$6a + 8{\cdot}00\beta$	[ring with H H]	$4a + 5{\cdot}46\beta$	$2{\cdot}54$
[naphthalene]	$10a + 13{\cdot}68\beta$	[naphthalene with H H]	$8a + 11{\cdot}38\beta$	$2{\cdot}30$
		[naphthalene with H H]	$8a + 11{\cdot}18\beta$ [3]	$2{\cdot}5$

[1] The introduction of a phenyl group into styrene (in the a-position), stilbene, benzene, diphenyl, etc., is associated with a change in the π-electron coupling energy of $8{\cdot}39 \pm 0{\cdot}01\beta$. Assumption of the same change on going from a-naphthylethylene ($E_\pi = 12a + 16{\cdot}12\beta$ *) gives the value in the table. [2] The replacement of a phenyl group by an a-naphthyl group in the benzyl radical is associated with a change in the coupling energy of $5{\cdot}77\beta$; the same replacement in triphenylmethyl, with a change of $5{\cdot}74\beta$. Assumption that the change on going from the diphenylmethyl ($17{\cdot}03\beta$) to the a-naphthyl-phenylmethyl radical is intermediate leads to the value given. [3] The π-electron energy of the p-isomer * is taken.

* Value from Syrkin and Diatkina (*loc. cit.*).

B	$(E_\pi)_B$	HB$^+$	$(E_\pi)_{HB^+}$	$-(\Delta E_\pi + 2\alpha)\beta^{-1}$
	$14\alpha + 19\cdot31\beta$		$12\alpha + 17\cdot30\beta$	2·01
			$12\alpha + 17\cdot0_7\beta$ [4]	2·2
			$12\alpha + 16\cdot8_4\beta$ [5]	2·6
	$14\alpha + 19\cdot45\beta$		$12\alpha + 17\cdot1_4\beta$ [6]	2·3
			$12\alpha + 17\cdot14\beta$ *	2·31
			$12\alpha + 17\cdot0_7\beta$ [4]	2·4
			$12\alpha + 16\cdot9_1\beta$ [7]	2·5
			$12\alpha + 16\cdot8_6\beta$ [8]	2·6
	$20\alpha + 28\cdot21\beta$ [9]		$18\alpha + 26\cdot4\beta$ [10]	1·8

[4] The difference in coupling energy between α- and β-naphthylcarbonium ion is $0\cdot07\beta$. The same relation being assumed to hold for the vinylogs, the value for the α-isomer ($17\cdot14\beta$) leads to the value in the table. [5] Introduction of a $\overset{+}{C}H_2$ group into the β-position of naphthalene changes the coefficient of β by $0\cdot74$. The same change is assumed to be affected by this substitution in β-naphthylethylene ($16\cdot10\beta$ *). [6] The π-electron energy of the p-isomer is taken. [7] Introduction of a $\overset{+}{C}H_2$ group into the α-position of naphthalene changes the coefficient of β by $0\cdot81$. The same change is assumed to occur from this substitution in β-naphthylethylene. [8] Introduction of $\overset{+}{C}H_2$ into the β-position of α-naphthylethylene ($16\cdot12\beta$ *); cf. footnote 5. [9] Approximate value given by Brown (*Trans. Faraday Soc.*, 1950, **48**, 1013). [10] Introduction of a phenyl group into (II)$^+$ is assumed to increase the coupling energy by $8\cdot6\beta$.

* Value from Syrkin and Diatkina (*loc. cit.*). † Most stable formulation of conjugate acid.

ticularly stable.* The low value of ΔE_π found for 3 : 4-benzopyrene is connected with this and is in accord with the qualitative observation of strong basicity of this compound.

Explanation of Table of Results.—The π-electron energies are expressed in terms of the Coulomb integral α and the resonance integral β. Since β is a negative quantity the stability of the conjugate acid cation will be greater the lower the numerical value given in col. 5. Thus the first of the two values for 1 : 1-diphenylethylene (1·51), corresponding to proton attachment to the methylene group, is lower than the second one (2·81) and therefore relates to the process which will occur in preference. Also, this value is lower than the lowest value for triphenylethylene (1·96) and therefore 1 : 1-diphenylethylene is the more basic hydrocarbon. The isomeric carbonium ions in col. 3 have been listed in order of decreasing stability.

Because of the complexity and lack of symmetry of some of the larger structures, not all the π-electron energies listed in the table have been obtained by solution of the appropriate secular equation. Instead, some of them have been obtained by the use of empirical additivity rules. The molecules concerned are marked with a small index and the method of evaluation is stated in footnotes. Most of the π-electron energies given in cols. 2 and 3 are in the literature; those marked with an asterisk are from Syrkin and Diatkina (*Acta Physicochim. U.R.S.S.*, 1946, **21**, 641), some of whose data have on recalculation been found to be in error by a few units in the second decimal place and not as reliable as the other values, which have been taken from Hückel (*Z. Elektrochem.*, 1937, **43**, 732) or Wheland (*J. Amer. Chem. Soc.*, 1941, **63**, 2025), or from our own calculations.