A Critique of the Resonance Energy Concept with Particular Reference to Nitrogen Heterocycles, Especially Porphyrins†

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I. Introduction

Porphyrins have now come to have a significance beyond the biological role they play as the organic structure in which iron is bound in the hemoproteins, and, in the form of dihydro and tetrahydro derivatives, the structure in which magnesium is bound in plant and bacterial chlorophylls (see Figure 1a–c).[1-4]

Not counting the biological macromolecules, porphyrins are some of the largest molecules found in living systems, and their biosynthesis thus provides an important test case for the hypothesis that building up large molecules from low molecular weight substrates is an energy-requiring process.[5] Their presence in petroleum is a crucial factor in establishing its origin and deciding its geochemical evolution.[6,7] The ease of their synthesis, given appropriate starting materials, is a pertinent consideration both in exobiology[8] and in cosmic chemistry, for it has recently been suggested that porphyrins are present in interstellar clouds.[9]

The stability of porphyrins is thus a topic with many ramifications, and, as has been customary with other aromatic structures, resonance stabilization has been regarded as an extremely important factor.[10] Furthermore, a diminution in this stabilization has been invoked in the case of the dihydro and tetrahydro ring systems. For example, "the dihydroporphyrins, commonly known as chlorins, include two extra hydrogen atoms on one of the pyrrole rings, saturating one of the double bonds, and thus impairing the resonance stability of the porphyrin structure by interfering with the conjugated bond system. The tetrahydroporphyrins carry four extra hydrogen atoms. As would be expected the resonance stability is further impaired."[10] It will be shown below in section V.A, where the nature and extent of the conjugation are examined, that this description of the reduced states is an oversimplification. Moreover, there appear to be no resonance energy values in the literature for the dihydro- and te-
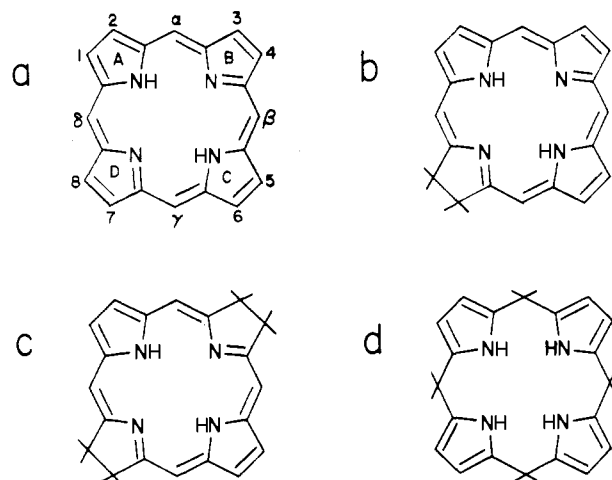
Figure 1. Kekulé structures for porphine derivatives. (a) Porphine (P): the biologically important porphyrins have substituents at positions 1 through 8, with hydrogen atoms at positions α through δ. One of the simpler organic syntheses gives $\alpha,\beta,\gamma,\delta$-tetrasubstituted derivatives. (b) Dihydroporphine (PH$_2$): generally known as chlorines; in the chlorophylls there is a subsidiary ring from C_6 to C_γ. (c) Tetrahydroporphine (PH$_4$): the ring structure present in the bacterial chlorophylls. (d) Porphyrinogen (PH$_6$): the cyclic tetrapyrrolic precursor of the porphyrins in the biosynthetic pathway. Porphine drawn to scale from data quoted by Tulinsky.[4]

trahydrorphyrins to support this contention (calculations for the former will be presented later in Table XV). In fact, despite the obvious importance of the resonance energy of porphyrins and the great interest shown over the years in the values for benzene and polycyclic aromatic hydrocarbons, there have been surprisingly few estimates of its magnitude.

Several theoretical studies have been carried out using free-electron, LCAO and MO models, but they have been concerned primarily with accounting for spectroscopic characteristics.[11-13] Resonance energies from 8.9β to 10.8β have been obtained for porphine and several substituted derivatives like those which occur naturally.[11] Putting β equal to 16 and to 18 kcal, these values would correspond to 142–173 and 160–195 kcal, respectively. In a later publication the value was rounded off at 200 kcal.[14] But the theoretical estimate is dependent not only upon the magnitude of β, but also on values chosen for other parameters to allow for heteroatoms in the aromatic structure.

At present the experimental studies are not particularly helpful in arriving at any more reliable a value. Until quite recently the only data available were the heats of combustion of a number of naturally occurring porphyrins and their derivatives reported by Stern and Klebs in 1933.[15] From this source, in 1950, Dorough and Shen[16] arrived at a value of about 250 kcal, but gave no details of their calculation procedure nor any indication of the particular porphyrin it referred to. The origin of the bond energy terms and heats of atomization of the elements was very probably the compilation published by Pauling in 1940.[17] On this basis, taking etioporphyrin I as the example, 225 kcal is obtained, compared to 39 kcal for the resonance energy of benzene. Corresponding values using the 1960 revision of the primary data[18] are set out for comparison in Table I. In their entirety, however, the Stern and Klebs' data give, as will as shown below, a great scatter of values from 78 to 179 kcal in relation to a value of 32 kcal for benzene. Furthermore, compared to these "low" values, the much more recent combustion experiments of Longo, Finarelli, Schmalzbach, and Adler[19] on porphine and its tetraethyl and tetraphenyl derivatives, with an

TABLE I. Heats of Atomization, $\Delta H_a°$, Total Bond Energy Terms, ΣE, and Resonance Energies, RE, for Benzene and Etioporphyrin I[a]

Compound	Property	Pauling, 1940	Pauling, 1960
Benzene	$\Delta H_a°$	1039	1323
	ΣE	1000	1283
	RE	39	40[b]
Etioporphyrin I	$\Delta H_a°$	6263[c]	7906[c]
	ΣE	6038	7690
	RE	225	216

[a] Calculated from the combustion data of Stern and Klebs[15] using Pauling's bond energy values in "The Nature of the Chemical Bond," 1940 and 1960.[17,18] [b] Pauling (ref 17, p 193) quotes 37 kcal/mol, but the bond energy terms listed for E(C–C) and E(C–H) in Table 3–4 (p 85), together with E(C=C) in Table 6–1 (p 189), give $\Sigma E = 1283$, not 1286, and hence RE = 40 kcal/mol. The origin of this discrepancy is obscure: $\Delta H_a° = 1323$ is correct according to the values given for the heat of combustion of benzene, 789.2 kcal/mol, and the heats of atomization of the elements in Table 3–5 (p 86). [c] Based on $\Delta H_f°$ (etioporphyrin I)$_c$ = −6.0 kcal/mol, calculated by Cox and Pilcher[20] from the combustion data of Stern and Klebs,[15] and an estimated $\Delta H_{sub}°$ of 26.5 kcal/mol.

identical calculation procedure, give "high" values from 450 to 500 kcal. The same compound was not burned by both groups of investigators, so there is a possibility, remote perhaps, that the difference may be real.

At the outset, the purpose of this review was to put thermochemical calculations for porphyrin reactions on a firmer basis. In the literature the enhanced stability had been envisaged in terms of resonance effects; hence resonance energy calculations in the traditional manner seemed the natural point of departure. New values were to be calculated for benzene, alkyl benzenes, polycyclic aromatic hydrocarbons, [18]annulene, pyridine, and pyrrole heterocycles, using the authoritative compilation of heats of formation of organic compounds published by Cox and Pilcher in 1970,[20] so that the issue of the likely magnitude of the porphyrin resonance energy—a "low" or "high" value—could be judged in relation to aromatic compounds in general on exactly the same basis. This approach was, in fact, employed, although not elaborated, in discussing thermodynamic aspects of porphyrin synthesis and biosynthesis.[5]

However, a closer examination of the procedures and the assumptions implicit in calculating resonance energies suggested that the treatment be broadened in scope, dealing first with resonance energy calculations and the manner in which the assumptions affect only theoretical considerations and not the validity of calculations of reaction heats; secondly, with an alternative approach using bond energy terms which include π-electron binding energies; and finally, with calculations of $\Delta H°$, $\Delta S°$, and $\Delta G°$ for various porphyrin reactions in which the porphine aromaticity is disrupted either by ring fission or by extensive reduction.

II. Sources of Data

The heats (enthalpies) of atomization, $\Delta H_a°$, of the elements from their standard states at 25° (H, 52.10 ± 0.06; C, 170.90 ± 0.45; N, 113.0 ± 0.5; O, 59.56 ± 0.03) have been taken from Cox and Pilcher,[20] also all the values for the heat (enthalpy) of formation of the compounds, $\Delta H_f°$, unless otherwise stated. The heat of atomization of a gaseous compound follows from a consideration of a simple Born–Haber cycle, i.e.

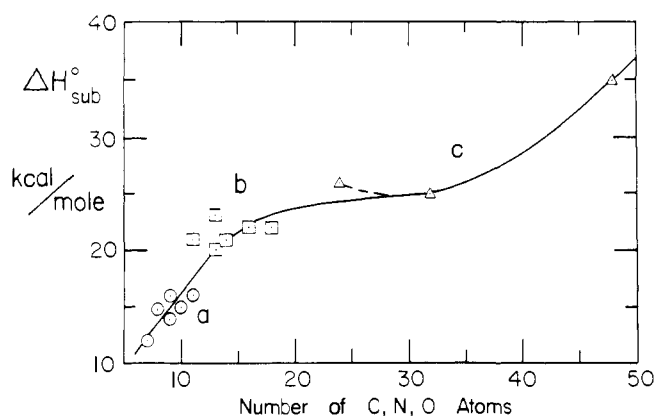$$\Delta H_a°(\text{compound})_g = \Delta H_a°(\text{elements})_{s.s.} - \Delta H_f°(\text{compound})_g$$

Figure 2. A plot of the heat of sublimation, $\Delta H_{sub}°$, against the number of structurally bonded carbon, nitrogen, and oxygen atoms in a molecule. (a and b) Compounds containing one and two aromatic rings, respectively, with C, N, and O substituent groups; data taken from Cox and Pilcher.[20] (c) From left to right, values for tetraethylporphine, porphine, and tetraphenyl-porphine.[21,4]

TABLE II. Bond Energy Terms (Laidler Parameters) Taken from Cox and Pilcher[20]

$E(C-C)$	85.48	$E(C=O)$	158.28
$E(C-H)_i$	98.19	$E(C_o-H)_1$	101.97
$E(C-H)_s$	97.27	$E(C_o-C)$	94.67
$E(C-H)_t$	96.53	$E(C_o-C_b)$	99.13
$E(C=C)$	133.00	$E(C-H)_s^{CO}$	98.19
$E(C_d-H)_2$	101.19	$E(C-H)_s^{CO}$	97.34
$E(C_d-H)_1$	100.53	$E(C-H)_t^{CO}$	95.53
$E(C_t-H)$	100.53	$E(COOH)$	383.34
$E(C_d-C)$	90.07		
$E(C_t-C)$	88.91	$E(N-H)_2$	91.57
		$E(N-H)_1$	90.21
$E(O-H)$	107.83	$E(C-N)$	74.00
$E(C-O)$	91.02	$E(C_b-N)$	81.87
$E(C-H)_i^O$	96.00	$E(C-H)_i^N$	97.59
$E(C-H)_s^O$	95.51	$E(C-H)_s^N$	97.12
$E(C-H)_t^O$	95.21	$E(C-H)_t^N$	97.32

" Explanation of symbols. (C-H)$_p$, (C-H)$_s$, and (C-H)$_t$ denote the C-H bond in a CH$_3$, CH$_2$, and CH group, respectively, the other bond(s) being to paraffinic carbon. The same symbols with the superscripts O, CO, and N indicate that the carbon is joined to these atoms, e.g., in alcohols, ethers, and esters, in aldehydes, ketones, carboxylic acids, and derivatives, and in amines, respectively. C, C$_d$, C$_t$, and C$_{co}$ denote carbon atoms in the following structural environments: paraffin, olefin, benzene (aromatic), carbonyl, carboxylic acid and derivatives. (C$_d$-H)$_1$, (C$_t$-H)$_2$ etc., denote the C-H bond in olefins where there are one and two hydrogen atoms, respectively, bound to the olefinic carbon atom. (COOH) denotes the carboxylic acid group comprising the C=O, C-O, and O-H bonds taken together.

For a number of compounds $\Delta H_f°$ is recorded only for the solid, so in these cases the heat of sublimation, $\Delta H_{sub}°$, has been estimated from the curve in Figure 2 where a selection of experimental values for $\Delta H_{sub}°$ are plotted as a function of the number of structurally bonded C, N, and O atoms in the molecule.[20,21] Any error involved is unlikely to exceed 3 kcal/mol, and for the majority of compounds where this estimation procedure has had to be employed, notably the pyrroles, chlorines, and porphyrins, the scatter in the values obtained for the resonance energies far exceeds this uncertainty.

For uncomplicated compounds $\Delta H_a°(compound)_g$ is simply equal to ΣE, the sum of the bond energy terms, the convention being that E is positive, i.e., enthalpy increases, for the breaking of a bond. In other cases, where resonance stabilization occurs or there is ring strain destabilizing the structure, the relationship becomes

$$\Delta H_a°(compound)_g = \Sigma E + RE - CRSE \qquad (2)$$

RE and CRSE denoting the resonance energy and the conventional ring strain energy respectively.

The symbols for the bond energy terms (Laidler parameters) employed by Cox and Pilcher[20] have been adopted, also the values they recommend (Table 50 in their monograph); see Table II. Additional values which had to be calculated for the present study are noted in passing.

All energies are quoted in kilocalories per mole, per atom, or per mole-bond at 25°C as the case may be. For brevity in the tables, a double bond is often abbreviated as DB. The ± sign following a mean value denotes the standard error.

III. Meaning of Resonance Energies

Resonance energies are obtained from heats of either combustion or hydrogenation by two well-known procedures.[17,18,22-26] The combustion heat is used to calculate the heat of atomization of the molecule via the heat of formation of the gaseous compound (see eq 1), and then the resonance energy is obtained using eq 2. Heats of hydrogenation are employed as follows: taking benzene as the example, the heat of hydrogenation of cyclohexene is used to estimate that for the (hypothetical) cyclic structure, cyclohexatriene, having three C—C and three C=C bonds. Experiment shows the heat of hydrogenation of benzene to be less favorable by about 36

kcal/mol; benzene is thus regarded as being 36 kcal/mol more stable than such a structure, and the 36 kcal/mol is identified as its resonance energy. Cyclohexene serves as the "reference" substance, the choice of which will be critically examined later. Combustion heats can also be used to calculate resonance energies in this way, and on occasion have been,[22] although the original procedure was that outlined above. Resonance energies calculated from hydrogenation data have generally been preferred on the grounds that, as the direct difference between relatively small experimental heats, they are more accurate than values arrived at as the difference between the much larger quantities involved in either procedure using combustion heats.

A. Resumé of Criticism of Bond Energy Terms and Resonance Energies

Even so, it has long been recognized that these "empirical" resonance energies obtained from thermochemical data are ambiguous quantities for a variety of reasons, some of which relate to the "state of the art," and others which are far more fundamental.

In the former category it is self-evident that in any calculation procedure which involves $\Delta H_a°$ and bond energy terms the magnitude of the resonance energy depends on the values adopted for the heats of atomization of the elements and on the particular values assigned to the various bond energy terms. Schofield's book[24] has a very instructive tabulation of resonance energy values calculated by various authors, with full references. With the high value now well established for the heat of atomization of graphite, it is improbable that further changes in $\Delta H_a°$ for carbon, hydrogen, oxygen, or nitrogen will exceed a few tenths of a kcal/(g atom). The assignment of bond energy terms is still, and, by their very nature, will remain a matter of choice, but the scheme adopted by Cox and Pilcher[20] is extremely satisfactory for taking next-nearest-neighbor interactions into account with a great diversity of functional groups. In any case, heats of

TABLE III. The Magnitude of the Thermal Energy, $H°_{298} - H°_0$, and the Zero Point Energy, ZPE, in Relation to the Heat of Atomization at 298°K, $\Delta H_a°$, for Various Hydrocarbons[20] [a]

Hydrocarbon	$\Delta H_a°$	$(H°_{298} - H°_0)$	ZPE
Methane	397.19	2.40 (0.60)	27.1 (6.82)
Ethane	674.64	2.86 (0.42)	45.2 (6.70)
n-Hexane	1794.72	6.99 (0.39)	116.2 (6.47)
Ethylene	537.75	2.53 (0.47)	30.5 (5.67)
Cyclohexane	1680.10	4.24 (0.25)	104.5 (6.22)
Benzene	1318.19	3.40 (0.26)	67.1 (5.09)

[a] Energies in kcal/mol: $(H°_{298} - H°_0)$ and ZPE also expressed as percentages of $\Delta H_a°$ in parentheses.

reaction calculated from any such data are independent of both $\Delta H_a°$ (elements) and the actual values of the bond energy terms, provided these data are used consistently.

In the latter category there are several more fundamental issues at stake. First, as Zahn pointed out in 1934,[27] the heat of atomization of a gaseous compound consists of energy contributions in addition to the chemical (i.e., electronic) binding energy, namely thermal energy of translation, rotation, and vibration at all temperatures above absolute zero, and, even at absolute zero, the zero-point energy. All derived thermochemical quantities, bond energy terms and resonance energies, are thus not purely electronic in origin. However, quantitative data for hydrocarbons[20] show that thermal energies, $H°_{298} - H°_0$, are a very small fraction amounting to about 0.2–0.6% of $\Delta H_a°$ (see Table III), and to a first approximation they are an additive function of molecular sructure. While the zero-point energies are some ten times greater in magnitude,[20] they still do not exceed 7% of $\Delta H_a°$, and for the n-alkanes at least they are to a fair approximation a bond additive function. The assumption that this would be true for other kinds of bonds is entirely reasonable, and heats of reaction calculated from bond energy terms are unlikely to be seriously in error on this account.

Secondly, quite apart from these complications, empirical resonance energies do not correspond to the stabilization energy of theoretical interest. In molecular orbital theory this is identified as the energy resulting from the delocalization of electrons originally constrained in isolated double bonds. In valence-bond theory it is identified as the difference between the actual energy of the molecule and the energy calculated for the most stable single contributing structure having the same geometry. Provided the "isolated double bond structure" of the MO treatment is the same as the "more stable single contributing structure" of the VB treatment, the stabilization energy is identical, and, to distinguish it from the empirical resonance energy, it is often referred to as the vertical resonance energy.[23,28,29] Empirical resonance energies thus differ from these theoretical stabilization energies by the energy needed to convert the single- and double-bond structure into the actual structure with bonds of intermediate length. Calculations have put this compression energy at about 27 kcal/mol in the case of benzene.[28]

This difference in molecular geometry is implicit in both thermochemical calculation procedures. In the benzene example cited above, it is self-evident that cyclohexatriene would have the geometry of a cyclic triolefin since its hydrogenation heat is based on that for the cyclic monoolefin, cyclohexene, as the reference compound. The difference is not quite so clear, however, in the case of the procedure using combustion heats to calculate $\Delta H_f°$, $\Delta H_a°$, and hence RE from eq 2. Opinion as

to the nature of the carbon–carbon bond appropriate to the structure for which $\Delta H_a°$ would simply be ΣE has changed over the years from C–C, as in paraffins,[30] to C_d–C_d, which takes cognizance of the different hybridization.[31,32] But since all calculations of this type employ a bond energy term for C=C obtained from olefins, it can be inferred that the structure must be one having double- and single-bond geometry; therefore the same argument regarding compression energy holds.

All these points have been discussed at length in the literature, and will not be elaborated any further here. There are two other thermochemical considerations though that have not been mentioned as yet. First, in taking cyclohexene as the reference compound in the case of benzene, the strain energy of the cyclohexene ring, which makes the heat of hydrogenation more favorable than it would otherwise be, appears quite irrelevantly as a component of the benzene resonance energy.[23] Obviously a correction can be made, but it leaves the calculation procedure itself, as a means of evaluating a property of benzene, open to question. Secondly, as Dewar and Schmeising pointed out in 1959,[31] a molecule such as cyclohexene is conjugatively stabilized by the presence of bonds of the sp^2–sp^3 type that are absent in benzene, and in addition hyperconjugation effects lead to variations in the C–H bond energy term. Therefore in using cyclohexene as the reference compound, the resonance energy obtained for benzene contains irrelevant contributions from conjugation and hyperconjugation effects too. For these reasons, since the choice of any reference reaction is an arbitrary one, they advocated that the simplest reaction, free from such effects, is preferable. Hence, instead of an olefin having some close structural resemblance to the conjugated compound as reference, they suggested ethylene and identified the empirical resonance energy as $\Delta H°$ for the reaction.

conjugated compound + ethane $\longrightarrow$

$\qquad\qquad$ fully reduced compound + ethylene $\quad$ (3)
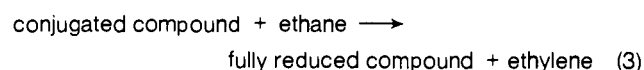
These criticisms of the empirical resonance energy concept on purely thermochemical grounds have been taken up by Mortimer,[23] Skinner and Pilcher,[33] Cox and Pilcher,[20] and others, but more as a matter of principle, not exploring how the magnitude of the resonance energy is dependent on the reaction chosen.

In fact, it does not yet appear to be generally appreciated that both classical procedures for calculating resonance energies from thermochemical data do not evaluate an energy that is the property of a molecule, but an energy that is the enthalpy change for a particular reaction. Before proceeding with new calculations of values for conjugated hydrocarbons and nitrogen heterocycles, it is thus necessary to make quite clear what underlying thermochemical assumptions are being made, and so the dependence of the values on the various reference reactions will be examined first. This analytical exercise is of theoretical interest because empirical resonance energies, with or without correction for strain energies and compression energies, are frequently compared with delocalization energies, e.g., β values, obtained from theory. It also has practical significance in the calculation of heats of reaction using bond energy terms, because it makes explicit the conditions under which these various criticisms do not affect the answer.
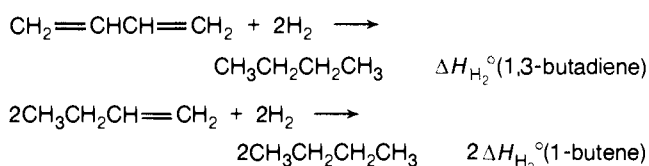
B. Calculation of $[nE(C_d-C_d) + RE]$ and the Consequences of Equating $\Delta H_{R_x}°$ with RE

Having decided upon the values for the bond energy

terms for the C—C bond and the three types of C—H bonds in alkyl groups, the two types of C—H bonds in olefins, C=C and C_d-C,[20] it is a matter only of simple arithmetic to evaluate the composite term $[nE(C_d-C_d) + RE]$ for any conjugated structure for which $\Delta H_f°$ of the gaseous compound and hence its heat of atomization are known, "n" being the number of C_d-C_d bonds, i.e., the single bonds between sp^2 hybridized carbon atoms.

This is the basis of the evaluation of an empirical resonance energy from the heat of combustion, and clearly its magnitude depends on that adopted for $E(C_d-C_d)$ since there is no assumption that can be made using this datum alone to divide up the composite term. Values of $[E(C_d-C_d) + RE]$ for three 1,3-dienes, the only compounds of this type for which data are available, are set out in Table IVA. The mean value is 98.03 ± 0.37.

The use of hydrogenation heats for the conjugated structure and a reference compound, i.e., two data, enables a split to be made, but there is an explicit assumption. Taking 1,3-butadiene and 1-butene as the test case, the appropriate difference between the heats of hydrogenation, $[\Delta H_{H_2}°(1,3\text{-butadiene}) - 2\Delta H_{H_2}°(1\text{-butene})]$,

$$CH_2{=}CHCH{=}CH_2 + 2H_2 \longrightarrow$$
$$CH_3CH_2CH_2CH_3 \quad \Delta H_{H_2}°(1,3\text{-butadiene})$$

$$2CH_3CH_2CH{=}CH_2 + 2H_2 \longrightarrow$$
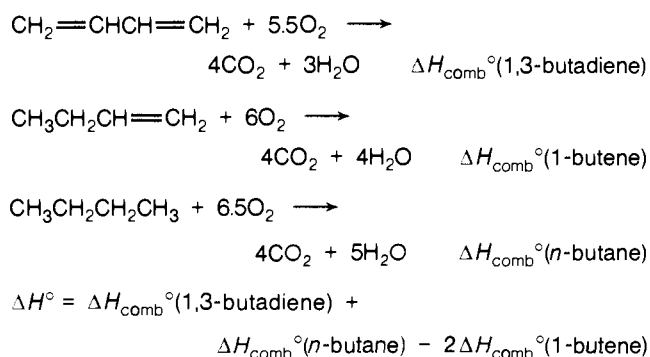$$2CH_3CH_2CH_2CH_3 \quad 2\Delta H_{H_2}°(1\text{-butene})$$

which is identified as the empirical resonance energy, turns out upon examination[33] to be $\Delta H°$ for the redistribution reaction

$$CH_2{=}CHCH{=}CH_2 + CH_3CH_2CH_2CH_3 \longrightarrow$$
$$2CH_3CH_2CH{=}CH_2$$
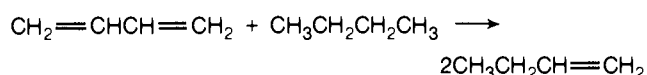
which is listed as reaction c in Table IV.C.1.

There is thus no a priori reason why empirical resonance energies calculated by these two methods should be the same, and this only occurs if the value of $E(C_d-C_d)$, derived from the hydrogenation data, is used in the calculation based on the atomization heat.

Provided no extraneous features such as steric hindrance are introduced, any other pair of addition reactions, e.g., halogenation, would serve the same purpose as hydrogenation. Furthermore, although the usual use of combustion data has been to evaluate $\Delta H_f°$, and hence RE via $\Delta H_a°$, the data for the conjugated compound, the olefin, and the paraffin could also be used to evaluate $\Delta H°$ for the redistribution reaction

$$CH_2{=}CHCH{=}CH_2 + 5.5O_2 \longrightarrow$$
$$4CO_2 + 3H_2O \quad \Delta H_{comb}°(1,3\text{-butadiene})$$

$$CH_3CH_2CH{=}CH_2 + 6O_2 \longrightarrow$$
$$4CO_2 + 4H_2O \quad \Delta H_{comb}°(1\text{-butene})$$

$$CH_3CH_2CH_2CH_3 + 6.5O_2 \longrightarrow$$
$$4CO_2 + 5H_2O \quad \Delta H_{comb}°(n\text{-butane})$$

$$\Delta H° = \Delta H_{comb}°(1,3\text{-butadiene}) +$$
$$\Delta H_{comb}°(n\text{-butane}) - 2\Delta H_{comb}°(1\text{-butene})$$

These various reactions exemplify the conclusion stated above in general terms, namely that the energy evaluated using this traditional method is not a property of the conjugated structure but $\Delta H°$ for one kind of reaction.

The characteristic feature of the butadiene/butane redistribution reaction, which is one of the simplest, is that the number and kind of C-H bonds are the same in reactants and products, likewise for the C_d-H bonds. Any number of similar reactions can be devised, for instance, reactions a, b, d, e, and f in Table IV.C.1, and the constancy of $\Delta H°$, 3.66 ± 0.08, is a measure of the accuracy of the various data. For all these reactions, by taking the difference between the heats of atomization of the products and reactants, it can be shown that

$$\Delta H° = 2E(C_d-C) - E(C-C) - E(C_d-C_d) - RE \quad (4)$$

i.e.

$$E(C_d-C_d) + RE = \Delta H° + 2E(C_d-C) - E(C-C) \quad (5)$$

Hence in identifying $\Delta H°$ as the empirical resonance energy, an implicit assumption is made,[31] namely that

$$E(C_d-C_d) = 2E(C_d-C) - E(C-C) \quad (6)$$

with the Cox and Pilcher bond energy term values,[20] $E(C_d-C_d)$ would thus be

$$2 \times 90.07 - 85.48 = 94.66$$

Dewar and Schmeising,[31] Skinner and Pilcher,[33] and Cox and Pilcher,[20] have examined the justification for this assumption, which will be taken up again later.

Given that $E(C_d-C_d)$ is fixed if $\Delta H°$ is identified as RE, the magnitude of the composite term $[E(C_d-C_d) + RE]$ can readily be determined without evaluating $\Delta H_a°$. For reaction C.1a in Table IV, for example, the value 98.55 is the sum of 94.66 and 3.89, and the same procedure has been used throughout Tables IV and V.

Other kinds of redistribution reactions can be devised in which the carbon–hydrogen bonds are not exactly matched in reactants and products. Two series of such reactions are set out in Table IV.C.2 and 3. As would be expected, $\Delta H°$ for these reactions, 0.80 ± 0.10 and −1.83 ± 0.10, differ from that for the previous series, and as a consequence, if $\Delta H°$ is nevertheless identified as the empirical resonance energy, different values result for the bond energy term $E(C_d-C_d)$, i.e., 97.43 and 100.20, respectively. The increment, 2.77, is quite a complex function of C–H and C–C bond energy terms, i.e.

$$3E(C-H)_p + E(C_d-H)_1 - 2E(C_d-H)_2 - 2E(C-H)_s +$$
$$E(C_d-C) - E(C-C)$$

If Dewar and Schmeising's suggestion is taken up and $\Delta H°$ for the reduction of the conjugated compound by a simple olefin is adopted as the empirical resonance energy,[31] a further series of RE and $E(C_d-C_d)$ values can be arrived at, as shown in Table IV.B.1–3. While it is true that the expressions for $E(C_d-C_d)$ do not involve any other C–C bond energy term, and in this respect could be regarded as more fundamental than that for the redistribution reactions discussed above, even the expression for the simplest of these reactions, the reduction of butadiene by ethane, involves the difference between no less that eight C–H bond energy terms, i.e.

$$E(C_d-C_d) = 4E(C-H)_s + 4E(C_d-H)_2 -$$
$$2E(C_d-H)_1 - 6E(C-H)_p + E(C-C) \cdot (7)$$

Moreover, the expressions become still more complex for the alkyl-substituted dienes; see Table IV.B.2 and 3.

Any assignment of bond energy terms that allows for different values of $E(C-C)$ and $E(C_d-C_d)$, i.e., conjugation

TABLE IV. Values of $E(C_d-C_d)$ and the Resonance Energy for 1,3-Butadiene and Its Methyl Derivatives, Based on $\Delta H°$ for Various Reactions

	$E(C_d-C_d) + RE$	$\Delta H° = RE$	$E(C_d-C_d)$
A. Atomization			
1. $CH_2=CHCH=CH_2 \rightarrow 4C + 6H$	98.27		
$E(C_d-C_d) + RE = \Delta H_a° - 4E(C_d-H)_2 - 2E(C_d-H)_1 - 2E(C=C)$			
2. $CH_2=CHCH=CHCH_3 \rightarrow 5C + 8H$	98.57		
$E(C_d-C_d) + RE = \Delta H_a° - 3E(C-H)_p - 2E(C_d-H)_2 - 3E(C_d-H)_1 - 2E(C=C) - E(C_d-C)$			
3. $CH_2=CHC(CH_3)=CH_2 \rightarrow 5C + 8H$	97.31		
$E(C_d-C_d) + RE = \Delta H_a° - 3E(C-H)_p - 4E(C_d-H)_2 - E(C_d-H)_1 - 2E(C=C) - E(C_d-C)$			
B. Reduction by Ethane and Propane			
1. $CH_2=CHCH=CH_2 + 2C_2H_6 \rightarrow CH_3CH_2CH_2CH_3 + 2C_2H_4$	98.03	8.91	89.12
$E(C_d-C_d) + RE = \Delta H° + 4E(C-H)_s + 4E(C_d-H)_2 - 2E(C_d-H)_1 - 6E(C-H)_p + E(C-C)$			
2. $CH_2=CHCH=CHCH_3 + 2C_2H_6 \rightarrow CH_3CH_2CH_2CH_2CH_3 + 2C_2H_4$	98.51	12.16	86.35
$E(C_d-C_d) + RE = \Delta H° + 6E(C-H)_s + 6E(C_d-H)_2 - 3E(C_d-H)_1 - 9E(C-H)_p + 2E(C-C) - E(C_d-C)$			
3. $CH_2=CHC(CH_3)=CH_2 + 2C_2H_6 \rightarrow CH_3CH_2CH(CH_3)_2 + 2C_2H_4$	97.52	10.47	87.05
$E(C_d-C_d) + RE = \Delta H° + 2E(C-H)_s + E(C-H)_t + 4E(C_d-H)_2 - E(C_d-H)_1 - 6E(C-H)_p + 2E(C-C) - E(C_d-C)$			
4. $CH_2=CHCH=CH_2 + C_2H_6 + C_3H_8 \rightarrow CH_3CH_2CH_2CH_3 + CH_2=CH_2 + CH_3CH=CH_2$	98.02	6.13	91.89
$E(C_d-C_d) + RE = \Delta H° + 2E(C-H)_s + 2E(C_d-H)_2 - E(C_d-H)_1 - 3E(C-H)_p + E(C_d-C)$			
C. Redistribution Reactions			
1a. $CH_2=CHCH=CH_2 + C_2H_6 \rightarrow 2CH_3CH=CH_2$	98.55	3.89	94.66
b. $CH_2=CHCH=CH_2 + C_3H_8 \rightarrow CH_3CH_2CH=CH_2 + CH_3CH=CH_2$	98.06	3.40	94.66
c. $CH_2=CHCH=CH_2 + CH_3CH_2CH_2CH_3 \rightarrow 2CH_3CH_2CH=CH_2$	98.51	3.85	94.66
d. $CH_2=CHCH=CHCH_3 + CH_3CH_2CH_2CH_2CH_3 \rightarrow CH_2=CHCH_2CH_2CH_3 + CH_3CH_2CH=CHCH_3$	98.38	3.72	94.66
e. $CH_2=CHC(CH_3)=CH_2 + CH_3CH_2CH(CH_3)_2 \rightarrow CH_2=CHCH(CH_3)_2 + CH_3CH_2C(CH_3)=CH_2$	98.29	3.63	94.66
f. $CH_2=CHCH=CH_2 + CH_3CH_2CH_2CH_2CH_3 \rightarrow CH_3CH_2CH=CH_2 + CH_3CH_2CH_2CH=CH_2$	98.12	3.46	94.66
$E(C_d-C_d) + RE = \Delta H° + 2E(C_d-C) - E(C-C)$			
2a. $CH_2=CHCH=CH_2 + C_3H_8 \rightarrow CH_3CH=CHCH_3 + CH_3CH=CH_2$	98.04	0.61	97.43
b. $CH_2=CHCH=CH_2 + CH_3CH_2CH_2CH_3 \rightarrow CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2$	98.49	1.06	97.43
c. $CH_2=CHCH=CH_2 + CH_3CH_2CH_2CH_2CH_3 \rightarrow CH_3CH_2CH=CH_2 + CH_3CH_2CH=CHCH_3$	98.29	0.86	97.43
d. $CH_2=CHCH=CH_2 + CH_3CH_2CH_2CH_2CH_3 \rightarrow CH_3CH=CHCH_3 + CH_3CH_2CH_2CH=CH_2$	98.10	0.67	97.43
$E(C_d-C_d) + RE = \Delta H° + 3E(C-H)_p + E(C_d-H)_1 - 2E(C_d-H)_2 - 2E(C-H)_s + 3E(C_d-C) - 2E(C-C)$			
3a. $CH_2=CHCH=CH_2 + CH_3CH_2CH_2CH_3 \rightarrow 2CH_3CH=CHCH_3$	98.47	−1.73	100.20
b. $CH_2=CHCH=CH_2 + CH_3CH_2CH_2CH_2CH_3 \rightarrow CH_3CH=CHCH_3 + CH_3CH_2CH=CHCH_3$	98.27	−1.93	100.20
$E(C_d-C_d) + RE = \Delta H° + 6E(C-H)_p + 2E(C_d-H)_1 - 4E(C_d-H)_2 - 4E(C-H)_s + 4E(C_d-C) - 3E(C-C)$			
D. Isomerization			
1. $CH_3CH=CHCH=CH_2 \rightarrow CH_2=CHCH_2CH=CH_2$	99.02	7.13	91.89
$E(C_d-C_d) + RE = \Delta H° + 2E(C-H)_s + 2E(C_d-H)_2 - E(C_d-H)_1 - 3E(C-H)_p + E(C-C)$, i.e., as in B4.			

effects, and takes next-nearest-neighbor interactions into account for the many kinds of C–H bonds, i.e., hyperconjugation effects, is bound to lead to similar conclusions. There is no resolution of the problem. If $\Delta H°$ is identified as RE, then a range of RE values results, and, as a consequence, a range of $E(C_d-C_d)$ values is obtained since the composite term $[E(C_d-C_d) + RE]$ is independent of any particular reaction—as it must be. In the case of these dienes the values of this composite term are 98.03 ± 0.37, 98.02 ± 0.20, and 98.30 ± 0.05 for the combustion (atomization), reduction, and redistribution reactions respectively; see Table IV.A–C. On thermochemical grounds alone, the division of this term into component parts is clearly a matter of choice, not principle, but before coming to a decision, the corresponding data for the benzene hydrocarbons will be examined because they present additional features of their own due to ring strain.

For aromatic compounds containing one benzene ring, the composite quantity calculated from $\Delta H_a°$ is $[3E(C_d-C_d) + RE]$. Values for benzene, four monoalkylbenzenes, and the three xylenes are given in Table V.A.1–3; the mean is 315.97 ± 0.10. Data for other alkylbenzenes are available, but these are the most accurate.

Similar values for reduction by ethane are set out in Table V.B.1–3; $[3E(C_d-C_d) + RE] = 315.94 ± 0.21$. Just as in the case of the dienes, the identification of $\Delta H°$ with RE leads to different values for $E(C_d-C_d)$ depending on the extent of substitution. The increment in going from benzene to the mono- and then the disubstituted derivatives is one-third of

$$2E(C-H)_s - E(C-H)_t - E(C_b-H) - E(C-C) + E(C_b-C) = 0.91$$

It is to be noted that the value of $E(C_d-C_d)$ for benzene, 89.12, is identical with that for butadiene.
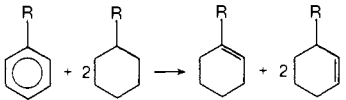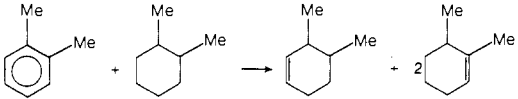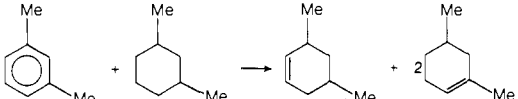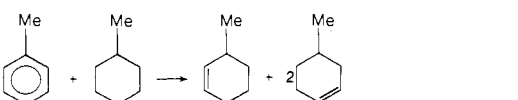
Turning to the values based on hydrogenation data (Table V.C.1), the value for benzene, 93.36, differs from the butadiene value, 94.66, by the conventional ring strain energy of cyclohexene. There are again differences in going from benzene to the mono- and disubstituted derivatives, the increment in this case being one-third of

$$E(C_d-C) - E(C_b-C) = 1.16$$

For these redistribution reactions the composite term $[3E(C_d-C_d) + RE] = 315.93 ± 0.08$. There is excellent agreement between the values calculated from the three sets of data, even though, as in the case of the dienes, the reduction reactions and the redistribution reactions lead to a series of values for RE and $E(C_d-C_d)$.

Hence any calculations of empirical resonance energies involve both choice and compromise. The identification of $\Delta H°$ for any particular reaction as an energy property of the conjugated structure is clearly without theoretical foundation, whereas to assume $E(C_d-C_d)$ has the

TABLE V. Values of $E(C_d–C_d)$ and the Resonance Energy for Benzene, Monoalkylbenzenes, and Xylene, Based on $\Delta H°$ for Various Reactions

	$3E(C_d–C_d) + RE$	$\Delta H° = RE$	$E(C_t–C_t)$
A. Atomization			
1. $C_6H_6 \rightarrow 6C + 6H$	316.01		
$\quad 3E(C_d–C_d) + RE = \Delta H_a° - 6E(C_b–H) - 3E(C{=}C)$			
2. $C_6H_5C_nH_{2n+1} \rightarrow (6 + n)C + (6 + 2n)H$			
$\quad$a. Toluene	315.98		
$\quad$b. Ethylbenzene	315.90		
$\quad$c. n-Propylbenzene	316.24		
$\quad$d. n-Butylbenzene	316.49		
$\quad 3E(C_d–C_d) + RE = \Delta H_a° - 5E(C_b–H) - 3E(C{=}C) - E(C_b–C) - (n - 1)E(C–C) - 3E(C–H)_p -$			
$\qquad 2(n - 1)E(C–H)_s$			
3. $C_6H_4(CH_3)_2 \rightarrow 8C + 10H$			
$\quad$a. o-Xylene	315.76		
$\quad$b. m-Xylene	315.78		
$\quad$c. p-Xylene	315.61		
$\quad 3E(C_d–C_d) + RE = \Delta H° - 4E(C_b–H) - 3E(C{=}C) - 2E(C_b–C) - 6E(C–H)_p$			
B. Reduction by Ethane			
1. $C_6H_6 + 3C_2H_6 \rightarrow C_6H_{12} + 3C_2H_4$	316.12	48.76	89.12
$\quad 3E(C_d–C_d) + RE = \Delta H° + 12E(C–H)_s + 12E(C_d–H)_2 -$			
$\qquad 6E(C_b–H) - 18E(C–H)_p + 3E(C–C)$			
2. $C_6H_5C_nH_{2n+1} + 3C_2H_6 \rightarrow C_6H_{11}C_nH_{2n+1} + 3C_2H_4$			
$\quad$a. Toluene	315.55	49.10	88.81
$\quad$b. Ethylbenzene	316.34	49.89	88.81
$\quad$c. n-Propylbenzene	316.46	50.01	88.81
$\quad$d. n-Butylbenzene	316.88	50.43	88.81
$\quad 3E(C_d–C_d) + RE = \Delta H° + 10E(C–H)_s + E(C–H)_t + 12E(C_d–H)_2 - 5E(C_b–H) - 18E(C–H)_p +$			
$\qquad 4E(C–C) - E(C_b–C)$			
3. $C_6H_4(CH_3)_2 + 3C_2H_6 \rightarrow C_6H_{10}(CH_3)_2 + 3C_2H_4$			
$\quad$a. o-Xylene	315.66	50.12[a]	88.51
$\quad$b. m-Xylene	315.34	49.80	88.51
$\quad$c. p-Xylene	315.20	49.66	88.51
$\quad 3E(C_d–C_d) + RE = \Delta H° + 8E(C–H)_s + 2E(C–H)_t + 12E(C_d–H)_2 - 4E(C_b–H) - 18E(C–H)_p +$			
$\qquad 5E(C–C) - 2E(C_b–C)$			
C. Redistribution Reactions			
1. Benzene + 2cyclohexane $\rightarrow$ 3cyclohexene	316.03	35.95	93.36
$\quad 3E(C_d–C_d) + RE = \Delta H° + 6E(C_d–C) - 3E(C–C) - 3CRSE \text{ (cyclohexene)}$			
2.			
$\quad$a. Toluene	315.76	34.51	93.75
$\quad$b. Ethylbenzene	315.78	34.53	93.75
$\quad$c. n-Propylbenzene[c]	315.90	34.65	93.75
$\quad$d. n-Butylbenzene[c]	316.32	35.07	93.75
$\quad 3E(C_d–C_d) + RE = \Delta H° + 7E(C_d–C) - 3E(C–C) - E(C_b–C) - \Sigma CRSE \text{ (alkylcyclohexenes)}[b]$			
3.[d]			
$\quad$a	316.14	33.75[a]	94.13
$\quad$b	315.82	33.43	94.13
$\quad$c.	315.68	33.29	94.13
$\quad 3E(C_d–C_d) + RE = \Delta H° + 8E(C_d–C) - 3E(C–C) - 2E(C_b–C) - \Sigma CRSE$			
$\qquad \text{(dimethylcyclohexenes)}$			

[a] $\Delta H°_f(o\text{-xylene})$ corrected by 0.4 kcal/mol to allow for the steric effect of the pair of ortho methyl groups. [b] 1-Methyl- and 1-ethylcyclohexene have CRSE values of 1.1 and 1.2 kcal/mol, respectively, within experimental error the same as that for cyclohexene, i.e., 1.3 kcal/mol: the latter value has therefore been adopted throughout for simplicity. [c] Reduction data for 1-ethylcyclohexene used in these calculations. [d] Calculation based on data for the reduction of cyclohexene and 1-methylcyclohexene.

same value in various structures is entirely in keeping with theoretical models and thermochemical practice. It would therefore seem desirable to have recourse to Occam's razor, and employ the same value of $E(C_d-C_d)$, not only for parent structures and substituted structures but also for both aliphatic conjugated polyenes and aromatic ring systems. The considerable wealth of heat of formation data can thus be used to calculate empirical resonance energies that are directly comparable, unlike those derived from hydrogenation reaction data where, in the case of ring structures, conventional ring strain energies of both the partially reduced and the fully reduced compound make irrelevant contributions. The issues underlying this important choice of a value for $E(C_d-C_d)$ will now be dealt with.

C. The Arbitrary Choice of a Value for $E(C_d-C_d)$

Despite the apparent simplicity of Dewar and Schmeising's proposal to base empirical resonance energies on reduction by ethane,[31] the resulting expression for $E(C_d-C_d)$, as shown above, involves a complex function of C–H bond energy terms (eq 7), i.e.

$$E(C_d-C_d) = E(C-C) + 4E(C-H)_s + 4E(C_d-H)_2 - $$
$$2E(C_d-H)_1 - 6E(C-H)_p$$

It seems very unlikely there can be any theoretical basis for such a relationship, and so, although by identifying $\Delta H°$ with RE a numerical value is immediately obtained, it is improbable that it has any direct bearing on C–C bond properties.

On the other hand, the expression derived from the "matched" redistribution reactions (eq 6)

$$E(C_d-C_d) = 2E(C_d-C) - E(C-C)$$

has the merit of being concerned only with the different kinds of C–C bonds. One kind of redistribution reaction also has a special significance. Reactions C.1c–e in Table IV for butadiene and its 1- and 2-methyl derivatives, and the reactions of benzene and all the alkylbenzenes listed in Table V.C.1–3, involve disproportionation between certain oxidation states of the molecular species, namely

$$C^{IV}_4 + C^0_4 \longrightarrow 2C^{II}_4 \tag{8}$$

for the former, and

$$C^{VI}_6 + 2C^0_6 \longrightarrow 3C^{II}_6 \tag{9}$$
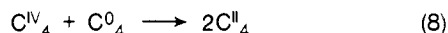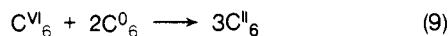
for the latter. In the case of the substituted compounds the product species consist of an appropriate mixture of isomers of the intermediate oxidation state. Unfortunately this significance is only of chemical interest and is of no help in solving the thermochemical problem of the appropriate value for $E(C_d-C_d)$.

Dewar and Schmeising,[31] Skinner and Pilcher,[33] and Cox and Pilcher[20] discussed the validity of eq 6 from the point of view of the electronegativity of carbon in its sp² and sp³ hybridization states. The general conclusion from inorganic thermochemistry is that the energy of a bond A–B is almost invariably larger than the mean of the energies of the A–A and B–B bonds, the difference becoming greater as the difference in the electronegativity of A and B increases, i.e.

$$E(B-B) < 2E(B-A) - E(A-A) \tag{10}$$

Now Walsh[34] has argued that "a carbon atom exerting hybrid valency has a stronger electronegativity the great-

TABLE VI. Resonance Energies for Butadiene and Its Methyl Derivatives, RE_I and RE_{II}[a]

	RE_I	RE_{II}
A. Ethane Reduction Data		
1. 1,3-Butadiene	8.91	
2. 1,trans-3-Pentadiene	9.39	
3. 2-Methyl-1,3-butadiene	8.40	
	m 8.90[b]	
B. Disproportionation Reaction Data		
1. 1,3-Butadiene		3.85
2. 1,trans-3-Pentadiene		3.72
3. 2-Methyl-1,3-butadiene		3.63
		m 3.73
C. Atomization Data		
1. 1,3-Butadiene	9.15	3.61
2. 1,trans-3-Pentadiene	9.45	3.91
3. 2-Methyl-1,3-butadiene	8.19	2.65
	m 8.93	m 3.39
D. Isomerization Data		
1,trans-3-Pentadiene →		
1,4-pentadiene	9.90	4.36

[a] Based on $E(C_d-C_d)_I = 89.12$ and $E(C_d-C_d)_{II} = 94.66$. [b] m = mean value.

er the proportion of s character in that valency . . . this can be regarded as a strongly founded theoretical conclusion or a simple deduction from experimental facts such as the acidity of acetylene." Hence in the present context, identifying A with C_{sp^3} and B with C_{sp^2}, the inference is that

$$E(C_d-C_d) < 2E(C_d-C) - E(C-C)$$

i.e.

$$E(C_d-C_d) < (2 \times 90.07 - 85.48) = 94.66$$

Using heat of isomerization data for bicyclic olefins and making certain assumptions about hybridization states, Staley[35] arrived at a lower value for the empirical resonance energy for the butadiene-type of redistribution reaction, RE > 1.9, which would thus raise the upper limit of $E(C_d-C_d)$ by about 3.85–1.9 = 1.95 to 96.61. An even higher value, 98.0, was adopted by Cox in his 1963 discussion of conjugation (resonance) energies of dienes and aromatic compounds.[32] This was based, however, on an argument advanced by Dewar and Schmeising from bond length considerations that the center bond in butadiene is especially strong so the conjugation energy would probably be less than 1.0.[36] Taking a value of 1.0 as small enough to be ignored in bond energy calculations gave the 98.0 value. The range of values that could be regarded as "acceptable" is thus from 98.0 down to 89.12, the value derived from the ethane reduction reactions. Somewhere in this range, spanning almost 10 kcal/mol, lies the true value, but a decision cannot be reached on the basis of thermochemical data alone—and at present there would not appear to be any lead from other experimental observations.

In the author's opinion the argument regarding electronegativity differences is the more convincing, but to leave the matter open, and demonstrate the numerical consequences of the choice of $E(C_d-C_d)$, empirical resonance energies are calculated below according to both the low value of 89.12, and the value 94.66, which is more likely to be the upper limit. To avoid confusion, these bond energy terms will be designated $E(C_d-C_d)_I = 89.12$ and $E(C_d-C_d)_{II} = 94.66$, and the corresponding empirical resonance energies RE_I and RE_{II}.

When a reliable value of $E(C_d-C_d)$ is decided upon, it will be an easy task to recalculate the appropriate RE values, since, as stressed throughout, the composite term $[nE(C_d-C_d) + RE]$ which can be calculated from the data in the tables is entirely independent of all these considerations.

The above analysis of the classical procedures for evaluating empirical resonance energies reveals the extremely arbitrary character of the numerical values that are so often quoted in the literature. It is not generally appreciated that the value of 36 kcal/mol for benzene obtained from the hydrogenation data is not only a function of the choice of reference compound but is also specific for this particular type of reaction, i.e., addition, and moreover it is inappropriate for even the simplest alkyl-substituted benzenes. Furthermore, if Dewar and Schmeising's suggestion is followed and the value based on reduction by ethane,[31] RE would be much higher, about 50 kcal/mol. The numerical comparisons that have been made from time to time between RE values based on hydrogenation data, or its equivalent, and stabilization energies calculated from theory would thus appear to have less significance than is usually supposed.

IV. Resonance Energy Calculations

A. Aliphatic Polyenes

RE values for the polyenes are listed in Table VI, including the two sets of values obtained from the atomization data. Only RE_I for (unsubstituted) butadiene is the same as that in Table IV, because the adoption of $E(C_d-C_d)_I$ = 89.12 throughout amounts to "correcting" RE for the substituted butadienes for hyperconjugation effects, i.e., the various C–H bond energy terms. Averaging the mean values in A, B, and C gives RE_I = 8.91 and RE_{II} = 3.56.

It is worthy of note that up to 1969, the time of the Cox and Pilcher tabulation,[20] despite the theoretical interest there has been in conjugated systems, the only experimental data for linear polyenes were those for just the three dienes treated above. Data for linear trienes and higher polyenes, especially those of biological significance such as the carotenes, are long overdue. In view of what follows for conjugated ring systems, it will be particularly interesting to see if there is any proportionality between the RE values and the number of conjugated double bonds. Since double bonds, by necessity, terminate a linear conjugated system, it may be necessary to count "one conjugated double bond" for butadiene, "two" for the trienes, etc., i.e., counting the number of C_d-C_d bonds.

B. Aromatic Hydrocarbons

RE values for benzene, the four monoalkyl benzenes, and the xylenes are listed in Table VII, including the two sets of values obtained from the atomization data. In this case not only are the RE_I values for the substituted compounds different from those in Table V, but also all the RE_{II} values. This is because the adoption of $E(C_d-C_d)_I$ = 89.12 amounts to "correcting" RE for the substituted compounds for hyperconjugation and also conjugation effects, i.e., the additional C–C bond energy terms; furthermore the adoption of $E(C_d-C_d)_{II}$ = 94.66 amounts to "correcting" RE for benzene and the substituted benzenes for the conventional ring strain energies of cyclohexene and the alkylcyclohexenes in addition to correcting for conjugation effects.

It should be noted that while the agreement between the corresponding RE values in Tables V and VII is about

TABLE VII. Resonance Energies for Benzene, Monoalkylbenzenes, and the Xylenes, RE_I and RE_{II}[a]

	RE_I	RE_I/DB	RE_{II}	RE_{II}/DB
A. Ethane Reduction Data				
1. Benzene	48.76	16.25		
2. Toluene	48.19	16.06		
3. Ethylbenzene	48.98	16.33		
4. n-Propylbenzene	49.10	16.37		
5. n-Butylbenzene	49.52	16.51		
6. o-Xylene	48.30	16.10		
7. m-Xylene	47.98	15.99		
8. p-Xylene	47.84	15.95		
m 48.58 ± 0.20				
B. Disproportionation Reaction Data				
1. Benzene			32.05	10.68
2. Toluene			31.78	10.59
3. Ethylbenzene			31.80	10.60
4. n-Propylbenzene			31.92	10.64
5. n-Butylbenzene			32.34	10.78
6. o-Xylene			32.16	10.72
7. m-Xylene			31.84	10.61
8. p-Xylene			31.70	10.57
m 31.94 = 0.08				
C. Atomization Data				
1. Benzene	48.65	16.22	32.03	10.68
2. Toluene	48.62	16.21	32.00	10.67
3. Ethylbenzene	48.54	16.18	31.92	10.64
4. n-Propylbenzene	48.88	16.29	32.26	10.75
5. n-Butylbenzene	49.13	16.38	32.51	10.84
6. o-Xylene	48.40	16.13	31.78	10.59
7. m-Xylene	48.42	16.14	31.80	10.60
8. p-Xylene	48.25	16.08	31.63	10.54
m 48.61 = 0.10		m 31.99 = 0.10		

[a] Based on $E(C_d-C_d)_I$ = 89.12 and $E(C_d-C_d)_{II}$ = 94.66.

the same for RE_I, it is appreciably better for RE_{II}. Averaging the mean values in Table VII.A–C gives RE_I = 48.60 and RE_{II} = 31.97. RE_{II} for benzene, namely the value originating from the hydrogenation data, is now 32.05 in contrast to the 35.95 (36.0) that appears in the literature, as a consequence of the built-in correction for the CRSE of cyclohexene, i.e., 3 × 1.3.

Based only on the atomization data, RE_I and RE_{II} per double bond in these structures have the values 16.2 ± 0.1 and 10.7 ± 0.1, respectively, which will be compared with the corresponding values for other aromatic compounds below.

Table VIII lists RE_I and RE_{II} values calculated from the atomization data for the polycyclic aromatic hydrocarbons so often discussed in the literature. In certain cases, indicated in the footnote, corrections for steric hindrance have been taken into account. Undoubtedly it is also present in the three most complicated structures (9,10-diphenylanthracene 9,9'-bianthryl, and 5,6,11,12-tetraphenyltetracene), but no attempt has been made to assess the magnitude. Even though these polycyclic hydrocarbons have far more complex structures than benzene, the RE per double bond is nevertheless remarkably constant and almost the same as that for benzene and its alkyl-substituted derivatives: RE_I/DB = 17.3 ± 0.2 and RE_{II}/DB = 10.6 ± 0.2. The higher values are associated with the more condensed structures, i.e., those with the higher C/H ratios, a feature which will be compared later with the RE values for graphite.

C. Nitrogen Heterocycles

In addition to deciding upon a value for $E(C_d-C_d)$, the

TABLE VIII. Resonance Energies for Benzene and Polycyclic Hydrocarbons, RE_I and RE_{II}[a]

Compound	Formula	No. of double bonds	RE_I	RE_I/DB	RE_{II}	RE_{II}/DB
Benzene	C_6H_6	3	48.7	16.2	32.0	10.7
Tetrahydronaphthalene	$C_{10}H_{12}$	3	46.0	15.3	29.4	9.8
Naphthalene	$C_{10}H_8$	5	85.8	17.2	52.6	10.5
Biphenyl[b]	$C_{12}H_{10}$	6	102.5	17.1	63.8	10.6
Diphenylmethane	$C_{13}H_{12}$	6	99.7	16.6	66.5	11.1
9,10-Dihydroanthracene	$C_{14}H_{12}$	6	97.9	16.3	64.7	10.8
1,8-Paracyclophane	$C_{21}H_{26}$	6	94.8	15.8	61.5	10.3
6,6-Paracyclophane	$C_{24}H_{32}$	6	105.5	17.6	72.3	12.1
Anthracene	$C_{14}H_{10}$	7	120.0	17.1	70.2	10.0
Phenanthrene[b]	$C_{14}H_{10}$	7	126.4	18.1	76.6	10.9
Pyrene	$C_{16}H_{10}$	8	155.8	19.5	94.9	11.9
5,12-Dihydrotetracene	$C_{18}H_{14}$	8	136.4	17.1	86.5	10.8
Tetracene	$C_{18}H_{12}$	9	158.8	17.6	92.3	10.3
3,4-Benzphenanthrene[b]	$C_{18}H_{12}$	9	163.4	18.2	96.9	10.8
1,2-Benzanthracene[b]	$C_{18}H_{12}$	9	162.6	18.1	96.1	10.7
Chrysene[b]	$C_{18}H_{12}$	9	167.2	18.6	100.7	11.2
Triphenylene[b]	$C_{18}H_{12}$	9	168.8	18.8	102.3	11.4
Triphenylmethane	$C_{19}H_{16}$	9	145.6	16.2	95.8	10.6
Perylene[b]	$C_{20}H_{12}$	10	186.9	18.7	109.3	10.9
1,3,5-Triphenylbenzene[b]	$C_{24}H_{18}$	12	213.3	17.8	130.2	10.9
9,10-Diphenylanthracene	$C_{26}H_{18}$	13	216.3	16.6	122.1	9.4
9,9'-Bianthryl	$C_{28}H_{18}$	14	249.6	17.8	144.3	10.3
5,6,11,12-Tetraphenyltetracene	$C_{42}H_{28}$	21	346.8	16.5′	191.7	9.1

[a] Calculated from $\Delta H_a°$ data with $E(C_d-C_d)$ = 89.12 and 94.66, respectively. [b] Corrections included for steric hindrance: biphenyl, 1.4; phenanthrene, 0.7; 3,4-benzphenanthrene, 4.4; 1,2-benzanthracene 0.7; chrysene, 1.4; triphenylene, 2.1; perylene, 1.4; and 1,3,5-triphenylbenzene, 4.2 kcal/mol.

calculation of an empirical resonance energy from $\Delta H_a°$ for aromatic heterocycles is further complicated by the choice of a value for the energy term for the C-heteroatom group.

1. Pyridine and Alkyl-Substituted Pyridines

For example, in the case of pyridine it follows from a consideration of the terms that make up $\Delta H_a°$ that given the values for $E(C=C)$ and $E(C_b-H)$

$$2E(C_d-C_d) + E(C=N-C_d) + RE$$

is the composite quantity that can be readily evaluated, just as $[3E(C_d-C_d) + RE]$ was in the case of benzene. The same values of $E(C_d-C_d)_I$ and $E(C_d-C_d)_{II}$ can obviously be adopted, and, in principle, RE_I and RE_{II} can be determined from hydrogenation and ethane reduction data, and hence corresponding values for $E(C=N-C_d)$. The disproportionation reaction that underlies the evaluation of RE_{II} from hydrogenation data can be written

(11)
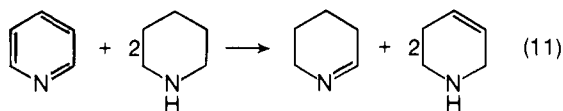
and RE_{II} evaluated using the heats of reduction of the 1,2- and 3,4-unsaturated compounds. The heat for the 3,4 derivative is readily obtained from $\Delta H_f°$ data, and a value for the 1,2 derivative can be estimated using bond energy terms together with the group energy $E(C=N-C)$ based on data for noncyclic aliphatic aldimines. This procedure was, in fact, employed in connection with the previous discussion of thermodynamic aspects of porphyrin synthesis and biosynthesis.[5] Taking $E(C_{C=N}-H) \equiv E(C_d-H)_1$ = 100.53, $E(C=N-C)$ = 202.42, and, with $E(C_d-C_d)$ = 93.74, a weighted mean of the values in Table V.C, making no correction for ring strain, RE was found to be 32.94. Hence $E(C=N-C_d)$ = 204.38. A better estimate would be to put $E(C_{C=N}-H)$ = $E(C_{CO}-H)$ =

101.97, which gives $E(C=N-C)$ = 200.98, but this does not affect the magnitude of either RE or $E(C=N-C_d)$. Updating the calculation and using $E(C_d-C_d)_{II}$ = 94.66 would give a revised value of 202.54 for $E(C=N-C_d)$.

However, as written, the above equation for the disproportionation reaction is not strictly correct. The reaction products should be
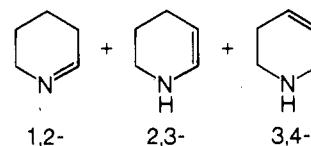
It does not necessarily follow that the heats of reduction of the 2,3 and 3,4 derivatives are identical. In the former case two C_d-C bonds are destroyed and replaced by two C-C bonds, whereas in the latter one C_d-C and one C_d-N bond are destroyed and replaced by one C-C bond and one C-N bond. Unfortunately, no experimental data are available at present relating to the 2,3 derivative, so another approach has been followed which is free from this particular uncertainty.

$\Delta H°$ for the reduction of pyridine by ethane, i.e., RE_I, can readily be obtained from $\Delta H_f°$ data as 51.76. Exami-

(12)
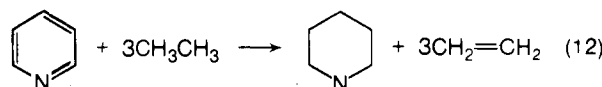
nation of the ratio RE_I/RE_{II} for benzene and the alkylbenzenes in Table VII shows it to be a constant well within experimental error, the ratio for benzene being 48.76/32.05 = 1.521 and the ratio from the overall means 48.58/31.94 = 1.520. In those cases where for any reason there is ambiguity or uncertainty in calculating RE_{II} directly from hydrogenation or equivalent data, it is proposed to evaluate RE_{II} from RE_I using this ratio. Hence for pyridine, RE_{II} = 51.76/1.52 = 34.05. It should perhaps be emphasized again that this RE_{II} value cannot be identified as $\Delta H°$ for the actual disproportiona-

tion reaction since $\Delta H°$ would also involve the conventional ring strain energies for the three product species. While in the previous calculation CRSE was automatically included for the reduction of the 3,4 derivative, it was not for the 1,2 derivative, but there is no purpose to be served in pursuing the comparison any further.

However, in general, the CRSE term for the reduced species also contributes to $\Delta H°$ for the ethane reduction reactions, and, if RE values based on hydrogenation data are to be criticized on this account, the neglect of the CRSE term in this case is just as inadmissible. The omission of the term in the above treatment of RE_I for benzene and the alkylbenzenes is justified because CRSE is zero for the corresponding cyclohexane derivatives. The same is true for pyridine, the CRSE value for piperidine actually being negative to a small extent, i.e., −0.13, which within experimental error implies zero strain.

Now if $\Delta H°$ for the reduction of pyridine by ethane is set up in terms of the heats of atomization of the reactant and product species, it can be shown that

$$E(C\!=\!\!\!=\!N\text{-}C_d) + 2E(C_d\text{-}C_d) + RE = \Delta H° +$$

$$E(C\text{-}C) + E(C\!=\!\!\!=\!C) + 2E(C\text{-}N) + 6E(C\text{-}H)_s + 4E(C\text{-}H)_s{}^N +$$

$$E(N\text{-}H)_1 - 5E(C_b\text{-}H) - 18E(C\text{-}H)_p = \Delta H° + 373.00$$

Thus, identifying RE_I with $\Delta H°$, and taking $E(C_d\text{-}C_d)_I =$ 89.12, it follows that the corresponding value for $E(C\!=\!\!\!=\!N\text{-}C_d)$, i.e., $E(C\!=\!\!\!=\!N\text{-}C_d)_I$, equals 194.76.

Since the RE_{II} value of 34.05 is to be identified with $\Delta H°$ for the disproportionation reaction with no strain energy contributions, the corresponding value of $E(C\!=\!\!\!=\!N\text{-}C_d)$ in this case, i.e., $E(C\!=\!\!\!=\!N\text{-}C_d)_{II}$ could be obtained in principle from the expression for $\Delta H°$ based on the atomization heats of reactants and products with no CRSE terms, i.e.

$$E(C\!=\!\!\!=\!N\text{-}C_d) + 2E(C_d\text{-}C_d) + RE = \Delta H° +$$

$$E(C\!=\!\!\!=\!N\text{-}C) + 4E(C_d\text{-}C) + E(C_d\text{-}N) - 2E(C\text{-}C) - E(C\text{-}N)$$

But unfortunately there are no data available at present to establish $E(C_d\text{-}N)$, so the only source of a value for $E(C\!=\!\!\!=\!N\text{-}C_d)$ is $\Delta H_a°$ for pyridine. The composite term derived from $\Delta H_a°$ is identical with the left-hand side of the above expression and is found to be 424.80. Hence with $RE_{II} = 34.05$, and $E(C_d\text{-}C_d)_{II} = 94.66$, $E(C\!=\!\!\!=\!N\text{-}C_d)_{II} = 201.43$.

Since nitrogen is undoubtedly more electronegative than carbon in any of its hybridization states, and since there is good reason for believing that C_{sp^2} is more electronegative than C_{sp^3}, the $N\text{-}C_d$ bond should be weaker than the $N\text{-}C$ bond. It is therefore interesting to note that compared to $E(C\!=\!\!\!=\!N\text{-}C)$, for which the value 200.98 was obtained from aldimine data,[5] $E(C\!=\!\!\!=\!N\text{-}C_d)_I$ is smaller, whereas $E(C\!=\!\!\!=\!N\text{-}C_d)_{II}$ is greater by 1.45. This substantiates the view that 94.66 for $E(C_d\text{-}C_d)$ is an overestimate, and the upper limit would be better put at $94.66 - 1.45 = 93.21$.

With values now established for $E(C\!=\!\!\!=\!N\text{-}C_d)_I$ and $E(C\!=\!\!\!=\!N\text{-}C_d)_{II}$, RE_{II} can be calculated from $\Delta H_a°$ data for the three mono- and six dimethylpyridines; see Table IX. Including that for pyridine, the mean values are $RE_I = 54.3 \pm 0.3$ and $RE_{II} = 36.5 \pm 0.3$, giving $RE_I/DB = 18.1 \pm 0.1$ and $RE_{II}/DB = 12.2 \pm 0.1$. While the values for benzene and the alkylbenzenes are the same within experimental uncertainty, it would appear that pyridine has an appreciably lower RE than any of its alkyl derivatives, but there may be a systematic experimental error somewhere.

TABLE IX. Resonance Energies for Pyridine and Its Mono- and Dimethyl Derivatives, RE_I and RE_{II}[a]

Compound	RE_I	RE_I/DB	RE_{II}	RE_{II}/DB
Pyridine	51.8	17.3	34.1	11.4
2-Methylpyridine	54.8	18.3	37.1	12.4
3-Methylpyridine	53.1	17.7	35.3	11.8
4-Methylpyridine	54.1	18.0	36.3	12.1
2,3-Dimethylpyridine	54.7	18.2	37.0	12.3
2,4-Dimethylpyridine	55.4	18.5	37.6	12.5
2,5-Dimethylpyridine	54.8	18.3	37.0	12.3
2,6-Dimethylpyridine	56.6	18.9	38.9	13.0
3,4-Dimethylpyridine	54.3	18.1	36.6	12.2
3,5-Dimethylpyridine	53.3	17.8	35.5	11.8

[a] Calculated from $\Delta H_a°$ data with $E(C_d\text{-}C_d)_I = 89.12$, $E(C\!=\!\!\!=\!N\text{-}C_d)_I = 194.76$, and $E(C_d\text{-}C_d)_{II} = 94.66$, $E(C\!=\!\!\!=\!N\text{-}C_d)_{II} = 201.43$.

2. Pyrrole and Substituted Pyrroles

The evaluation of RE values for pyrroles presents similar kinds of problems as those encountered with the pyridines, this time centered on establishing a value for the group energy term $E(C_d\text{-}NH\text{-}C_d)$. A value for RE_{II} cannot as yet be obtained from $\Delta H°$ for the disproportiona-

$$\text{(13)}$$
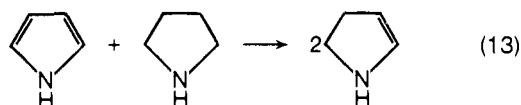
tion reaction because $\Delta H_f°$ is not known for 2,3-dihydropyrrole. A value could be arrived at using cyclopentene data, but too many assumptions have to be made about strain energies for it to be of any use.

On the other hand, a reliable value for RE_I can be calculated from ethane reduction data, and RE_{II} calculated from the RE_I/RE_{II} ratio of 1.52 as for pyridine. $\Delta H°$ for

$$+ \ 2CH_3CH_3 \ \longrightarrow \ + \ 2CH_2\!=\!CH_2 \quad (14)$$
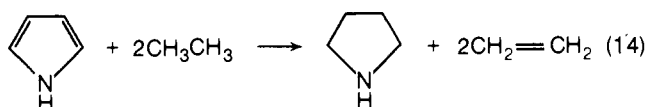
the ethane reduction reaction (eq 14), 38.70 from $\Delta H_f°$ data, is given by the expression

$$\Delta H° = [E(C_d\text{-}C_d) + E(C_d\text{-}NH\text{-}C_d) + RE] + 4E(C_b\text{-}H) +$$

$$12E(C\text{-}H)_p - 2E(C\text{-}N) - E(N\text{-}H)_1 - E(C\text{-}C) - 4E(C\text{-}H)_s -$$

$$4E(C\text{-}H)_s{}^N - 8E(C_d\text{-}H)_2 + CRSE(\text{pyrrolidine})$$

But $CRSE(\text{pyrrolidine})$ is 5.91. So in this case the simple identification $RE_I = \Delta H° = 38.70$ would result in a value for RE_I enhanced by this amount, which is clearly quite irrelevant. $\Delta H°$ should therefore be corrected, i.e.

$$RE_I = \Delta H° - CRSE(\text{pyrrolidine}) = 38.70 - 5.91 = 32.79$$

Putting $\Delta H° - CRSE(\text{pyrrolidine})$ equal to RE_I thus gives

$$E(C_d\text{-}C_d)_I + E(C_d\text{-}NH\text{-}C_d)_I = E(C\text{-}C) + 2E(C\text{-}N) +$$

$$E(N\text{-}H)_1 + 4E(C\text{-}H)_s + 4E(C\text{-}H)_s{}^N + 8E(C_d\text{-}H)_2 -$$

$$4E(C_b\text{-}H) - 12E(C\text{-}H)_p$$

i.e., $E(C_d\text{-}C_d)_I + E(C_d\text{-}NH\text{-}C_d)_I = 330.49$ from which $E(C_d\text{-}NH\text{-}C_d)_I = 241.37$.

From the ratio $RE_I/RE_{II} = 1.52$, it follows that RE_{II} for pyrrole equals 21.57. But the corresponding group energy term, $E(C_d\text{-}NH\text{-}C_d)_{II}$, again cannot be evaluated from the expression for $\Delta H°$ for the disproportionation reaction because the bond energy term $E(C_d\text{-}N)$ would

TABLE X. Resonance Energies for Substituted Pyrroles, RE_I and RE_{II}[a]

Compound	ΔH_{sub}° [b]	RE_I	RE_{II}
2,4,5-Trimethyl-3-ethylpyrrole	16	27.5	16.4
2,4-Dimethyl-3-ethyl-5-formylpyrrole	17.5	45.1	34.0
2-Methyl-3-carbethoxypyrrole	17.5	30.5	19.4
2,4-Dimethyl-3-carbomethoxypyrrole	17.5	39.3	28.3
2,4-Dimethyl-5-carbomethoxypyrrole	17.5	39.3	28.3
2,5-Dimethyl-3-carbethoxypyrrole	19	43.3	32.3
2,4-Dimethyl-5-carbethoxypyrrole	19	42.5	31.6
2,3-Dimethyl-4-carbethoxypyrrole	19	41.6	30.6
2,4-Dimethyl-3-carbethoxypyrrole	19	39.6	28.6
2,3-Dimethyl-5-carbethoxypyrrole	19	36.3	25.3
2,4,5-Trimethyl-3-carbethoxypyrrole	20	38.2	27.1
2,4-Dimethyl-3-vinyl-5-carbethoxypyrrole	21	58.6	47.6
2,4-Dimethyl-3-ethyl-5-carbethoxypyrrole	21	41.8	30.7
2,4-Dimethyl-3-propyl-5-carbethoxy-pyrrole	21.5	44.7	33.7
2,4-Diethyl-3,5-dipropionylpyrrole	22.5	34.0	23.0
2,4-Dimethyl-5-carbethoxy-3-formyl-pyrrole	21	51.7	40.7
2,4-Dimethyl-3-carbethoxy-5-formyl-pyrrole	21	52.9	41.9
2,4-Dimethyl-3-acetyl-5-carbethoxy-pyrrole	21.5	42.3	31.2
2,4-Dimethyl-3-propionyl-5-carbethoxy-pyrrole	22	42.7	31.7
2,4-Dimethyl-5-propionyl-3-carbethoxy-pyrrole	22	43.2	32.2
2,4-Dimethyl-3,5-dicarbomethoxypyrrole	21.5	49.8	38.8
2,4-Dimethyl-5-carbomethoxypyrrole-3-propionic acid methyl ester	22.5	40.7	29.6
2,4-Dimethyl-3,5-dicarbethoxypyrrole	22.5	49.7	39.6
4-Methyl-3,5-dicarbethoxy-2-hydroxy-methylpyrrole	23	47.1	36.1
4-Methyl-3,5-dicarbethoxy-2-α-hydroxy-ethylpyrrole	23.5	56.2	45.2
3,5-Dicarbethoxy-2-α-hydroxypropyl-4-methylpyrrole	23.5	39.0	27.9

[a] Calculated from ΔH_a° data with $E(C_d-C_d)_I = 89.12$, $E(C_d-NH-C_d)_I = 241.37$, and $E(C_d-C_d)_{II} = 94.66$, $E(C_d-NH-C_d)_{II} = 246.87$. [b] ΔH_{sub}° estimated on the basis of the number of structurally bonded C, N, and O atoms according to Figure 2.

be needed. Hence for the present, $E(C_d-NH-C_d)_{II}$ has to be based on the atomization heat of pyrrole. Expressing this as the sum of the various bond energy terms, it follows that

$$E(C_d-C_d)_{II} + E(C_d-NH-C_d)_{II} + RE_{II} = 363.10$$

and thus $E(C_d-NH-C_d)_{II} = 246.87$. Neither $E(C_d-NH-C_d)_I$ nor $E(C_d-NH-C_d)_{II}$ is less than $E(C-NH-C)$, i.e., 238.21, which might have been expected at first from electronegativity considerations. However, the involvement of the lone pair of electrons on the N atom in the aromaticity of pyrrole might affect the strength of the N–H bond similar to the alteration in C–H bond strength in going from $E(C-H)_t = 96.53$ to $E(C_b-H) = 100.53$. An increase in the $E(N-H)$ component of $E(C_d-NH-C_d)$ would thus decrease the contribution of $E(C_d-N)$, which would be in the direction anticipated.

The very recent combustion and evaporation data for 2,5-dimethylpyrrole give $\Delta H_f^{\circ} = +9.50 \pm 0.21$ for the gaseous compound.[37] From an evaluation of ΔH_a°, RE_I and RE_{II} are found to be 33.29 and 22.25, in excellent agreement with the values for pyrrole itself.

Twenty-six RE_I and RE_{II} values can be calculated for heavily substituted pyrroles from the old combustion data of Stern and Klebs,[38,39] and in addition values for four di-

TABLE XI. Resonance Energies for Phenylpyrrole, Polypyrroles, Pyrromethenes, etc., RE_I and RE_{II}[a]

Compound	ΔH_{sub}° [b]	RE_I	RE_{II}
2-Phenylpyrrole	17.5	83.9	50.7
Di-α-pyrrylmethane	17.5	68.8	46.8
4,4'-Dicarbethoxy-2,2',5,5'-tetra-methyl-3,3'-pyrromethane	24.5	79.9	57.8
5,5'-Dicarbethoxy-2,2',4,4'-tetra-methyl-3,3'-pyrromethane	24.5	75.0	52.9
2,2',4,4'-Tetramethyl-3,3'-dicarb-ethoxydipyrrylmethane	24.5	78.6	56.5
2,2',4,4'-Tetramethyl-3,3'-dicarb-ethoxydipyrrylmethylmethane	24.5	77.1	55.0
3,3',5,5'-Tetramethyl-4,4'-diethyl-2,2'-pyrromethene	23.5	78.6	44.3
2,2',4,4'-Tetramethyl-3,3'-dicarb-ethoxydipyrrylmethene	24.5	103.9	69.5
2,9-Diacetyl-1,3,5,6,8,10-hexamethyl-4,7-diethyltetrapyrro-14-ene	28	158.6	93.2

[a] Calculated from ΔH_a° data with $E(C_d-C_d)_I = 89.12$, $E(C=N-C_d)_I = 194.76$, $E(C_d-NH-C_d)_I = 241.37$, and $E(C_d-C_d)_{II} = 94.66$, $E(C = N-C_d)_{II} = 201.43$, $E(C_d-NH-C_d)_{II} = 246.87$. [b] ΔH_{sub}° estimated on the basis of the number of structurally bonded C, N, and O atoms according to Figure 2.

pyrrylmethanes, two pyrromethenes, and a tetrapyrromonoene derivative; see Tables X and XI and the summary in Table XII. A few data for carboxylic acids have not been worked on because of the much greater uncertainty in estimating the sublimation heats, and a 3-hydroxy compound has been omitted because of the possibility of a tautomeric shift to give the 3-oxo structure. For these substituted pyrroles there is a much greater scatter in the values compared to the substituted pyridines, Table IX; furthermore the mean value for RE_{II}, 32, is half as much again as that for pyrrole and 2,5-dimethylpyrrole obtained from the more recent experimental work.[37] It seems unlikely that this discrepancy could originate in the estimation of the sublimation heats of the substituted compounds, and further experimental studies are much needed. It may be noted that RE_I and RE_{II} for phenylpyrrole, 83.9 and 50.7, respectively, support a lower value since the sum of the individual values for benzene and pyrrole are 81.5 and 53.6. The RE values per ring are a little less for the dipyrrylmethanes compared to the substituted pyrroles, and, judging by the values for pyrromethenes and the tetrapyrromonoene, partial oxidation of the ring system has little effect on the RE.

3. Pyridine, Pyrrole, and Related Polycyclics

The fusion of a benzene ring onto pyridine and pyrrole has a systematic influence on the resonance energy, as shown in Table XIII. The molecular structures of pyridine, quinoline, isoquinoline, and acridine are strictly comparable to those of benzene, naphthalene, and anthracene, so it is interesting to see how close RE per double bond is to the values for the aromatic hydrocarbons.

The evaluation of a similar parameter for pyrrole, indole, and carbazole is not straightforward, since in these cases the lone pair of electrons on the N atoms is an integral part of the aromaticity. There are several possibilities: to assume that the structures have the equivalent of three, five, and seven double bonds; to evaluate RE/DB on the basis of the increment in going from pyrrole to indole to carbazole; or to use the actual number of double bonds in the Kekulé structures, i.e., 2, 4, and 6. Any choice is arbitrary, and all three possibilities give values for the parameter quite close to those for pyridine, quinoline, and acridine and the polycyclic hydrocarbons. In

TABLE XII. Summary of Resonance Energies for Pyrrole, Substituted Pyrroles, Polypyrroles, etc.

Class of compd	Range of RE_I	Mean RE_I	RE_I per ring	Range of RE_{II}	Mean RE_{II}	RE_{II} per ring
Pyrrole	32,8	—	33	21,6	—	22
26 Tri- and tetrasubstituted pyrroles	27.5–58.6	$43,0 \pm 1,4$	43	16.4–47,6	$32.0 \pm 1,4$	32
4 Hexasubstituted dipyrrylmethanes	75,0–79,9	77.7	39	52.9–57.8	55.6	28
2 pyrromethenes	78,6, 103.9	91.3	46	44,3, 69,5	56,9	28
Decasubstituted tetrapyrro-14-ene	158,6	—	40	93,2	—	23

TABLE XIII. Resonance Energies for Pyridine, Pyrrole, and Related Polycyclic Compounds, RE_I and RE_{II}[a]

Compound	No. of DB	RE_I	RE_I/DB	RE_{II}	RE_{II}/DB
Pyridine	3	51.8	17.3	34.1	11.4
Quinoline[b]	5	88.3	17.7	53.9	10.8
Isoquinoline[b]	5	91.1	18,2	56.7	11.3
Acridine	7	124.6	17.8	73.6	10,5
Pyrrole[c]	"3"	32.8	10.9	21.6	7,2
Indole[c,d]	"5"	74.5	14.9	46.8	9.4
Carbazole[c]	"7"	115.2	16.5	70.9	10.1

[a] Calculated from $\Delta H_a°$ data with $E(C_d–C_d)_I = 89.12$, $E(C=N–C_d)_I = 194.76$, $E(C_d–NH–C_d)_I = 241.37$, and $E(C_d–C_d)_{II} = 94.66$, $E(C=N–C_d)_{II} = 201.43$, $E(C_d–NH–C_d)_{II} = 246.87$. [b] Values for quinoline and isoquinoline calculated from old[22] and very recent[37] combustion data, respectively, assuming a heat of evaporation of 14 in each case. [c] The lone pair of electrons on the N atom, which contributes to the aromaticity, is taken to be equivalent to a double bond in the evaluation of RE/DB. [d] Value based on very recent combustion data[37] with $\Delta H_{sub}° = 16.7$.

Table XIII the first has been adopted, because, while the values for pyrrole are low, it shows how in the limit with a benzene ring fused on either side (carbazole) the values approach those for the analogous polycyclic hydrocarbon (anthracene).

4. Pyrimidine, Pyrazine, Imidazole, and Adenine

The introduction of another N atom into the aromatic system in place of C–H would appear to result in a perceptible increase in RE values; see Table XIV. The case of adenine calls for special comment, since $RE_I = 117$ and $RE_{II} = 86.0$ are 14 kcal/mol higher than would be expected on the basis of combining a pyrimidine with an imidazole ring system, viz. 103 and 72, respectively. Data for other purines are much needed to establish whether this enhanced stability is real.

5. Porphyrins and Chlorines

As in the case of the substituted pyrroles,[38,39] the combustion data of Stern and Klebs lead to a great scatter of RE_I and RE_{II} values for porphyrins and chlorines[15] that seems unlikely to be due entirely to errors in the estimation of sublimation heats. The values are presented in detail in Table XV and summarized in Table XVI. A few data for compounds with carboxylic acid side chains have again been omitted. Despite the uncertainties, the magnitude of the parameter RE/DB appears to be somewhat greater than the values for the other simpler aromatic structures reported above. Or, put another way, the average value of RE_I and RE_{II} per five-membered ring would be about 56 and 36, respectively.

In even greater contrast, however, are the values obtained from the recent combustion studies of Longo, Finarelli, Schmalzbach, and Adler[19] on porphine itself and the meso-substituted tetraethyl and tetraphenyl derivatives. Exactly the same calculation procedure leads to RE_I of about 570, and RE_{II} of about 480, so that RE_I/DB is more than twice, and RE_{II}/DB about three times, the Stern and Klebs' values; see Table XVII. Further discussion of this discrepancy will be taken up in section V below.

TABLE XIV. Resonance Energies for N Heterocycles with More Than One N Atom per Ring, RE_I and RE_{II}[a]

Compound	RE_I	RE_{II}
Pyrimidine	57.3	38.4
Pyrazine	57,4	38.5
Imidazole	45.8	33.6
Adenine	117.2	86.1

[a] Calculated from $\Delta H_a°$ data with $E(C_d–C_d)_I = 89.12$, $E(C=N–C_d)_I = 194.76$, $E(C_d–NH–C_d)_I = 241.37$, and $E(C_d–C_d)_{II} = 94.66$, $E(C=N–C_d)_{II} = 201.43$, $E(C_d–NH-C_d)_{II} = 246.87$.

TABLE XV. Resonance Energies for Porphyrins (A and C) and Chlorines (B and D) Calculated from $\Delta H_a°$ Based on the Combustion Data of Stern and Klebs[15] [a]

Compound	$\Delta H_{sub}°$ [b]	RE_I	RE_{II}
A. Etioporphyrin I	26.5	240	155
Octaethylporphyrin	28.5	257	171
Pyroporphyrin XV monomethyl ester	27.5	257	171
γ-Phylloporphyrin monomethyl ester	28	246	161
Desoxophylloerythrin monomethyl ester	28,5	206	120
Verdoporphyrin dimethyl ester	30	251	166
Rhodoporphyrin XXI dimethyl ester	30	203	117
Protoporphyrin dimethyl ester	31.5	259	163
Mesoporphyrin IX dimethyl ester	31.5	265	179
Coproporphyrin I tetramethyl ester	40	243	157
Isouroporphyrin II octamethyl ester	60	164	78
B. Methylpheophorbide b	33	227	147
Chlorine p_6 trimethyl ester	33	281	201
Dimethylpheopurpurin 7	35	209	129
C. (i) Phylloerythrin monomethyl ester[c]	29,5	221	135
(ii) Chloroporphyrin e_4 dimethyl ester	30.5	225	139
(iii) Pheoporphyrin a_5 dimethyl ester	32.5	211	126
(iv) Chloroporphyrin e_6 trimethyl ester	34	214	129
D. (i) Pyropheophorbide a mono-methyl ester[c]	29.5	223	143
(ii) Chlorine e_4 dimethyl ester	30,5	215	136
(iii) Methylpheophorbide a	32.5	203	123
(iv) Chlorine e_6 trimethyl ester	34	205	125

[a] RE_I and RE_{II} evaluated using $E(C_d–C_d)_I = 89.12$, $E(C=N–C_d)_I = 194.76$, $E(C_d–NH–C_d)_I = 241.37$, and $E(C_d–C_d)_{II} = 94.66$, $E(C=N–C_d)_{II} = 201.43$, $E(C_d–NH–C_d)_{II} = 246.87$. [b] $\Delta H_{sub}°$ estimated on the basis of the number of structurally bonded C, N, and O atoms according to Figure 2. [c] C(i) and D(i) isomers; likewise, C(ii) and D(ii), etc.

D. [18]Annulene

In view of the structural relationship between porphine and [18]annulene, which will be described shortly, the

TABLE XVI. Summary of Resonance Energies for Porphyrins and Chlorines[a]

Class of compd	Range of RE_I	Mean RE_I	RE_I/DB[b]	Range of RE_{II}	Mean RE_{II}	RE_{II}/DB[b]
11 porphyrins, Table XV.A	164–265	236 ± 9	26	78–179	149 ± 9	17
3 unrelated chlorines, Table XV.B	209–281	239	26	129–201	159	18
4 porphyrins, Table XV.C	211–225	218 ± 3	24	126–139	132 ± 3	15
4 isomeric chlorines, Table XV.D	203–223	212 ± 7	24	123–136	132 ± 7	15

[a] Calculated from the data of Stern and Klebs.[15] [b] On the basis of nine double bonds in the macrocyclic ring, as in the [18]annulene model.

TABLE XVII. Resonance Energies for Porphine and Tetraethyl- and Tetraphenylporphine (TEP and TPP)[a]

Compd	RE_I	RE_I/DB[b]	RE_{II}	RE_{II}/DB[b]
Porphine	582	65	497	55
TEP	580	64	495	55
TPP	560[c]	62	452[c]	50

[a] Calculated from ΔH_a° based on the combustion data of Longo, Finarelli, Schmalzbach, and Adler[19]; RE_I and RE_{II} evaluated using $E(C_d–C_d)_I = 89.12$, $E(C=N–C_d)_I = 194.76$, $E(C_d–NH–C_d)_I = 241.37$, and $E(C_d–C_d)_{II} = 94.66$, $E(C=N–C_d)_{II} = 201.43$, $E(C_d–NH–C_d)_{II} = 246.87$. [b] On the basis of nine double bonds in the macrocyclic ring as in the [18]annulene model. [c] After allowing for the contribution of the benzene rings using 1217.67 kcal for the C_6H_5 group energy.

resonance energy for this 18-membered ring containing nine conjugated double bonds is of the greatest interest.

Beezer, Mortimer, Springall, Sondheimer, and Wolovsky[40] determined its heat of combustion and calculated ΔH_f° for the crystalline compound, $+39.0 \pm 4$ kcal/mol. Assuming 28 ± 2 kcal/mol for the sublimation heat on the basis of values ranging from 26 to 30 for several C_{18} polycyclic hydrocarbons, ΔH_f° for the gaseous compound was obtained as $+67.0 \pm 6$ kcal/mol. With ΔH_f°(benzene)$_g = +19.8$, ΔH° for the hypothetical isomerization reaction

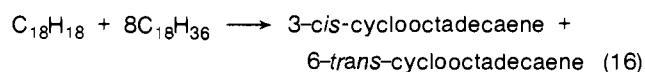$$3C_6H_6 \longrightarrow [18]\text{annulene} \qquad (15)$$
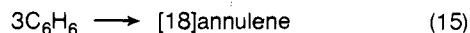
was found to be $+8.0 \pm 6$ kcal/mol. Hence, taking the C–H bond energy terms to be identical in the two compounds, it follows that with an RE value for benzene of 36 kcal/mol, the value for [18]annulene is $(3 \times 36) - 8 = 100 \pm 6$ kcal/mol. Thus the magnitude of what is approximately RE_{II}, as defined in this review, is in little doubt, and it can be seen immediately that an approximate value of RE_{II}/DB is 11 kcal.

Values for RE_I and RE_{II} have been obtained as follows. A revised estimate of 22 kcal/mol has been adopted for the sublimation heat because the value for porphine, with six more structurally bonded atoms in a similar almost planar structure, is 26.[21,41] Furthermore, the C_{18} hydrocarbons used as the basis for the 26 value are polycyclic structures for which the intermolecular interaction in the crystalline state is likely to be greater than that with the more open [18]annulene structure. ΔH_f° for the gaseous compound thus becomes $+61.0 \pm 6$ kcal/mol. ΔH_f° for cyclooctadecane gas has been calculated using the C–C and (C–H)$_s$ bond contributions of -0.03 and -2.44 evaluated by Cox and Pilcher,[20] and found to be -88.38. ΔH° for the ethane reduction reaction

$$[18]\text{annulene} + 9CH_3CH_3 \longrightarrow C_{18}H_{36} + 9CH_2=CH_2$$

is thus 144.83. CRSE for the C_{18} cycloparaffin is likely to be very nearly zero, the values for the C_{15}, C_{16}, and C_{17} compounds being 1.8, 1.8, and -3.4, respectively; so ΔH° for the above reaction can be identified as RE_I. A value for RE_{II} can be obtained from ΔH° for the disproportionation reaction

$$C_{18}H_{18} + 8C_{18}H_{36} \longrightarrow 3\text{-}cis\text{-cyclooctadecaene} +$$
$$6\text{-}trans\text{-cyclooctadecaene} \qquad (16)$$

the cis and trans reduction products taking into account the disposition of cis and trans double bonds in the Kekulé structure for [18]annulene. The heats of reduction for the two cyclic olefins can be taken as equal to those for cis- and trans-2-butene, i.e., -28.50 and -27.37, respectively, and, in this way, assuming there is no ring strain in the cyclic olefins, $RE_{II} = 100.34$. What is probably a rather more reliable value is obtained from the heat of atomization, which gives

$$9E(C_d–C_d)_{II} + RE_{II} = 946.46$$

from which $RE_{II} = 94.52$. It is to be noted that with this value the ratio RE_I/RE_{II}, 1.53, is very close to the 1.52 characteristic of benzene and the alkylbenzenes. RE_I/DB and RE_{II}/DB are 16.1 and 10.5, respectively.

On this topic of the resonance energy of [18]annulene, there appears to be a serious conflict between experiment and theory. In an earlier form, a semiempirical SCF–MO treatment gave 3.188 eV,[42] i.e., 73.5 kcal, while in a later more refined state, the very low value of 0.382 eV, i.e., 8.8 kcal, was obtained.[43,44] Even though resonance energy is defined somewhat differently in the theoretical treatments, these values can be judged in relation to that adopted for benzene, namely, 1.318 eV, i.e., 30.4 kcal. There is thus a very real discrepancy.

E. Graphite

Finally, in any assessment of empirical resonance energies for aromatic compounds, graphite, in which there are infinite sheets of conjugated double bonds in the Kekulé structure, is the limiting case; RE/DB for graphite is therefore likely to be the maximum attainable —at least for polycyclic hydrocarbons. Judging from the values in Table XIII, the substitution of C–H by N atoms in conjugated structures has little effect on RE/DB, so the graphite value is probably the maximum for nitrogen heterocycles too.[45]

An LCAO calculation has given RE per C atom as 0.58β,[47] which with $\beta = 18$ (a value based on RE = 35.64 for benzene), equals 10.44.[48] A different treatment gave 0.846 eV, i.e., 19.50, which after correction for the compression energy, 8.5, gives 11.0.[49] An experimental value was obtained by Barrow[50] using an empirical equation suggested by Mulliken and Parr[51] for the calculation of heats of formation of gaseous hydrocarbons at 298°K, namely

$$\Delta H_I^\circ = -4.14N_{C-H} + 4.90N_{C-C} +$$
$$26.50N_{C=C} - 0.78n - \Delta \qquad (17)$$

where N_{C-H}, N_{C-C}, and $N_{C=C}$ are the number of C–H, C–C, and C=C bonds, respectively, n is a branching factor, and a positive value for Δ is the resonance energy. Having estimated the cohesion energy of graphite, i.e., the interaction energy between the layers, to be 1.6 kcal/g-atom, on the basis of the sublimation heats of polycyclic aromatic hydrocarbons, ΔH_f° is thus $+1.6$ and putting $N_{C-H} = 0$, $N_{C-C} = 1$, $N_{C=C} = 0.5$, and $n = 8$, the resonance energy, was found to be approximately 10

kcal/g-atom. Since there is half a double bond per carbon atom in the Kekulé structure for graphite, these resonance energy values are equivalent to about 20–22 in terms of RE/DB.

To calculate the corresponding values of RE_I/DB and RE_{II}/DB, the following procedure has been adopted. First, although there have been direct experimental measurements that give values for the cohesion energy up to about 4 kcal/g-atom,[52,53] a value based on sublimation heats has again been chosen as the more reliable, the values for benzene, biphenyl, naphthalene, anthracene, phenanthrene, pyrene, tetracene, triphenylene, chrysene, and perylene[20] giving a mean of 1.61 ± 0.04 kcal/g-atom. The heat of atomization of graphite is 170.9; hence the bonding energy per carbon atom in the layered structure in the hypothetical ideal gas state is 170.9 − 1.61 = 169.29. A consideration of the bonding shows that per carbon atom it amounts to

$$2 \times {}^1\!/_2 E(C_d\text{--}C_d) + {}^1\!/_2 E(C\!\!=\!\!C) + {}^1\!/_2 RE/DB$$

Hence, making the appropriate substitutions, RE_I/DB = 27.34 and RE_{II}/DB = 16.26, with the resonance energies per carbon atom, 13.67 and 8.13, respectively.

Reference to Table VIII shows that graphite, in relation to all the polycyclic hydrocarbons for which data are available, has resonance energy stabilization which is greater by some 50–60%.

V. Structure of Porphine in Relation to the Magnitude of Its Resonance Energy

### A. Complexity of the Structure

Even though the correct molecular structure for porphyrins was proposed by Küster and Deihle in 1913,[54] and, after much controversy and several false leads, fully established through the synthetic studies of Fischer and his colleagues by 1929,[55] it is often described in a misleading fashion and the character of the aromatic ring system poorly defined.

The many organic syntheses from substituted pyrroles and the biosynthetic route via porphobilinogen—a trisubstituted pyrrole—have led to the widespread description of porphyrins as tetrapyrrole compounds, or, a little better, as tetrapyrrole derivatives. In innumerable places in the literature the porphine structure is referred to as a fully conjugated cyclic system in which four pyrrole rings are linked together via the 2 and 5 positions by four –CH= groups to give a 16-membered ring.[56-59] But in the classical Kekulé structure (Figure 3a), only one of the four small rings, ring A, is a pyrrole; rings B and D are of the pyrrolenine type, and ring C is related to maleimide.[60] In the delocalized electron structure (Figure 3b), none are pyrrole rings.[61] Designation as a tetrapyrrole derivative obscures the fact that porphyrins are six equivalents above the oxidation state of a tetrapyrrole. It is as if benzene, six equivalents above the oxidation state of cyclohexane, was persistently referred to as a cyclohexane derivative: true in a way, but misleading.

This could be regarded as pedantry because the oxidation–reduction relationship is readily appreciated, but more is at stake in the precise definition of the macrocyclic aromatic system. The structure is complex, and aromaticity can be achieved, on paper at least, in three quite distinct ways.

1. Inner 16-Membered Ring

In the Kekulé structure the inner 16-membered ring
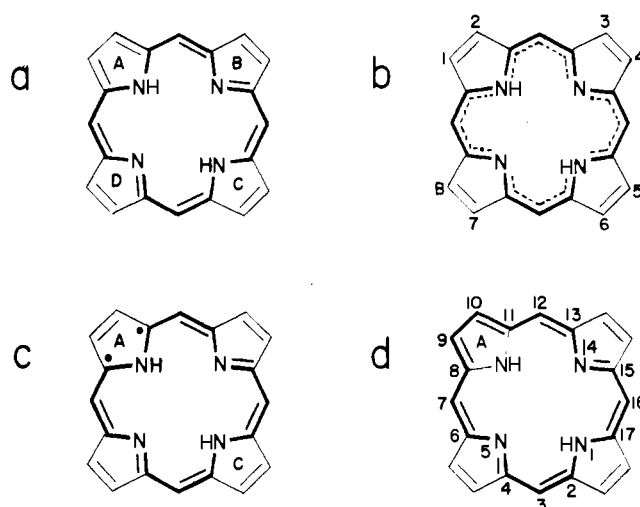
Figure 3. Porphine structures. (a) The Kekulé structure with the "inner 16-membered" ring emphasized; note the broken conjugation in this ring at the two NH groups: (b) Delocalized electron structure; note the four peripheral double bonds at positions 1,2, 3,4, 5,6, 7,8. (c) Diradical structure. (d) Kekulé structure with a 17-membered ring emphasized.

does not contain alternating, i.e., conjugated, double and single bonds; see Figure 3a. Conjugation is broken at both NH groups, especially in ring A where there is a run of four single bonds. However, in pyrrole, the aromatic character is understood to arise from the lone pair of electrons on the NH group combining with four electrons from the four carbon atoms to give a total of six delocalized electrons, as in benzene. Similar contributions in the case of the inner 16-membered ring of porphine do nothing to achieve a conjugated ring system, but aromaticity can be attained with 18 delocalized electrons, in accord with Hückel's rule, i.e., (4n + 2) delocalized electrons, 12 from the 12 carbon atoms, 2 from the two pyrrolenine N atoms, and 4 from the 2 N–H groups. As in the case of pyridine, the lone pairs of electrons on the pyrrolenine N atoms would not be involved.

This pattern of delocalization, illustrated schematically in Figure 3b, has been the basis for the majority of theoretical treatments,[12] and, as a consequence of emphasizing the inner 16-membered ring as the origin of the aromaticity, the rest of the structure has been regarded as peripheral in nature, with the carbon–carbon bonds at the 1:2, 3:4, 5:6, 7:8 positions predominantly olefinic in character. Recent X-ray studies have been taken to support this model:[4,62] the bond lengths in the 16-membered ring being 1.38 Å, those to the peripheral carbon atoms appreciably longer, 1.43–1.45 Å, and the peripheral bonds 1.35–1.36 Å, close to that for an isolated double bond.

But this theoretical model is not necessarily unique in predicting this kind of geometry. Moreover the model suggests that porphine should have four two-equivalent reduction states as each of the peripheral "double" bonds are progressively reduced, i.e., P → PH_2 → PH_4 → PH_6 → PH_8. However, the PH_8 state has not yet been discovered, and the PH_6 state does not have this type of structure at all, but is porphyrinogen, a true tetrapyrrole; see Figure 1d. This reduction behavior can be taken to suggest that the delocalization energy associated with four individual pyrrole rings exceeds that of the 16-membered aromatic ring, which in turn casts some doubt on the 16-membered ring system as the source of the aromaticity.

Furthermore, if hydrogen atoms were to replace the peripheral double bond carbon atoms, the molecule $C_{12}H_{14}N_4$ would be obtained, consisting of the 16-mem-

bered ring alone. At first sight it is strange that if this ring is the source of the aromaticity the compound is still unknown. However, unlike pyrrole, for which a paired electron structure can readily be written, this cannot be done for $C_{12}H_{14}N_4$. Starting with single and double bonds in sequence from one NH group, for instance, ring C in Figure 3c, results in a diradical structure about the opposite NH group, ring A. Perhaps this is the reason $C_{12}H_{14}N_4$ as such has not yet been prepared: it would be the two-equivalent oxidation product of $C_{12}H_{16}N_4$, for which there are several tautomeric forms depending on the position of the two CH_2 groups.

2. 17-Membered Ring

The diradical structure for the inner ring system can be circumvented by omitting one of the NH groups and including the two peripheral carbon atoms of that ring, e.g., ring A in Figure 3d. This structure, containing 17 atoms, can be regarded as a pyrrole ring enlarged by the insertion of a C_{12} polyene chain with –CH= substituted by –N= at positions 5 and 14. Aromaticity is again achieved by 18 delocalized electrons, but in this case 14 from the 14 carbon atoms, 2 from the two pyrrolenine N atoms, and 2 from the single NH group.

In referring to either the 16- or 17-membered ring structures, a clear distinction needs to be made between conjugation and aromaticity. Neither ring is conjugated.

3. Conjugated 18-Membered Ring: An [18]Annulene Derivative

It has long been recognized that the Kekulé ring structure does contain a fully conjugated system. Including the four peripheral carbon atoms of the rings with NH groups, and omitting the nitrogen atoms, it contains 18 in all (16 carbon and 2 nitrogen) with 18 delocalized electrons, one from each.

The possibility that this ring system may be of comparable or even greater significance in determining the electronic structure of porphyrins has been considerably enhanced by the recent discovery of the cyclic polyene [18]annulene (see Figure 4a) and the demonstration that it possesses aromatic character.[63]

Porphine is related to this structure by substitution of –N= for –CH= at positions 1 and 10 giving 1,10-diaza[18]annulene, bridging NH groups inside the ring at positions 4,7 and 13,16, and external –CH=CH– bridges at positions 9,11 and 18,2; compare Figures 4a and 4b.[25] This way of assessing the structure of porphine has the merit that while in the PH_2 and PH_4 reduction states the porphine conjugation remains intact, it is inevitably disrupted in the PH_6 reduction state, and thus the tetrapyrrole structure for porphyrinogen follows as a natural consequence; see Figures 1b–d.

The stability of $C_{12}H_{14}N_4$ and the entire question of the relative stability of porphine and its reduction states, including PH_8, on the basis of the 16-, 17-, and 18-membered ring systems merit a critical theoretical evaluation.

B. Estimation of the Resonance Energy

In this section the likely magnitude of the porphyrin resonance energy will be discussed in terms of the structural elements that make up the macrocyclic ring.

On the one hand, if the pyrrole and pyrrolenine N atoms are an integral part of the aromatic system, then the porphyrin RE might be expected to be closely related to values for simpler partially oxidized pyrrole derivatives. Even though there are only three data, the RE values per ring for the two pyrromethenes and the tetrapyrromo-

noene are of the same order of magnitude, i.e., RE_{II} about 25 kcal, as those for pyrrole and the monosubstituted derivatives. Adopting rather wide limits it could therefore be concluded that $100 < RE_{II} < 150$. These considerations, however, do not take into account the possibility that the linking of the four rings to give the macrocyclic ring introduces some extra stabilization. Nor does it allow for the possibility that there are important differences between ring-substituted and methine-substituted porphyrins. New experimental data, as they become available, could be profitably examined against this background.

On the other hand, if the porphyrin structure can properly be regarded as a modification of [18]annulene in the manner described above, then the likely magnitude of its RE can be approached in the following way. First, the values for pyridine, quinoline, isoquinoline, and acridine give no indication that the substitution of –N= for –CH= at positions 1 and 10 would markedly affect the RE. Moreover, the introduction of –NH– bridging groups inside the ring at positions 4, 7 and 13, 16 would be expected to contribute only to the rigidity and planarity of the macrocyclic ring and not have any direct influence on the RE. This leaves the effect of the external –CH=CH– bridging groups at positions 9,11 and 18,2 to be assessed.

1. Resonance Energy of Styrene Compared to Benzene. Effect of an Olefinic Double Bond Conjugated to an Aromatic Structure

One of the simplest compounds in which there is an olefinic double bond peripheral to, but conjugated with, an aromatic system is styrene; and it has long been known that the resonance energy of styrene is only a little greater than that of benzene, e.g., styrene 38, compared to benzene, 35 kcal/mol.[22]

In terms of RE_I and RE_{II} values this difference can be calculated as follows. The composite bond energy term $[nE(C_d–C_d) + RE]$ for any aromatic hydrocarbon is given by the expression

$$[nE(C_d-C_d) + RE] = \Delta H_a^\circ - \Sigma E(C_b-H) - \Sigma E(C_d-H) - $$

$$\Sigma E(C-H) - \Sigma E(C=C) - \Sigma E(C_b-C) - E(C-C) \quad (18)$$

Denoting this quantity by $\delta \Delta H_a^\circ$, the difference between RE for styrene and that for benzene is

$$RE(styrene) - RE(benzene) = \delta \Delta H_a^\circ(styrene) - $$

$$\delta \Delta H_a^\circ(benzene) - E(C_d-C_d) \quad (19)$$

which, substituting the values of ΔH_a° obtained from heat of formation data, gives $[(411.4 - 316.01) - E(C_d-C_d)] = [95.13 - E(C_d-C_d)]$. Hence, with $E(C_d-C_d)_I = 89.12$ and $E(C_d-C_d)_{II} = 94.66$

$$RE_I(styrene) - RE_I(benzene) = 6.01$$
$$RE_{II}(styrene) - RE_{II}(benzene) = 0.47$$

2. Resonance Energies of Acenaphthylene and Acenaphthene Compared to Naphthalene. Effect of –CH=CH– and –CH₂–CH₂– Groups Bridging an Aromatic Structure

A corresponding treatment of the data for naphthalene and acenaphthylene shows that a –CH=CH– bridging group generating a five-membered ring, like the 9,11 and 18,2 bridges to [18]annulene described above, has scarcely any more effect on the resonance energy of the

TABLE XVIII. The Effect, on the Resonance Energy, of an Olefinic Double Bond Conjugated to an Aromatic Structure, and $-CH_2-CH_2-$ and $-CH=CH-$ Groups Bridging an Aromatic Structure

Compound	Group	RE_I	RE_{II}
Benzene		48.7	32.0
Styrene	$-CH=CH_2$	54.7	32.5
Naphthalene		85.8	52.6
Acenaphthene[a]	$-CH_2-CH_2-$	84.8	51.6
Acenaphthylene[a]	$-CH=CH-$	96.6	52.2

[a] Value corrected by 5.81 in each case to allow for the conventional ring strain energy in the five-membered ring, based on data for cyclopentene and cyclopentadiene.[20]

TABLE XIX. Mean Resonance Energy per Double Bond for the Major Classes of Aromatic Compounds together with Values for [18]Annulene and Graphite

| Compound	RE_I/DB	RE_{II}/DB
Benzene and 7 alkylbenzenes	16.2 ± 0.1	10.7 ± 0.1
Benzene and 22 polycyclics	17.3 ± 0.2	10.6 ± 0.2
Pyridine and 9 alkylpyridines	18.1 ± 0.1	12.2 ± 0.1
Pyridine, quinoline, isoquinoline, and acridine	17.8 ± 0.2	11.0 ± 0.2
Limit: pyrrole → indole → carbazole	16.5	10.1
Cyclooctadecanonaene, i.e., [18]annulene	16.1	10.5
Graphite	27.3	16.3

primary aromatic system. But this case is more complicated because strain energy has to be taken into account and there is no exact structural counterpart to this particular kind of ring system in simple C_5 ring compounds. The "strain" in cyclopentane is understood to arise primarily through adverse eclipsing interactions between H atoms on adjacent carbons, and the introduction of a double bond would clearly diminish this particular destabilization. On the other hand, an examination of molecular models (Courtauld design) shows bond angle deformation in both cyclopentene and cyclopentadiene which would increase destabilization again. On a *priori* grounds it is difficult to decide which would be the more important; however, the CRSE values for cyclopentane, cyclopentene, and cyclopentadiene calculated from ΔH_f° — 6.16, 5.71, and 5.91, respectively, show there is almost complete compensation, and for acenaphthylene the mean of the CRSE values for cyclopentene and cyclopentadiene, 5.81, has been adopted. The cyclopentadiene value was obtained by assuming $[E(C_d-C_d) + RE]$ to be the same as the butadiene value, 98.27, based on the ΔH_a° data.

Setting up the corresponding equation for the RE difference, and substituting for $\delta\Delta H_a^\circ$,

RE(acenaphthylene) − RE(naphthalene) =

$$\delta\Delta H_a^\circ(\text{acenaphthylene}) + \text{CRSE(acenaphthylene)} -$$

$$\delta\Delta H_a^\circ(\text{naphthalene}) - 2E(C_d-C_d) =$$

$$189.06 - 2E(C_d-C_d) \quad (20)$$

Hence for RE_I the difference is 10.82, and for RE_{II}, −0.26, i.e., about zero. The low value of $E(C_d-C_d)_I$ used in computing RE_I always accentuates RE differences.

A check on the validity of this calculation is provided by acenaphthene in which the bridging group is saturated, i.e., $-CH_2CH_2-$, and which should therefore not affect RE at all. Again taking CRSE for the new ring to be 5.81, the RE difference is
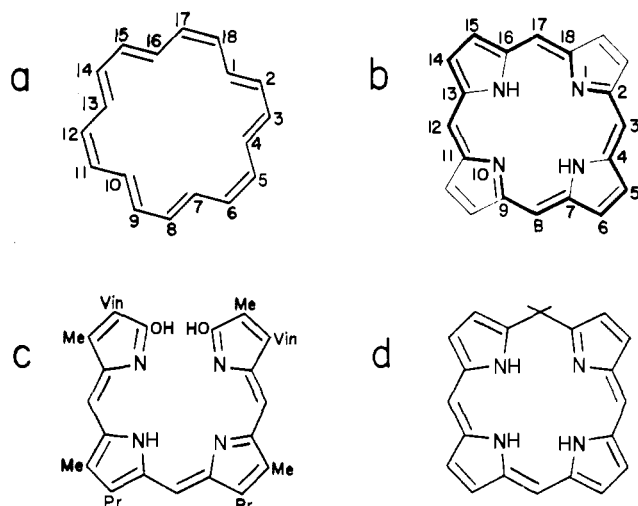
Figure 4. Additional Kekulé structures. (a) [18]Annulene. (b) Porphine, showing its structural relationship to ⌊18⌋annulene, namely substitution of $=N-$ for $=CH-$ at positions 1 and 10, internal $-NH-$ bridges at positions 4,7 and 13,16 and external $-CH=CH-$ bridging groups at positions 9,11 and 18,2. (c) Biliverdin: formed by the oxidation of heme, ferrous protoporphyrin IX; Me, Vin, and Pr denote methyl, vinyl, and propionic acid side chains, respectively. (d) Phlorine: an isomer of dihydroporphine; see Figure 1b.

RE(acenaphthene) − RE(naphthalene) =

$$\delta\Delta H_a^\circ(\text{acenaphthene}) + \text{CRSE(acenaphthene)} -$$

$$\delta\Delta H_a^\circ(\text{naphthalene}) \quad (21)$$

i.e., −0.97. This bears out the expectation, and for purposes of comparison, the RE_I and RE_{II} values for benzene and styrene, and for naphthalene, acenaphthene, and acenaphthylene have been brought together in Table XVIII.

3. Resonance Energy per Double Bond in Aromatic Structures

In the above discussion of the resonance energy of aromatic compounds, attention has been drawn to the magnitude of the quantity RE/DB. The values have been brought together in Table XIX to show that RE_I/DB and RE_{II}/DB are sensibly independent of variations in structure, and do not exceed about 18 and about 12, respectively. Only for graphite, with its infinite sheet of conjugated double bonds in the Kekulé structure, do the values reach about 27 and 16, respectively.

4. Adoption of RE_I and RE_{II} Values for Porphine and the Resulting Heat of Atomization

If, on structural grounds, the [18]annulene model is a good approximation for porphine, then, in the light of the negligible effect of $-CH=CH-$ bridging groups (section 2, above) and the approximately constant values of RE/DB for many types of aromatic structure (section 3, above), the resonance energy of [18]annulene can reasonably be regarded as a lower limit for porphine.[6] The RE_{II} values, as calculated in this review, being based on hydrogenation data, are closest to those in common usage, and for this reason the RE_{II} value for [18]annulene, 94.52, will be adopted for porphine, and the corresponding RE_I value obtained in a self-consistent manner.

The sum of the bond energy terms for porphine is made up as shown. The heat of atomization, ΔH_a°, is given by the sum of these bond energy terms plus the resonance energy. Thus, with $RE_{II} = 94.52$, $\Delta H_a^\circ =$

1.36

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	I	II
$12E(C_b-H)$	1206.36	1206.36
$9E(C{=}C)$	1197.00	1197.00
$2E(C{=}N-C_d)$	389.52	402.86
$2E(C_d-NH-C_d)$	482.74	493.74
$11E(C_d-C_d)$	980.32	1041.26
	4255.94	4341.22

$4341.22 + 94.52 = 4435.74$; as a consequence, since $\Delta H_a{}^\circ$ has to be independent of any particular assignment of $E(C_d-C_d)$ and RE values, $RE_I = 4435.74 - 4255.94 = 179.80$.

The RE values calculated from the combustion data of Longo, Finarelli, Schmalzbach, and Adler[19] can equally reasonably be taken as the upper limit, i.e., $RE_I = 582.02$ and $RE_{II} = 496.74$. Hence on this basis, $\Delta H_a{}^\circ$ (porphine) $= 4255.94 + 582.02 = 4341.22 + 496.74 = 4837.96$.

Finally, in the later discussion of the feasibility of various porphyrin reactions, it is useful to have some intermediate value of $\Delta H_a{}^\circ$(porphine) to correspond to RE values like those calculated from the combustion data of Stern and Klebs.[15] For this purpose the actual values obtained for etioporphyrin I have been adopted, i.e., $RE_I = 240.48$ and $RE_{II} = 155.20$. Hence on this basis, $\Delta H_a{}^\circ$ (porphine) $= 4255.94 + 240.48 = 4241.22 + 155.20 = 4496.42$.

Summarizing, the choice of low, intermediate, and high values for the resonance energy leads to values for $\Delta H_a{}^\circ$ (porphine) of 4435.74, 4496.42, and 4837.96, respectively.

VI. Alternative Approach Using Bond Energy Terms Which Include π-Electron Binding Energies

All the problems surrounding both the concept and the evaluation of resonance energies are avoided by "absorbing" the extra stabilization energy that characterizes aromatic compounds into the C–C bond energy terms. This approach has been developed by Tatevskii, Korolov, and Mendzheretskii,[65] Mackle and O'Hare,[66] Cox,[67] Lovering and Nor,[68] McGinn,[69] and Bernstein.[70] On the basis of their revision of the $\Delta H_f{}^\circ$ data, Cox and Pilcher[20] propose the following values for the three types of $C_{ar}-C_{ar}$ bond, which would be used with the value of 100.53 for

Type A: 119.17   Type B: 114.30   Type C: 112.80
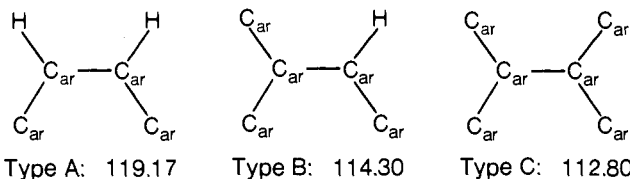
$E(C_{ar}-H)$ and 88.91 for $E(C_{ar}-C)$ corresponding to the terms $E(C_b-H)$ and $E(C_b-C)$, respectively, in Table II. With these values $\Delta H_a{}^\circ$ calculated for benzene and eight polycyclic aromatic hydrocarbons agrees with experiment to within 0.5 kcal/mol in six of the cases, the greatest discrepancy being noted with 3,4-benzphenanthrene for which it is generally acknowledged there is substantial steric hindrance. Excellent agreement is also obtained for [18]annulene, despite the large multiplication factors involved, with experimental and calculated $\Delta H_a{}^\circ$ values of 3953.00 and 3954.60, respectively.
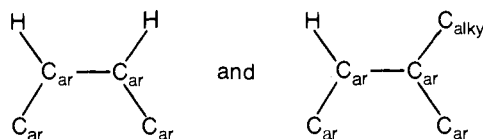
To extend this approach so as to cover aromatic N-heterocycles and porphyrins, values have to be established for the $C_{ar}-N_{ar}-C_{ar}$ and $C_{ar}-N_{ar}H-C_{ar}$ group energy terms.

A. Group Energy Terms for $C_{ar}-N_{ar}-C_{ar}$ and $C_{ar}-N_{ar}H-C_{ar}$

There are three types of structural environment in each case (see Table XX) which present the values calculated from the $\Delta H_a{}^\circ$ data for pyridine, quinoline and acridine, pyrrole, indole, and carbazole.[20] In order to carry out these calculations, certain assumptions specified in the upper part of the table have to be made; or, to put the point another way, the values quoted for the $C_{ar}-N_{ar}-C_{ar}$ and $C_{ar}-N_{ar}H-C_{ar}$ group energy terms are linked to the adoption of 119.17, 114.30, and 112.80 for the $C_{ar}-C_{ar}$ bonds where one of the next-nearest-neighbor atoms is nitrogen instead of carbon.

It can be seen that the three values for $C_{ar}-N_{ar}-C_{ar}$, i.e., D, E, and F, show a regular decrease, E having a value of 209.10 very close to the mean of D and F, 209.02. The new $\Delta H_f{}^\circ$ for isoquinoline,[37] which leads to an independent value for D, 216.73, substantiates this trend, but since the heat of evaporation had to be estimated, the pyridine value is to be preferred. On the other hand, the three values for the $C_{ar}-N_{ar}H-C_{ar}$ bonds cannot be taken as indicative of a similar trend because G and H, which are almost identical, are derived from the most recent and reliable combustion data. The mean of G, H, and I, 270.42 ± 1.34, has, therefore, been employed in later calculations.

The data for alkylbenzenes give within experimental error the same value for the $C_{ar}-C_{ar}$ bond energy term as benzene itself. For toluene, ethylbenzene, n-propylbenzene, and n-butylbenzene, the values are 119.17, 119.16, 119.20, and 119.24, respectively, and for o-, m-, and p-xylene, 119.06, 119.13, and 119.10, respectively (mean 119.15 ± 0.02). Hence with bond energy assignments of 100.53 and 88.91 for $C_{ar}-H$ and $C_{ar}-C$, respectively, the following structures can be regarded as equivalent energetically, and data for alkylpyridines and alkyl-

pyrroles can, therefore, be used to test the reliability of the $C_{ar}-N_{ar}-C_{ar}$ and $C_{ar}-N_{ar}H-C_{ar}$ bond energy terms, types D and G, in Table XX.

For the 2-, 3-, and 4-methylpyridines, the values for the type D bond energy term are 217.12, 215.40, and 216.41, and for the 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dimethylpyridines, 216.65, 217.00, 217.09, 218.94, 216.23, and 215.57, respectively. The mean values, 215.76 and 216.91, are a little greater than the value for pyridine, 214.12, but they simply reflect the same slightly higher stability shown by the RE_I and RE_{II} values of Table IX; they fully bear out the larger value for type D compared with types E and F.

For C-alkylpyrroles, $\Delta H_f{}^\circ$ is available only for the 2,5 derivative,[37] and this leads to 272.27 for the type G bond energy term, in satisfactory agreement with the value of 271.59 obtained from the pyrrole data.

B. Application to Nitrogen Heterocycles with Two Nitrogen Atoms per Ring

With these values for the bond energy terms, $E(C_{ar}-N_{ar}-C_{ar})$ and $E(C_{ar}-N_{ar}H-C_{ar})$, it is possible to predict the heats of atomization of pyrimidine, pyrazine, imidazole, and adenine. For the first two compounds the agreement is quite good, as shown in Table XXI, but imidazole,

TABLE XX. Bond Energy Terms for the C_{ar}–C_{ar} Bonds and Group Energy Terms for C_{ar}–N_{ar}–C_{ar} and C_{ar}–$N_{ar}H$–C_{ar} in Aromatic Structures

and especially adenine, are apparently much more stable than the calculations suggest. This is in accord with the conclusion reached in the case of adenine from the RE values, and again stresses the need for more data on pyrimidines and purines in general.

C. Estimation of the Heat of Atomization of Porphine

Just as in the case of the estimation using RE values, it is first necessary to establish the effect of a bridging –C=C– group on an aromatic structure. A different method has to be followed, however, because there is no quantity corresponding to the resonance energy to be evaluated; instead, the decrease in stability can be calculated from that expected on the presumption that the entire structure is fully aromatic.

Taking acenaphthylene again, $\Delta H_a° = 2406.00$; and subtracting $8E(C_{ar}$–H$) = 804.24$ gives 1601.76, which is ΣE for all the C–C bonds. Now if the structure were fully aromatic, ΣE would be equal to $(5A + 6B + 3C)$, i.e., 1620.05. The decrease in stability attributable to the bridging –C=C– group not being fully conjugated with the major naphthalene structure is thus $1620.05 - 1601.76 = 18.29$. Acenaphthene provides a useful check on this calculation. The experimental $\Delta H_a° = 2534.40$, whereas the calculated value 2540.58 is 6.18 greater; i.e., the strain energy in the five-membered ring is 6.18, which is quite in keeping with the values of 6.16, 5.71, and 5.91 for cyclopentane, cyclopentene, and cyclopentadiene.

Fluoranthene provides an example similar to acenaphthylene in which the bridging group consists of adjacent

TABLE XXI. Observed and Calculated Heats of Atomization of N Heterocycles with More Than One N Atom per Ring

Compd	$\Delta H_a°$(obsd)	$\Delta H_a°$(calcd)	δ(obsd-calcd)
Pyrimidine	1071.01	1068.70	2.31
Pyrazine	1071.14	1068.70	2.34
Imidazole	916.50	905.30	11.20
Adenine	1631.00	1595.91	35.09

carbon atoms of another benzene ring. In this case $\Delta H_a° - 10E(C_{ar}$–H$) = 3185.62 - 1005.30 = 2180.32 = \Sigma E$. If the structure were fully aromatic, ΣE would be equal to $(7A + 6B + 6C) = 2196.79$; hence the lack of stabilization amounts to $2196.79 - 2180.32 = 16.47$.

These two values, 18.29 and 16.47, are in surprisingly close agreement considering the substantial differences in the bridging groups, the one olefinic and the other aromatic, and the mean, 17.38, can confidently be adopted for the 9,11 and 18,2 olefinic bridges in the [18]annulene model for porphine.

The heat of atomization of porphine can now be computed:

$12E(C_{ar}$–H$)$	=	1206.36
$4E$(type A)	=	476.68
$16E$(type B)	=	1828.80
$2E$(type F)	=	407.82
$2E$(type G/H/I)	=	540.84 (mean)
		4460.50
less 2 × 17.38, destabilization		34.76
		4425.74

In view of the completely different calculation procedure, it is quite striking and very satisfying that this value

TABLE XXII. Total π-Electron Binding Energies for Aromatic Hydrocarbons, and the Average Binding Energy per Bond, and per Carbon Atom, According to Two Values, for the C–C σ Bond Energy Term, $E(C_\sigma - C_\sigma) = 89.12$ and 94.66

Compound	No. of C	No. of bonds	Bond/C	$E(C-C)_{\sigma I} = 89.12$			$E(C-C)_{\sigma II} = 94.66$		
				$E_{\pi b}$	$E_{\pi b}/Bd$	$E_{\pi b}/C$	$E_{\pi IIb}$	$E_{\pi b}/Bd$	$E_{\pi b}/C$
Benzene	6	6	1.00	180.29	30.05	30.05	147.05	24.51	24.51
Naphthalene	10	11	1.10	305.19	27.74	30.52	244.29	24.43	22.21
Biphenyl[a]	12	13	1.08	365.81	28.14	30.48	293.81	24.48	22.60
Anthracene	14	16	1.14	427.18	26.70	30.51	338.54	24.18	21.16
Phenanthrene[a]	14	16	1.14	433.38	27.09	30.96	344.74	24.62	21.55
Pyrene	16	19	1.18	506.88	26.68	31.68	401.62	25.10	21.14
Tetracene	18	21	1.16	553.72	26.37	30.76	437.38	24.30	20.83
3,4-Benzphenanthrene[a]	18	21	1.16	558.32	26.59	31.02	441.98	24.55	21.05
1,2-Benzanthracene[a]	18	21	1.16	557.53	26.55	30.97	441.19	24.51	21.01
Chrysene[a]	18	21	1.16	562.12	26.77	31.23	445.78	24.77	21.23
Triphenylene[a]	18	21	1.16	563.72	26.84	31.32	447.38	24.85	21.30
Perylene[a]	20	24	1.20	625.66	26.07	31.28	492.70	24.64	20.53
1,3,5-Triphenylbenzene[a]	24	27	1.12	739.82	27.40	30.83	590.24	24.59	21.86

[a] Corrections included for steric hindrance: biphenyl, 1.4; phenanthrene, 0.7; 3,4-benzphenanthrene, 4.4; 1,2-benzanthracene, 0.7; chrysene, 1.4; triphenylene, 2.1; perylene, 1.4; and 1,3,5-triphenylbenzene, 4.2 kcal.

TABLE XXIII. π-Electron Binding Energies Associated with the Three Main Types of Carbon–Carbon Bond in Cyclic Aromatic Structures

Type	Structure	$E(C_{ar}-C_{ar})$	$E_{\pi b}/Bd$	
			$E(C-C)_{\sigma I}$	$E(C-C)_{\sigma II}$
A	H $\diagdown$ $\diagup$ H C_{ar}—C_{ar} C_{ar} $\diagdown$ $\diagup$ C_{ar}	119.17	30.05	24.51
B	C_{ar} $\diagdown$ $\diagup$ H C_{ar}—C_{ar} C_{ar} $\diagdown$ $\diagup$ C_{ar}	114.30	25.18	19.64
C	C_{ar} $\diagdown$ $\diagup$ C_{ar} C_{ar}—C_{ar} C_{ar} $\diagdown$ $\diagup$ C_{ar}	112.80[a]	23.68	18.14

[a] Cox and Pilcher[20] do not specify the data from which they calculated this value for the type C bond energy term. It could be calculated from data for the hydrocarbons pyrene or perylene, or that for graphite. In the latter case, using the heat of atomization of carbon from the infinite sheet as estimated in section IV.E, 169.29, the value for the bond energy term, and hence those for $E_{\pi b}/Bd$, would differ by only 0.06, i.e., 112.86, 23.74, and 18.20, respectively, which is negligible.

differs by only 10 kcal/mol from that obtained above in section V.B.4 using the more conventional bond energy terms and the resonance energy of [18]annulene.

VII. Evaluation of the π-Electron Binding Energy per Bond and per Carbon Atom in Aromatic Structures

This alternative method of assigning bond energy terms for aromatic structures has the advantage of being closer conceptually to current theoretical treatments in which the binding is envisaged as a combination of σ bonds with additional bonding arising from π-electron interactions. Once a term value is chosen for the σ bond between sp^2-hybridized carbon atoms, it is a simple matter to evaluate the π-electron binding energy, $E_{\pi b}$. The values adopted for $E(C_d-C_d)$ in the resonance energy treatment can be taken for this bond too because both in principle and practice they are the same. The resonance energy treatment merely separates $E_{\pi b}$ artificially into two parts, one the sum of the extra binding energy of the

nominal C=C bonds above that of C_d-C_d bonds, and the other part the resonance energy as such, i.e.

$$E_{\pi b} = \Sigma [E(C=C) - E(C_d-C_d)] + RE \qquad (22)$$

However, to avoid confusion in terminology, this σ bond will be denoted by a different symbol in the present context, i.e., $E(C-C)_\sigma$, and the limiting values will be specified as before by subscripts: $E(C-C)_{\sigma I} = 89.12$ and $E(C-C)_{\sigma II} = 94.66$.

A. Values for Benzene and Polycyclic Hydrocarbons

Values of $E_{\pi b}$ have been calculated directly from ΔH_a° for benzene and a number of polycyclic aromatic hydrocarbons using the expression

$$E_{\pi b} = \Delta H_a^\circ - N_{C-H} E(C_{ar}-H) - N_{C-C} E(C-C)_\sigma \qquad (23)$$

where N_{C-H} and N_{C-C} are the number of C–H and C–C bonds, respectively. The values are listed in Table XXII, and also a breakdown in terms of $E_{\pi b}$ per C–C bond and $E_{\pi b}$ per carbon atom. It is immediately apparent that $E_{\pi b}/Bd$ shows a greater variation than $E_{\pi b}/C$, and that in general the more condensed the structure, i.e., the greater the quotient "number of C–C bonds per carbon atom," the lower the value. The origin of this behavior lies in the variation of $E_{\pi b}/Bd$ for the three main types of aromatic C–C bond, A, B, and C; see Table XXIII. $E_{\pi b}/Bd$ decreases as the number of C–C bonds per carbon atom increases from 1.0 for benzene, the lower limit, to 1.5 for graphite, the upper limit. For the polycyclic hydrocarbons in Table XXII, the peripheral C–H bonds are nevertheless a sizable fraction of the total number of bonds. The fraction is smallest for pyrene and perylene, but even so it still amounts to about 0.38, and the number of C–C bonds per carbon atom does not exceed 1.20. It is understandable therefore that $E_{\pi b}/Bd$ for none of these polycyclic hydrocarbons approaches the value for graphite.

The reason for the near constancy of $E_{\pi b}/C$ can be sought in a similar way by evaluating $E_{\pi b}$ for the several types of carbon atom that can be distinguished. There are two groups, depending on whether the carbon atom in question is bonded to H or to C, and then in each group there are three subgroups which take into account the bonding to the next-nearest-neighbor carbon atoms. Values of $E_{\pi b}/C$ for these six types have been obtained from the appropriate simultaneous equations that can be

TABLE XXIV. π-Electron Binding Energies per Carbon Atom for the Various Structural Elements in Aromatic Hydrocarbons

Type	Structural element	$E(C-C)_{\sigma I} = 89.12$	$E(C-C)_{\sigma II} = 94.66$
a	(H H H) C—C—C / C C	30.05	24.51
b[a]	(H H C) C—C—C / C C	30.75	24.29
c[b]	(C H C) C—C—C / C C	31.10	24.18
d[a]	(H H) C—C—C / C C C	30.75	24.28
e[c]	(H C) C—C—C / C C C / C C	31.41	24.69
f	C—C—C / C C C	35.61	27.30

[a] Mean value: $[2E(b) + E(d)]/3$. [b] Mean value: $[E(c) + E(d)]/2$. [c] Mean value: $[4E(b) + E(d) + 2E(e)]/7$.

set up for $E_{\pi b}$ for the various polycyclic hydrocarbons. For self-consistency in the results the $E_{\pi b}$ values are based on the A, B, and C bond energy terms. Unique solutions can only be arrived at for type (a) and type (f) carbon atoms, those in benzene and graphite, respectively. The particular combinations of bonds that are present in polycyclic hydrocarbons do not permit the separate evaluation of the other types. Average values are worked out in these cases as indicated in the footnote to Table XXIV.

The near constancy of $E_{\pi b}/C$ for the polycyclic hydrocarbons, 30.9 and 24.6 for $E(C-C)_\sigma = 89.12$ and 94.66, respectively, thus comes about because $E_{\pi b}/C$ does not vary very much for carbon atoms of type (a) through (e), although there is a perceptible but slight increase in $E_{\pi b}/C$ as the number of C–C bonds per carbon atom increases; see Figure 5. The really large difference comes with the type (f) carbon atom, characteristic of the graphite structure, but these are only present in pyrene and perylene, and only to a small extent, 2 out of 16 and 20 carbon atoms, respectively.

B. Polycyclic Hydrocarbons Compared to Graphite

Polycyclic hydrocarbons have to be very large before the C–H bonds constitute a negligible part of the structure and the fraction $N_{C-H}/(N_{C-H} + N_{C-C})$ reaches very low values. This can be readily demonstrated by taking circumbenzene as the model; see Figure 6. An alternative structure, with similar trigonal symmetry, also has a benzene-type ring as the core but with an array of benzene- and radialene-type rings surrounding it. This model and the rectangular grid model with an hexagonal array
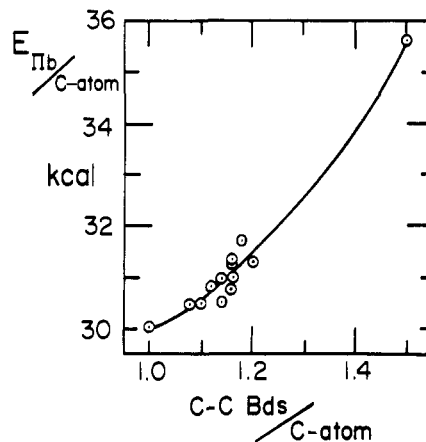
Figure 5. A plot of the π-electron binding energy per carbon atom against the number of C–C bonds per carbon atom for polycyclic hydrocarbons and graphite.
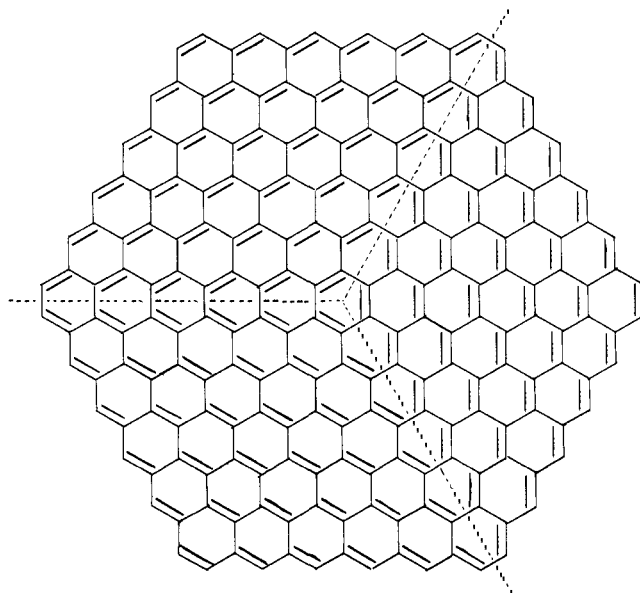


Figure 6. Kekulé structure for the circumbenzene with $n = 5$, n being the number of rings around the benzene core. The dotted lines indicate the trigonal symmetry defining three segments, each containing p-benzoquinone-type conjugation.

of carbon atoms utilized by Bradburn, Coulson, and Rushbrooke[71,72] in their theoretical study of graphite-like crystallites give substantially the same results; however, the summation procedures involved are somewhat more complicated.

The general formula for a circumbenzene is $C_{6(n+1)^2}H_{6(n+1)}$, where n is the number of rings around the C_6 core: i.e. for benzene, C_6H_6, $n = 0$: for coronene, $C_{24}H_{12}$, $n = 1$, etc. The number of C–H bonds is simply $6(n + 1)$, and summation procedures show the total number of C–C bonds to be $(9n^2 + 15n + 6)$, made up of $(6n^2 + 12n + 6)$ bonds in the annular rings and $(3n^2 + 3n)$ bonds joining the rings together. With $n = 10$, the molecular formula is $C_{726}H_{66}$ and the molecular weight 8778, yet one bond in 17 is a C–H bond. Even with $n = 100$, $C_{61206}H_{606}$, molecular weight 735,078, one bond in 152 is still a C–H bond. The way the fraction varies with n, from 0.5 for benzene to 0 for graphite, is shown in Figure 7a.

The other important structural parameter, the average number of bonds per carbon atom, approaches the limiting value of 1.5 characteristic of graphite rather more rapidly, as can be seen from the plot in Figure 7b.

This analysis points up the need for new combustion
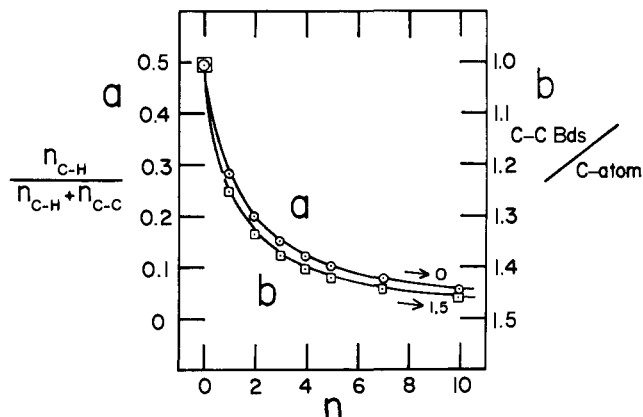
Figure 7. Structural relationships for circumbenzenes. (a) The fraction of the total bonds present as C–H. (b) The number of C–C bonds per C atom. Note: the number of C atoms for $n = 0$, 1, 2, 3, 4, 5, 7, and 10 is 6, 24, 54, 96, 150, 216, 384, and 726, respectively. As $n \rightarrow \infty$, *i.e.*, the graphite structure, curve a approaches zero, and curve b approaches 1.5.

and sublimation studies on larger condensed aromatic hydrocarbons so as to follow up the emergence of graphite-like bonding properties. At the same time it suggests very strongly that the porphine molecule is far too small for its bonding characteristics to approach, let alone exceed, those of graphite, unless there is some difference in kind that far outweighs the difference in degree.

C. Comparison of π-Electron Binding Energies per Carbon Atom in Aliphatic and Aromatic Structures

Far fewer π-electron binding energies can be calculated for aliphatic polyenes because so few data are available. Following the same procedure as that used for the aromatic hydrocarbons, the average values for the conjugated diene structure based on the $\Delta H_a{}^\circ$ data for 1,3-butadiene, 1-*trans*-3-pentadiene, and 2-methyl-1,3-butadiene are 96.7 ± 0.4 and 80.1 ± 0.3 for the low and high values of $E(C-C)_\sigma$, respectively. Assuming that the four carbon atoms in the conjugated diene structure participate equally in the π-bonding, $E_{\pi b}$ per carbon atom is 24.2 and 20.0, respectively.

These values are to be compared with $E_{\pi b}$ for a simple olefinic bond which is just $[E(C=C) - E(C-C)_\sigma]$, *i.e.*, 43.88 and 38.34 for the low and high values of $E(C-C)_\sigma$, respectively, or 21.9 and 19.2 per carbon atom since the π-bonding involves only two atoms.

These values, together with those for the aromatic hydrocarbons and graphite, are brought together in Table XXV and are presented schematically in Figure 8. The customary designation of the olefinic bond as a double bond, and the attribution of the increased stability in conjugated polyenes, aromatic hydrocarbons, and graphite to resonance effects, implies a difference in kind rather than one of degree. No matter what subtle differences there may be in the various π-electron interactions, from a purely thermochemical point of view there is only a progressive increase in binding energy per carbon atom from the olefin to the polyene, to the aromatic hydrocarbon, and finally to graphite; and in the olefin at least half the increase characteristic of graphite has already been achieved.

D. π-Electron Binding Energies in Nitrogen Heterocycles

Given the primary assignment of bond energy terms there is only one additional assumption involved in evalu-

TABLE XXV. A Comparison of π-Electron Binding Energies per Carbon Atom in Aliphatic and Aromatic Structures, and the Percentage Values with Respect to Graphite

Structure	$E_{\pi b}$ per carbon atom	
	$E(C-C)_{\sigma I} = 89.12$	$E(C-C)_{\sigma II} = 94.66$
Simple olefin	21.9 (61%)	19.2 (70%)
Aliphatic polyene[a]	24.2 (67%)	20.0 (73%)
Aromatic hydrocarbon[b]	30.9 (86%)	24.6 (90%)
Graphite	35.6 (100%)	27.3 (100%)

[a] Average of values for 1,3-butadiene, 1,*trans*-3-pentadiene, and 2-methyl-1,3-butadiene. [b] Average value for the hydrocarbons listed in Table XXII.

ating $E_{\pi b}$ for hydrocarbons, namely deciding upon a value (or limiting values) for $E(C-C)_\sigma$. Several extra assumptions, however, have to be made in dealing with nitrogen heterocycles, and the values arrived at below are included more by way of illustration to round out the present treatment than provide numbers that are strictly comparable to those for the hydrocarbons.

To calculate $E_{\pi b}$ for the ring N atoms in pyridine and its homologs, a value is needed for the bond energy term $E(C-N)_\sigma$. To use the same procedure as that employed in evaluating $E(C-C)_\sigma$, $E(C=N)$ would be required. In principle this could be obtained by splitting the group energy term $E(C=N-C)$ obtained from the aldimine data, *i.e.*, 200.98, into its component parts, but to do this $E(N_d-C)$ has to be known, and at present there is no very satisfactory resolution of this problem. Solely in the interest of simplicity, therefore, limiting values for $E(C-N)_\sigma$ have been estimated from the corresponding values for $E(C-C)_\sigma$ by simple proportion, using the ratio $E(C-N)/E(C-C)$. Thus, $E(C-N)_{\sigma I} = 74.00/85.48, \times 89.12 = 77.15$, and $E(C-N)_{\sigma II} = 74.00/85.48, \times 94.66 = 81.95$.

With these values $E_{\pi b}$ per C–N bond in HC–N–CH and C–N–C, *i.e.*, pyridine- and acridine-type structures, can readily be calculated from the D and F group energies, 214.12 and 203.91, respectively; see Table XX. In the former case the values are 29.91 and 25.11 compared with 30.05 and 24.51 for the corresponding C–C bonds, and in the latter case, 24.81 and 20.01 compared with 23.68 and 18.14; see Table XXIII. Despite the uncertainty in $E(C-N)_\sigma$, values of this magnitude for $E_{\pi b}$ for the C–N bonds are to be expected since the resonance energies for benzene and pyridine homologs are so very similar.

Assuming that the contribution to $E_{\pi b}$ per carbon atom in pyridine is the same as that in benzene, the contribution to $E_{\pi b}$ by the nitrogen atom can be determined from the expression

$$E_{\pi b}/N = \Delta H_a{}^\circ(\text{pyridine}) - 5E(C_{ar}-H) -$$
$$4E(C-C)_\sigma - 2E(C-N)_\sigma - 5E_{\pi b}/C$$

i.e., 29.87 and 25.71 for the low and high values, respectively, for the σ bonds. These are to be compared with 30.05 and 24.51 for the carbon atoms in benzene; again the values are very close, as might be expected. Similar calculations can be made for the N atom in quinoline and acridine.

To extend the calculations to the pyrrole-type heterocycles, a further assumption has to be made, namely, a value for the N–H bond energy term. It could be argued that by analogy with C–H bonds the value should be somewhat greater than the secondary amine value, $E(N-H)_1$; but in the absence of any direct evidence this amine value, 90.21, will be adopted. With the average value of 270.42 for the C–NH–C group energy term in pyrrole, indole, and carbazole, $E_{\pi b}$ per C–N bond in these five-

membered aromatic rings is thus 12.99 and 8.16 for the low and high values, respectively, for the σ bonds. $E_{\pi b}$'s *in toto* for pyrrole are 117.23 and 91.07 which are less than $4E_{\pi b}/C$ using the benzene value. The five-membered aromatic N-heterocyclic ring thus has appreciably less stabilization energy than benzene—a result which is already obvious from a comparison of the empirical resonance energies. A contributing factor to this lower value may well be ring strain since the bond angles of about 108° are substantially less than the 120° characteristic of sp²-hybridized carbon.

VIII. $\Delta H°$, $\Delta S°$, and $\Delta G°$ Calculations for Various Porphyrin Reactions

Despite the stability of the porphyrin ring, there are two kinds of reaction that destroy its aromaticity: oxidative fission in which the macrocyclic ring is actually broken, e.g., biliverdin formation or combustion, and reduction to either the phlorine (PH₂) state, isomeric with the dihydroporphines, or the porphyrinogen (PH₆) state, both of which leave the ring intact but break the conjugation; see Figures 4c,d and 1b,d. Undoubtedly there are differences in the ease, or otherwise, with which different porphyrins undergo these reactions. In the following calculations their gross feasibility is examined by making estimates of the standard free energy changes. The calculations relate to the porphyrin and its oxidized or reduced product in the gas phase—an idealized situation—but the thermodynamics of solvation are likely to be rather similar, and since the difference is involved when considering the reactions in solution, the present calculations can be taken as a reliable guide to practical conditions.

For simplicity, porphine itself is chosen as the model porphyrin, and three values are adopted for its RE as explained in section V.B.4 (a lower limit, a middle value, and an upper limit) which give $\Delta H_a°$ values of 4435.7, 4496.4, and 4838.0, respectively. For all the individual rings in the oxidative fission product and in phlorine and porphyrinogen, a compromise RE_{II} value of 25 is adopted (compare Table XII), giving extra weight to the lower values of 21.6 and 22.3 obtained for pyrrole and 2,5-dimethylpyrrole which are the most reliable.

$\Delta H°$ for the stepwise reduction of porphine to the dihydro and tetrahydro states, P → PH₂ → PH₄, has been calculated according to the [18]annulene-type structure whereby these first two steps would merely reduce the bridging -CH=CH- groups at positions 9,11 and 18,2 without substantially affecting the aromaticity of the macrocyclic ring. The major change in the formation of porphyrinogen, PH₆, is thus identified with the last step, PH₄ → PH₆, in which the aromaticity of the porphine ring is finally lost, to be replaced by that of the true cyclic tetrapyrrole, porphyrinogen.

The evaluation of the standard entropy changes for these reduction reactions is based on the assumption that since the macrocyclic ring remains intact the only difference in entropy between P, PH₂, PH₄, and PH₆ arises from the saturation of double bonds, which, according to Cobble's empirical treatment,[73] can be taken as 3.5 eu in each case, the reduced compound having the higher entropy. It would seem unlikely that the resulting uncertainty in $\Delta S°$ would exceed 5 eu even for P → PH₆, *i.e.*, 1.5 kcal/mol in the $T\Delta S°$ term.

The calculation of $\Delta S°$ for any reaction in which the macrocyclic ring is broken is subject to much greater uncertainty, since separate estimates have to be made for the cyclic and the open-chain structures. A value for porphine has been estimated by plotting $S°$ for the aromatic hydrocarbons—benzene, naphthalene, azulene, anthra-
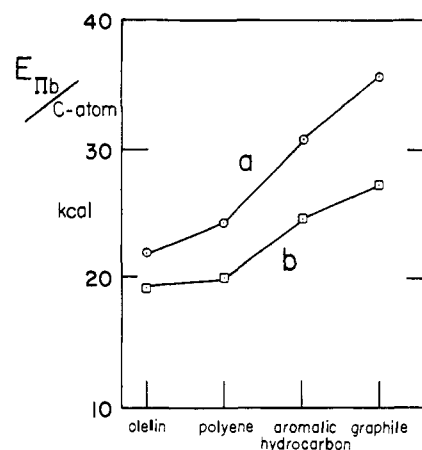
Figure 8. Schematic diagram showing how the π-electron binding energy per carbon atom increases in going from the olefin to the aliphatic conjugated polyenes, the aromatic hydrocarbons, and finally to graphite.

cene, and phenanthrene—as a function of N, the number of structurally bonded atoms (ignoring hydrogen); extrapolation to $N = 24$, for porphine, gives an $S°$ value of about 95 eu.[5]

Two independent approaches suggest that the value for the corresponding open-chain compound, with the biliverdin-type structure, is about 210 eu. First, Cobble's empirical equation can be used

$$S° = 26 + \tfrac{3}{2}R \ln M + 9.2N - S°_s \qquad (24)$$

where M is the molecular weight, N the number of structurally bonded atoms (ignoring hydrogen), and $S°_s$ structural correction terms to allow for the decrease in entropy due to branched chains, multiple bonds, and rings.[70] For $N \geq 14$, Cobble suggested replacing the $9.2N$ term by $(10.1N - 0.1N^2)$. But later data for long unbranched paraffins do not support this, e.g., $S°(n\text{-}C_{20}H_{42}) = 223.3$[74] compared with calculated values of 226.8 using $9.2N$ and 204.8 using $(10.1N - 0.1N^2)$. The simpler form of the equation is therefore to be preferred. The structural correction term for the biliverdin-like molecule can be computed as follows. A comparison of $S°$ for five cyclopentanes and their acyclic analogs[74] give values of $S°_s$ ranging from 11.6 to 14.6, mean 12.8, whereas for five cyclopentenes and their acyclic analogs the values of $S°_s$ range from 10.6 to 13.4, mean 12.3, a decrease of 0.5. On this basis the correction for a five-membered ring containing two double bonds has been put at 11.8. Hence for the biliverdin-like structure with four such rings joined by three -CH= groups, *i.e.*, three extra double bonds, the total correction factor works out to be 4 × 11.8 plus 3 × 3.5, *i.e.*, 57.7 eu. Using the above equation, this leads to an $S°$ value of about 215.5.

Secondly, the increase in $S°$ in going from benzene, 64.34, to biphenyl, 93.85, is 29.5, *i.e.*, 46% of the benzene value. Using this proportionality factor and 70 eu for $S°(\text{pyrrole})$,[5] a chain of four such rings linked together with five additional structurally bonded atoms might be expected to have an entropy value of about 70 + (3 × 0.46 × 70) + (5 × 9.2), *i.e.*, 212.6. The three extra double bonds would reduce this to about 202.1. It thus seems very probable that the entropy for the biliverdin-like structure is a little greater than 200 eu, and in the calculations below a compromise value of 210 eu has been adopted.

The uncertainty in this value and in that for porphine is unlikely to be greater than ±15 eu. Hence $\Delta S°$ for the oxidation reaction will have an uncertainty of ±30 eu,

which is equivalent to almost ± 10 kcal/mol in the $T\Delta S°$ term. Nevertheless, it will appear that an uncertainty even of this magnitude in no way affects the conclusions regarding permissible values for the porphine resonance energy.

A. Oxidative Fission

1. Biliverdin Formation

This is the rather remarkable process in which the heme of hemoglobin, ferrous protoporphyrin IX, undergoes enzymatic oxidative degradation, the macrocyclic ring breaking between rings A and B with the elimination of the α-methine C atom as carbon monoxide.[75] The process involves many steps including the oxidation itself, removal of the prosthetic group from the globin, and ejection of the iron. At some stage the underlying fission reaction occurs, which, taking porphine as the model, can be represented

$$\text{porphine} + \frac{3}{2}O_2 \longrightarrow \text{biliverdin analog} + CO \quad (25)$$
$$C_{20}H_{14}N_4 \qquad\qquad\qquad C_{19}H_{14}N_4O_2$$
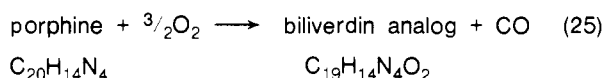
However the actual mechanism is more complicated,[76,77] a mixed function oxygenase being involved, whereby NADPH is simultaneously oxidized to NADP$^+$. Replacing this two equivalent coenzyme reducing agent by H_2, which is justified in the present context because these redox couples have extremely similar thermodynamic characteristics, the fission reaction becomes

$$\text{porphine} + 3H_2 + 3O_2 \longrightarrow$$
$$\text{biliverdin analog} + CO + 3H_2O \quad (26)$$
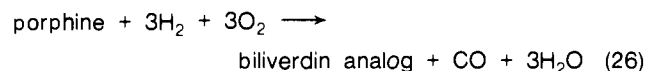
Taking RE_{II} = 25 for each ring in the biliverdin analog, $\Delta H_a°$ works out to be 4472.45, which gives for the heat of the reaction the three values set out in the first column of Table XXVI, according to whether porphine is assigned the low, middle, or high value for its resonance energy. The enol structure has been used for the biliverdin compound, Figure 4c. However, the physicochemical properties of hydroxypyridines, hydroxypyrroles, and biliverdin itself indicate that the carbonyl tautomer, the lactam, is the more stable.[75] No very precise evaluation of $\Delta H_a°$ can as yet be made for this structure, but amide, α,β unsaturated aldehyde, and polyene data[20] provide a rough estimate of about 4490. This would have the effect of making the heats of reaction in Table XXVI more favorable by about 18 kcal/mol, but the marked contrast between the first two, very favorable, and the third, very unfavorable, value is unaltered.

With the $S°$ values discussed above, $\Delta S°$ is +57 eu. The $\Delta G°$ values listed in the third column are thus very favorable for the low and middle porphine RE values, but extremely unfavorable, owing to the adverse $\Delta H°$ of

+114 (or +96) for the high value of the porphine RE. At least in the case of protoporphine, therefore, these calculations would appear to rule out the high value completely.

It needs to be emphasized that the mixed function oxygenase reaction, which can be generalized

$$AH + H_2 + O_2 \longrightarrow AOH + H_2O$$
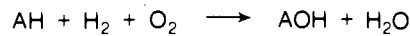
entails a prodigious expenditure of energy, since for each mole of AH oxidized to AOH, one mole of H_2O is formed for which $\Delta H_f°$, $\Delta S_f°$, and $\Delta G_f°$ are -57.8 kcal/mol, -10.6 eu, and -54.64 kcal/mol, respectively.[74] In the above formation of biliverdin, $\Delta H°$, $\Delta S°$, and $\Delta G°$ thus contain contributions amounting to -173.4 kcal, -31.8 eu, and -163.9 kcal, respectively, from this source. In actuality the process squanders material substance too, the precious reduced coenzyme NADPH. On purely thermodynamic grounds this mixed function reaction would be unnecessary if the porphyrin had low or middle RE values, because the fission reaction itself, reaction 25, would still be a favored process with $\Delta H°$ and $\Delta G°$ -115 and -141, -54 and -81 kcal, respectively. Even so, despite the additional driving force provided by the formation of water (or NADP$^+$) in the mixed function reaction, it is still far from sufficient to result in favorable $\Delta H°$ and $\Delta G°$ values for any porphyrin with a high RE.

2. The Biliprotein Prosthetic Groups

Biliverdin formation from heme is essentially a degradation reaction leading to the excretion of the elements of the once useful iron porphyrin structure. Linear-chain tetrapyrroles, phycocyanobilin, and phycoerythrobilin do, however, play a more positive biological role as the photoactive prosthetic groups of the biliproteins in blue and red algae.[77,78] Phytochrome, the pigment in higher plants responsible for many of their photoresponses, has a similar prosthetic group.[79] The details of the formation of these particular open-chain derivatives are not yet fully worked out, but there is evidence to suggest that a porphyrin ring is formed first, which is then opened to give the linear tetrapyrrole.[80] Whatever the mechanism may be, the porphyrin resonance energy would again be an important factor in determining the heat of the step in which fission of the macrocyclic ring actually occurs.

3. Combustion

The macrocyclic ring must be broken at some stage in the combustion reaction, and, although the nature of the fission reaction is not yet established, the resonance energy is obviously an important factor again. The reaction of dioxygen with an olefinic double bond to give a dialdehyde

$$(27)$$
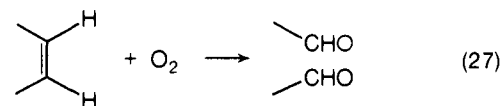
which is known to occur in the conversion of β-carotene to retinal,[81] will be employed to examine this feature, because it is both simple in principle and probably has a more favorable heat of reaction than any actual intermediate step involving free radicals—and favorability is the point at issue. The combustion, of course, is a high-temperature process; nevertheless, heats of reaction do not vary greatly with temperature, and values based on the 25°C data are reliable enough to demonstrate the critical role of the resonance energy.

TABLE XXVII. Values of RE_{II} for the [18]Annulene Structure That Would Result in Thermoneutrality for Oxidative Fission by Dioxygen Attack at the Double Bonds Giving Aldehyde Groups[a]

| No. of O_2	RE_{II}	No. of O_2	RE_{II}
1	104.6	5	362.1
2	169.0	6	426.5
3	233.4	7	490.9
4	297.7	8	555.3

[a] The first reaction, $n = 1$, breaks the macrocyclic ring, and the additional reactions for which $n = 2, 3$, etc., produce glyoxal.

Clearly the more stable the aromatic compound, i.e., the larger its resonance energy, the less favored the reaction. Taking benzene as the example, with $RE_{II} = 32.03$, $\Delta H°$ for reaction 28 is found to be -51.21 kcal/

$$\text{(benzene)} + O_2 \longrightarrow \text{(diene-CHO, CHO)} \tag{28}$$
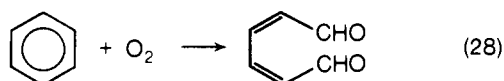
mol, using $E(C_d-C_{CO}) = 100.84$ from crotonaldehyde data,[20] and 3.56 for the RE_{II} associated with the central C_d-C_d bond; see section IV.A. For [18]annulene, with $RE_{II} = 94.52$, $\Delta H°$ for the corresponding fission reaction is -10.08; or, put another way, if RE_{II} had the value 104.60, the fission reaction would be thermoneutral. Any higher RE_{II} value would make the reaction endothermic, and therefore less acceptable as a key step in the combustion process. Even with the middle value adopted for RE_{II} of porphine, 155.20, the reaction would be endothermic to the extent of 50.6 kcal/mol, and with the high value, as great as 392 kcal/mol.

Endothermicity of this primary fission reaction could be offset by additional oxidation at the α,β double bond conjugated to the aldehyde group with the concomitant formation of glyoxal, i.e.

$$-CH=CH-CHO + O_2 \longrightarrow$$
$$-CHO + CHO-CHO \tag{29}$$
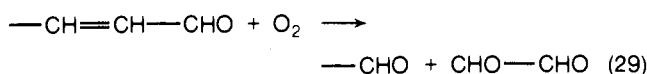
Calculations show that for each such reaction $\Delta H° = -64.38$. Hence thermoneutrality in the overall fission reaction would be achieved with RE_{II} values given by the equation

$$RE_{II} = 184.60 + 64.38(n - 1) \tag{30}$$

where n is the total number of O_2 molecules reacting simultaneously with the [18]annulene structure. RE_{II} values for n from 1 to 8 are listed in Table XXVII.

Now although the combustion of a porphyrin is a far more complicated process than that of the [18]annulene structure, the above reaction(s) simulates oxidative attack at double bonds in the 1,2 or 3,4 positions, etc. Porphyrins with substituents at these positions would give ketones, not aldehydes, but the $\Delta H°$ values would be quite similar. To break the macrocyclic ring the stabilization due to the resonance energy has to be met. The resonance energy of any five-membered ring left in the oxidation product would have a compensatory effect. But with RE_{II} values of about 25 kcal per ring this would lead to a thermoneutral or exothermic fission reaction only if the porphyrin had a low to middle RE_{II} value. These considerations would clearly have to be taken into account in arriving at a fully satisfactory mechanism for the fission reaction.
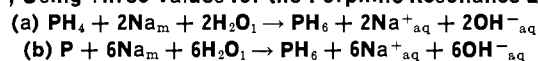
B. Reduction to Porphyrinogen

In this reaction too the stabilization of the porphyrin ring has to be overcome, and again high values for the

TABLE XXVIII. $\Delta H°$, $\Delta S°$, and $\Delta G°$ at 25° for the Stepwise and Overall Hydrogenation of Porphine (P) to Porphyrinogen (PH_6) in the Gas Phase, Using Three Values for the Porphine Resonance Energy

Reaction	RE	$\Delta H°$, kcal/mol	$\Delta S°$, eu	$\Delta G°$, kcal/mol
$P + H_2 \rightarrow PH_2$		-25	-28	-17
$PH_2 + H_2 \rightarrow PH_4$		-25	-28	-17
$PH_4 + H_2 \rightarrow PH_6$	Low[a]	-26	-28	-18
$P + 3H_2 \rightarrow PH_6$	Low[a]	-75	-83	-51
$PH_4 + H_2 \rightarrow PH_6$	Middle[b]	$+35$	-28	$+43$
$P + 3H_2 \rightarrow PH_6$	Middle[b]	-15	-83	$+10$
$PH_4 + H_2 \rightarrow PH_6$	High[c]	$+376$	-28	$+385$
$P + 3H_2 \rightarrow PH_6$	High[c]	$+327$	-83	$+352$

[a]–[c] See corresponding footnotes in Table XXVI.

TABLE XXIX. $\Delta G°$ Values for the Reduction of Tetrahydroporphine (PH_4) and Porphine (P) by Metallic Sodium and Water at 25°, Using Three Values for the Porphine Resonance Energy

(a) $PH_4 + 2Na_m + 2H_2O_l \rightarrow PH_6 + 2Na^+_{aq} + 2OH^-_{aq}$
(b) $P + 6Na_m + 6H_2O_l \rightarrow PH_6 + 6Na^+_{aq} + 6OH^-_{aq}$

	$\Delta G°$, kcal/mol		
Reaction	Low RE[a]	Middle RE[b]	High RE[c]
(a) $PH_4 \rightarrow PH_6$	-105	-44	$+298$
(b) $P \rightarrow PH_6$	-312	-251	$+91$

[a]–[c] See corresponding footnotes in Table XXVI.

porphine resonance energy would make the reaction very unfavorable.

1. By Hydrogen

Using the data discussed at the beginning of this section, $\Delta H°$, $\Delta S°$, and hence $\Delta G°$ values have been calculated for the gas-phase hydrogenation of porphine to the dihydro-, tetrahydro-, and porphyrinogen oxidation states; see Table XXVIII. Even with the middle value for the resonance energy, $RE_{II} = 155.2$, the final reduction stage, $PH_4 \rightarrow PH_6$, and the overall reduction $P \rightarrow PH_6$ would appear to be somewhat unfavored. With the high value, extremely positive values are obtained for $\Delta G°$. Hence for those porphyrins which are known to undergo reduction to the porphyrinogen state by hydrogen in the presence of catalysts,[82] high values for the resonance energy would appear to be ruled out.

2. By Sodium Plus Water

The same is true (see Table XXIX) for the reduction by sodium and water, a reaction which is often carried out using the mercury amalgam. A similar contrast between the $\Delta G°$ values would be obtained for reduction by sodium and an alcohol.

C. Thermal Decomposition of Porphyrinogen

The ease, or otherwise, of the hydrogenation of P to PH_6, and PH_4 to PH_6, has an interesting consequence in connection with the stability of the porphyrinogen toward thermal decomposition. In Table XXX, $\Delta H°$ values are listed for the decomposition of various hydrocarbons, several explosives, and porphyrinogen decomposing into PH_4 and P with the liberation of one and three molecules of hydrogen, respectively. Although instability is a kinetic as well as a thermodynamic phenomenon, it is very striking that porphyrinogen would rank with other ordinary stable organic compounds provided the porphine resonance energy had a low to middle value, while with the high value, in the neighborhood of 500 kcal/mol its ther-

TABLE XXX. $\Delta H°$ for Various Thermal Decomposition Reactions at 25°

	Reaction	$\Delta H°$, kcal/mol
	A. Hydrocarbons	
Acetylene	$C_2H_2\ _g \rightarrow 2C_c + H_2\ _g$	−54
Benzene	$C_6H_6\ _g \rightarrow 6C_c + 3H_2\ _g$	−20
Naphthalene	$C_{10}H_8\ _g \rightarrow 10C_c + 4H_2\ _g$	−36
Anthracene	$C_{14}H_{10}\ _g \rightarrow 14C_c + 5H_2\ _g$	−55
Chrysene	$C_{18}H_{12}\ _g \rightarrow 18C_c + 6H_2\ _g$	−63
9,10-Diphenyl-anthracene	$C_{26}H_{18}\ _g \rightarrow 26C_c + 9H_2\ _g$	−111
5,6,11,12-Tetra-phenyltetracene	$C_{42}H_{28}\ _g \rightarrow 42C_c + 14H_2\ _g$	−187
	B. Explosives	
Silver azide	$2AgN_3\ _c \rightarrow 2Ag_c + 3N_2\ _g$	−134
Gunpowder	$2KNO_3\ _c + 3C_c + S_c \rightarrow$ $K_2S_c + N_2\ _g + 3CO_2\ _g$	−147
Mycomycin	$C_{13}H_{10}O_2\ _c \rightarrow 11C_c +$ $2H_2O_l + C_2H_6\ _g$	−224
Glycerol trinitrate	$C_3H_5(NO_3)_3\ _l \rightarrow$ $2.5H_2O_l + 3CO_2\ _g +$ $1.5N_2\ _g + 0.25O_2\ _g$	−364
	C. Porphyrinogen Dehydrogenation	
$PH_6\ _g \rightarrow PH_4\ _g + H_2\ _g$		+26^a −35^b −376^c
$PH_6\ _g \rightarrow P_g + 3H_2\ _g$		+75^a +15^b −327^c

$^{a-c}$ See corresponding footnotes, in Table XXVI.

modynamic instability would exceed that of several explosives and be very comparable to that of glycerol trinitrate, which is readily detonated by mechanical means.

D. Summary and Data for a Porphine/Phlorine Couple

All these calculations suggest that although differences might be expected from one porphyrin to another, a low to middle value for the resonance energy is more in keeping with the known chemical properties in the majority of cases. The importance of porphyrins, their dihydro and tetrahydro derivatives, and porphyrinogen, in biology, geochemistry, and cosmic chemistry points up the need for new experimental studies to establish beyond doubt the thermodynamic relationships between the oxidation states and the variation that could be brought about by substitution around the porphine ring.

At present the only piece of quantitative data which bears on these problems, other than the heats of combustion, is the oxidation–reduction potential of −0.041 V with respect to the silver|silver chloride electrode, obtained by Wilson for the porphine/phlorine couple of $\alpha,\beta,\gamma,\delta$-tetramethylpyridinium porphine.[83] The porphine type of aromaticity is destroyed in this reduction process (compare Figures 1a and 4d); hence, by making certain assumptions, it is possible to arrive at a value of the porphyrin resonance energy.

The $E°$ value was determined by cyclic voltametry using very acidic solution in which, from the point of view of the ring nitrogen atoms, the porphyrin was present as the dication, and the phlorine, the monocation. The pK for the ionization of the porphyrin giving its monocation was estimated as about 3. Putting these data together gives −12.35 kcal/mol for the reaction

$$\text{porphyrin} + H_2 \longrightarrow \text{phlorine} \qquad (31)$$
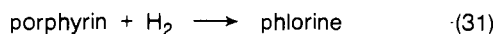
TABLE XXXI. Thermodynamic Data for Various Porphine Reactions Based on $RE_{II} = 103.15$ Calculated from Wilson's Data[83] on the Porphine/Phlorine Couple for $\alpha,\beta,\gamma,\delta$,-Tetramethylpyridinium Porphine

Reaction	$\Delta H°$, kcal/mol	$\Delta S°$, eu	$\Delta G°$, kcal/mol
Biliverdin analog formation	−106	89	−133
$PH_4 + H_2 \rightarrow PH_6$	−17	−28	−9
$P + 3H_2 \rightarrow PH_6$	−66	−83	−42
$PH_4 \xrightarrow{Na} PH_6$			−96
$P \xrightarrow{Na} PH_6$			−303

with both species present as monocations. Assuming that the entropy change for the reduction is determined solely by the saturation of the double bond and loss of the hydrogen molecule, $\Delta S° = -27.7$, i.e., $T\Delta S° = -8.26$. With these values it follows that $-12.35 = \Delta H° + 8.26$, i.e., $\Delta H° = -20.61$. Assuming the solvation heats to be the same for porphyrin and phlorine, which is a reasonable approximation since the charge is the same, this value for $\Delta H°$ can be identified with the gas-phase value. $\Delta H_a°$ for the unsubstituted phlorine structure corresponding to porphine is calculated to be 4569.17; hence, using the data for porphine from section V.B.4

$$4341.22 + RE_{II}(\text{porphyrin}) + 104.20 - 4569.17 = -20.61$$

i.e., RE_{II} (porphyrin) = 103.14.

It is interesting that this value is "low," much nearer the [18]annulene value even than those based on the combustion data of Stern and Klebs.[15] In fact, a value 50 kcal/mol greater than this would alter $E°$ by more than 2 V, and as a consequence the reaction would be very difficult to study electrometrically.

Using this RE_{II} value, thermodynamic data for the various reactions discussed in this section have been recalculated; see Table XXXI. It is to be noted that in all cases where, from observation, the reaction is in general known to occur, the $\Delta G°$ values are appropriately negative; and, conversely, porphyrinogen is stable with respect to thermal decomposition, the $\Delta G°$ values for $PH_6 \rightarrow PH_4$ and $PH_6 \rightarrow P$ being +9 and +42 kcal/mol, respectively. Furthermore, with this low value, fission of the macrocyclic ring in the combustion reaction would present no problem.

IX. References and Notes

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(45) Although this finding is at variance with some traditional values in the literature, for example, 36.0 for benzene and 23.0 for pyridine,[22] this is by no means always the case as can be seen by referring to Schofield's tabulation.[24] Pauling's values,[18] which date back to the original paper of Pauling and Sherman[46] in 1933, are 39 and 43 respectively. Overall, the values Schofield lists for benzene range from 35.9 to 41, while those for pyridine range from 21 to 43. More recently, Cox[32] has obtained 22 for benzene and 19 for pyridine. Leaving aside the issue of better experimental combustion data over the years, these different values should occasion no surprise since, as stressed throughout this review, a resonance energy is not simply a property of a molecule but a reaction parameter. It is empirical in this respect, and, moreover, an arbitrary element enters into its evaluation since the value actually obtained depends on certain bond energy assignments, notably $E(C_d–C_d)$ in the case of aromatic hydrocarbons and, in addition, the group energy term $E(C=N–C_d)$ in the case of pyridine and its homologs. The problem of deciding upon a value for this latter term has been discussed at length in section IV.C.1. Very similar problems arise in connection with the group energy term $E(C_d–NH–C_d)$ in dealing with pyrrole and its homologs; see section IV.C.2. Given the arbitrary nature of all RE calculations, any correlation with structural features is circumstantial. Nevertheless, provided self-consistent use is made of bond and group energy terms along with the corresponding RE values, it is entirely justifiable to take advantage of any such correlation in the estimation of heats of atomization and hence reaction heats.

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(64) It should be emphasized that this choice does not mean that the porphine value is being regarded as a "function" of the [18]annulene value. Whatever is finally decided upon for [18]annulene will in no way invalidate the discussion of thermodynamic aspects of porphyrin reactivity which follows later in this review. Attention has already been drawn to the discrepancy between the only experimental value available at present, reported by Beezer, Mortimer, Springall, Sondheimer, and Wolovsky,[40] and theoretical calculations which point toward a lower value.[42–44] In choosing a "low" value for porphine any number substantially lower than the Stern and Klebs' values, Table XVI, could have been adopted—say, 40, 50, 60, 70, 80, or 90—with no reference at all to [18]annulene. If, in fact, the value for [18]annulene turns out to be less than the current experimental value, this will serve only to accentuate the issue of the porphine resonance energy: the Stern and Klebs' values will, by comparison, appear ever greater, and those of Longo, Finarelli, Schmalzbach, and Adler, Table XVII, greater still.

Exactly the same conclusion holds with regard to the effect of ring strain and nonplanarity of ring structure on resonance energies. Both effects would tend to diminish a value for porphine actually calculated on the basis of structures that are essentially strain-free and planar. But in the present context these considerations do not enter since a value is merely being adopted, not calculated, in order to explore the consequence of resonance energies of various magnitudes on $\Delta H°$ for several porphine reactions. It is perhaps worth noting, however, that the effect of both ring strain and nonplanarity would be negligible compared to the present uncertainty of several hundred kcal/mol raised by the experimental porphyrin values. Strain energies are less than 10 kcal/mol for five-, six-, and seven-membered rings,[20] and there is no particular reason to anticipate a substantial strain in the macrocyclic ring. It is not so simple to arrive at an estimate for the effect of nonplanarity due to puckering of the five-membered rings within the macrocyclic porphine ring system. In 3,4-benzphenanthrene, 9,9'-bianthryl, and 9,10-diphenylanthracene, the rings are prevented for steric reasons from lying in a single plane: yet RE_{II}/DB is still 10.3, 10.3, and 10.1, respectively, compared to 10.7 for benzene. In 1,8-paracyclophane, 2,2-metacyclophane, and dianthracene there is undoubtedly nonplanarity and distortion of the π-electron systems: yet RE_{II}/DB has values of 10.3, 8.9, and 9.5, respectively. Against this background it is difficult to see how any departure from planarity in the porphine ring could diminish the resonance energy by more than about 10 kcal/mol from the value that would otherwise characterize a perfectly planar structure.

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