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AROMATIC ENERGIES OF SOME HETEROAROMATIC MOLECULES

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Abstract ——— Heats of formation derived from the AM1 semiempirical method were used to determine the aromatic energies (AE) of the following systems: pyridine, pyridazine, pyrimidine, pyrazine, 1,2,4,5-tetraazine, phosphabenzene, 1,2-, 1,3-, 1,4-diphosphabenzene, hexaazine, hexaphosphabenzene, silabenzene, thiophene, pyrrole and furan. Two methods were employed for AE estimates. One used the heats of union of atomic pairs (with elimination of H_2) of appropriate nonaromatic precursors. The other method used a comparison of the heats of hydrogenation of aromatic species to estimate the AE.

INTRODUCTION

While the nature of aromaticity has been a major concern of organic chemists for over a hundred years, there is still no general agreement concerning the best way to define it or the procedures to be used in assessing its importance in specific molecules[1-16]. However, while a wide variety of molecular properties has been used in this connection, there are good reasons for insisting on thermochemical criteria, because the abnormal chemical behaviour of aromatic species is due simply to the fact that their molecular energies are more negative than would be expected for an analogous nonaromatic molecule, i.e. one with localized[17] single and multiple bonds.

This was first recognized by Pauling[18] who introduced the term resonance energy to describe the difference in energy between a given molecule and a nonaromatic analog with localized bonds. It was generally believed at that time that the bonds in saturated molecules, and in molecules with isolated multiple bonds, can be well represented in terms of two-center bonds formed by sharing of pairs of electrons between atoms. This belief, however, has proved to be incorrect. Bonds that are localized in this sense are found only in diatomic molecules. While one can write arbitrary "localized" wave functions for larger molecules, corresponding to bonding by localized pairs of electrons, these do not correspond to real states of the systems in question. Relaxation of the restraints responsible for localization leads to delocalization of the electrons and a concommitant decrease in energy. Since this is true for all polyatomic molecules, the energy of any such molecule is necessarily more negative than that of any localized analog. Thus in this literal sense, all polyatomic molecules are resonance stabilized, a conclusion which would vitiate any value that the concept of *resonance stabilization* might otherwise have.

Any property of a localized molecule is, by definition, an additive sum of contributions by the individual bonds. The properties of such a molecule can then be equated to an appropriate sum of fixed bond properties. Chemists have known for many years that certain properties of saturated molecules, in particular their energies, geometries, and dipole moments, can indeed be expressed to a good approximation in this way, as additive sums of empirically determined bond properties. This result was formerly taken as evidence that the bonds in such molecules are indeed localized, being formed by localized pairs of electrons, and theoreticians have spent much fruitless effort in attempts to explain this "fact". Further confusion was caused by the fact that other properties of such molecules (e.g. light absorption and ionization energy) are not additive.

The situation was clarified many years ago by Dewar[19] who pointed out that, in MO terms, the properties of a molecule can be divided into two categories, collective properties that depend collectively on all the valence electrons and one-electron properties that depend on the electrons occupying specific MOs. Only collective properties show additivity. This additivity results moreover not from bond localization but from additivity of the interactions between the valence electrons. If we start with an analog of such a molecule in which the bonds are artificially localized and if we then allow them to interact with one another, the interaction energies are themselves additive functions of the bonds[20]. If appropriate corrections are absorbed into the values of the bond energies, the heat of atomization of a molecule can then be written as a sum of the corresponding bond energies. While the additivity is not perfect, the errors due to departure from it are small. Similar comments apply to other collective properties of molecules, e.g. geometries and dipole moments.

The only satisfactory definition of bond localization depends on this result[21]. If the collective properties of a molecule can be expressed as additive functions of bond properties, the molecule, and the bonds in it, are regarded as localized. It was formerly assumed that this kind of localization holds only for molecules that are saturated or contain only isolated multiple bonds. This, however, is not the case. It is true for all classical molecules, a classical molecule being one for which only a single classical (unexcited resonance) structure can be written. Classical conjugated polyenes are localized in this sense[21].

Additivity breaks down in the case of nonclassical molecules. The heat of formation of a classical analog of a nonclassical molecule can be approximated by a sum of the corresponding bond energies. Comparison with the actual heat of formation of the molecule itself then provides a measure of the stabilization, or destabilization, due to delocalization. The quantities found in this way have been termed "Dewar resonance energies". However, in view of the ambiguity of the term "resonance energy", the term stabilization energy (SE) seems more appropriate.

Following the same reasoning, the aromatic energy (AE) of a cyclic conjugated molecule can be equated to minus the difference between its energy and that of an analog where one of the bonds in the ring has been replaced by a localized bond. Following the convention used in defining resonance energies, a positive AE corresponds to stabilization. In the case of a ring with an even number of atoms, the AE is equal to the stabilization energy, because localizing a bond in the ring turns the molecule into a classical species. This is not generally the case for odd-numbered rings because corresponding open chain analogs are also delocalized; cf cyclopentadienate anion (1) with pentadienate ion (2).

AEs, unlike resonance energies, are clearly defined quantities which can in principle be determined by experiment, by comparing the heat of reaction for any process that converts the molecule in question into one or more classical molecules with an analogous process involving only classical molecules. Use of different reactions in this scheme should in principle lead to identical estimates of AEs. However, since the additivity of bond energies is not exact, different estimates of the AE of a given compound will show a similar variation. It is also difficult to avoid complications due to steric and hyperconjugative interactions that are present in one of the systems being compared but not in the other.

Lack of the necessary thermochemical data presents a further problem. Theoretical calculations have then to be used instead. These suffer from the fact that no current procedure gives accurate estimates of heats of formation. Indeed, few systematic studies of AEs have as yet been carried out. Calculations of this kind were reported[22] some time ago for a wide range of aromatic hydrocarbons, using a π SCF MO procedure[23]. While this proved remarkably successful for conjugated hydrocarbons, reproducing the heats of formation of unstrained alternant hydrocarbons (AH) as accurately as they can be measured by current procedures, and while analogous calculations have been reported[24] for some heteroaromatic species, the results for molecules containing heteroatoms were clearly less reliable and use of π approximations in connections such as this now seems in any case a bit old fashioned. We therefore decided to carry out a systematic study of the aromatic energies of a wide range of monocyclic aromatic compounds, using a more modern procedure, partly to illustrate the procedure and partly to test the potential of theoretical calculations in this connection.

In connections such as this, high level ab initio procedures are usually the methods of choice, provided that the necessary calculations do not require a prohibitive amount of computing time. We decided instead to use the AM1 model[25] because our objective was to illustrate the ways in which AEs can be estimated, rather than to obtain the most accurate possible results for a few simple systems. Since AM1 provides results comparable with those from good ab initio models at less than one-thousandth the cost[26], it is in any case prudent to try it first before embarking on a very expensive and possibly unnecessary ab initio study. We also hoped to extend our calculations to polycylic aromatic systems where use of adequate ab initio methods would involve a prohibitive amount of computation.

PROCEDURE

The calculations were carried out using the AM1 procedure[25] as implemented in the AMPAC program[27]. All geometries were fully optimized, assuming only that the aromatic species were planar. Aromatic energies were estimated in the way indicated above, using appropriate comparisons of the aromatic species with a nonaromatic analog.

Attempts to parametrize MNDO or AM1 for phosphorus and sulfur failed until recently to give satisfactory results for compounds containing these elements in their higher valence states (P^{V}, S^{IV}, and S^{VI}). We had assumed that this failure was due to omission of d AOs in MNDO and AM1. This problem now seems to have been overcome. AM1 parameters have been developed that seem to give satisfactory results for compounds of both sulfur[28] and phosphorus[29] in all their valence states, even though d AOs are still not included. These were used in the present work.

Early attempts to estimate "resonance energies" of aromatic compounds were often based on comparisons of their heats of hydrogenation with those of nonaromatic models. As has often been pointed out, complications commonly arise in this approach from ring strain and hyperconjugation. We have been careful to allow for these in estimating AEs from heats of hydrogenation.

We also used an alternative approach, based on heats of union (HOU), the HOU of two conjugated molecules being the change in heat content when the molecules combine by elimination of hydrogen and formation of a σ bonds; e.g.:

$$H_2CCH_2 \xleftrightarrow{u} H_2CCH_2 \rightarrow H_2C{=}CH{-}CH{=}CH_2 + H_2$$

If the bonds in classical polyenes are indeed localized, the HOU of two classical polyenes to form a single classical species should have a fixed value, which can be determined from appropriate thermochemical data. The energy of a classical analog of a given nonclassical species (equivalent classical energy; ECE) can then be found from the heat of reaction for its formation by intramolecular union of a classical precursor or intermolecular union of classical precursors. The stabilization energy of a nonclassical molecule is equal to the difference between its energy and its ECE. In the case of a cyclic molecule, this is, by definition, its aromatic energy (AE).

HEATS OF FORMATION

Table I lists the molecules studied here together with their calculated heats of formation and experimental values where these are available. Unless otherwise noted, the experimental values for heats of formation, here and subsequently, are from a recent compilation by Pedley et al[30]. The geometries are not reproduced since they presented no unusual features. AM1 calculations have already been reported for a number of these molecules. Appropriate references are given in Table I. Our results agree with the published values. ARCHIVE files suitable for input to AMPAC are available.[31]

The large positive errors for furan and pyrrole have been noted previously[26]. AM1 performs erratically for five-membered rings. Otherwise the agreement with experiment is reasonable.

Table I. Heats of Formation for Molecules Calculated in this Study (kcal/mol).

Molecule	ΔH_f (calc.)	ΔH_f (exp.)	Molecule	ΔH_f (calc.)	ΔH_f (exp.)
(6)	22.0	19.8[a]	(41)	55.2	
(9)	17.5	25.4[a]	(42)	47.5	
(11)	27.0	25.4[b]	(43)	76.7	
(13)	32.0	34.6[a]	(44)	80.3	
(14)	25.1		(45)	56.3	
(15)	30.2		(46)	66.4	
(16)	27.5		(47)	62.4	
(17)	19.2		(48)	86.5	
(18)	39.6		(49)	53.4	
(19)	35.2		(50)	53.3	
(23)	60.9		(51)	80.7	
(24)	55.8		(52)	21.6	
(25)	55.3	53.7[b]	(53)	19.4	
(26)	47.0		(54)	46.3	
(27)	43.9	46.8[a]	(55)	27.6	
(28)	36.4		(56)	-60.5	
(29)	40.6		(57)	-3.2	
(30)	44.2	46.9[a]	(62)	169.8	
(31)	39.1		(63)	162.2	
(32)	63.3		(64)	184.2	
(33)	63.4		(65)	176.3	
(34)	97.5		(66)	188.6	
(35)	87.0		(67)	182.0	
(36)	44.4		(68)	198.4	
(37)	65.0		(69)	192.4	
(38)	39.2		(70)	188.5	
(39)	34.2		(71)	39.7	
(40)	38.2				

[a] J. B. Pedley and G. Rylance. "Sussex-N.P.L. Computer Analysed Thermochemical Data: *Organic and Organometallic Compounds*", Sussex Univ., 1977. [b] J. B. Pedley, R. D. Naylor and S. P. Kirby. "Thermochemical Data of Organic Compounds, 2nd Ed.", University Press: Cambridge, 1986.


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$H_2C{=}CH_2$
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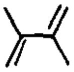
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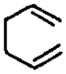
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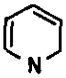
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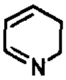
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H_2CNH

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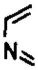
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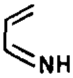
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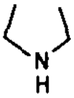
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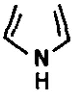
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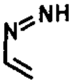
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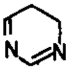
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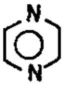
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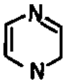
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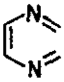
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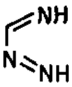
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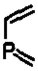
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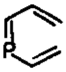
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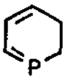
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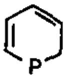
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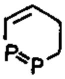
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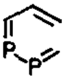
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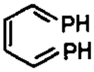
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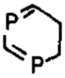
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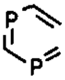
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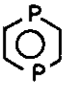
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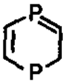
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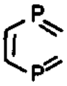
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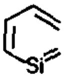
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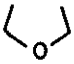
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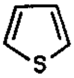
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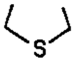
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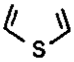
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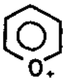
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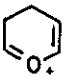
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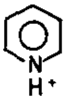
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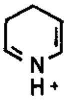
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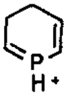
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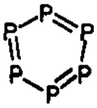
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HEATS OF UNION

In order to determine aromatic energies in the manner indicated above, we need to know the HOUs for the various possible types of union. These can be found from the energetics of specific examples, preferably by using experimental heats of formation if accurate values are available. Thus the HOU for union via two carbon atoms (HOU/CC) can be found from the HOU for union of two molecules of ethylene (3) to form 1,3-butadiene. The result depends on whether the product of union is cis (4; Figure 1a) or trans (5; Figure 1b). Since the links in conjugated rings are normally all cis, HOUs should refer to the formation of cis isomers.

(a)	3	←u→	3	→	4	HOU, 3.5 kcal/mol
			12.5		28.5	
(b)	3	←u→	3	→	5	HOU, 1.2 kcal/mol
			12.5		26.3	
(c)	7	←u→	7	→	8	HOU, 1.2 kcal/mol
			4.8		10.8	
(d)	6	←u→	3	→	$Ph\text{-}CHCH_2$	HOU, 3.1 kcal/mol
	19.8		12.5		35.4	
(e)	6	←u→	6	→	Ph-Ph	HOU, 3.9 kcal/mol
			19.8		43.4	

Mean HOU(cis), 3.5 kcal/mol

Figure 1.
Estimation of the Heats of Union for Coupling of Hydrocarbons (HOU/CC)

The cis isomers are higher in energy, the difference in the case of butadiene being 2.3 kcal/mol. This could, however, be due to steric repulsion between the terminal methylene groups in 4. Since such repulsions are absent in benzene (6), it would then be appropriate to use the HOU for union of 3 to 4. However, the HOU for union of two molecules of propene (7) to form trans-2,3-dimethylbutadiene (8) is the same as the HOU for union of two molecules of ethylene (3) to form trans-1,3-butadiene (5); cf. Figures 1b and 1c. Since the steric repulsions in 8 are similar to those in 4, they can play at most a minor role in the difference in energy between 4 and 5.

Figures 1d and 1e show two further estimations of HOU/CC, using different types of union. Note that the HOU for union of any two even alternant hydrocarbons is expected to have a fixed value[21]. The three values for HOU/CC, found by using experimental heats of formation, agree as well as could be expected, given that bond energies are not accurately additive. We will adopt their mean, 3.5 kcal/mol.

Estimation of the HOU for union involving heteroatoms is more difficult because experimental values for the relevant heats of formation are often not available and because the theoretical values that have to be used are subject to appreciable uncertainty. Table II lists the mean values of HOUs for various types of union, found by schemes similar to that in Figure 1 and using calculated heats of formation from Table I.

Table II. Heats of Union (kcal/mol)

XY	CC	CN	CSi	NN
HOU/XY	3.5	4.7	-4.0	19.6

AROMATIC ENERGIES OF BENZENE AND HETEROBENZENES

Aromatic energies were estimated for benzene and a number of its heteroaromatic analogs, using the approach indicated above. The comparisons used for the individual compounds, and the derived AEs, are discussed below while Table III compares means of the various estimates for each molecule with AEs and resonance energies obtained by other procedures.

Table III. Mean Values of Aromatic Energies (kcal/mol).

Compound	Mean AE	Previous Estimate
Benzene (6)	28.3	24.8[a]
Pyridine (13)	25.6	25.4[a]
Pyridazine (25)	22.7	24.2[a] 12.3[b]
Pyrimidine (27)	25.0	26[c]
Pyrazine (30)	24.6	24.03[d]
1,2,4,5-Tetraazine (34)	12.4	-
Phosphabenzene (38)	26.0	15.24[e]
1,2-Diphosphabenzene (41)	24.6	-
1,3-Diphosphabenzene (46)	25.3	-
1,4-Diphosphabenzene (49)	25.6	-
Silabenzene (52)	25.3	22[f]
Hexaazine (70)	non-aromatic	-
Furan (58)	12.1	23.7[g]
Pyrrole (22)	22.5	-
Thiophene (59)	16.5	29.3[h]

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A. Benzene. Since adequate thermochemical data were available for the species involved in *estimating the AE of benzene* (6), there was no need for recourse to theoretical calculations. The processes used to estimate the aromatic energy of benzene (6) included reduction of 6 to 1,3-cyclohexadiene (9), and formation of 6 by union of 3 with 4 or union of three molecules of 3; see Figure 2.

(a) $\underset{19.8}{6} \rightarrow \underset{\substack{23.6\\ \text{strain}\\ \text{free}}}{9} \leftarrow \underset{20.1}{10}$ $\delta\Delta H_f$, +3.8 kcal/mol

(b) $\underset{56.4}{\underline{\text{trans}}\text{-PhCHCHPh}} \rightarrow \underset{\underline{58.6}}{\underline{\text{cis}}\text{-PhCHCHPh}} \rightarrow \underset{\underline{34.2}}{\underline{\text{cis}}\text{-PhCH2-CH2Ph}}$ $\delta\Delta H_f$, -24.4 kcal/mol

AE (a and b), 28.2 kcal/mol

(c) $\underset{28.5}{4} + \underset{12.5}{3} \rightarrow \underset{19.8}{6}$ AE, 28.2 kcal/mol

(d) $3 + 3 + \underset{12.5}{3} \rightarrow \underset{19.8}{6}$ AE, 28.3 kcal/mol

Mean AE, 28.3 kcal/mol

Figure 2.
Estimations of the Aromatic Energy (AE) of Benzene

Problems arise in the first reaction because 9 is stabilized by two hyperconjugative (sp^2/sp^3) interactions and destabilized by ring strain, *factors that were commonly ignored* in early attempts to estimate the "resonance energy" of 6 from its heat of hydrogenation. An estimate (23.6 kcal/mol) of the heat of formation of "strain-free" 1,3-cyclohexadiene can be obtained by constructing it by intramolecular union from 1,5-hexadiene (10); see Figure 2. The heat of hydrogenation of 6 to strain-free 1,3-cyclohexadiene is thus +3.8 kcal/mol. A suitable nonaromatic model for the conversion of 6 to 1,3-cyclohexadiene is provided by the reduction of <u>cis</u>-stilbene to <u>cis</u>-1,2-diphenylethane; see Figure 2b. Here again complications arise from the steric strain in <u>cis</u>-stilbene, which is much greater than that in 4. An appropriate value for the heat of formation of <u>cis</u>-stilbene in this context can, however, be obtained by assuming the cis-trans energy difference to be the same as for 1,3-butadiene (5 → 4), i.e 2.2 kcal/mol; see Figure 2b.

The other two estimates of the AE of 6 (see Figures 2c and 2d) used estimates of the ECE of benzene derived from union of 3 with 4 or of three molecules of 3. As Figure 2 shows, the three values agreed closely, their mean being 28.3 kcal/mol.

This is much greater than the value (20.0 kcal/mol) given by the earlier π SCF approximation[22], a surprizing result in view of the high accuracy of the heats of formation it gives for alternant hydrocarbons. The discrepancy is, however, easily explained. The earlier estimate depended on the assumption that the heat of atomization of a classical molecule is equal to a sum of the corresponding bond energies. The values for these were derived from the heats of formation of classical polyenes in their ground state conformations where adjacent double bonds are trans to one another. The estimate of the ECE of benzene is thus too low by three times the difference in energy between 4 and 5, i.e. 7 kcal/mol. This accounts quantitatively for the discrepancy.

As noted above, other estimates of the AE of benzene are subject to errors of this kind. The one possible exception, based on a recent high level ab initio calculation[32], led to a value agreeing with ours to within the limits of error of the procedure used[33].

B. Pyridine. Our estimates of the AE of benzene could be, and were, based entirely on experimental values for the relevant heats of formation. This unfortunately was not the case for the other aromatic species studied here. Theoretical values therefore had to be *used for some* or all of the relevant compounds. In such cases it is usually advisable to use calculated heats of formation throughout because errors in the values for related molecules are likely to be similar. The notable exception to this was the use of the *experimental ΔH_f for ethylene throughout the paper.*

The AE of pyridine (13) was again deduced both from its heat of hydrogenation and from the heats of union from suitable precursors. In this case the *complications that normally arise* in use of heats of hydrogenation were avoided by comparing the heat of hydrogenation of 13 to 3,4-dihydropyridine (14) with that of benzene (6) to 1,3-cyclohexadiene (9); see Figure 3. It is reasonable to assume that any complicating effects are the same in both cases. For reasons indicated above, AM1 values for heats of formation were used throughout. The results indicated that the AEs of benzene and pyridine are similar, a conclusion supported by the other estimates indicated in Figure 3.

(a) 6 → 9
22.0 17.5
} AE, 25.8 kcal/mol
(b) 13 → 14
32.0 25.1

(c) 18 + 3 → 13 AE, 27.1 kcal/mol
39.6 12.5 32.0

(d) 19 + 3 → 13 AE, 23.9 kcal/mol
35.2 12.5 32.0

Mean AE, 25.6 kcal/mol

Figure 3.
Estimations of the Aromatic Energy (AE) of Pyridine

Organic chemists have generally assumed that the aromatic energy of pyridine (13) must be close to that of benzene, a conclusion supported by PMO theory[33] as well as the present estimates. Indeed, PMO theory predicts[33] the AEs of <u>all</u> the azabenzenes to be the same, to a first approximation. It has been suggested[34] that the aromaticity of pyridine should be decreased by the electron-attracting nitrogen atom. Neither our results, nor the <u>ab initio</u> ones referenced above, support this suggestion in the case of pyridine itself. However, in view of their limited accuracy, no definite conclusions can be drawn. Positive evidence for the suggestion is presented below in the form of calculations for molecules containing two or more hetero atoms.

C. Pyridazine, Pyrimidine, and Pyrazine. The AEs of pyridazine (25), pyrimidine (27), and pyrazine (30) were estimated in a similar, manner; see Figures 4-6. The AEs were determined, as before, from comparisons of heats of hydrogenation and energies of union. The AEs of the diazines are much less than those for benzene or pyridine, the difference being least for pyrimidine.

(a) 25 → 26
55.3 47.0
} AE, 21.9 kcal/mol
(b) 13 → 16
32.0 25.5

(c) 23 + 3 → 25 AE, 25.1 kcal/mol
60.9 12.5 55.3

(d) 24 + 3 → 25 AE, 21.2 kcal/mol
55.8 12.5 55.3

Mean AE, 22.7 kcal/mol

Figure 4.
Estimations of the Aromatic Energy (AE) of Pyridazine

(a) 27 → 28
43.9 36.4

) AE, 25.3 kcal/mol

(b) 13 → 16
32.0 27.5

(c) 27 → 29
43.9 40.6

) AE, 26.5 kcal/mol

(d) 13 → 15
32.0 30.2

(e) 18 + 17 → 27 AE, 23.1 kcal/mol
39.6 19.2 43.9

Mean AE, 25.0 kcal/mol

Figure 5.
Estimations of the Aromatic Energy (AE) of Pyrimidine

(a) 30 → 31
44.2 39.1

) AE, 25.0 kcal/mol

(b) 13 → 15
32.0 30.2

(c) 32 → 30 AE, 26.1 kcal/mol
63.3 44.2

(d) 18 + 17 → 30 AE, 22.8 kcal/mol
39.6 19.2 44.2

Mean AE, 24.6 kcal/mol

Figure 6.
Estimations of the Aromatic Energy (AE) of Pyrazine

Few alternative estimates are available and, for reasons indicated above, little attention need be paid to them. A previous estimate of the AE of pyridazine (12.3 kcal/mol; Table III) is clearly too small.

Various attempts have been made to deduce the relative aromaticities of the azines, using miscellaneous criteria. Thus Papadopoulos and Waite[15], using polarizability as a criterion, predicted the order: pyridazine > pyrimidine ≈ pyridine > pyrazine. Bird[11], using a cyclic bond variation method, predicted the order: pyridazine > pyrimidine ≈ pyridine > pyrazine. Our predicted order (pyridine > pyrimidine > pyrazine > pyridazine) differs from either of the earlier ones. This, however, is not surprising because there is no valid reason why either of these properties should correlate with the corresponding AEs. The differences are in any case too small for our predictions to carry much weight.

D. 1,2,4,5-Tetraazine. 1,2,4,5-Tetraazine (34) presents problems because the difference in energy between single and double NN bonds is much greater than the corresponding differences *for CC or CN bonds.* This problem seems to be avoided by the comparisons in Figure 7 which lead to similar values for the AE, both much less than the AEs of benzene, pyridine, or the diazines. These results account for the well known *chemical instability of the tetraazine* ring.

(a) 34 → 35
97.5 87.0
) AE, 16.9 kcal/mol
(b) 13 → 15
32.0 30.2

(c) 33 + 17 → 34 AE, 9.5 kcal/mol
63.4 19.2 97.5

Mean AE, 13.2 kcal/mol

Figure 7.
Estimations of the Aromatic Energy (AE) of 1,2,4,5-Tetraazine

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E. Phosphabenzene. Figure 8 shows the comparisons used to estimate the AE of phosphabenzene (38). The agreement between the three values is acceptable, their mean (26.0 kcal/mol; Table III) being only a little less than that for benzene or pyridine. This is surprising, *because it has* usually been assumed that phosphorus forms only weak π bonds to second period elements. The only previous estimate[35] (15.24 kcal/mol.) was derived from a much less reliable procedure, i.e. graph theory, *and is therefore likely* to be incorrect.

(a) 38 → 39
39.2 34.2
) AE, 26.8 kcal/mol
(b) 13 → 16
32.0 25.5

(c) 37 → 38 AE, 26.3 kcal/mol
65.0 39.2

(d) 36 + 3 → 38 AE, 24.7 kcal/mol
44.4 12.5 43.9

Mean AE, 26.0 kcal/mol

Figure 8.
Estimations of the Aromatic Energy (AE) of Phosphabenzene

This apparent inconsistency can be attributed to the tendency of Group V elements to avoid using hybridized AOs to form bonds[36]. The ground state valence shell configuration of a Group V element (X) is s^2p^3, the s AO being filled while the p AOs are each singly occupied. Consider a corresponding molecule XY_3, where X is trivalent. If X uses sp^3 hybrid AOs to form the bonds to Y, the lone pair AO will also be a sp^3 hybrid. The corresponding valence state of X will then be $(sp^3)^5$, i.e. $s^{1.25}p^{3.75}$, corresponding to promotion of 0.75 electrons from the s AO to the p AO. Since the sp separation is of the order of 10 eV, there is a strong tendency for X to use p AOs to form the XY bonds, the lone pair AO being essentially an s AO. The bond angles of such molecules are indeed usually close to 90°, except when X is nitrogen, when repulsions between the ligands (Y), due to the small size of the nitrogen atom, increase the bond angles and lead to hybridization of the nitrogen AOs. Otherwise the unshared electrons of X cannot be used to form π bonds unless the lone pair AO acquires some p character, which involves promotion of s electrons and a corresponding decrease in the strength of the resulting π bond. The apparent reluctance of the later Group V elements to form π bonds does not therefore indicate that such bonds are necessarily any weaker than in the case of nitrogen. The situation in **38** is different because the planar geometry of phosphorus ensures that the p AO involved in π bonding remains unhybridized. The corresponding π bonds can therefore form without hindrance so the AE of phosphabenzene is comparable with that of pyridine.

F. Diphosphabenzenes. Figures 9-11 show the comparisons used to estimate the AEs of 1,2- (**41**), 1,3- (**46**), and 1,4- (**49**) diphosphabenzene.

(a) 41 → 42
55.2 47.5
} AE, 23.4 kcal/mol
(b) 38 → 39
39.2 34.1

(c) 43 → 41 AE, 25.0 kcal/mol
76.7 55.2

(d) 44 → 41 AE, 29.2 kcal/mol
80.3 55.2

(e) 45 + 3 → 41 AE, 20.6 kcal/mol
56.3 12.5 55.2

Mean AE, 24.6 kcal/mol

Figure 9.
Estimations of the Aromatic Energy (AE) of 1,2-Diphosphabenzene

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(a) 46 → 47
66.4 62.4
} AE, 27.0 kcal/mol
(b) 38 → 39
39.2 34.2

(c) 48 → 46 AE, 23.6 kcal/mol
86.5 66.4

Mean AE, 25.3 kcal/mol

Figure 10.
Estimations of the Aromatic Energy (AE) of 1,3-Diphosphabenzene

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(a) 49 → 50
53.4 53.3
} AE, 26.9 kcal/mol
(b) 38 → 40
39.2 38.2

(c) 51 → 49 AE, 24.3 kcal/mol
80.7 53.4

Mean AE, 25.6 kcal/mol

Figure 11.
Estimations of the Aromatic Energy (AE) of 1,4-Diphosphabenzene

While the different estimates of the AEs of the diphosphabenzenes show more variation than usual, it is nevertheless possible to conclude that these molecules are less aromatic than their nitrogen counterparts, as would be expected in view of the general assumption, that CP π bonds are weak.

This result is in fact quite intelligible and the explanation raises a point of general concern. In nonclassical conjugated hydrocarbons, and indeed in most of their heteroatom-containing counterparts, the various classical structures contain similar bonds and so should have similar energies, within the limits of additivity of bond energies. This, however, is not the case for 41. Here one of the two classical (Kekulé) structures contains a P=P double bond and two P-C single bonds while the other contains two P=C double bonds and one P-P single bond. The definition of AE in such a system is ambiguous, depending on the classical structure used as the reference. Problems of this kind become extreme in odd conjugated ions containing heteroatoms. It is often difficult to find satisfactory definitions of the stabilization energies ("resonance energies") of such systems.

The other results require no special comment except that, in contrast to the corresponding azines, the AEs of the 1,2- 1,3- and 1,4- diphosphabenzenes are similar to that of phosphabenzene. This difference presumably reflects the fact that phosphorus differs much less in electronegativity from carbon than does nitrogen.

G. **Silabenzene** The reactions used to estimate the AE of silabenzene (52), and the three concordant values obtained, are shown in Figure 12. The average AE (25.3 kcal/mol; Table III) is close to that for benzene. This is significantly larger than previous estimates from _ab initio_ calculations (22 kcal/mol[37] and 20-25 kcal/mol[6]; Table III). The discrepancy is probably due to the factors indicated above.

(a) 52 → 53
21.6 19.4
) AE, 22.3 kcal/mol
(b) 6 → 9
22.0 17.5

(c) 54 → 52 AE, 28.2 kcal/mol
46.3 21.6

(d) 55 + 3 → 52 AE, 25.5 kcal/mol
27.6 12.5 21.6

Mean AE, 25.3 kcal/mol

Figure 12.
Estimations of the Aromatic Energy (AE) of Silabenzene

H. **Pyrilium(62), Pyridinium(64), Phosphilium(68), and Thiapyrilium(66).** These four ions are well known aromatic species. Use of union to estimate their aromatic energies seemed dubious because the effect of the positive charge on energies of union is uncertain. The AEs were therefore estimated relative to that of benzene by appropriate comparisons of heats of hydrogenation to dihydro derivatives; see Table IV. Since the heats of formation of the ions and their dihydro derivatives were estimated using AM1, it seemed appropriate to also use AM1 energies to calculate the energetics of the reference reaction, i.e. the hydrogenation of benzene. The procedure used is indicated in detail in Table IV, together with the resulting AEs. These are all much less than that of benzene, supporting the suggestion[34] concerning the effect of electronegative atom on the aromaticity of benzene. The effect should be much greater for a positively charged substituent than for a neutral one.

Table IV. Aromatic Energies of Cyclic Ions and Benzene.

Molecule	ΔH_f^a	Dihydro derivative	ΔH_f^a	$\delta\Delta H_f^b$	AE^c
Benzene (6)	22.0	9	17.5	-4.5	28.3
Pyrilium (62)	169.76	63	162.16	-7.6	25.2
Pyridinium (64)	184.16	65	176.30	-7.9	24.9
Phosphilium (68)	198.36	69	192.44	-5.9	26.9
Thiapyrilium (66)	188.57	67	181.99	-6-6	26.2

[a] AM1 heat of formation (kcal/mol).
[b] Heat of hydrogenation (kcal/mol).
[c] Aromatic energy (kcal/mol).

I. Hexaheterobenzenes. AM1 predicts the *NN bonds in hexaazabenzene* (70) to alternate in length. However, the symmetrical aromatic structure is predicted to be only 2 kcal/mol higher in energy, being the transition state for interconversion of the two Kekulé isomers. Similar conclusions have been drawn from previous calculations[1,14-15,38-40]

The AM1 results for P_6 *(hexaphosphabenzene, 71)* illustrate a known failing of the new parameters for phosphorus[29]. In order to allow calculations to be carried out for compounds of phosphorus in both its valence states (P^{III} and P^{V}), an additional repulsive Gaussian term had to be included in the core repulsion function, peaking at 3 Å. This leads to energies that are too positive in situations where some other atom is at this distance from phosphorus. While *the error is relatively small* and rarely causes complications, problems arise in the case of 71 if it has C_{3v} or D_{6h} symmetry because the P_1P_3 distance is then ca 3Å. As a result, the molecule distorts into a lozenge-shaped structure, the P_1P_3 distances being alternately greater and less than 3Å.

NEUTRAL AROMATIC COMPOUNDS WITH FIVE-MEMBERED RINGS

Problems arise in attempts to estimate the AEs of heteroaromatic compounds containing five-membered rings, in particular furan (58), pyrrole (22), and thiophene (59), due to the complicating effects of ring strain and the difficulty of finding suitable nonaromatic species for comparison. AM1 moreover gives erratic results for these compounds. However, reasonable estimates of their AEs can be obtained by the approach indicated above, using experimental values for the heats of formation (ΔH_f); see Figure 13.

(a)	11 →	12(strain free)		12(obs.)	Strain Energy, 3.4 kcal/mol
	25.2	28.7		32.1	
(b)	56 →	57 →	58(classical)	58(obs.)	AE, 12.1 kcal/mol
	-60.2	-3.2	3.6	-8.5	
(c)	20 →	21 →	22(classical)	22(obs.)	AE, 22.5 kcal/mol
	-17.3	39.7	46.6	24.1	
(d)	60 →	61 →	59(classical)	59(obs.)	AE, 16.4 kcal/mol
	-20.0	37.0	43.9	27.5	

Figure 13.
Estimations of the Aromatic Energy (AE) of Neutral Five-Membered Ring

The ΔH_f of strain-free cyclopentadiene (12) can be estimated to be 28.7 kcal/mol by considering its formation by intramolecular union from 1,4-pentadiene (11) (ΔH_f, 25.2 kcal/mol). Comparison with the observed ΔH_f of cyclopentadiene (32.1 kcal/mol) leads to an estimate of the strain energy, i.e. 3.4 kcal/mol. Since this is small and since replacement of the methylene group by a heteroatom is unlikely to lead to any large percentage change in the strain energy, it can resonably be assumed that the strain energies in these compounds are all the same as in 12, i.e. 3.4 kcal/mol.

The heat of formation of strain-free "classical" furan can be estimated to be 0.25 kcal/mol by considering its formation by intramolecular union from divinylether (57; ΔH_f, -3.25 kcal/mol^{30}). Since the strain energy is assumed to be 3.4 kcal/mol, the ΔH_f of "classical" furan is then 3.65 kcal/mol. Comparison with the observed ΔH_f (-8.45 kcal/mol^{30}) leads to an estimate (12.1 kcal/mol) for its AE (Table III).

This argument cannot be applied directly to pyrrole (22) or thiophene (59) because no experimental values seem to be available for the ΔH_f of divinylamine (21) or divinylsulfide (61). These can, however, be estimated from the heats of formation of diethylamine (20) (-17.3 kcal/mol^{30}) and diethylsulfide (60) (-20.0 kcal/mol^{30}) on the reasonable assumption that the heats of hydrogenation of 21 and 61 are similar to that (-57.0 kcal/mol) of divinylether (57). The values obtained in this way (39.7 and 37.0 kcal/mol, respectively), together with the observed ΔH_f for 22 (24.1 kcal/mol^{30}) and 59 (27.5 kcal/mol^{30}), lead to estimated AEs for pyrrole (22.5 kcal/mol) and thiophene (16.4 kcal/mol).

The values obtained in this way imply that aromaticity decreases in the order pyrrole > thiophene > furan, which agrees with the qualitative evidence from chemical reactivity. Table III compares our values with earlier estimates of resonance energies. These are naturally much larger than ours because they represent estimates of the stabilization relative to hypothetical reference structures with "pure" single and double bonds.

CONCLUSIONS

The calculations reported here illustrate the ease with which aromatic energies can be estimated, accurately and without ambiguity, from experimental data when these are available. They also illustrate both the usefulness and limitations of the AM1 *semiempirical model* in this connection, as a source of thermochemical information in cases where experimental data are lacking. The techniques developed here should also be generally useful in assessing the stabilities of aromatic, or potentially aromatic, rings, in particular ones with odd numbers of atoms which present well known problems. Our AEs seem to be in much better general agreement with the chemistry of such systems than the resonance energies derived earlier by other methods.

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