MO STUDIES OF SOME NONBENZENOID AROMATIC SYSTEMS

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ABSTRACT

A new version of (MINDO/3) of the MINDO semiempirical SCF MO method has been developed which seems to avoid the serious defects of earlier treatments. Very extensive tests show that it gives results at least comparable with those of the best *ab initio* SCF procedures at one-hundred-thousandth of the cost. Calculations are reported for the benzynes, for various cyclic polymethines, including $(CH)_3^+$, $(CH)_3$, $(CH)_3^-$, $(CH)_4$, $(CH)_5^+$, $(CH)_5$, $(CH)_5^-$, $(CH)_9^+$, and $(CH)_{18}$, for azulene and pentalene, for the cycloheptatriene–norcaradiene equilibrium, for spironoatetraene, for silabenzene, for a variety of polyazines and polyazoles, and for various aromatic and potentially aromatic sulphur-containing compounds.

INTRODUCTION

While theoretical organic chemistry has long been based on the results of quantum mechanical treatments, in particular simplified versions of the molecular orbital (MO) method, these until recently have been too inaccurate to give results of more than qualitative significance. Many problems have therefore remained outside the scope of current theory since their solution depended on quantitative estimates of the relative energies of atoms and molecules. Recently it has become possible to carry out such quantitative calculations and the results are already proving of major chemical interest in a number of areas. The purpose of this lecture is to report some preliminary studies of this kind of various aromatic systems and problems connected with them.

There is of course no question of obtaining accurate solutions of the Schrödinger equation for molecules large enough to be of chemical interest. As yet only very approximate solutions can be obtained and this situation seems unlikely to change in the forseeable future. In the case of organic molecules, the energies given by the best available procedures are in error by amounts which are vast in a chemical sense. Thus *ab initio* SCF calculations approaching the Hartree–Fock limit can still give heats of atomization that are in error by ± 100 per cent. Any approach to the calculation of 'chemical' quantities must therefore at present be purely empirical, based on a demonstration that the procedure in question can in practice give satisfactory results even though its inherent accuracy is wholly inadequate.

Tests of this kind suggest that *ab initio* SCF calculations may give reasonable estimates of heats of reaction for reactions involving 'normal' molecules, provided that a very large basis set is used; unfortunately the cost of such calculations becomes wholly prohibitive for any but the simplest molecules. This problem is aggravated by the need to calculate molecular geometries: calculations using assumed geometries are of course of little or no chemical value. Because of the cost, very few calculations of this kind have been reported so it is difficult to tell whether or not the results are likely to prove generally reliable. Present indications in any case suggest that the energies of 'nonclassical' species and of transition states are poorly reproduced. The future of such calculations for chemical purposes therefore seems at best uncertain. It is difficult to see how any possible improvement in computers could ever make them feasible for molecules large enough to be of real interest to organic chemists and there is no assurance that the results even then would be of value.

Since we predicted this situation twelve years ago, our approach has followed a quite different course. We start with the most sophisticated treatment that is still simple enough for the necessary calculations to be feasible for molecules of reasonable size and we then try to upgrade its accuracy by introducing adjustable parameters. Such parametric ('semiempirical') treatments have of course been around for some time; however, none has so far aspired to high accuracy. Apart from earlier π approximations, all have either been based on hopelessly crude approximations, e.g. the 'extended Hückel' or Wolfberg–Helmholz method, or have been directed to reproducing the results of current *ab initio* calculations (CNDO, INDO). We have been virtually alone in trying to parametrize such a treatment to reproduce heats of atomization and molecular geometries with the object not only of carrying out calculations at less cost than that required for *ab initio* ones but also of obtaining results of *greater* accuracy.

While we have been successful in this endeavour in the sense that we now have a treatment that is apparently more accurate than any available *ab initio* one and which produces results at one-hundred-thousandth of the cost, and while we have already produced results of major chemical significance in several fields, we ourselves are by no means satisifed. The accuracy we have attained is still insufficient for many chemical purposes and we know that our approach is still capable of almost unlimited improvement. However, we do feel that we have established that calculations of chemical behaviour by other methods at the present time either represent a waste of money or are chemically worthless.

This lecture reports some preliminary applications of MINDO/3, and of a prototype of an even more advanced method, to the subject of this symposium, i.e. aromaticity in nonbenzenoid systems.

PROCEDURE

The course to be followed in developing simplified versions of the Roothaan–Hall *ab initio* SCF method has been charted by Pople and his collaborators. The calculations are confined to the valence electrons, these being assumed to move in a fixed field due to the nuclei and inner shell electrons. The valence electrons are treated by the usual Roothaan–Hall method, using a minimum basis set. The calculations are further simplified by neglecting various electron repulsion integrals and overlap integrals that involve differential overlap. Our own work has been mostly concerned with an INDO-type approach in which all such integrals are neglected other that the one-centre exchange integrals (*ij*, *ij*). We also estimate the one-centre integrals from spectroscopic data for atoms while the two-centre integrals are equated to suitable empirical functions. Parameters in the latter are adjusted to give the best overall fit to the observed geometries and heats of atomization of a carefully chosen set of standard molecules. We term our treatments MINDO (≡ *m*odified INDO) to distinguish them from the original INDO treatment of Pople *et al.*

Apart from a preliminary version (MINDO/1[1]), in which geometries were assumed and only heats of atomization calculated, there have been just two versions of MINDO prior to our present one. MINDO/2[1] was the first treatment that gave both molecular energies and geometries; however, although it already proved superior to most *ab initio* SCF treatments, in particular those using minimum basis sets (e.g. STO-3G), we were not ourselves satisfied since it suffered from a number of serious defects. Some of these were eliminated by a small change in the parameters (MINDO/2′[2]) while most of the rest have now been overcome by a complete reparametrization (MINDO/3[3]).

MINDO/3 has been parametrized for H, C, N, O, F and (without 3*d* AOs) for Si, P, S and Cl. Calculations for several hundred molecules, ions and radicals show that it reproduces heats of atomization with an average error of ~ ± 6 kcal/mole, bond lengths to *ca.* ± 0.02 Å, and bond angles to a few degrees. The results for small ring compounds (the Achilles' heel of earlier treatments) are now comparable with those for compounds of other types. Somewhat larger, but not excessive, deviations occur in the case of compounds with compact globular molecules, e.g. $C(CH_3)_4$ and aromatics, where the calculated heats of atomization are too small, and in compounds where adjacent heteroatoms have unshared pairs of electrons in hybrid AOs, e.g. hydrazines and peroxides, where the calculated heats of atomization are too large and the bond lengths too short. The latter error is due to an inherent failing of MINDO, arising from the neglect of one-centre overlap[1]. This can be avoided by using the rather more complicated NDDO approximation; we already have a preliminary but working version of NDDO (MNDDO/1[4]) in which this problem does not arise.

Studies of chemical behaviour require the calculation of differences in energy between the reactants and products in a reaction, or between the reactants and the transition state. Such calculations are meaningful only if the geometries of the various species are calculated by minimizing the energy with respect to all the geometrical variables involved. One advantage of approximations of the INDO/NDDO type is that derivatives of the energy with respect to the geometrical variables can be calculated very easily; this allows the use of very efficient procedures for the energy minimization. Our current geometry programme enables the geometry of a molecule with up to twenty atoms to be calculated by only about thirty SCF calculations. The number moreover increases only slowly with the size of the molecule. Thus a recent complete geometry calculation[5] for lysergic acid diethylamide (LSD), a molecule with forty-nine atoms and hence one-hundred-and-forty-one geometrical variables to be optimized, required only ninety SCF calculations.

While MINDO/3 was parametrized solely to reproduce heats of atomization and molecular geometries, we have found that it also gives good results for a wide variety of other ground state properties. This of course greatly reinforces our confidence in it. It has previously been generally assumed that different parameters are needed in any given semiempirical treatment to reproduce different properties or even to deal with molecules of different types; our work has shown that this is not true if the parameters are properly chosen (a task which incidentally is far from trivial). Thus MINDO/3 reproduces dipole moments[3] about as well as *ab initio* SCF methods and the predicted charge distributions are also similar. MINDO/3 also gives values[6] for the electron polarizabilities of molecules that agree well with experiment and the same seems also to be true of some preliminary calculations of hyperpolarizabilities[7]. ESCA chemical shifts[8] are again well reproduced as also are ^{14}N nuclear quadrupole coupling constants[9]. And finally· a calculation[7] of the electronic band structure of polyethylene gave results which were much superior to those from other treatments, including an *ab initio* SCF calculation, the predicted band gap agreeing almost exactly with experiment.

A particularly striking test has been provided by recent MINDO/3 calculations[10] for CH_2, O_2 and $C_3H_7^+$, systems small enough for rather elaborate *ab initio* calculations to have been carried out. Not only were the MINDO/3 calculations much faster (by several orders of magnitude) but the results are also in better agreement with experiment.

AROMATIC AND POTENTIALLY AROMATIC SYSTEMS

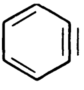
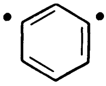
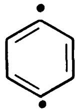
A. Introduction

In the year which has elapsed since the development of MINDO/3, our main concern has been to study a number of mechanistic problems of current interest. This work showed that MINDO/3 can apparently give good estimates of the energies of transition states, the calculated activation energies for several dozen reactions of various kinds agreeing with experiment with an average error of less than ± 5 kcal/mole. In this way some rather startling conclusions have been reached concerning the mechanisms of pericyclic reactions[11] and chemiluminescence[12]; these, however, are not relevant to the present Symposium. Here I will confine myself to some recent studies of a number of cyclic conjugated systems which are of relevance to the general theory of aromaticity.

B. The benzynes

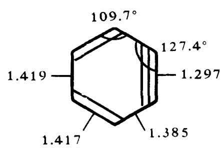
The benzynes are perhaps not strictly 'nonbenzenoid' systems; however, we have included our calculations for them by way of introduction. *Table 1* shows the heats of formation calculated for the three isomers in both singlet and triplet forms; the singlet calculations were also carried out with inclusion of configuration interaction (CI) with the lowest doubly excited con-

Table 1. Calculated heats of formation of benzynes

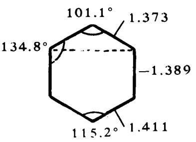
Compound	Heat of formation, kcal/mole Singlet (without CI)	Singlet (with CI)	Triplet
	118.3	114.3	126.9
	117.6	107.2	125.9
	133.9	116.9	123.1

figuration, a refinement known[13] to be essential in the case of systems with significant biradical character. In normal molecules, inclusion of such CI lowers the energy by only 1–3 kcal/mole; a larger decrease occurs in the case of biradical-like species. The results in *Table 1* indicate that *o*- and *m*-benzyne must have singlet ground states since the heats of formation calculated for them without CI are already less than that for the triplet. In the case of *p*-benzyne the situation is more equivocal. However, we feel that our results still indicate a singlet ground state to be favoured, albeit one with much biradical character.

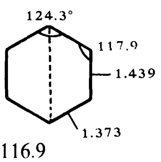
The calculated geometries (bond lengths in Å) and heats of formation (ΔH_f, kcal/mole) of the three singlet species are shown below. Evidently the singlet is favoured in the *meta* and *para* isomers because of long range bonding interactions between the radical centres, leading to corresponding distortions of the benzene rings. It is interesting that bicyclo[2,2,0]-hexatriene was also found to be a stable species, corresponding to complete 1,4 bonding in *p*-benzyne. The bicyclohexatriene is, however, much less stable and is separated from *p*-benzyne only by a low barrier (4.7 kcal/mole). Note also that *m*-benzyne is predicted to be similar to the *ortho* isomer in stability. This suggests that *m*-benzynes may also play a role as reaction intermediates.



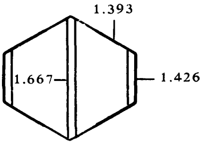
ΔH_f, 114.3



ΔH_f, 107.2



ΔH_f, 116.9



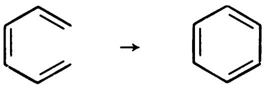
ΔH_f, 152.8

C. The monocyclic polymethines

The only true criterion of aromaticity is provided by a comparison of the heat of formation of a given cyclic conjugated molecule with the value that would be expected if it had a structure similar to that of an open chain analogue. We may term this difference the *aromatic stabilization energy* (ASE) of the cyclic system. In view of the sign convention used for the analogous quantity, resonance energy, a positive ASE corresponds to an aromatic system, i.e. one that is more stable than would be expected from analogy with cyclic systems.

In the case of benzene, the ASE can be estimated from experimental thermochemical data as follows:

$2H_2C{=}CH_2 \rightarrow$  $+ H_2; \Delta H = +1.1$ kcal/mole (1)

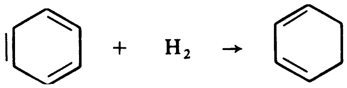


$+ H_2; \Delta H = -24.5$ kcal/mole (2)

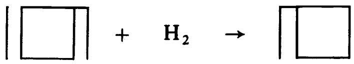
If benzene were non-aromatic, the two heats of union[14] should be equal. The ASE of benzene is thus equal to the difference between them;

$$\text{ASE (benzene)} = 25.6 \text{ kcal/mole} \quad (3)$$

Next let us consider cyclobutadiene. Here complications arise partly through lack of thermochemical data and partly because of ring strain. These can be avoided by using calculated (MINDO/3) heats of formation to estimate the following heats of reaction:



; ΔH, + 5.6 kcal/mole (4)



; ΔH, − 61.9 kcal/mole (5)

The difference between the two heats of reaction should be equal to the difference between the corresponding ASE; hence

$$\text{ASE (benzene)} - \text{ASE (cyclobutadiene)} = 67.5 \text{ kcal/mole} \quad (6)$$

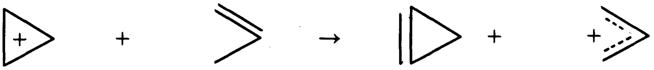
Using equation 3,

$$\text{ASE (cyclobutadiene)} = -41.9 \text{ kcal/mole} \quad (7)$$

This is a remarkably large negative value; clearly cyclobutadiene is *very* anti-aromatic, a conclusion which is certainly supported by its extreme reactivity. The large negative value is the more surprising because MINDO/3, in common with most other treatments, predicts singlet cyclobutadiene to have a reactangular structure (CC bond lengths, 1.535 and 1.342 Å). Such bond alternation should reduce the unfavourable effect of cyclic conjugation[14].

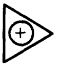
The $(CH)_4$ system is of some interest in view of the current controversies concerning the stability of tetrahedrane and the multiplicity of the ground state of cyclobutadiene. We have studied[15] the singlet and triplet surfaces in some detail. MINDO/3 predicts tetrahedrane to be a stable species, separated from the more stable cyclobutadiene by a 10.8 kcal/mole barrier. Cyclobutadiene is predicted to have a singlet ground state, the square triplet (CC, 1.433 Å) lying higher in energy by 5.3 kcal/mole. Recently Chapman *et al.*[16] have obtained a species in matrices at low temperatures that appears to be cyclobutadiene but whose infra-red spectrum indicates a square geometry. Our calculated vibration frequencies for triplet cyclobutadiene correspond closely to those observed so there seems little doubt that the species studied by Chapman *et al.* was indeed triplet cyclobutadiene. This result is not inconsistent with our conclusions because the photochemical procedure used by Chapman *et al.* would have been expected to give cyclobutadiene in its triplet state and because our calculations imply that the life of the triplet should be long at the low temperatures used. The long life is due partly to a significant energy barrier (3.5 kcal/mole) and partly to a mismatch of vibrational energy levels (which should make the intersystem crossing difficult and the Arrhenius pre-exponential factor correspondingly small).

Next let us consider the $(CH)_3$ system[17]. The ASE for the two ions and the radical can be estimated from the heats of reaction for hydrogen transfer from propene to give the corresponding allyl ion or radical; e.g.

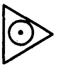


(8)

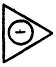
Apart from minor uncertainties due to differences in ring strain and hyperconjugation, the heat of reaction should be equal to the ASE of the $(CH)_3$ species. Using MINDO/3 heats of formation to calculate the heats of reaction, we find:



; ASE, 34.7 kcal/mole



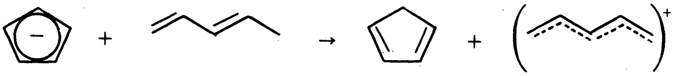
; ASE, − 5.9 kcal/mole



; ASE, − 68.0 kcal/mole (9)

The radical is thus virtually non-aromatic, as simple PMO theory predicts[14], while the cation has a very large positive ASE and the anion an even larger negative one. These results are consistent with those for benzene and cyclobutadiene since the aromatic stabilization and anti-aromatic destabilization should both increase with decreasing ring size.

The various $(CH)_5$ species can be discussed likewise, in terms of reactions such as:



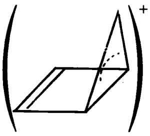
(10)

The ASE found from the corresponding MINDO/3 heats of formation[18] are as follows:

$$\begin{aligned} &(CH)_5^- \text{; ASE, } + 13.1 \text{ kcal/mole} \\ &(CH)_5 \text{; ASE, } - 0.3 \text{ kcal/mole} \\ &(CH)_5^+ \text{; ASE, } - 17.7 \text{ kcal/mole} \end{aligned} \tag{11}$$

The value for the anion may be too small because MINDO/3 tends to underestimate resonance energies. The negative ASE for the cation is much less than that for $(CH)_3^-$ or $(CH)_4$; this is because the $(CH)_5^+$ cation can relieve the unfavourable anti-aromatic interactions not only by bond alternation but also by departure from coplanarity (**1**).

The structures of the $(CH)_5$ anion and radical are not in themselves of much interest. As expected, the former has D_{5h} symmetry while the latter undergoes mild Jahn–Teller distortion[19]. The corresponding cation, however, is interesting because the anti-aromatic destabilization might lead to conversion to isomeric structures; indeed Stohrer and Hoffmann[20] have suggested that the most stable form of the ion might be the 'nonclassical' square pyramid **2**, isoelectronic with pentaborane. Indeed, their EH calculations[21], and CNDO/2 calculations by Kollmar[22], predicted **2** to be more stable than **1** by 60–70 kcal/mole. The situation is made even more intriguing by the fact that an *ab initio* SCF calculation by Hehre[23] led to the diametrically opposite conclusion that **2** should be only marginally stable, lying 65 kcal/mole above **1** in energy, and by experimental evidence that **1** and **2** cannot be too dissimilar in energy and that a dimethyl derivative of **2** can exist as a stable species in solution.



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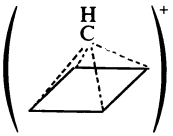

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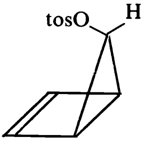

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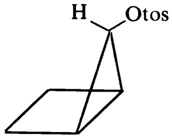

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We have therefore studied the $(CH)_5^+$ potential surface in detail[19], examining all the structures that have been suggested. We found only two minima, corresponding to **1** and **2**, **1** being the lower in energy by 14 kcal/mole. Isomerization of **2** to **1** should, however, be difficult since we predict a barrier to interconversion of no less than 43 kcal/mole. Our results are clearly in much better accord with experiment than those from the other calculations. It is of course well known that EH and CNDO/2 greatly overestimate the stabilities of 'nonclassical' structures such as **2**, a failing also present to a lesser extent in the earlier versions of MINDO. It now seems likely that the *ab initio* SCF methods err in the opposite direction, seriously underestimating the stabilities of 'nonclassical' structures.

Our calculations lead to the conclusion that **1** and **2** should both be stable at room temperature, once formed. An amusing prediction (from further MINDO/3 calculations) is that the isomeric bicyclic tosylates **3** and **4** should solvolyse in different ways, **3** giving **1** and **4** giving **2**.

We have also studied the $(CH)_5^+$ triplet surface[24]; this contains a single minimum, with D_{5h} symmetry, lying 1.6 kcal/mole below **1**. This result is in agreement with the experimental finding[25] that the ground state of $(CH)_5^+$ is a triplet. Our calculated zero field splitting (0.153 cm^{-1}) agrees well with that observed[25] (0.1868 cm^{-1}).

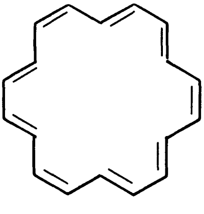
In view of these results, we have also studied in detail the potential surface for the next higher anti-aromatic polymethine cation, $(CH)_9^+$. Here the ground state is predicted to be a singlet, composed of one or other of two nonplanar Jahn–Teller-distorted structures. We have also located five other minima, four being bicyclic structures and one a pyramidal ion akin to **2**. While the interconversions of the various species are of interest in connection with the theory of pericyclic reactions, they are not relevant here. The same applies to the interconversions of benzene with the other $(CH)_6$ isomers which we have also studied in detail.

The last polymethine to be discussed is [18]annulene (**5**). We calculated[26] the structure of this by a complete energy minimization, no assumptions being made (not even planarity!). At the time this was by far the largest molecule whose geometry had been calculated by an SCF MO procedure; recently this record has been beaten by a similar calculation for LSD.

Our results are compared in *Table 2* with those from an earlier π SCF calculation[27] and from molecular mechanics[28]. It will be seen that the three entirely different methods lead to very similar results, predicting definite bond alternation. This result is at variance with an x-ray structure determination[29] which implied that **5** is 'aromatic'; however, the n.m.r. spectrum of **5** seems to be inconsistent with a structure in which bond alternation is absent. We cannot attribute this discrepancy to a difference in structure between the crystal and solution because, according both to MINDO/3 and the π SCF procedure, the symmetrical D_{6h} structure is very much higher

Table 2. Bond lengths in [18]annulene

Bond	Length (Å)			
	x-ray	MINDO/3	πSCF	Molecular mechanics
1,2	1.381	1.458	1.462	1.463
2,3	1.419	1.355	1.352	1.361
3,4	1.383	1.458	1.462	1.463
4,5		1.351	1.353	1.357
5,6		1.466	1.458	1.467
6,7		1.350	1.354	1.357



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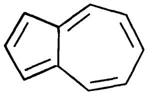

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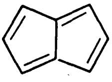

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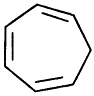
in energy than that indicated in *Table 2*. We feel that these results at least throw doubt on the validity of the conclusions drawn from the x-ray diffraction studies, particularly since no case has yet been found when a compound definitely crystallizes as a disordered mixture of Kekulé forms. In the absence of such a case, there is no experimental evidence concerning the difference in diffraction patterns to be expected between an aromatic compound and one crystallizing as a mixture of Kekulé forms.

D. Other hydrocarbons

We were somewhat surprised to find[17] that MINDO/3 predicts azulene (**6**) also to have alternating bond lengths round the periphery of the ring. It has been generally assumed that **6** has a symmetrical C_{2v} structure with peripheral bonds of 'aromatic' length. Since the calculated (MINDO/3) difference in energy between the C_{2v} structure and the C_s one was very small (1.6 kcal/mole) and since there is some evidence that MINDO/3 may underestimate resonance energies, we repeated the calculations using MINDO/2′ and also our preliminary version of NDDO (MNDDO/1), both of which had given good heats of formation for benzene and naphthalene. However, the results were the same as before, the alternating C_s structure being predicted to be lower than C_{2v} and in each case by a small margin (MINDO/2′, $\delta\Delta H_f = 1.1$; MNDDO/1, $\delta\Delta H_f = 1.3$ kcal/mole). We therefore suspect that the potential surface for azulene has two minima, corresponding to the two Kekulé structures and separated by a very low barrier. If so, **6** should behave at room temperature almost as though it has a single very flat minimum. Since the crystals of **6** are moreover disordered, one would expect the resulting x-ray diffraction pattern to be almost impossible to interpret. The results of several different analyses indeed show quite remarkable variations. Since the problem is of some theoretical importance, it is to be hoped that it will be studied further.

We have also calculated[17] pentalene (**7**). As expected, the bond lengths in this anti-aromatic compound alternate and the difference in energy between the alternating C_s structure and a symmetrical C_{2v} one is large (13.3 kcal/mole).

We have also studied the effects of homoconjugation and spiroconjugation by carrying out calculations for the cycloheptatriene (**8**) $\rightleftarrows$ norcaradiene (**9**) equilibrium[30] and for the series of spiranes **10**, **11** and **12**[17].



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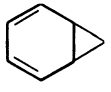

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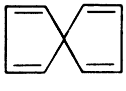

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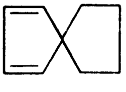

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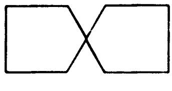
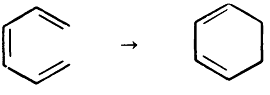


12

Cycloheptatriene (**8**) is predicted, correctly, to be more stable than **9** while the 7,7-dicyano derivative is predicted, again correctly, to be more stable than the norcaradiene. For the 7-monocyano derivative, MINDO/3 predicts the cycloheptatriene to be more stable than the norcaradiene by 2.1 kcal/mole; in practice both seem to be similar in stability. Thus the calculated heat of reaction for **8** → **9** (10.2 kcal/mole) is probably quite near the truth. Using this value we can estimate the homo-aromatic stabilization (ASE) of **8** as follows:



; ΔH, − 25.7 kcal/mole

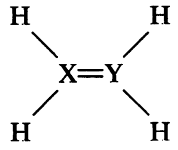
$$\mathbf{8} \rightarrow \mathbf{9};\ \Delta H,\ +\ 10.2\ \text{kcal/mole} \qquad (12)$$

The difference between the two values (35.9 kcal/mole) should be equal to a sum of the strain energy in **9** plus the ASE of **8**. Since it seems unlikely that the strain energy of **9** could be much greater than that of cyclopropane (27 kcal/mole), the homoconjugative stabilization of **8** must be significant, probably close to 9 kcal/mole.

The second problem, that of spiroconjugation, was studied by calculating the heats of formation of **10**, **11** and **12**. Since the differences in strain energy between **10** and **11**, and between **11** and **12**, should be similar, the differences in heat of formation between **10** and **11**, and between **11** and **12**, should be the same if spiroconjugation in **10** is energetically unimportant. This in fact proved to be the case, the differences being − 64.7 and − 63.7 kcal/mole respectively. Any spiroconjugative stabilization of **10** would have made the first difference numerically the smaller.

E. Silene derivatives

There has been much interest recently in the chemistry of silenes, i.e. species containing C=Si bonds, in particular in the ability of silicon to π bond to carbon. We estimated[31] the strengths of C=C, C=Si and Si=Si π bonds from the corresponding heats of hydrogenation (calculated by MINDO/3) as follows:



$$H_2X{=}YH_2 + H_2 \rightarrow H_3X{-}YH_3$$

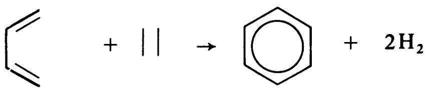
$$\Delta H = E^{\pi}_{XY} - E_{HX} - E_{HY} \qquad (13)$$

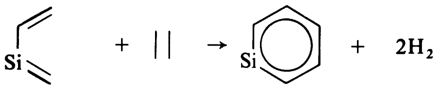
Here E_{HB} and E_{HY} are the corresponding bond energies for which we assumed standard values. The π bond energies (E^{π}_{XY}) found in this way were:

$$E^{\pi}_{CC},\ 60.3;\ E^{\pi}_{C\,Si},\ 42.2;\ E^{\pi}_{Si\,Si},\ 20.0\ \text{kcal/mole} \qquad (14)$$

Our procedure is admittedly naïve, ignoring effects of changes in hybridization; on the other hand the CC value is close to the observed barrier to rotation in ethylene (65 kcal/mole), so it represents a reasonable estimate of the CC π bond strength. On this basis it can be seen that the CSi π bond, while weaker than CC, should still be strong and that even the SiSi π bond should have appreciable strength. This conclusion is supported by the following estimate of the ASE of silabenzene.

Consider the two following reactions:

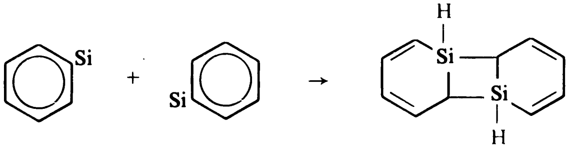

(15)


(16)

If the products were non-aromatic, the heats of reaction should each be just double that for equation 1, i.e. 2.2 kcal/mole. Deviations from this value are measures of the ASE of the two species; thus the difference between the two heats of reaction should be equal to the difference between the two ASEs. Using MINDO/3 data, we find:

$$\text{ASE (benzene)} - \text{ASE (silabenzene)} = 5\ \text{kcal/mole} \tag{17}$$

Since the ASE of benzene is 24.5 kcal/mole (equation 2), that of silabenzene is about four-fifths that for benzene. On this basis we would expect silabenzene to be a stable species because the loss of aromatic stabilization during dimerization,


(18)

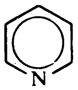
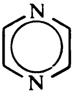
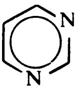
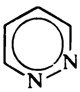
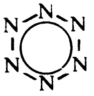
should balance the gain in bond energy.

F. Heterocyclic species

We have carried out calculations for a number of hetero-aromatic compounds, mainly with the object of testing our theoretical procedures. We expect MINDO/3 to be generally satisfactory for compounds in which there are no important lone pair repulsions. When such repulsions are important, MINDO/3 will give heats of formation that are too negative; it will then be necessary to use NDDO. At present, however, we have only a preliminary version of NDDO (MNDDO/1), parametrized for compounds derived from C, H, N or C, H, O (but not yet for compounds containing both N and O). Moreover the parametrization is by no means fully optimized. The results reported here must therefore be regarded as tentative.

Table 3 compares calculated[18] and observed heats of formation of a number of azines. It will be seen that MINDO/3 gives a good result for pyridine but values that are too negative for the diazines. The deviation moreover increases rapidly as the distance between the lone pairs decreases. This is because, as noted above, MINDO/3 fails to take into account repulsions due to the dipole component of the field arising from lone pair electrons in a hybrid AO. The effect becomes extreme in hexazine, which MINDO/3 predicts to be stable. The MNDDO/1 results are generally more satisfactory. Here pentazine and hexazine are predicted to be unstable, decomposing without activation to ($2N_2$ + HCN) and $3N_2$ respectively.

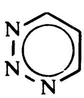
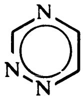
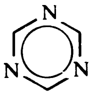
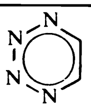
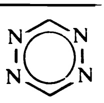
Table 3. Calculated and observed heats of formation of azines

Compound						
$\Delta H_f^{\dagger}$(obs.)	33.5	46.9	47.0	66.5	—	—
$\Delta H_f^{\dagger}$(MINDO/3)	34.2	41.3	35.4	22.5	−23.0	−57.8
$\Delta H_f^{\dagger}$(MNDDO/1)	26.9	41.0	48.4	41.4	(215)‡	(323)‡

† Heat of formation (kcal/mole).
‡ Dissociates without activation into $(2N_2 + HCN)$ or $3N_2$.

Table 4 shows MNDDO/1 heats of formation[18] for various polyazines, together with the heat of reaction for dissociation into N_2, HCN and HCCH. Note the predicted instability of 1,2,3-triazine and the (apparently correct) prediction that the most stable tetrazine is the 1,2,4,5 isomer.

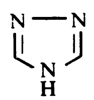
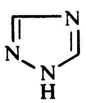
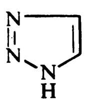
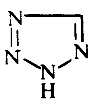
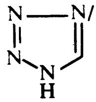
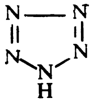
Table 4. MNDDO/1 calculations for polyazines

Compound						
$\Delta H_f^{\dagger}$	86.3	72.2	86.8	130.5	137.1	125.6
$\Delta H_d^{\ddagger}$	−0.8	+13.3	+6.8	−76.2	−74.7	−63.2

† Heat of formation calculated by MNDDO/1 (kcal/mole).
‡ Heat of reaction for dissociation into most stable binuclear products (N_2, HCN, HC≡CH).

Table 5 shows MNDDO/1 results[18] for a number of polyazoles, together with calculated heats of reaction for dissociation into HN_3 + N_2, HCN or C_2H_2. The calculations seem to lead to correct predictions of the preferred isomer in the triazoles and tetrazole. They also account well for the high thermal stability of the 1,2,4-triazoles.

Table 5. MNDDO/1 calculations for polyazoles

Compound						
$\Delta H_f^{\dagger}$	92.2	84.3	71.4	139.4	127.8	213.0
$\Delta H_d^{\ddagger}$	—	—	53.2	−37.9	−26.3	−142.7

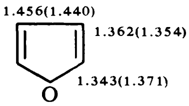
† See *Table 3*.
‡ Heat of dissociation into HN_3 + (C_2H_2, HCN or N_2).

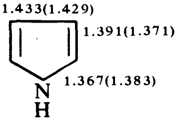
G. Sulphur compounds

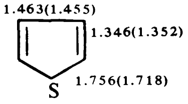
While MINDO/3 has been parametrized for phosphorus and sulphur, 3*d* AOs have not yet been included. It is therefore interesting to find that for thiophene it gives quite good estimates of the heat of formation (calc. 32.5; obs. 27.6 kcal/mole) and vertical ionization potential (calc. 8.87; obs. 8.92 eV).

This supports earlier conclusions[32] that $p\pi:d\pi$ bonding is not important in compounds of this type and that the aromaticity of thiophene does not depend to any large extent on it.

The calculated geometries of furan[3], pyrrole[3] and thiophene[33] are in good agreement with experiment, the calculated (observed) bond lengths (Å) being:

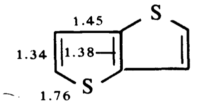




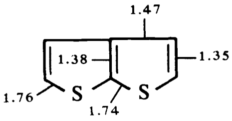


Note that bond alternation increases in the series pyrrole < furan < thiophene. Thus thiophene is the *least* aromatic of the three, as would be expected if $p\pi:d\pi$ bonding were unimportant. The apparently greater chemical stability of thiophene is an illusion, being due merely to its lower basicity. This protects it from cationic polymerization by electrophiles.

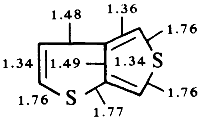
Strong bond alternation is also predicted[18] in the three 'classical' thiophthenes, the calculated bond lengths (Å) and heats of formation (kcal/mole) being as follows:



ΔH_f. 43.9

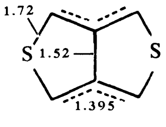


49.4



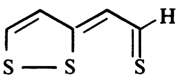
48.4

The fourth 'nonclassical' isomer is predicted[18] to be biradical-like in character, being in effect an internal disulphide derived from 2,2′-biallyl.

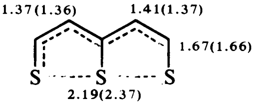


We have not yet calculated the corresponding triplet.

It has been shown by x-ray crystallography of derivatives that the disulphide thioaldehyde **13** exists preferentially as the symmetrical 'nonclassical' isomer **14**. It seems to be generally accepted that the bonding in **14** makes use of sulphur *d* AOs. We were therefore somewhat surprised to find[18] that MINDO/3 also led to this conclusion although 3*d* AOs are not as yet included in it. The calculated bond lengths (Å) are shown in **14** together with experimental values in parentheses. The agreement is quite good. For comparison we also calculated the 'classical' isomers **15** and **16**; the corresponding heats of formation (kcal/mole) are listed under the formulae. It will be seen that **14** is predicted to be much the most stable of the three.

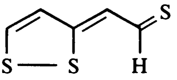


13



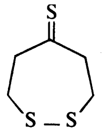
ΔH_f. 15.5

14



37.7

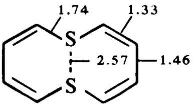
15



62.7

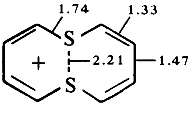
16

This result suggested that similar 'nonclassical' species might be formed by compounds analogous to **13** in which sulphur is replaced by O, NH or PH. However, MINDO/3 predicts[18] all three compounds to have 'classical' structures analogous to **13**, the corresponding symmetrical nonclassical isomers being unstable and much higher in energy. A similar negative result came from calculations of the naphthalene analogue **17** and the mono (**18**) and di (**19**) cations derived from it. The bond lengths and heats of formation are indicated on and below the formulae. It will be seen that **17** has a structure corresponding to a butadiene disulphide. Equal bond alternation is retained even in the dication **19** although this is isoconjugate with naphthalene. These results again emphasize the very low ability of sulphur to form π bonds to carbon.



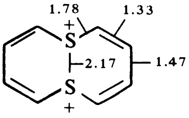
ΔH_f. 53.5

17



ΔH_f. 202.7

18



ΔH_f. 476.4

19

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