

THE THEORETICAL DESIGN OF NOVEL STABILIZED SYSTEMS

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ABSTRACT

Simple symmetry and bonding arguments, coupled with detailed molecular orbital calculations, are used in the design of three novel stabilized systems: (1) Spirarenes—allylic radicals coupled in a spiro system. (2) Diradicals converted by heteroatom replacement or substitution into singlet ground state zwitterions. (3) The stabilization of planar tetracoordinate carbon.

To devise novel types of aromaticity is not easy. There are a lot of very clever theoreticians around, likely to think of these things before us. More important there is Nature to contend with. If a system is indeed extremely stable there is a good chance that it occurs naturally. Or if an unnatural act is needed to produce such a molecule it is probable that the compound has already serendipitously fallen out of one of the many pots that organic chemists keep boiling around the world. Nevertheless it has been our fortune to come upon some novel means of conferring stabilization upon a molecule. Though not yet experimentally achieved these cases are theoretically amusing, and I would like to recount the story of three such systems to you.

THE SPIRARENES AND SPIROCONJUGATION

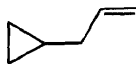
The well known molecular orbitals of an allyl system are shown in *Figure 1*. If two allyl radicals are brought together in such a way as to produce little interaction among the energy levels then the ground state of the system of the two radicals is likely to be a triplet. If the radicals are brought together so that the levels interact appreciably then it is possible that the nonbonding levels may interact strongly enough so that the ground state of the six electron system is a stabilized singlet (*Figure 4*). Such stabilization has been effectively achieved in the various collapse products of two allyl radicals, e.g. **1**, **2**, **3**, **4**.



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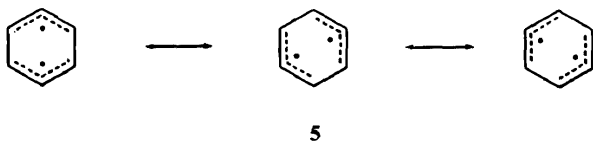


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Even more efficient is the coupling of allyl radicals in aromatic molecules. A perfectly adequate, if somewhat unpopular, way of viewing benzene is as two strongly interacting allyl radicals, **5**. The molecular orbitals of benzene

are indeed clearly related to those of two interacting allyls, as shown in *Figure 3*.

In searching for still different topologies for interaction of two allyl radicals my collaborators and I came upon the idea of incorporating the allylic moieties into a spiro system¹. The simplest species of this type, which we called a [3,3]-spirarene is **6**, [3,5], [5,5] and [3,7]-spirarenes are shown



in **7**, **8**, **9**. The [3,3]-spirarene is redrawn in *Figure 4* to emphasize the perpendicularity of the spiro arrangement and to define the planes used in the subsequent analysis.

In the evaluation of the stabilization of any system two questions must be faced, in the indicated sequence: (1) Does the topology and symmetry of the system allow any stabilizing interaction? (2) If so, what is the magnitude

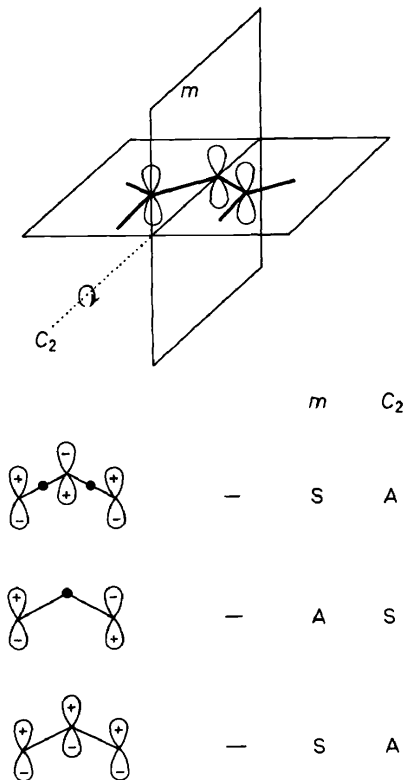


Figure 1. The π molecular orbitals of an allyl system. Two symmetry operations are defined in the figure and the allyl orbitals classified as symmetric (S) or antisymmetric (A) under those operations.

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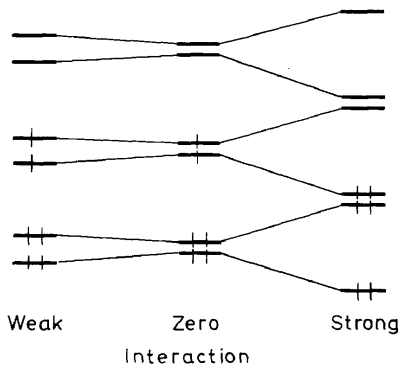


Figure 2. Two allyl radicals (centre) may interact weakly (left), with a likely triple ground state resulting, or strongly (right), leading to a stabilized singlet.

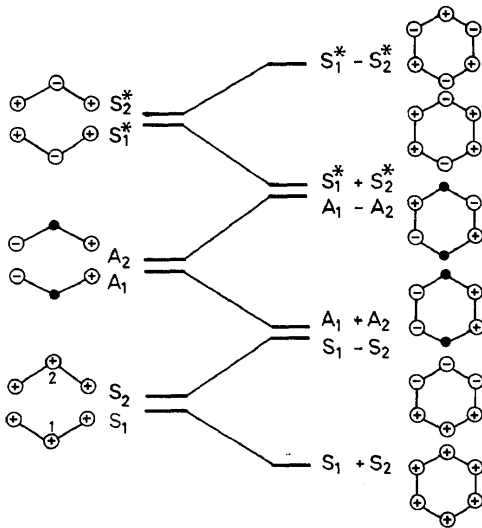


Figure 3. The formation of the benzene orbitals (right) from the molecular orbitals of two interacting allyl systems (left).

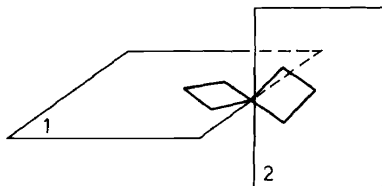
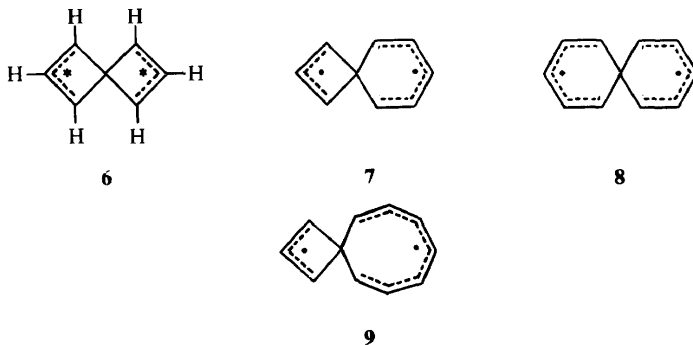
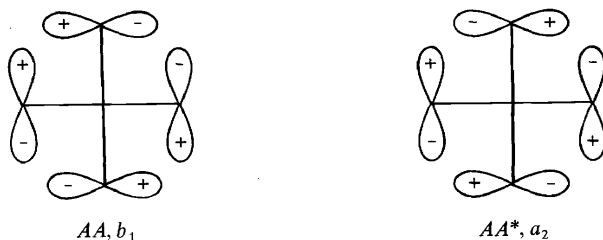


Figure 4. Definition of perpendicular planes for [3,3]-spirarene.

of that stabilization? The important interaction in our case is that between the nonbonding orbitals of the two allyl groups. Using the planes defined in *Figure 4* we can classify in symmetry the individual orbitals and form the interaction diagram of *Figure 5*. The symmetric allyl orbitals do not interact (in fact they form a degenerate e orbital in the D_{2d} geometry) but the anti-symmetric nonbonding orbitals are both of symmetry AA and so may interact.



The middle levels of the [3,3]-spirarene after interaction are shown below. The view is end on, along the S_4 axis of the molecule. AA is characterized by four sideways interactions of p orbitals of an allyl in one ring with an allyl



in the other. The splitting between AA and AA^* is given by an extended Hückel calculation as 1.0 eV for a C—C distance of 1.45 in each perfect four-membered ring, 0.75 eV for a C—C distance of 1.54. The overlap which gives rise to each interaction would appear to be quite inefficient; in fact at a ring C—C distance of 1.45 Å the two carbons are separated by 2.51 Å and the overlap is 0.025. One can make a rough estimate of the stabilization to be expected by comparing with benzene, imagined as arising from the interaction of two allyl systems. In benzene the two allyl fragments are coupled by π - π overlaps at a distance of 1.40 Å—each having the value of approximately

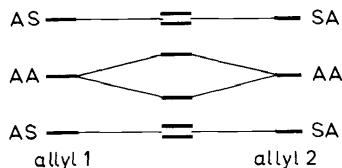
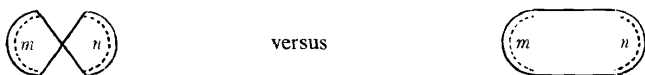


Figure 5. Interaction diagram for [3,3]-spirarene. Symmetry designations are with respect to the planes defined in *Figure 4*.

0.25. Thus it would seem that the overlap in benzene is ten times as efficient as in [3,3]-spirarene. However, benzene has only two such overlaps but *AA* contains four.

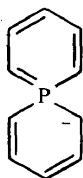
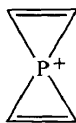
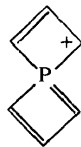
When the splitting of two levels is small and two electrons are to be placed in these levels, it is critical to determine if the ground state of the system is expected to be a singlet or a triplet. The extended Hückel method is useless for this purpose and we attacked the question with the aid of a Pariser-Parr-Pople calculation² ably adapted by Dr Akira Imamura for a general nonplanar molecule. An important feature of calculations on near diradicals such as **6** is that it is crucial to include at least one doubly excited configuration. The ground state emerges as a stabilized singlet, a heavy mixture of configurations $(AA)^2$ and $(AA^*)^2$. The stabilization is not excessive, since the triplet arising from the configuration $(AA)^1(AA^*)^1$ is calculated to lie only 0.64 eV above the ground state singlet.

Interaction diagrams similar to *Figure 5* readily show that there is some symmetry allowed interaction of nonbonding orbitals in **9**, but none in **7** and **8**. The generalization to an arbitrary case $[m,n]$ is simple. An interaction leading to a stabilizing interaction can only occur when the nonbonding orbital of both systems has *AA* symmetry which occurs for the cases $m.n =$



3,7,11, etc., i.e. both *m* and *n* must be $4q + 3$ where $q = 0,1,2 \dots$. This stabilization rule for a spiro system is thus in interesting contrast to Hückel's rule for a lateral interaction of two allylic fragments, which states that stabilization will occur whenever $m + n = 4q + 2$.

When the central spiro carbon atom is replaced by a second row atom, presumed to possess relatively low-lying unoccupied *d* orbitals, an interesting further stabilization may occur³. The *d* orbitals contain a set of functions of the proper symmetry to interact with *AA*, b_1 and *AS*, *SA*, *e* orbitals. They can thus enhance the stability of the above spirarenes or even create novel stabilized systems. Likely candidates are **10**, **11** and **12**, or the isoelectronic species with P replaced by S^+ or Si^- .

**10****11****12**

The more general concept of through space interaction reaching across a spiro centre is, of course, not limited to the spirarenes. For polyenes or lone pairs coupled in this manner the interaction manifests itself in changes in electronic spectra, ionization potentials, and reactivity. The general mode of

interaction has been analysed independently by us¹ and by Simmons and Fukunaga⁴, who aptly named the phenomenon 'spiroconjugation'. Though no spirarenes have been synthesized there is accumulating evidence for spiroconjugation as a real phenomenon^{4,5}.

DIRADICALS INTO ZWITTERIONS

Molecules whose every classical valence structure is at best a diradical one generally emerge theoretically and experimentally as triplet ground states. Rolf Gleiter and I⁶ have developed several procedures for stabilizing the singlet states of diradicals by heteroatom replacement.

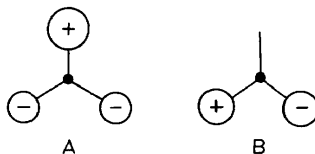


Figure 6. The nonbonding molecular orbitals of trimethylenemethane.

Consider trimethylenemethane, **13**, a typical π diradical, which in a D_{3h} geometry possesses a degenerate pair of nonbonding π -orbitals. These orbitals, shown in Figure 6, are to be occupied by a pair of electrons. Theoretically⁷ and experimentally⁸ the ground state of the system appears to be a triplet.

Of the two nonbonding orbitals *A* has density at C_1 whereas orbital *B* by symmetry does not. Substitution in trimethylenemethane of an oxygen atom



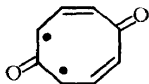
for CH_2 at the C_1 position would be anticipated to break the degeneracy of *A* and *B* by stabilizing *A* and leaving *B* unaffected. The resulting species is oxyallyl, **14**, the ring-opened zwitterionic form of cyclopropanone. A previous calculation which we carried out on this molecule⁹ showed that the lowest singlet was considerably stabilized, but that a triplet remained the ground state of the molecule by 0.1 eV. In order to obtain diradicals with singlet ground states we scrutinized the molecular orbitals of a large number of carbon diradicals, keeping an eye out for those molecules in which one nonbonding molecular orbital possessed electron density at one or more carbon atoms which did not appear in the other nonbonding orbital. After substituting the appropriate number of oxygens in these differentiated positions we carried out Pariser-Parr-Pople calculations with extensive configuration interaction.

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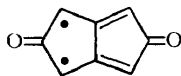
We discovered three species, (**15–17**), which were definitely singlet ground states, and a number of other borderline cases.



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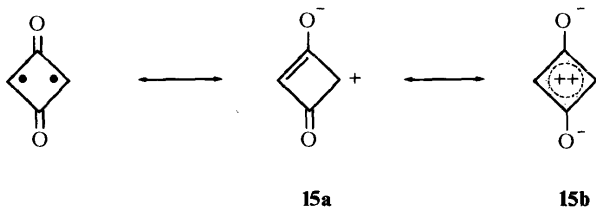


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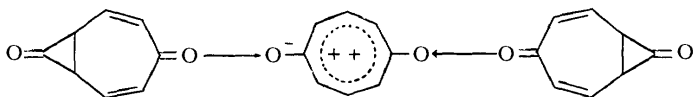


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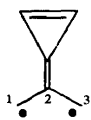
I have drawn diradical valence structures for **15–17**, but the calculations in each case showed final charge distributions characteristic of the expected zwitterionic resonance structures such as **15a** and **15b**. Each of these molecules



would be expected to be highly coloured. Substituted derivatives of **15** are known¹⁰, and are strong chromophores. The stabilization of **16** is of great interest, since it suggests the possibility of achieving a Cope rearrangement with a negative activation energy:



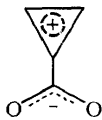
A related class of molecules is exemplified by **18**. The classical valence structure **18a** implies a diradical; however, the resonance structure **18b** clearly suggests a closed shell. The simple Hückel calculation gives a gap of



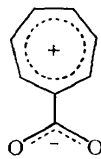
18a



18b



19



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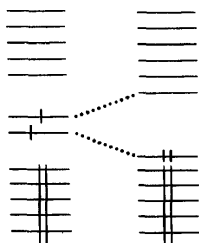
0.704 β between occupied and unoccupied levels. Nevertheless, according to our SCF calculations the ground state of **18** is a triplet, some 1.1 eV below the lowest singlet—the energy gap is thus not large enough for stabilization of the singlet state.

We noticed, however, that the highest occupied MO of **18** was an essentially localized nonbonding allyl orbital at C-1 and C-3, whereas the lowest

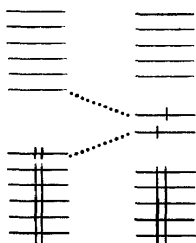
unoccupied MO was localized in the three-membered ring. Replacement of the methylene groups at C-1 and C-3 by oxygens produced the necessary selective stabilization of the highest occupied MO.

The ground state of cyclopropenium carboxylate, **19**, is computed to be a singlet, with a triplet state 1.0 eV above it. Similarly we find a singlet ground state for cycloheptatrienylium carboxylate **20**.

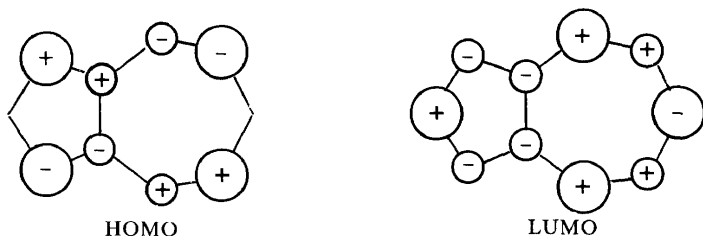
In the systems discussed above, as well as in some related work on stabilizing cyclobutadienes and cyclooctatetraenes¹¹, the basic strategy is the modification of the levels of a diradical toward that of a stable molecule, as shown schematically below. It occurred to us that it might be amusing to try



to pursue the converse strategy, i.e. so to modify by heteroatom replacement or substitution the levels of a stable molecule that it might be converted into a triplet ground state¹². The general pattern we wished to impose is shown below.



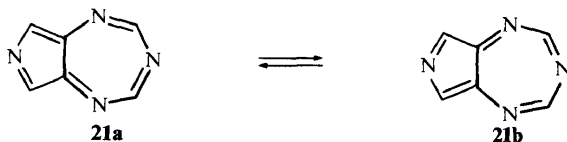
A little reflection indicates that nonalternants are likely candidates for this manoeuvre. Consider the highest occupied (HOMO) and lowest unoccupied (LUMO) π molecular orbitals of azulene, a perfectly stable molecule.



Note that HOMO and LUMO differ greatly in their electron distributions—HOMO has maxima of density at carbons 1, 3, 5 and 7; while LUMO has maxima at 2, 4, 6 and 8. If we now replace the CH groups at sites 2, 4, 6 and 8

8 by N then we would expect to lower the energy of LUMO while leaving HOMO more or less unaffected. We were very happy when a calculation showed this effect and predicted a triplet ground state for the tetraazaazulene. Destabilization of HOMO, stabilization of LUMO may also be achieved by substitution of a π donor, such as NH_2 , for H at positions 1, 3, 5 and 7 and a π acceptor, such as NO_2 , at 2, 4, 6 and 8.

However, we had underestimated the ingenuity of the molecule in evading the fate we had constructed for it. When we allowed the molecule to move away from C_{2v} symmetry it immediately returned to a singlet ground state by localizing double bonds¹³. The 2,4,6,8-tetraazaazulene **21** should thus not be a ground state triplet but, losing the aromaticity of the azulene parent, should exist in a real equilibrium between destabilized, double-bond-localized structures **21a** and **21b**.



In fact all our attempts to ruin the virtue of stable molecules met a similar fate—the molecule chose to localize double bonds rather than remain a delocalized triplet.

PLANAR TETRACOORDINATE CARBON

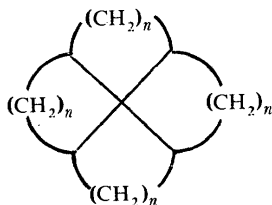
Attempts to subvert something as basic to organic chemistry as the tetrahedral tetracoordinate carbon atom should perhaps be viewed as acts appropriately described by the Yiddish word *chutzpah* and/or the Greek *hubris*. Nevertheless in some recent work with R. Alder and C. F. Wilcox¹⁴, this is precisely what we set out to do, namely to derive the conditions for stabilizing planar tetracoordinate carbon.

That molecules with a simple centre of chirality do not racemize spontaneously sets a lower limit of perhaps 60 kcal/mole for the energy of an achiral coordination geometry, such as the planar one, above the favoured tetrahedral form. Theoretical estimates of $\Delta E = E_{(\text{planar})} - E_{(\text{tetrahedral})}$ for CH_4 are much higher: 5.5 eV in an extended Hückel calculation¹⁴, 8.1 eV from CNDO/2¹⁴, 10.8 eV from an approximate SCF calculation¹⁵. We thus have to overcome a great preference for the tetrahedral geometry.

To those schooled in the philosophy of Aristotle or Mao Tse-tung it will not come as a great surprise that there are two ways in which ΔE can be lowered: either by destabilizing the tetrahedral form or stabilizing the planar one. No great ingenuity is required to write down molecules which will be very unhappy in a tetrahedral geometry, e.g. species such as **22** with $n < 3$. Creativity enters in the synthesis of such a highly strained system. We concentrated on the theoretically less obvious task of deriving the criteria for stabilizing the planar geometry.

Let me momentarily digress here on the role of theory in chemistry. Objectively viewed, the calculation of the electronic structure of molecules

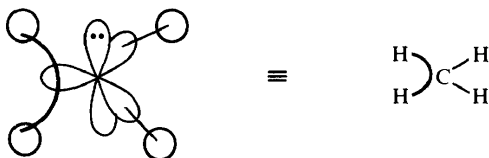
has not played a great role in the progress of chemistry. Our discipline remains an experimental science. Nevertheless there are a few areas where theory is in an absolute sense useful. I believe that we have such a case at hand.



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To obtain any experimental information on such an unstable species as square planar methane is impossible. But for a theoretician a calculation on a square planar methane is just as easy as a calculation on a tetrahedral conformation, and the results should be just as good (or bad). Of course the intelligent use of theory demands that we do not stop with the calculation of ΔE but that we examine closely the electronic structure of planar CH_4 in order to devise the optimum strategy for stabilizing the high energy conformation.

Let us begin the theoretical analysis of square planar methane in the valence-bond framework. We form a normal set of sp^2 hybrids at the carbon. Two hybrids engage in normal two-electron two-centre bonds with two hydrogens, using up two of the four carbon valence electrons. The third hybrid participates in a two-electron three-centre bond¹⁶ with the remaining two hydrogens. This three-centre bond utilizes only the hydrogen electrons. The remaining two valence electrons of carbon are placed in the $2p$ orbital perpendicular to the molecular plane, **23**. Resonance among equivalent structures with different



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relative placement of three-centre and two-centre C—H bonds achieves equivalence of all hydrogens. Alternatively the molecular orbitals of planar CH_4 are shown in *Figure 7*.

The following characteristics of a planar methane emerge from either procedure:

(1) All C—H bonds are weaker than in tetrahedral methane. In the valence-bond picture the three-centre C—H bonds have an approximate bond order of 1/2, leading to an average bond order for all C—H bonds of 3/4. In the MO picture it is clear that there are only six bonding electrons in planar CH_4 , while there are eight in tetrahedral CH_4 . This σ bond weakening cannot be cured, but we must plan to compensate for it in other ways.

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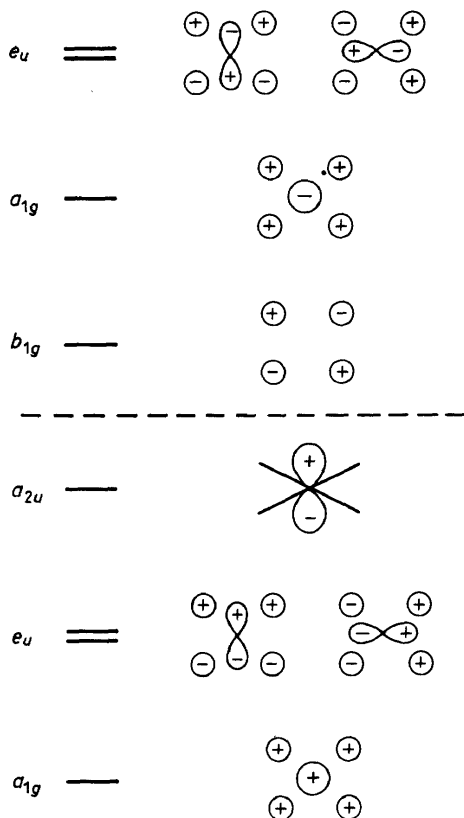


Figure 7. The molecular orbitals of planar methane. Levels below the dashed line are occupied. The representation of the e_u levels is of course not unique.

(2) There is considerable electron transfer from H to C. This is most apparent in the valence-bond scheme, where the three-centre bonding uses only hydrogen electrons, but locates considerable electron density on carbon.

(3) The planar carbon atom possesses a pure $2p$ lone pair perpendicular to the molecular plane.

(4) There are two obvious ways of transforming the tetrahedron into a square. These motions are shown in Figure 8. They may be described as

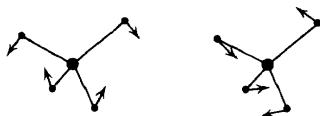
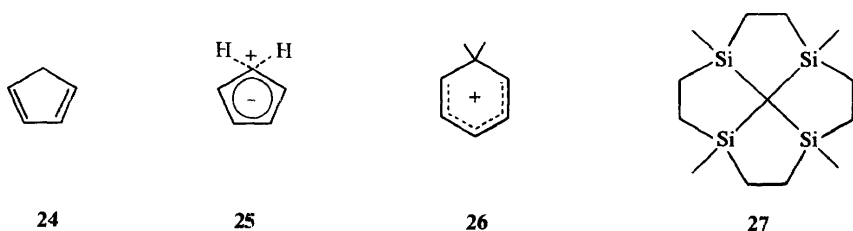


Figure 8. Two distortions of a tetrahedral methane which carry it over to a square planar geometry. 'Squashing' is shown at left, 'twisting' at right.

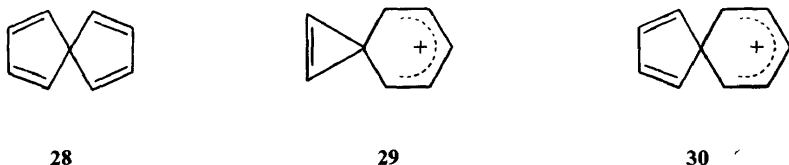
twisting ($T_d \rightarrow D_2 \rightarrow D_{4h}$) and squashing ($T_d \rightarrow D_{2d} \rightarrow D_{4h}$). Actually they both resemble the components of a degenerate normal mode of vibration, E symmetry, of tetrahedral methane. Given the molecular orbitals of square planar methane it can be shown that its transformation into tetrahedral methane is a symmetry-allowed process.

Conclusions 2 and 3 above are the departure points for our strategy. Delocalization of the lone pair may be accomplished by attaching substituents to carbon which are good electron acceptors, as in $C(CN)_4$. The planar-tetrahedral energy difference ΔE is reduced to 3.4 eV (this and all subsequent values of ΔE quoted are from extended Hückel calculations). Alternatively we may incorporate the lone pair as part of a $4n + 2 \pi$ -electron system, as in the planar geometry of cyclopentadiene, **24**. ΔE for **24** is 4.2 eV and the planar geometry is best described as a σ cation of an aromatic anion, **25**. In a model

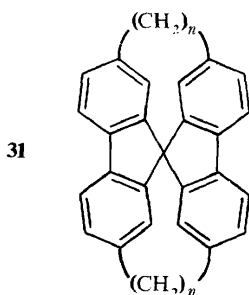


benzenonium ion **26** ΔE is reduced to 2.9 eV. Substitution of H by less electronegative groups lowers ΔE still further—in $C(BH_2)_4$ to 1.8 eV, in $C(SiH_3)_4$ to 2.9 eV. In the latter case $3d$ orbitals on Si were included; Si then acts as a σ donor and π acceptor. The hypothetical molecule **27** combines these factors with destabilization of the tetrahedral form. Further favourable effects of an electronegativity differential are observed on Li substitution or replacement of C by N^+ .

New types of stabilization in planar systems with tetracoordinate carbon may be probed with standard Hückel calculations. Thus the neutral spiro-nonatetraene **28** and the cations **29** and **30** in their planar geometries are stabilized 10, 8 and 10 π -electron systems respectively, superimposed on a positively charged σ core. Their highest occupied and lowest unoccupied

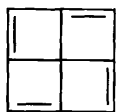


MOs are at $+0.62$ and -0.62β for **28**, $+0.37$ and -1.00 for **29**, $+0.62$ and -0.29 for **30**. In an extended Hückel calculation on **29** we find the tetrahedral form favoured by only 1.1 eV. Vespirenes, **31**, are interesting known chiral derivatives of **28**¹⁷.

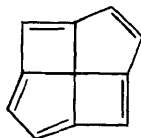


With the extra benzene rings in **31** the steric problems apparent already in the planar geometry of **28** are exacerbated. There is some indication of a twisting distortion in the vespirenes¹⁸; whether this is an indication of stabilization of near planar geometries remains to be seen.

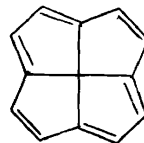
While it is difficult to define clearly the criteria for π stabilization in these species, it is clear that such stabilization must be significant in order to overcome the bond weakening in the σ system. As a preliminary criterion for stability we take the absence of nonbonding molecular orbitals, the occupation of only bonding orbitals and the presence of a sizable gap between highest filled and lowest unfilled molecular orbitals. Most obvious candidates,



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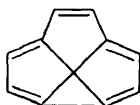


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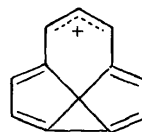
e.g. **32–34** fail one or the other of these tests. The best stabilized molecules we have found are **35–40** and especially the fascinating structures **41–43**.



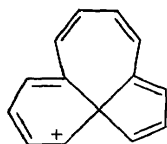
35



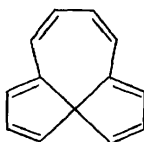
36



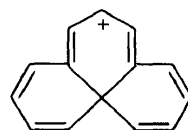
37



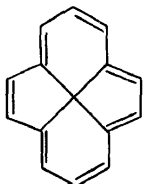
38



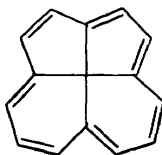
39



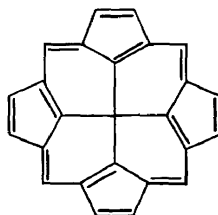
40



41



42



43

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