teraction, is found between the carbene p and adjacent orbitals. We find the lack of this node and clear stabilization for formyl-, nitro-, and cyanomethylenes. The cyanomethylenes are a case where as a result of required lack of discrimination between $p_o$ and $p_i$ both are stabilized. We think methoxycarbene is an example of a weak destabilization of $p_o$ by interaction with a high-lying occupied orbital—the oxygen lone pair. Fluoro- and difluoromethylenes are more drastic examples of destabilization of p by occupied nonbonding orbitals.

The case of cyclopropyl is puzzling. This is the only clear-cut case (the other minor one is methoxymethylene) where $p_o$ is destabilized more than $p_i$. A discriminating interaction with the two levels is easy to accept if one is aware of the theoretical and experimental evidence for $\pi$-like orbitals in cyclopropane. But that these levels should destabilize $p_o$ greatly implies that the interaction with the bonding Walsh level is considerably more efficient than with the antibonding. This is not apparent and we plan to investigate it further.

**Acknowledgment.** Our original interest in the electronic structure of methylenes was aroused by the exciting observations of E. Wasserman and coworkers. We are grateful for generous support of this work by the National Institutes of Health, the National Science Foundation, the Sloan Foundation, and the Chevron Research Company.

# Benzynes, Dehydroconjugated Molecules, and the Interaction of Orbitals Separated by a Number of Intervening σ Bonds

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*Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850.* *Received May 31, 1967*

**Abstract:** From a variety of molecular orbital methods we have deduced significant and specific interactions among radical lobes in the same molecule separated by a number of intervening $\sigma$ bonds. These are explored in detail for benzynes and didehydroconjugated molecules. The interaction (1) is shown to depend only on the orientation of the $\sigma$ bonds between the radical lobes and the orientation of the lobes themselves, not on the specific molecule; (2) factors into direct (through-space) interactions proportional to the direct overlap and indirect (through-bond) coupling dependent on significant vicinal *cis* and, more important, *trans* overlaps; and (3) leads to the simpler splitting patterns as shown in the text by compounds **1–6** (Figure 3) where S and A beneath the geometrical outline indicate whether the symmetric (S, $n_1 + n_2$) or the antisymmetric (A, $n_1 - n_2$) combination of radical lobes is at lower energy. For a through-bond interaction over an odd number of $\sigma$ bonds we give an argument for A falling naturally below S. The filling of A or S has a direct consequence on the stereochemistry of the reactions of the lowest singlet of these species.

Our calculations on benzynes and other dehydroconjugated molecules were stimulated by three experimental and one theoretical paper. In the first of these Berry and coworkers attempted to generate the *m*-benzyne and *p*-benzyne species.[1] At the same time we learned of some calculations on *o*-benzyne by Simmons.[2] The extended Hückel method makes it possible to do a calculation on any molecule desired, and the impedance to undertaking a series of calculations is not the ability to perform the computation but instead one's doubt as to the degree to which the calculation may be trusted.[3] To assuage this doubt it is useful to calibrate the reliability of the method for the series of molecules to be studied by examining how it performs for some known simpler member of the series. Unfortunately there was little that was exactly known about the geometry or electronic structure of even *o*-benzyne.[4–6]

Nevertheless some calculations were carried out on the three benzynes. The main point of interest in the results and the primary problem in the electronic structure of these species is the extent to which the two radical lobes, the two half-occupied lone pairs, interact or feel each other. As we will see below, such an interaction can be direct (through space) or through bond. The primary measure of interaction in quantum mechanics is the energy splitting between two levels which would be accidentally degenerate in the absence of any interaction. If one removes two hydrogens from a normal benzene molecule, there are left behind two $\sigma$ orbitals, approximately nonbonding. Common preconception takes these as $sp^2$ hybrids, but in fact their precise composition is (1) immaterial to the argument, and (2) in these calculations somewhat delocalized and quite different from $sp^2$ locally. Let us simply call them $n_1$ and $n_2$

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(1) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Letters*, 1003, 1011 (1965).

(2) H. E. Simmons, to be published; also H. E. Simmons, *J. Amer. Chem. Soc.*, 83, 1657 (1961).

(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); 40, 2745, 2474, 2480 (1964); *Tetrahedron*, **22**, 521, 539 (1966).

(4) For recent reviews on the chemistry of benzynes, see R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960); R. Huisgen in "Organometallic Chemistry," H. H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 36; J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961).

(5) The intermediacy of benzyne was established by the work of J. D. Roberts, H. E. Simmons, L. A. Carlsmith, and C. W. Vaughan, *J. Amer. Chem. Soc.*, **75**, 3290 (1953), and R. Huisgen and H. Rist, *Naturwissenschaften*, **14**, 358 (1954).

(6) R. S. Berry, G. N. Spokes, and R. M. Stiles, *J. Amer. Chem. Soc.*, **82**, 5240 (1960); **84**, 3570 (1962), and references therein.

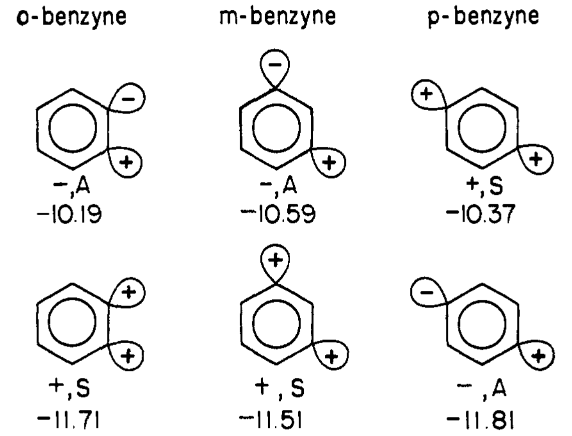


Figure 1. The nonbonding energy levels of the benzynes. +,S stands for the symmetric combination $n_1 + n_2$, −,A for the antisymmetric $n_1 - n_2$.

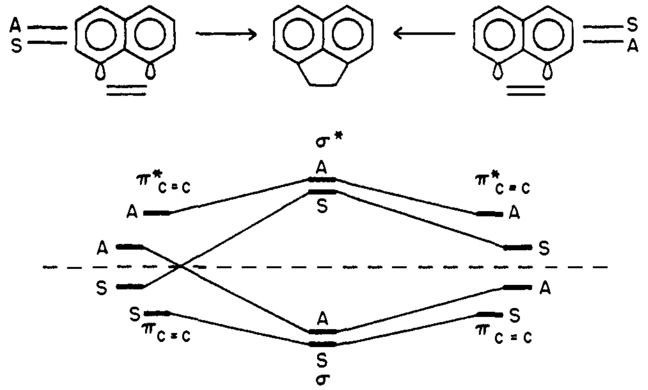


Figure 2. Level correlation diagrams for the addition of two possible kinds of 1,8-dehydronaphthalenes to ethylene. The right-hand diagram, that for the ordering A below S, gives rise to an allowed reaction.

to establish a mnemonic connection with the corresponding problem of the interaction of lone pairs in the diazines. The point groups of *o*-, *m*-, and *p*-benzyne are $C_{2v}$, $C_{2v}$, and $D_{2h}$, respectively, but to stress the common features of the interaction of $n_1$ and $n_2$ we will only use the twofold axis interchanging $n_1$ and $n_2$ as a classifying symmetry element, and the symbols S (symmetric) and A (antisymmetric) to describe the transformation properties. Thus from $n_1$ and $n_2$ one forms the symmetry adapted (but unnormalized) combinations

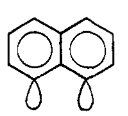
$$\text{S} \quad n_1 + n_2$$
$$\text{A} \quad n_1 - n_2$$

In the absence of any interaction between $n_1$ and $n_2$, S and A will be degenerate. If there is any interaction they will split in energy, and we will use the magnitude of the splitting $\Delta = E(\text{A}) - E(\text{S})$ as a measure of the extent of interaction. The results of the first extended Hückel calculations on the three benzynes are summarized in Figure 1.

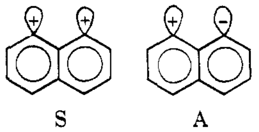
The splitting for *m*- and *p*-benzynes was surprising. For *o*-benzyne one anticipated a large direct interaction. Such an interaction would always place the positive overlap S molecular orbital below the A. The results here checked this point. For *m*-benzyne the direct overlap is much smaller and so while one might have expected S to come below A the observed splitting was larger than had been anticipated. For *p*-benzyne the direct overlap (over a distance of 2.8 Å) is minute. If, as one in ignorance supposed, the direct interaction were all that mattered, the splitting should have been correspondingly minute, but as small as it might be still putting the S MO below the A. The calculations remarkably showed a very large splitting with the antisymmetric combination A at lower energy than S.

Several years ago one of us carried out some extended Hückel calculations on pyridazine, pyrimidine, and pyrazine, as well as pyridine.[7] The diazines of course form a parallel series of compounds to the benzynes with what was an interaction between radical lobes in the latter, a two-electron problem, transformed into a four-electron problem, the interaction between two lone pairs, in the former. The interactions of the lone pairs in the diazines precisely paralleled in direction and magnitude the conclusions quoted above for the benzynes.[7a]

In early 1965, Rees and coworkers published their work on a most interesting reaction which could be rationalized by postulating the existence of a 1,8-dehydronaphthalene reactive intermediate.[8]



Accepting without any direct evidence the intermediacy of such a species, it was most interesting that it added *stereospecifically* 1,2 to olefins. In contrast *o*-benzyne, which does undergo 1,2 cycloadditions, when offered the opportunity prefers to add 1,4.[9,10] This behavior of *o*-benzyne is easily understood. If the molecule is a ground-state singlet with two electrons in the lower S orbital, then its electronic structure at the reactive site resembles another (partial) $\pi$ bond, *i.e.*, it is like an olefin. Using the selection rules previously derived for concerted cycloadditions[11] such an *o*-benzyne should in fact add in a concerted manner 1,4. Accepting the existence of a 1,8-dehydronaphthalene and its apparent concerted 1,2 addition we reasoned backward and concluded that of the two orbitals of this species the A combination had to be the lower. That



an A below S ordering would give allowed 1,2 addition but S below A would be forbidden is shown with the aid of correlation diagrams in Figure 2.

The ordering was surprising, particularly in view of our previous calculation for a 1,3-diradical *m*-benzyne, which gave the reversed pattern. A calculation was

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(7) R. Hoffmann, *J. Chem. Phys.*, **40**, 2745 (1964).

(7a) Note Added in Proof. The remarkable splitting of $S(a_1)$ and $A(b_2)$ lone-pair combinations in pyrazine has been also recently observed in *ab initio* calculations: E Clementi, *J. Chem. Phys.*, **46**, 4737 (1967). In the latter calculation A emerges more than 4 eV below S in one-electron energy!

(8) C. W. Rees and R. C. Storr, *Chem. Commun.*, 193 (1965).

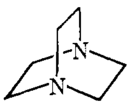
(9) R. G. Miller and R. M. Stiles, *J. Amer. Chem. Soc.*, **85**, 1798 (1963).

(10) G. Wittig, *Angew. Chem.*, **69**, 245 (1957).

(11) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

quickly carried out on 1,8-dehydronaphthalene and it clearly showed the expected ordering, A below S. This clear (but indirect) connection between a computation and reality reinforced our belief that the calculations were mirroring some actual facts of the electronic structure of these molecules. We proceeded to calculate a number of other dehydroconjugated molecules, and the results will be discussed below.

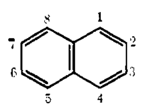
The third experimental stimulation came from some extremely interesting work on triethylenediamine (TED) and its radical cation by McKinney and Geske.[12] This radical cation is the first higher nitrogen radical in which one can be fairly confident that the lost electron comes from a nitrogen lone pair. The remaining electron serves *via* its spin resonance spectrum as a probe of the electron distribution in the molecule. In TED$^+$ were found equal hyperfine couplings with both nitrogen nuclei and the 12 protons. This can be interpreted in two ways: either the electron is in fact delocalized over the molecule or that it is jumping back and forth faster than the characteristic time of the spectrum. We would, of course, like to believe the former since it would be evidence for coupling of the two N lone pair orbitals, as well as delocalization of the spin density to the hydrogens. Another most interesting observation of McKinney and Geske concerned the parent molecule, TED. A vapor-phase ultraviolet spectrum of this molecule revealed a beautifully fine-structured series of absorption bands near 2550 Å, with $\epsilon \sim 1000$.[13] On examination, the literature revealed that saturated amine spectra had been grossly neglected and considered to be of no analytical value by organic chemists. The only pertinent work was a study of the uv spectra of some trialkyl amines by Tannenbaum, Coffin, and Harrison.[14] This showed some absorption and fine structure for triethylamine in the 2300-Å region, but the spectrum of TED remains uniquely red shifted from these compounds.



A calculation on TED clearly showed a large interaction of the two lone pairs, with the level ordering A below S, just as had been observed for *p*-benzyne and pyrazine. The allowed transition, n → $\sigma^*$ in character, was consequently red shifted from that in a normal amine. These calculations will also be described below, and they further reinforced our confidence in the level ordering.

## The Identification of the Basic Coupling Unit and Some Model Molecules

The splitting pattern for 1,8-dehydronaphthalene came out to be opposite to that calculated for *m*-benzyne, another 1,3 diradical. This implied some sort of molecular or conformational dependence of the interaction. Having the coordinates of a large number of aromatic systems from previous calculations, it was an easy matter systematically to remove two hydrogens from molecules I → VII.



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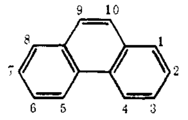

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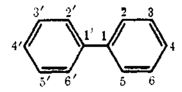

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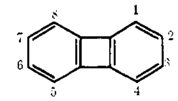

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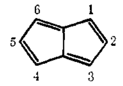

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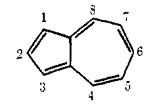

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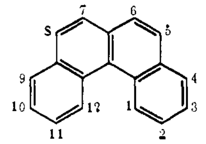

VII

In Table I below we list the observed interaction patterns. The S and A symbols of course do not strictly apply in cases where the symmetry is lacking (*e.g.*, 1,2-dehydronaphthalene). Nevertheless the combinations $c_1n_1 \pm c_2n_2$ with $c_1$ approximately but not precisely equal to $c_2$ are clearly recognizable.

**Table I.** Splittings between $n_1 + n_2$ and $n_1 - n_2$ for Some Dehydroaromatic Molecules

| Radical type | Molecule | Lower energy MO | Splitting, eV |
|---|---|---|---|
| 1,2 | *o*-Benzyne | S | 1.52 |
| | 1,2-I | S | 1.40 |
| | 2,3-I | S | 1.59 |
| 1,3 | *m*-Benzyne | S | 0.92 |
| | 1,3-I | S | 0.90 |
| | 1,8-I | A | −0.44 |
| | 1,6-V | A | −0.68 |
| | 1,8-VI | A | −0.52 |
| 1,4 | *p*-Benzyne | A | −1.44 |
| | 1,4-I | A | −1.49 |
| | 1,7-I | S | 0.38 |
| | 4,5-II | S | 0.50 |
| | 2,2′-III | S | 0.31 |
| | 4,5-I | S | 0.59 |
| | 1,5-I | A | −0.95 |
| 1,5 | 1,6-I | S | 0.06 |
| | 2,7-I | S | 0.48 |
| | 1,12-VII | S | 2.74 |
| 1,6 | 2,6-I | A | −0.57 |

The pattern that emerged was a fairly consistent one. Figure 3 shows some arrangements of radical lobes and intervening $\sigma$ bonds; the molecules of Table I can be classified according to the cases of Figure 3. For the *o*-benzynes in Table I (case **1** of Figure 3) S was below A. For 1,3-diradicals of the *m*-benzyne geometry (case **4**) S was also below A, but for those of the 1,8-dehydronaphthalene configuration (case **3**; 1,6-dehydropentalene, 1,8-dehydroazulene) the trend was reversed and A emerged below S. For 1,4 diradicals of the *p*-benzyne type (case **6**; 1,4-dehydronaphthalene) A was also below S, but for case **5** (4,5-dehydrophenanthrene, 2,2′-dehydrobiphenyl, 1,8-dehydrobiphenylene) S returned to below A. The consistency of the splittings given a specified local connectivity of the radical

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[12] T. M. McKinney and D. H. Geske, *J. Amer. Chem. Soc.*, **87**, 3013 (1965).

[13] The spectrum has also been independently observed by Cookson in connection with R. C. Cookson, J. Henstock, and J. Hudec, *ibid.*, **88**, 1060 (1966).

[14] E. Tannenbaum, E. M. Coffin, and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953).

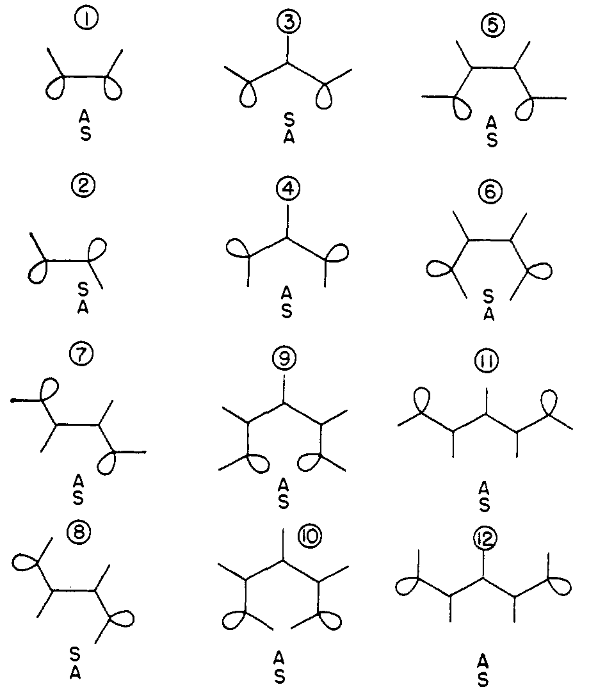

Figure 3. Some model arrangements of orbital lobes and intervening $\sigma$ bonds. The symbols below each case give the ordering obtained on model compounds.

lobes and its independence of the actual molecule in which the local unit was embedded made us try to simplify the study by calculating the electronic structures of a set of simplest model molecules for cases **1**–**12**: *cis*- and *trans*-dehydroethylenes ($C_2H_2$), *cis,cis*- and *trans,trans*-1,3-dehydroallyls-($C_3H_3$), *cis,cis*- and *trans,trans*-1,4-dehyrobutadienes ($C_4H_4$) in *s-cis* and *s-trans* forms; and *cis,cis*- and *trans,trans*-1,5-dehydropentadienyls ($C_5H_5$) in both U- and W-shaped geometries. This series of extended Hückel calculations was in fact based on some realistic geometries for the parent hydrocarbons: C–C 1.34 for cases **1** and **2**, 1.45 for cases **3**, **4**, **7**, **8**, **9**, **10**, and 1.34 and 1.48 Å for cases **5** and **6**. HCH and CCC angles were taken throughout at 120° and C–H at 1.10 Å. The parameters are those of ref 3 except for a hydrogen Slater exponent of 1.3. Some *cis–trans* configurations were also studied. The results are summarized in Table II. The model compound interaction patterns agree with those of the dehydroconjugated molecules. Thus the interaction is a function only of the $\sigma$ orbitals in the vicinity of the radical lobes and is not dependent on the specific molecule. Our further attempts to understand *why* the interaction sometimes puts S and sometimes A at lower energy will be then confined to the model compounds.

**Table II.** Interaction Patterns in Model Compounds **1–12**

| Compd | Lower energy MO, eV | | Higher energy MO, eV | | $\Delta = E(A) - E(S)$, eV |
|---|---|---|---|---|---|
| **1** | S | −12.382 | A | −10.773 | 1.61 |
| **2** | A | −13.948 | S | −9.716 | −4.23 |
| **3** | A | −11.924 | S | −11.659 | −0.26 |
| **4** | S | −12.364 | A | −11.149 | 1.21 |
| **5** | S | −11.805 | A | −11.344 | 0.46 |
| **6** | A | −11.791 | S | −11.084 | −0.71 |
| **7** | S | −11.611 | A | −11.554 | 0.06 |
| **8** | A | −12.128 | S | −10.798 | −1.33 |
| **9** | S | −12.755 | A | −10.183 | 2.58 |
| **10** | S | −11.781 | A | −10.391 | 1.39 |
| **11** | S | −11.821 | A | −11.726 | 0.10 |
| **12** | S | −11.870 | A | −11.334 | 0.54 |

## Calculations Using Linear Combinations of Hybridized Molecular Orbitals

To obtain an independent numerical check on the peculiar splitting patterns obtained by extended Hückel calculations we have investigated the model compounds **1**–**6** by another method capable of treating the $\sigma$ systems of molecules. This is the hybridized molecular orbital method which was originally introduced by Sandorfy[15] and extensively applied to organic molecules by Fukui and coworkers.[16] In our calculations the Coulomb integrals were taken from Fukui's work,[16] and the resonance integrals were estimated for *all* pairs of atomic orbitals assuming a proportionality of the resonance integral to the corresponding overlap integral, *i.e.*

$$\beta_{ij} = \beta_0 \frac{S_{ij}}{S_0}$$

where $\beta_0$ is the standard resonance integral between two $sp^2$ hybrids on adjacent carbons directed toward each other, and $S_0$ is the corresponding large overlap integral. In constructing the secular determinant, however, we neglected all off-diagonal overlap integrals.

In the resulting molecular orbitals—linear combinations of $sp^2$-hybridized carbon orbitals and 1s hydrogen orbitals—the symmetric and antisymmetric nonbonding orbitals of interest to us were easily recognizable. Their deviation from the nonbonding energy was always small enough so that they were the highest occupied and lowest unoccupied orbitals of the system. While the MO's were somewhat delocalized, these characteristic orbitals had by far the larger coefficients for the two nonbonding orbitals. Table III shows the calculated location of these energy levels.

**Table III.** Energy Levels and Symmetries of Highest Occupied and Lowest Unoccupied Molecular Orbitals Obtained from Fukui-Sandorfy Calculations[a]

| Model molecule | Energy Levels S | Energy Levels A | $\Delta = E(A) - E(S)$ | Symmetry of HOMO |
|---|---|---|---|---|
| **1** | 0.1180 | 0.2632 | +0.1452 | S |
| **2** | 0.4013 | −0.1671 | −0.5684 | A |
| **3** | 0.2743 | 0.1269 | −0.1474 | A |
| **4** | 0.0563 | 0.3729 | +0.3166 | S |
| **5** | 0.1740 | 0.2636 | +0.0896 | S |
| **6** | 0.2495 | 0.2146 | −0.0349 | A |

[a] Energies are in units of $\beta_0$.

In every case the splitting pattern parallels that obtained from extended Hückel calculations. Since this method of calculation is quite different from extended Hückel theory we think that the observed correspondence of the results of the two numerical experiments reflects a real physical fact. The magnitudes of $\Delta$ also

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(15) C. Sandorfy, *Can. J. Chem.*, **33**, 1337 (1955).

(16) K. Fukui, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jap.*, **34**, 442, 1111 (1961); K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura, and C. Nagata, *ibid.*, **35**, 38 (1962).

show a correlation between the two methods, except for models **5** and **6**.

The extended Hückel method is not very well adapted to the obvious procedure that suggests itself for probing the role of various interactions: drop some interactions and see how the splitting is affected. The reason is twofold; if the interactions dropped are sizable the artifact of linear dependence and level inversion may be introduced; also the transformation properties may be affected. On the other hand the Fukui–Sandorfy calculations are quite convenient for picking out significant interactions in this manner.

In the first series of calculations we dropped only the direct interaction from a whole molecule calculation, with the results of Table IV. We also calculated the splittings, $\Delta = E(\mathrm{A}) - E(\mathrm{S})$, for the isolated direct interaction of the two radical lobes. The results may be found in the third column of Table V and are there compared with the Δ's obtained when the direct interaction is dropped and with those of the whole molecule.

**Table IV.** Fukui–Sandorfy Calculations with *Only* the Direct Interaction Dropped

| Model molecule | Energy levels | | $\Delta = E(\mathrm{A}) - E(\mathrm{S})$ | Symmetry of highest occupied MO |
|---|---|---|---|---|
| | Sym | Anti | | |
| **1** | 0.24202 | 0.16747 | −0.07455 | A |
| **2** | 0.26831 | −0.01676 | −0.28507 | A |
| **3** | 0.31342 | 0.07075 | −0.24267 | A |
| **4** | 0.06647 | 0.36094 | +0.29447 | S |
| **5** | 0.22562 | 0.21022 | −0.01540 | A |
| **6** | 0.25796 | 0.20465 | −0.05331 | A |

**Table V.** Comparison of Fukui–Sandorfy Calculations for Only Direct Interaction Dropped, Isolated Direct Interaction, and Total Molecule Calculations

| Model molecule | Δ direct interact, dropped | | Δ direct | | Δ total | |
|---|---|---|---|---|---|---|
| **1** | −0.0746 | A | +0.3164 | S | +0.1452 | S |
| **2** | −0.2851 | A | −0.3386 | A | −0.5684 | A |
| **3** | −0.2427 | A | +0.1376 | S | −0.1474 | A |
| **4** | +0.2945 | S | +0.0348 | S | +0.3166 | S |
| **5** | −0.0154 | A | +0.1684 | S | +0.0896 | S |
| **6** | −0.0533 | A | +0.0296 | S | −0.0349 | A |

First of all, it is a direct consequence of the assumptions of the method that the location of the two energy levels in the case of the isolated direct interaction depends on the sign of the overlap integral, and their separation is directly proportional to the magnitude of the overlap. Significant direct interactions are present in cases **1**, **2**, **3**, **4**, and **5**. The sign of the direct interaction in case **2** will be discussed in detail below. Second, the "direct interaction only" and "direct interaction dropped" columns sum approximately to the "total molecule" calculation. The contributions are sometimes of the same sign and sometimes competitive. The approximate summability supports the idea that the total interaction can be partitioned into direct (through-space) and indirect (through-bond) contributions. In case **1** the two are of opposite sign and the direct interaction wins out; in case **2** the effects reinforce to create a large splitting in favor of A. In case **3** they compete again but the indirect interaction dominates, whereas in case **4** they operate in the same direction. In case **5** they are opposite in sign but the direct interaction is large and dominates. In case **6** the contributions are once again opposite in sign, both small, and the indirect coupling is the larger.

In another series of calculations we have used a perturbation approach to study the relative contributions of the direct (through-space) and indirect (through-bond) interaction of the nonbonding orbitals. First, only the direct interaction was taken into account. The results are the first entries in Table VI. We then calculated the energy levels of the system with the two nonbonding orbitals missing and used perturbation theory to study the effect of the interaction between the nonbonded orbitals and the rest of the $\sigma$ system. The change in energy of the nonbonded levels is given to second order by the expression

$$\Delta E_i = 2\sum_{\mathrm{all}\,j} \frac{(C_{j1}\beta_1 + C_{j2}\beta_2 + \cdots + C_{jn}\beta_n)^2}{E_i - E_j}$$

where $i$ denotes the nonbonding MO and $j$ is one of the remaining levels. $E_j$ is the energy of the $j$th MO for the system without the nonbonding orbitals, $C_{jk}$ is the coefficient of the $k$th atomic orbital in the $j$th molecular orbital, and $\beta_k$ is the resonance integral between the $k$th AO and one of the nonbonding hybridized orbitals. In this formula if $i$ denotes the symmetric MO, then the summation covers only the symmetric levels, and if $i$ is antisymmetric, $j$ goes over only the antisymmetric levels. Two procedures were tried, to be called PT1 and PT2. In the first the nonbonded levels were allowed to interact directly and then the perturbation applied. The $E_i$ are then the first entries in Table VI. In PT2 the perturbation was applied before the direct interaction, *i.e.*, $E_i$ in the perturbation formula was 0.0 for both S and A levels. The results are also shown in Table VI. The main significance of the perfect agreement in ordering and satisfactory agreement in magnitude between PT1 or PT2 and the total MO calculation is that it makes sense to partition the observed splittings into an effect of a direct coupling plus an interaction with all the other $\sigma$ and $\sigma^*$ bonds, *i.e.*, a through-bond coupling. The effects are comparable in size since in model compounds **3** and **6** through-bond coupling is sufficiently strong to overcome the direct effect.

We have also noticed the following trend in the contributions of individual orbitals to the perturbation sum. There is a general but imperfect trend for lower energy orbitals to contribute more to the perturbation sum than higher energy orbitals. This contribution is mainly through larger numerators in the perturbation sum. This is true for both antisymmetric and symmetric levels (with the exception of A of model **2**) and manifests itself in Table VI in the destabilization of both S and A with respect to the nonbonding energy line. We attribute this effect to the more efficient overlap of $n_1 \pm n_2$ with framework orbitals with less nodes (bonding). The fewer nodes in the orbital, the fewer changes of sign in the numerator of the perturbation sum, and so the larger the numerator for those levels.

**Table VI.** Contribution of the Direct and Indirect Interactions Evaluated from Perturbation Theory

| Model | | I, direct interaction | II, indirect PT1 | III, total I + II | IV, indirect PT2 | V, total I + IV | VI, MO calculation |
|---|---|---|---|---|---|---|---|
| **1** | S | −0.1582 | 0.4488 | 0.2905 | 0.3241 | 0.1659 | 0.1180 |
| | A | 0.1582 | 0.1735 | 0.3317 | 0.2859 | 0.4442 | 0.2632 |
| **2** | S | 0.1693 | 0.2958 | 0.4652 | 0.3486 | 0.5180 | 0.4013 |
| | A | −0.1693 | 0.0024 | −0.1669 | −0.0189 | −0.1882 | −0.1671 |
| **3** | S | −0.0688 | 0.7224 | 0.6537 | 0.6102 | 0.5415 | 0.2743 |
| | A | 0.0688 | 0.0712 | 0.1400 | 0.0881 | 0.1569 | 0.1269 |
| **4** | S | −0.0174 | 0.1474 | 0.1301 | 0.1254 | 0.1081 | 0.0563 |
| | A | 0.0174 | 0.5701 | 0.5874 | 0.5863 | 0.6037 | 0.3729 |
| **5** | S | −0.0842 | −1.2780 | −1.3622 | 0.4969 | 0.4127 | 0.1740 |
| | A | 0.0842 | 0.3113 | 0.3955 | 0.4496 | 0.5338 | 0.2636 |
| **6** | S | −0.0148 | 0.6208 | 0.6060 | 0.5847 | 0.5699 | 0.2495 |
| | A | 0.0148 | 0.2961 | 0.3109 | 0.3038 | 0.3186 | 0.2146 |

## SCF Calculations

To verify further the reality of the interaction patterns we have also carried out some self-consistent field Hartree–Fock–Roothaan calculations with limited Gaussian basis sets on model compounds **1**, **2**, **3**, and **4**. The program used was POLYATOM, kindly made available by the former MIT group through the Quantum Chemistry Program Exchange.[17]

For $C_2H_2$ we used a 532 basis set (five s-type Gaussians on each C, three p-type for $p_x$, $p_y$, $p_z$ on C, 2 s-type orbitals on each H) for a total of 32 orbitals. The exponents were taken from some previous work[18] as Cs: 0.32, 1.60, 8.40, 200; Cp: 0.1852, 0.9259, 4.63; Hs: 0.27, 1.80. The geometries studied were those of models **1** and **2**, with C–C 1.40 Å, C–H 1.10 Å; angle HCH 120°. Examining one-electron energies makes little sense in an SCF procedure because whichever orbitals are occupied are forced to be bonding. So utilizing the same set of integrals we carried out the closed-shell SCF procedure twice—once with A doubly occupied, the other time with S doubly occupied. The total electronic energies (*i.e.*, not including nuclear repulsions) are

| | | | |
|---|---|---|---|
| model **1** | *cis* | $(S)^2$ | −98.7146 au |
| | | $(A)^2$ | −98.5052 |
| model **2** | *trans* | $(S)^2$ | −98.3370 |
| | | $(A)^2$ | −98.7214 |

Thus for **1** the configuration $(S)^2$ is at lower energy by 0.2094 au, while for **2** $(A)^2$ is lower by 0.3844 au. The preferences agree exactly with those obtained from semiempirical methods. We also carried out these calculations with smaller 321 basis sets and whereas the total energy was about 3 au poorer with the smaller basis set the difference between the $(S)^2$ and $(A)^2$ configuration energies was changed by only 0.01 au!

Models **1** and **2** are nothing other than bent and stretched acetylenes. There are available several SCF calculations on these and they again check that S is occupied in **1**, A in **2**.[19] There are also some Gaussian SCF calculations on *cis*- and *trans*-diimide, $N_2H_2$.[20] This molecule is the four-electron case comparable to our two-electron models, and the calculations show the ordering S below A for *cis*, A below S by still more for *trans*.

For models **3** and **4** we were constrained to a rather poor 321 basis set (exponents Cs: 0.6047, 5.0990, 42.98; Cp: 0.2469, 1.4810; Hs: 0.38) which for $C_3H_3$ added up to 30 orbitals. We were here faced with specifying a closed-shell state for completing the calculation, and we chose to study both $(S)^2$ and $(A)^2$ singlets of $C_3H_3^+$ and $C_3H_3^-$, *i.e.*, didehydroallyl cation and anion. The geometries were again idealized, with C–C distances of 1.40 Å, C–H 1.10 Å; all angles 120°. The total electronic energies were

| | | | |
|---|---|---|---|
| model **3** | $C_3H_3^+$ | $(S)^2$ | −161.7831 au |
| | | $(A)^2$ | −161.8532 |
| | $C_3H_3^-$ | $(S)^2$ | SCF diverged |
| | | $(A)^2$ | −162.0037 |
| model **4** | $C_3H_3^+$ | $(S)^2$ | −162.4308 |
| | | $(A)^2$ | −162.2842 |
| | $C_3H_3^-$ | $(S)^2$ | −162.6249 |
| | | $(A)^2$ | −162.4662 |

Thus model **3** favored the configuration $(A)^2$ over $(S)^2$ in $C_3H_3^+$ by 0.0701 au; model **4** favored $(S)^2$ by 0.1466 au in $C_3H_3^+$ and 0.1587 au in $C_3H_3^-$. Again the results confirm the semiempirical calculations.

## Through-Space *vs.* Through-Bond Interaction

Consider two normalized, equivalent orbitals, $\phi_1$ and $\phi_2$, interacting *via* a Hamiltonian $H$. The energy levels of the system after the interaction are given by

$$E_\pm = \frac{H_{11} \pm H_{12}}{1 \pm S_{12}}$$

where $H_{ij} = \int \phi_i^* H \phi_j \, d\tau$ and $S_{12} = \int \phi_1^* \phi_2 \, d\tau$. The splitting of the two orbitals is given by

$$\frac{2H_{12}}{1 - S_{12}^2}$$

(if the energy zero is taken as $H_{11}$) and its sign is determined by the sign of $H_{12}$. For all molecular systems which we know, $H_{12}$ has the opposite sign to the overlap integral $S_{12}$. A proportionality of $H_{12}$ to $S_{12}$ of the type normally assumed in extended Hückel calculations does not in fact hold absolutely for real interactions, but the sign relation seems to be universal for electronic interaction. In turn this implies that the positive overlap combination in the case of a direct, through-space interaction will always be put at lower energy. Since

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(17) The POLYATOM program was authored by I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, S. Seung, B. T. Sutcliffe, and M. P. Barnett, MIT, Cambridge, Mass., 1965.

(18) J. W. Moskowitz and M. C. Harrison, *J. Chem. Phys.*, **42**, 1726 (1965).

(19) L. Burnelle, *ibid.*, **35**, 311 (1961).

(20) M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Amer. Chem. Soc.*, **89**, 1564 (1967).

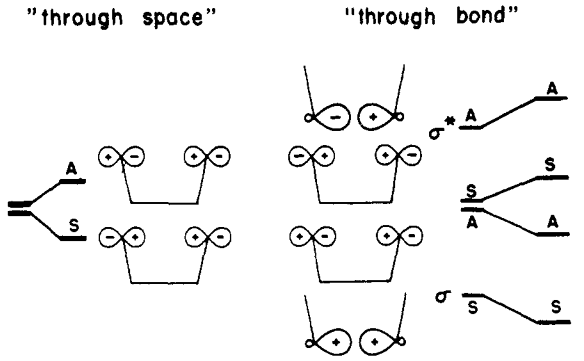
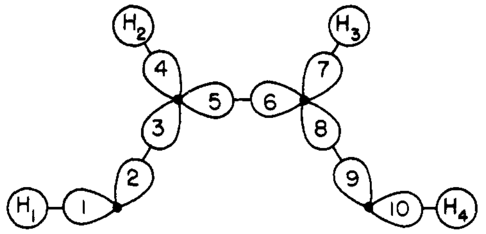


Figure 4. Through-bond *vs.* through-space coupling over three σ bonds. See text for explanation.



overlaps (>0.06)

| | | | |
|---|---|---|---|
| 1–3 | 0.1226 | 2–8 | 0.0631 |
| 1–4 | 0.1180 | 2–9 | 0.0628 |
| 1–5 | −0.1263 | 1–$H_1$ | 0.6795 |
| 2–3 | 0.7458 | 2–$H_1$ | 0.0818 |
| 2–6 | 0.1961 | 3–$H_1$ | 0.1534 |

Figure 5. A trigonal chain of carbons and hydrogens, C–C 1.40 Å, C–H 1.10 Å. An sp$^2$-hybridized basis set is formed and overlaps evaluated between hybrids. The figure lists all over-laps greater than 0.06.

there is a well-established general quantum mechanical correlation between increasing energy and increasing number of nodes in a wave function, the association of positive overlap with lower energy is hardly surprising.

Is it then possible that an antisymmetric, noded combination such as $n_1 - n_2$ can emerge at lower energy than the symmetric combination, $n_1 + n_2$, which appears to have less nodes? The answer is, yes, if $n_1 + n_2$ and $n_1 - n_2$ interact in different ways with other available orbitals.

Consider the case of $n_1 \pm n_2$ and three intervening σ bonds illustrated in Figure 4. For the moment let us single out the 2–3 σ-bond orbitals and construct a "before–after" picture of their interaction with $n_1 \pm n_2$. It will be useful to classify all levels with respect to the twofold axis which passes through the 2–3 bond and interchanges $n_1$ and $n_2$. With respect to this axis $n_1 + n_2$ is S and $n_1 - n_2$ is A, while the 2–3 σ orbital is S and the 2–3 σ* is A. The fact that we chose to represent the 2–3 bond as the overlap of two unspecified hybrids is only a matter of convenience—the only *real* thing about the σ orbital is that it concentrates electron density between 2 and 3, with approximate cylindrical symmetry around the 2–3 axis, and that it is symmetric with respect to the above-defined twofold axis or a mirror plane intersecting the 2–3 axis. In turn the only *real* properties of the σ* orbital are similar to those described for σ except that it is antisymmetric with respect to the axis or plane, *i.e.*, it has an obvious node between atoms 2 and 3.

Returning to Figure 4 we now allow the four orbitals to interact. The standard restriction is that only orbitals of like symmetry interact with each other. These "repel" each other, regardless of the sign of the interaction. Thus $n_1 + n_2$, which is of S symmetry, mixes with σ, and as a result of the interaction moves to higher energy. On the other hand, $n_1 - n_2$, which is of A symmetry, mixes not with σ but with σ* and is forced to lower energy as a consequence of that interaction. The magnitude of the shifts is a function of the overlap of $n_1 \pm n_2$ with σ or σ*, and we will return to this shortly. However the direction of the interaction is unambiguous; $n_1 - n_2$ emerges at lower energy than $n_1 + n_2$.

At this point one could legitimately ask: Why single out the 2–3 σ bond? Why not let the 1–2 and 3–4 bonds mix as well, also the C–H bonds from atoms 2 and 3? The answer is that one can allow these bonds to enter the interaction scheme, but that they will not change the general splitting pattern. The reason for this is that while the 2–3 bond is uniquely located on the axis, the other bonds (1–2 and 3–4 say) always enter in symmetry-related pairs. Thus 1–2 and 3–4 yield an S and A pair of σ orbitals and an S and A pair of σ* orbitals. In the first approximation the effect on $n_1 + n_2$ of having one S level below it and one above it will cancel out. More precisely if one has a large, odd number, say $2N + 1$, of intervening σ bonds between $n_1$ and $n_2$, we would not like to say that it is the central bond only which causes the splitting of $n_1 + n_2$ and $n_1 - n_2$. Rather it is that below the nonbonding orbitals $n_1$ and $n_2$ there are $N + 1$ Sσ levels, but above them are $N$ Sσ* levels. It is likely then that the nonbonding S combination, $n_1 + n_2$, will be destabilized by interaction with all the σ and σ* levels of like symmetry. On the other hand below $n_1 - n_2$ there are $N$ Aσ levels but above it are $N + 1$ Aσ* levels; it is likely that as a result $n_1 - n_2$ will be stabilized by interaction with the greater number of A levels above it. The general result of this argument is: *through-bond coupling over an odd number of intervening σ bonds will always place $n_1 - n_2$ below $n_1 + n_2$.*

There is another factor in the through-bond coupling which must be considered. It is the more effective overlap of $n_1 \pm n_2$ with bonding levels below than with antibonding levels above, and we have already discussed this in a previous section. This preferential interaction destabilizes both A and S and is most readily apparent in the results of the Fukui–Sandorfy calculations in Table III. Thus a more accurate statement of our conclusions would be: as a result of through-bond coupling over an odd number of σ bonds both S and A are destabilized, but S is destabilized more than A.

We now return to the question of the magnitude of the interactions, which we propose to measure approximately by the magnitude of the overlap. Figure 5 shows some sp$^2$ hybrids, disposed in a chain with 120° angles and at C–C distances of 1.40 Å. Some of the overlaps evaluated with a carbon Slater exponent of 1.625 for 2s and 2p are also indicated in this figure. The largest overlaps, of course, are the optimally oriented types 2–3 which lead to σ and σ* levels. Particularly significant are the signs and magnitudes of the 1–3, 1–4, 1–5, and 2–6 overlaps. Probably the

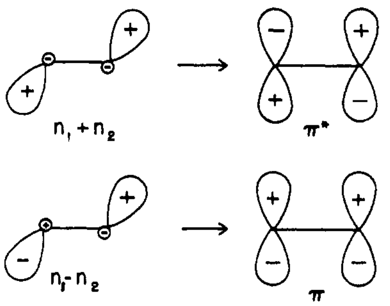


Figure 6. An illustration showing how the A orbital of *trans*-dehydroethylene transforms into $\pi$ of acetylene, and S goes over to $\pi^*$.

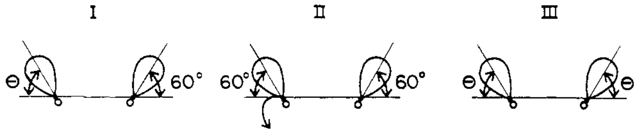


Figure 7. Three relative motions of two vicinal C hybrids at a C–C distance of 1.40 Å. In I (left) one $sp^2$ hybrid is fixed at a 60° angle from the internuclear axis while the other one is moved toward the axis, all in plane. In II (center) both $sp^2$ hybrids are at 60° and then one is rotated around the C–C axis away from coplanarity. In III (right) two $sp^3$ hybrids, coplanar, are both bent toward the axis through the same angle.

most nonintuitive result is that the *trans* 1–5 overlap is negative and in fact in magnitude slightly larger than the *cis* 1–4 overlap. We urge the reader to convince himself of this fact by evaluating the overlap integral between the hybrids by decomposing them into the basic (2s|2s), (2s|2p$\sigma$), (2p$\sigma$|2p$\sigma$), and (2p$\pi$|2p$\pi$) overlap integrals. The values (chosen positive) for the seare respectively 0.407, 0.413, 0.331, and 0.244 at the specified distance and exponent. The overlaps calculated show that one cannot always trust one's intuition as to the size and sign of an overlap guessed from the direction and extent of two hybrids.

The negative sign of the 1–5 overlap implies that considering only direct coupling in say a *trans*-dehydroethylene (Figure 6) the symmetric combination $n_1 + n_2$ (negative overlap) will be at higher energy than the antisymmetric $n_1 - n_2$ (positive overlap). This has been previously pointed out by Robin and Simpson.[21] Another way to see that this is reasonable is to think of the distortion of the *trans*-dehydroethylene to what it would really like to be, an acetylene. As this distortion occurs $n_1 + n_2$ becomes $\pi^*$ but $n_1 - n_2$ becomes $\pi$ of the acetylene.

The general magnitudes of the vicinal overlaps (1–3, 1–4, 1–5) are approximately 0.1. Of then onvicinal overlaps only 2–6 is significant. Thus the primary effects in through-bond coupling will be a consequence of the vicinal overlaps. A consequence of this model is that the splitting of two coupled nonbonded orbitals will be somewhat insensitive to rotation around the unique central $\sigma$ bond but quite sensitive to rotations around all the other $\sigma$ bonds. Since the vicinal overlaps are $^1/_6$ of the $\sigma$-bond overlap (2–3) it is not surprising that the $n_1 \pm n_2$ splittings obtained by through-bond coupling are of the order of 0.1–1.0 eV.

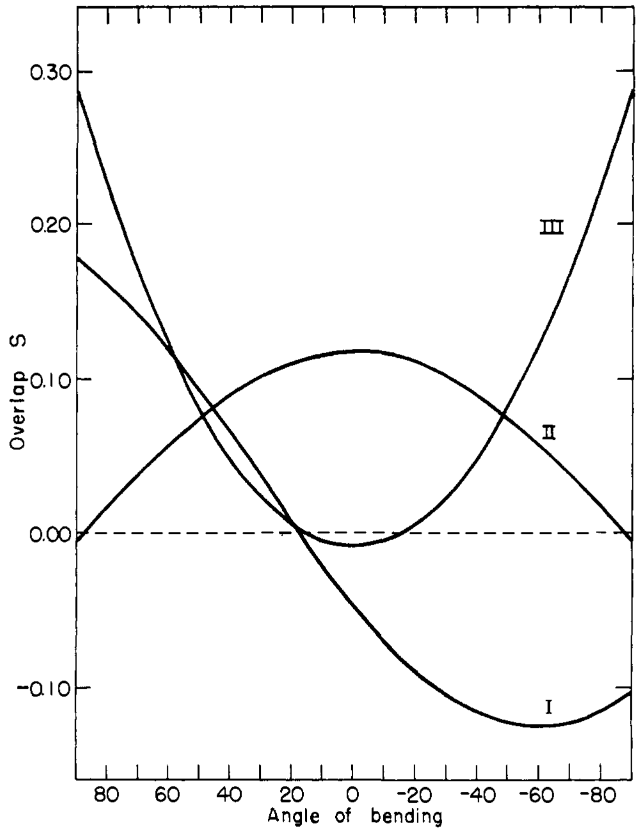


Figure 8. Overlaps for the motions described in Figure 7.

The sensitivity of the interaction to bending and rotation may be approximately probed by studying the dependence of the vicinal overlap of two hybrids on adjacent carbons on their orientation. Three motions are characteristic (Figure 7). In the first (I) we have taken two $sp^2$ hybrids, kept one fixed at a 60° angle with respect to the internuclear axis, and varied the orientation of the other hybrid in plane (left side of Figure 7). In the second motion we began again with two $sp^2$ hybrids, both at an angle of 60° with respect to the internuclear axis, and now we rotated one of them out of plane around the internuclear axis (II, center of Figure 7). In III (right side, Figure 7) we took two $sp^3$ hybrids both making an angle $\theta$ with respect to the internuclear axis and simultaneously bent them both in the same plane. The results are plotted in Figure 8. The overlap in motion I decreases rapidly as the other hybrid is bent from 60°, goes to zero at about 18° (on the *cis* side), and then becomes increasingly negative, with a maximum magnitude overlap at $-60°$ *trans*. A given amount of strain imposed on one of two hybrids would be thus expected to have a significant effect on their interaction, particularly on the *cis* side. Motion II illustrates that the interaction is very sensitive to a rotation around the internuclear axis, and goes to zero when the hybrids lie in perpendicular planes. III is another probe of bending of hybrids. If strain is imposed on both centers so that they are both pinned back, then the interaction is sharply and seriously diminished. A colinear interaction is very small.

We feel we now understand the pattern of interaction in at least model compounds **1**, **2**, **5**, and **6** of Figure 3. In each of these the primary through-bond coupling puts A below S. In **6** the direct interaction is essentially

(21) M. B. Robin and W. T. Simpson, *J. Chem. Phys.*, 36, 580 (1962).

negligible and the splitting is due mainly to the indirect coupling. In **5** and **1** the direct coupling is strong enough to overcome the indirect stabilization of A. In **2** the direct coupling also favors A, creating the largest splitting observed. Case **9** is also an instance of a large direct coupling.

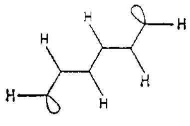
Of the simple systems cases **3** and **4** remain most puzzling. When two orbitals are separated by an even number of $\sigma$ bonds then there is no unique $\sigma$ bond which couples with $n_1 + n_2$ and not $n_1 - n_2$. There is a bond which sits on the symmetry axis—the C–H bond on the central carbon. But both $\sigma$ and $\sigma^*$ levels of this C–H bond have the same symmetry properties; they mix with $n_1 + n_2$ and not $n_1 - n_2$. The perturbation treatment carried out earlier shows that this C–H bond is a most important contributor to the interaction, but we do not have a simple interpretation of its action.

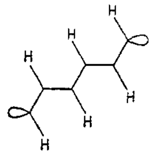
Returning to the reactions of the dehydro conjugated systems we make no prediction here as to the true ground state of the species. It seems likely that the better candidates for a possible singlet ground state are systems **1** and **6**, especially where one can enhance the coupling by building in the same feature twice (*p*-benzyne) or three times (the 1,4 diradical of bicyclo[2.2.2]-octane).

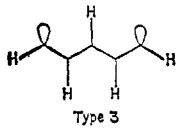
The lowest singlet state of every system with S below A may add in a concerted manner 1,4 or 1,8, etc., to a polyene, while every case with A below S may add 1,2 or 1,6 or 1,10, etc. Since cases **2**, **4**, and **6** would require a long polyene to reach around, they are unlikely partners for cycloaddition. It would seem to us profitable to search for additional examples of 1,3 diradicals such as case **3**, and to try to confirm the prediction that a case **5** molecule, such as 4,5-dehydrophenanthrene, should undergo stereospecific 1,4 additions.

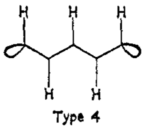
## The Distance Dependence of Through-Bond Coupling

It was interesting to determine how the coupling between radical lobes was affected by an increasing separation of the radical centers. The direct or through-space coupling is a short-range effect, negligible beyond a separation of ~2.5 Å. The through-bond coupling is a longer range phenomenon but we would also expect it to decrease at large distances since it depends on a propagation of small effects. To probe this phenomenon we calculated (extended Hückel method) a series of $\alpha,\omega$-dehydropolyenes and dehydropolyenyl systems, $C_nH_n$, $n$ = 3–10. The conformations were throughout *trans*, with C=C in the polyenes of 1.34 Å, C–C of 1.48 Å, C–C in the polyenyl systems of 1.45 Å; 120° angles everywhere. Four conformations were studied, illustrated below for the cases with $n$ = 5 and 6.


Type 1


Type 2


Type 3


Type 4

We have not included the $n$ = 2 case, dehydroethylene, in these series since it does not quite possess analogous structural features. The results presented in Table VII very clearly show a greater coupling at a given separation if the radical lobes have the carbon chain *trans* to them (types 2 and 4) rather than *cis* (types 1 and 3). This is an interesting result since while the magnitude of the vicinal *trans* overlap was larger than that of the *cis* (Figure 5), the specific difference was not very great. The *trans*-coupled conformations (types 2 and 4) show a regular exponential diminution of the coupling with distance, while the *cis*-coupled types 1 and 3 are consistently very small. The *cis*-dehydroallyl case splitting is probably still the result of a moderate through-space coupling. Aside from the anomalous cases of *cis* conformation with $n$ = 3 all $n$ = even couplings, independent of magnitude, have the A molecular orbital lower than S, but all $n$ = odd cases reverse the splitting pattern. We have described an argument above for the $n$ = even case (coupling over an odd number of intervening $\sigma$ bonds). That an opposite trend occurs for the $n$ = odd case makes it likely that there is an underlying rationale for S going below A here.

**Table VII.** The Distance Dependence of Coupling in $\alpha,\omega$-Dehydropolyenes and Polyenols

| Molecule | $n$ | Lower energy MO | Higher energy MO | $\Delta = E(A) - E(S)$ |
|---|---|---|---|---|
| Type 1 | 4 | S −11.611 | A −11.554 | +0.057 |
| | 6 | A −11.603 | S −11.548 | −0.055 |
| | 8 | A −11.591 | S −11.558 | −0.033 |
| | 10 | A −11.581 | S −11.566 | −0.015 |
| Type 2 | 4 | A −12.128 | S −10.799 | −1.329 |
| | 6 | A −11.602 | S −11.078 | −0.524 |
| | 8 | A −11.416 | S −11.194 | −0.222 |
| | 10 | A −11.345 | S −11.247 | −0.098 |
| Type 3 | 3 | A −11.924 | S −11.659 | −0.265 |
| | 5 | S −11.821 | A −11.726 | +0.095 |
| | 7 | S −11.776 | A −11.769 | +0.007 |
| | 9 | S −11.775 | A −11.769 | +0.006 |
| Type 4 | 3 | S −12.364 | A −11.149 | +1.215 |
| | 5 | S −11.870 | A −11.334 | +0.536 |
| | 7 | S −11.672 | A −11.446 | +0.226 |
| | 9 | S −11.597 | A −11.500 | +0.097 |

## Benzynes

The calculations were carried out on idealized geometries obtained by removing two hydrogens from a $D_{6h}$ benzene with C–C 1.40 Å, C–H 1.10 Å. The stability order was *ortho* more stable than *para*, which in turn was at lower energy than *meta*. The crucial splitting of the radical lobes has already been indicated in Figure 1, and Figure 9 illustrates the charges and Mulliken overlap populations which were calculated for the lowest energy configuration, *i.e.*, two electrons in S for *o*- and *m*-benzyne, two electrons in A for *p*-benzyne. Benzene itself is included for comparison.

**1.** ***o*-Benzyne.** Even with all distances kept the same, the increased 1–2 overlap population indicates the partial triple-bond character. With the same parameters an acetylene with a C≡C distance of 1.40 Å has an overlap population of 1.6020, while a normal acetylene with C≡C at 1.21 Å has 1.9095. The overlap population of the 4–5 bond actually increases over that of benzyne. If the overlap populations are indicators of

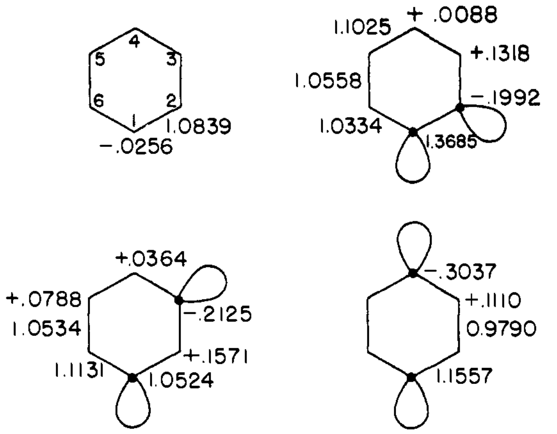
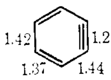
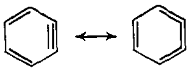


Figure 9. Mulliken overlap populations (unsigned numbers) and charges for the benzynes. Benzene is included for comparison.

equilibrium bond lengths, then benzyne will have quite different distances from those estimated by Coulson and shown below[22] (VIII). In fact if we try to translate



VIII

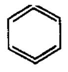


IXa IXb

the MO results into VB language, the overlap populations seem to be telling us that a sizable contribution enters from the resonance structure IXb, not only from IXa. The charge redistribution in benzyne is also worth noting. There appear no gross changes in nonbonded overlap populations.

2. *m*-**Benzyne**. The only striking feature of the population analysis here is the nonbonded 1-3 overlap population which is +0.0409 compared to −0.0825 in benzene. This is the largest such change in the entire benzyne series and from our experience definitely indicative of incipient or partial 1-3 bonding. In VB language one would say that the resonance structures Xa and Xb contribute significantly.

Xa Xb



XI

3. *p*-**Benzyne**. Here there are two significant features of the population analysis. First the bonded 1-2, 3-4, 4-5, 6-1 populations are large and the 2-3, 5-6 are small. Second there is a significant change in the 1-4 overlap population from −0.0431 in benzyne to −0.1185 in *p*-benzyne. A repulsion is indicated and perhaps the resonance structure XI contributes. Incidentally were it *not* for the observed ordering of $n_1 \pm n_2$ the reaction taking *p*-benzyne into the hypothetical bicyclohexatriene would be a thermally allowed reaction. This is shown in the correlation diagram of Figure 10.

Population analyses were also carried out for the lowest excited configurations $(S)^1(A)^1$ of the benzynes. As might have been expected these gave a much more uniform electron distribution, close to that of an unperturbed benzene.

Extended Hückel calculations on benzyne in the geometry suggested by Coulson, dehydronaphthalenes, and cyclopentynes have been carried out by Yonezawa and coworkers.[23]

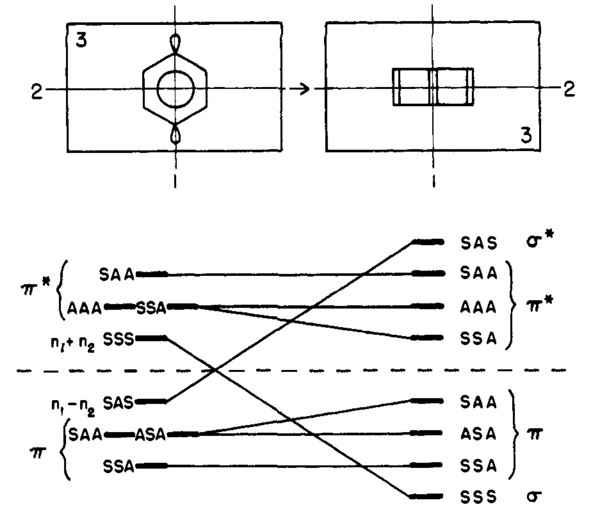
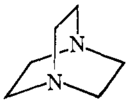


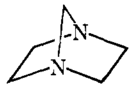
Figure 10. A level correlation diagram for the hypothetical conversion of a *p*-benzyne to a bicyclotriene.

## Bridgehead Diazabicyclic Alkanes

The original molecule in this series which was studied most extensively was triethylenediamine or 1,4-diazabicyclo[2.2.2]octane (XII). Later the study was extended to the 2.2.1, 2.1.1, and 1.1.1 systems with nitrogen at both bridgeheads (XIII, XIV, XV). The calculations



XII



XIII

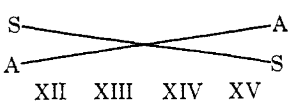
XIV

XV

were in fact carried out on idealized geometries of the hydrocarbons, with N substituted at the bridgehead for C-H. The unrealistic C-N distances of 1.54 Å thus came about. A $D_{3h}$ conformation was used for XII, coordinates for XIII and XIV given by Wilcox[24] were used, and a reasonable guess was made at the geometry of bicyclo[1.1.1]pentane.

We would like to discuss the results on XII in some detail first. The two highest occupied and the lowest unoccupied MO's came at −13.422 eV ($a_2''$), −11.849 ($a_1'$), −3.257 ($e'$). Thus there is a large interaction of the nitrogen lone pairs, and the splitting pattern puts A($a_2''$) below S($a_1'$) precisely as in pyrazine or *p*-benzyne. The transition $a_1' \rightarrow e'$ is allowed and $a_2'' \rightarrow e'$ forbidden in $D_{3h}$ symmetry. The highest occupied orbital, $a_1'$, which presumably contains the odd electron in the radical cation of XII, is considerably delocalized in these calculations. If one electron is placed in this orbital 0.292 of it will be on each N, 0.060 on each C, and 0.0005 on each H. Table VIII summarizes the results obtained for the compounds XII → XV.

Progressing along this series there is a clear interchange of the order of S and A which can be summarized as below.



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(22) C. A. Coulson, Special Publication No. 12, The Chemical Society, London, 1958, p 85.

(23) T. Yonezawa, H. Konishi, M. Kato, K. Morokuma, and K. Fukui, *Kogyo Kagaku Zasshi*, **69**, 869 (1966).

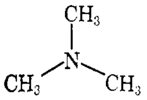
(24) C. F. Wilcox, Jr., *J. Amer. Chem. Soc.*, **82**, 414 (1960).

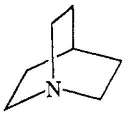
Table VIII. Energy Levels of Diazabicyclic Compounds

| Molecule | XII ($D_{3h}$) | XIII ($C_{2v}$) | XIV ($C_{2v}$) | XV ($D_{3h}$) |
|---|---|---|---|---|
| E(LUMO) | $-3.257$ e′ | $-3.269$ $b_2$ | $-4.259$ $a_2$ | $-5.175$ e″ |
| E(HOMO) | $-11.849$ $a_1$′S | $-12.618$ $a_1$S | $-12.519$ $b_1$A | $-11.885$ $a_2$″A |
| E (other lone pair combination) | $-13.422$ $a_2$″A | $-12.989$ $b_1$A | $-13.124$ $a_1$S | $-14.763$ $a_1$′S |

This can be interpreted as follows. Each two-carbon bridge is in the most favorable orientation for through-bond coupling of the two lone paris. This coupling puts A below S. As one-carbon bridges are substituted for two-carbon bridges the through-bond coupling becomes inefficient while the through-space coupling increases since the bridgeheads come closer together. This direct coupling always puts S below A.

To provide some models in which lone-pair interaction is lacking we have calculated trimethylamine (XVI) and quinuclidine (XVII). The lone-pair orbitals are at $-12.754$ in XVI and $-12.261$ eV in XVII.


XVI


XVII

We have not been able to find any reports of the molecules XIII, XIV, and XV in the literature.[25] Our calculations predict a red shift in the n → $\sigma^*$ transition in XII and XV but less for XIII and XIV. It seems to us that the synthesis of XIII should be feasible; the molecule would be of considerable theoretical interest.

**Acknowledgment.** We are grateful to H. E. Simmons for some stimulating discussions. The Quantum Chemistry Program Exchange kindly provided the POLYATOM program authored by I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, S. Seung, B. T. Sutcliffe, and M. P. Barnett. This work has been supported in part by the National Science Foundation, the National Institutes of Health, and the Chevron and Sloan Foundations.

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(25) A diquaternary salt of XIII is known: G. R. Pettit and J. A. Settepani, *Chem. Ind.* (London), 1805 (1964).

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# Hydrogen Bonding in Pyridine[1]

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*Received June 9, 1967*

**Abstract:** The pyridine–water and pyridine–methanol hydrogen-bonded systems have been examined using the extended Hückel theory (EHT). Of the various conformations studied, the one in which the hydrogen approaches the pyridine lone pair forming a linear arrangement of the O–H···N grouping is of lowest energy. In this case, for both water and methanol, a reasonable potential energy curve is obtained for the hydrogen-bonded system. From this curve it is concluded that the heat of formation is $-2.3$ kcal/mol, the equilibrium distance between the oxygen and nitrogen atom 2.76 A, and the force constant $0.10–0.11 \times 10^5$ dyn/cm. The nitrogen lone-pair orbital shifts progressively to lower energy as water or methanol approachs the pyridine molecule. The calculated blue shift is about twice as large for water than methanol. At fixed positions of the heavy nuclei, the proton was transferred from oxygen to the nitrogen atom. A double energy minimum was obtained with an energy barrier of approximately 0.7 eV for the proton transfer at the equilibrium distance of O–N separation. As the proton shifts over from oxygen to nitrogen, as expected, the O–H overlap population decreases and the H–N increases. While the charge on oxygen increases and for nitrogen decreases, it stays essentially constant at about $+0.4$ electron for hydrogen during the transfer. For the $(n,\pi^*)$ excited state, the results parallel qualitatively those for the ground state. Finally, it is of interest to mention that the carbon-13 chemical shifts, calculated from the EHT wave function, are in reasonable agreement with the experimental values.

A great number of facts about the hydrogen bond are fairly well understood; what is not so clear is the interpretation that should be given to them. Pimentel and McClellan,[3] Coulson,[4] and Bratoz[5] provided reviews of the concepts used in the theoretical interpretation of the hydrogen bond. These will be presented in brief form before discussing our calculations.

The classical electrostatic model of the hydrogen bond has enjoyed substantial support and there are two main

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(1) This work was supported by a research grant from the University of Puerto Rico. It was presented at the Euchem Symposium held on April 16–21, 1967, in Mittenwald, Germany.

(2) Cornell University, Ithaca, N. Y.

(3) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Chapter 8.

(4) C. A. Coulson in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, London, 1959.

(5) S. Bratoz in "Advances in Quantum Chemistry," Vol. III, P. O. Löwdin, Ed., Academic Press Inc., New York, N. Y., 1967.