Molecular Orbital Theory of SN2 Reactions[1]

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Abstract: MO calculations of anionic and neutral base attacks on CH_4 and CH_3F are analyzed in terms of substrate MO's. Charge polarization is shown to occur in concert with bond weakening under C_3 but not under C_2 attack by H^- on CH_4. F^- attack on CH_3F proceeds analogously. Neutral base produces a weaker perturbation, but still causes F charge buildup and C–F bond weakening in C_3 attack of CH_3F. MO's which are important for these processes cannot be predicted from their orbital energies alone.

Experimental evidence strongly supports the view that SN2 displacement reactions proceed through back-side displacement, or Walden inversion.[2] Partial explorations of the reaction surface for hydride attack on methane have been carried out using MO methods.[3–6] These studies are consistent with a reaction path passing through a structure with D_{3h} symmetry. In view of the importance of this reaction process, it appeared worthwhile to attempt to extract a simple physical interpretation for MO calculations of SN2 inversion. Our strategy will be to analyze and interpret the ways in which MO's of the substrate molecule participate in forming MO's in the base–substrate complex.

All calculations reported in this paper are of the CNDO type.[7] This level of calculation gives qualitative agreement with *ab initio* calculations of hydride attack on methane (compare ref 3 and 4) and is extremely cheap to perform. We have avoided doing calculations using the extended Hückel method[8] because that method ignores ionic interactions likely to be important in this study.

Hydride Attack on Methane

Analysis of this system will be made in terms of the MO's of unperturbed methane. These MO's are highly symmetry determined. The carbon 2s AO is totally symmetric and combines with the symmetric hydrogen AO combination ($1s_a + 1s_b + 1s_c + 1s_d$) in two ways to produce two nondegenerate MO's. The lower energy one is isotropically C–H bonding, the other is antibonding. The 2p AO's on carbon are degenerate in a tetrahedral field. Each of these AO's is symmetric for reflection in two Cartesian axis planes and antisymmetric in the third, and they combine with linear combinations of hydrogen AO's having the same symmetry. Again, these combine both in C–H bonding and antibonding ways. The coordinate system for the molecule is shown in Figure 1, where idealized sketches of the MO's also appear. This system was used to study the effect of hydride attack from the $+x$ direction, along a C_2 axis.

Table I. Molecular Orbitals of Methane with y Axis Coincident with a C_3 Axis[a]

AO	MO 1	2	3	4	5	6	7	8
C_{2s}	0.7288	0.0	0.0	0.0	−0.6848	0.0	0.0	0.0
C_{2p_x}	0.0	0.7054	0.0	0.0	0.0	0.7088	0.0	0.0
C_{2p_y}	0.0	0.0	0.7054	0.0	0.0	0.0	0.7088	0.0
C_{2p_z}	0.0	0.0	0.0	0.7054	0.0	0.0	0.0	0.7088
H_{1s_a}	0.3424	0.0	−0.6138	0.0	0.3644	0.0	0.6109	0.0
H_{1s_b}	0.3424	0.5786	0.2046	0.0	0.3644	−0.5759	−0.2036	0.0
H_{1s_c}	0.3424	−0.2893	0.2046	0.5012	0.3644	0.2880	−0.2036	−0.4990
H_{1s_d}	0.3424	−0.2893	0.2046	0.5012	0.3644	0.2880	−0.2036	+0.4990
MO energies, au	−1.2613	−0.7232	−0.7232	0.7232	0.3045	0.3266	0.3266	0.3266

[a] Atom populations: C = 4.0479, H = 0.9880.

A different methane orientation is convenient for studying attack along a C_3 axis behind a C–H bond. We used the orientation shown in Figure 2, allowing the hydride to attack from the $+y$ direction. For this orientation, it is apparent that the hydrogen on the $-y$ axis has a different relation to the carbon p AO's than do the other three hydrogens. This hydrogen can enter an MO with p_y, but not with p_x or p_z, since it lies in their nodal planes. Methane MO's for this coordinate orientation are given in Table I and sketched in Figure 2.

Calculations were performed on methane–hydride ion systems with the hydride ion at a distance of 5 Å along

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[3] C. D. Ritchie and G. A. Chappell, *J. Amer. Chem. Soc.*, **92**, 1819 (1970).

[4] N. L. Allinger, J. C. Tai, and F. T. Wu, *ibid.*, **92**, 579 (1970).

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[6] J. J. C. Mulder and J. S. Wright, *ibid.*, **5**, 445 (1970).

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[8] R. Hoffmann, *ibid.*, **39**, 1397 (1963).

Table II. Molecular Orbital Results for C_3 Attack by Hydride Ion 5 Å from Methane

AO	MO 1	2	3	4	5	6	7	8	9	Atom population
C_{2s}	0.7286	−0.0090	0.0	0.0	−0.0010	−0.6754	0.1137	0.0	0.0	4.0456
C_{2p_x}	0.0	0.0	0.0	0.7079	0.0	0.0	0.0	−0.7063	0.0	
C_{2p_y}	−0.0017	−0.6998	0.0	0.0	−0.0002	0.1259	0.7032	0.0	0.0	
C_{2p_z}	0.0	0.0	−0.7079	0.0	0.0	0.0	0.0	0.0	−0.7063	
H_{1s_a}	0.3482	0.6191	0.0	0.0	0.0009	0.4574	0.5351	0.0	0.0	1.0090
H_{1s_b}	0.3405	−0.2057	0.0	0.5767	0.0	0.3260	−0.2623	0.5780	0.0	0.9818
H_{1s_c}	0.3405	−0.2057	−0.4995	−0.2884	0.0	0.3260	−0.2623	−0.2890	0.5005	0.9818
H_{1s_d}	0.3405	−0.2057	0.4995	−0.2884	0.0	0.3260	−0.2623	−0.2890	−0.5005	0.9818
H (5 Å)	0.0005	−0.0007	0.0	0.0	1.000	−0.0011	−0.0002	0.0	0.0	2.0000
MO energies, au	−1.1561	−0.6214	−0.6161	−0.6161	0.1108	0.4092	0.4291	0.4337	0.4337	

the $+x$ axis of Figure 1 and the $+y$ axis of Figure 2. The methane molecule was not allowed to distort, as that would obscure any subsequent analysis in terms of methane MO's.

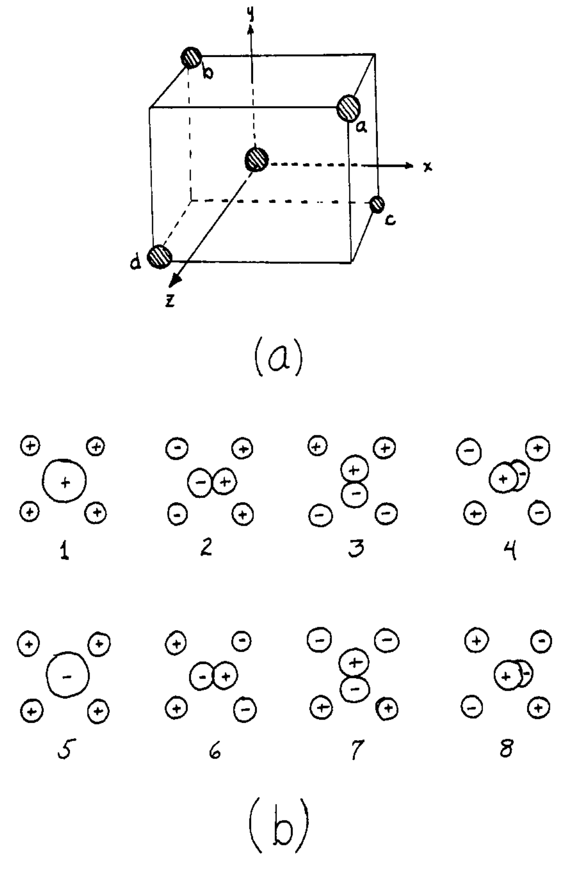

Figure 1. (a) Methane orientation having C_2 axes coincident with Cartesian axes. (b) Idealizations of the MO's.

We first discuss C_3 attack from the $+y$ direction in Figure 2. MO's for this methane hydride complex appear in Table II. One important effect of approach by a hydride ion is polarization of the methane molecule. This was observed in earlier calculations,[3–5] where it was noted that negative charge builds up on the hydrogen of methane most distant from the hydride, the other hydrogens and carbon becoming somewhat positive. Simple electrostatics leads us to expect this to be the favored charge distribution for the process of polarization exclusive of formation of incipient bonds and charge transfer. Let us, therefore, consider the nature of polarization of methane by a negative charge on the $+y$ C_3 axis.

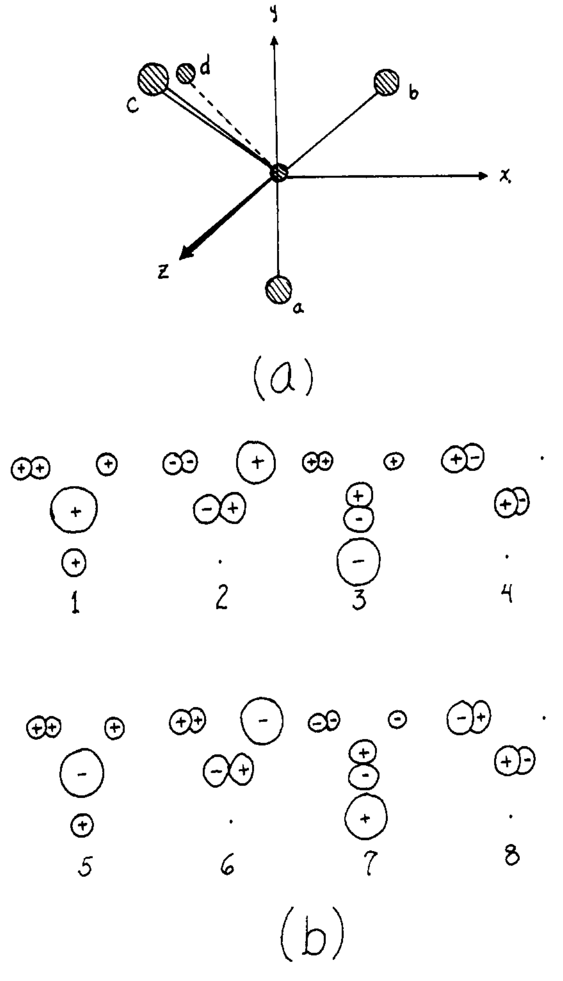

Figure 2. (a) Methane orientation producing data of Table I. (b) Idealizations of the MO's of Table I.

MO theory effects polarization by mixing together the filled and empty MO's of the unperturbed molecule. In Figure 2, idealized sketches of the MO's appear. We wish to mix these to cause increased orbital size on the $-y$ hydrogen. Ways of doing this are indicated in Figure 3. Mixing MO 1 with a small amount of MO 7 and likewise MO 3 with a small amount of MO 5 pro-

Table III. Resolution of MO's of Table II in Terms of MO's of Table I[a]

Complex MO	Methane MO 1	2	3	4	5	6	7	8
1	+0.1000D 01	0.0	−0.5925D − 02	0.0	0.1734D − 03	0.3405D − 04	0.2405D − 01	0.0
2	−0.5874D − 02	0.0	−0.9999D 00	0.0	0.6892D − 02	−0.2057D − 04	−0.2449D − 01	0.0
3	0.0	0.0	0.0	−0.1000D 01	0.0	0.0	0.0	0.3259D − 02
4	−0.3424D − 04	0.9999D 00	−0.2046D − 04	0.0	−0.3644D − 04	0.3520D − 02	−0.2306D − 04	0.0
5	−0.4206D − 03	0.0	−0.6935D − 03	0.0	0.1013D − 02	0.0	−0.4080D − 03	0.0
6	−0.7506D − 03	0.0	0.8157D − 02	0.0	0.9856D 00	0.3260D − 04	−0.1431D 00	0.0
7	−0.3352D − 02	0.0	0.6593D − 02	0.0	−0.1696D 00	−0.2623D − 04	−0.1007D 01	0.0
8	0.0	0.3422D − 02	0.0	0.0	0.0	−0.1000D 01	0.0	0.0
9	0.0	0.0	0.0	0.3477D − 02	0.0	0.0	0.0	0.1000D 01

[a] Read −0.3424D − 04 as −0.3424 × 10^{-4}.

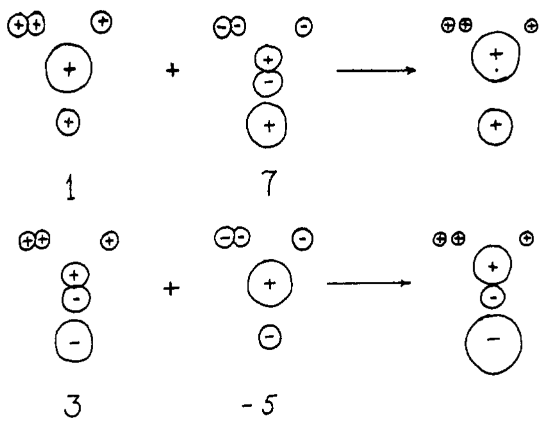

Figure 3. Ways in which filled MO's of Figure 2 can be mixed with small amounts of empty MO's to cause charge polarization from the three $+y$ hydrogens to the $-y$ hydrogen.

duces polarized MO's wherein charge is built up on the $-y$ hydrogen. Mixing together MO's 2 and 6 or 4 and 8 allows charge to shift between carbon and the three equivalent hydrogens, but has no effect on the $-y$ hydrogen. We might expect, then, that the MO's of Table II contain more contribution from empty MO's 5 and 7 than from 6 and 8. This is indeed the case. Table III shows the resolution of the methane part of the MO's of Table II in terms of the unperturbed methane MO's of Table I. These were obtained by calculating the scalar products between that part of a complex MO on methane and each of the MO's of unperturbed methane. Thus, the 1,2 element of Table III is the scalar product between column 2 of Table I and column 1 of Table II, the final element excepted. The coefficients in the last four columns of the first five rows indicate the extent to which empty methane MO's participate in filled MO's of the hydride–methane system. The contributions from coefficients of columns 5 and 7 are much larger than those due to columns 6 and 8. Columns 1–4 of rows 6–9 indicate the extent to which filled methane MO's get mixed into empty MO's of the hydride–methane system. MO 3 is by far the dominant here, so this MO is the one which is mainly lost in the perturbation caused by hydride attack.

The net result is that charge polarization due to hydride approach along the $+y$ C_3 axis mixes in some empty methane MO which is C–H antibonding mainly in the C–H bond where charge is accumulating. Also, the MO partially mixed out is one which was bonding mainly in that same C–H bond. Hence, the effect of charge polarization is to transfer charge from the rest of the methane substrate to the $-y$ hydrogen, simultaneously weakening the bond to that hydrogen. These concerted effects make the loss of the $-y$ hydrogen energetically easier than the loss of any other hydrogen.

For purposes of comparison, hydride attack from the $+x$ direction of Figure 1 was treated similarly. Polarization of charge to the two equivalent $-x$ hydrogens is effected by mixing filled with empty methane MO's as depicted in Figure 4. In this case, all of the empty MO's can participate in shifting charge to these hydrogens. CNDO MO coefficients for the system having a hydride ion at 5 Å on the $+x$ axis were resolved in terms of the methane MO's of Figure 1. All of the empty MO's contribute about equally except for

Table IV. Molecular Orbitals of CH_3F with C_3 Axis Coincident with y Axis

AO	MO 1	2	3	4	5	6	7	8	9	10	11	Atom population
C_{2s}	−0.3684	0.6202	0.0	0.0	0.0043	0.0	0.0	0.6832	0.0	0.0	0.1133	3.8134
C_{2p_x}	0.0	0.0	0.0173	0.5366	0.0	0.0401	0.4502	0.0	−0.7122	0.0140	0.0	
C_{2p_y}	0.2418	0.2223	0.0	0.0	0.5416	0.0	0.0	0.0531	0.0	0.0	−0.7720	
C_{2p_z}	0.0	0.0	−0.5366	0.0173	0.0	−0.4502	−0.0401	0.0	−0.0140	−0.7122	0.0	
F_{2s}	−0.8693	−0.3696	0.0	0.0	0.1617	0.0	0.0	−0.0893	0.0	0.0	−0.2714	7.1891
F_{2p_x}	0.0	0.0	0.0231	0.7168	0.0	−0.0612	0.6865	0.0	0.1031	−0.0020	0.0	
F_{2p_y}	−0.0816	0.2730	0.0	0.0	−0.7851	0.0	0.0	−0.2020	0.0	0.0	−0.5116	
F_{2p_z}	0.0	0.0	−0.7168	0.0231	0.0	0.6865	0.0612	0.0	0.0020	0.1031	0.0	
H_{1s_b}	−0.1204	0.3439	0.0117	0.3626	0.1463	0.0410	−0.4605	−0.4007	0.5667	−0.0111	0.1364	0.992
H_{1s_c}	−0.1204	0.3439	−0.3199	−0.1712	0.1463	−0.4193	0.1947	−0.4007	−0.2737	0.4963	0.1364	0.992
H_{1s_d}	−0.1204	0.3439	0.3082	−0.1914	0.1463	0.3783	0.2658	−0.4007	−0.2930	−0.4852	0.1364	0.992
MO energies, au	−1.7454	−1.1821	−0.8940	−0.8940	−0.7902	−0.6423	−0.6423	0.2547	0.2929	0.2929	0.3443	

MO 6 which participates much more weakly. Furthermore, MO's 2, 3, and 4 are about equally mixed out, MO 1 suffering very little loss. This indicates that the first combination in Figure 4 is brought in less by the perturbation than are the other three. This makes sense because this combination mixes the methane MO's of lowest and highest energy (see Table I). The other three combinations mix MO's of uniformly smaller energy difference. When all the MO's are roughly equally capable of effecting a charge shift, we expect the energy difference to dominate the relative weightings.

If all the filled or empty methane MO's participate equally, an isotropic bonding or antibonding interaction results. In C_{2v} attack, the filled and empty sets participate about equally except for one member in each set. However, each of these members is itself isotropic with respect to C–H bonding (see Figure 1). Hence, the bonding–antibonding character of methane under C_{2v} attack is quite isotropic even though the charge distribution is not. (This conclusion is borne out by an investigation of the density matrix for C_{2v} methane hydride.)

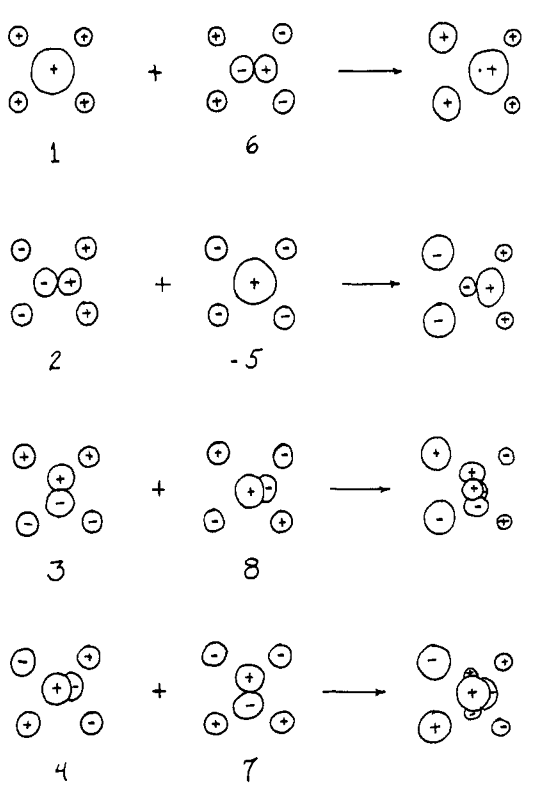

Figure 4. Ways in which filled MO's of Figure 1 can be mixed with small amounts of empty MO's to cause charge polarization from the two $+x$ hydrogens to the two $-x$ hydrogens.

The reaction we are considering requires charge accumulation and bond breakage to occur in one bond. The need to produce a *single* C–H bond different from the others in itself makes the C_3 approach seem more promising than a C_2 approach or anything between these extremes. What we have shown here is that, in addition to this gross symmetry consideration, there is a convenient reinforcement between anisotropic charge polarization and bond weakening in the C_{3v} mode attack, but not in the C_{2v} mode.

F^- Attack on CH_3F

Replacing a hydrogen of CH_4 with a fluorine amounts to adding three more AO's and six more electrons to the molecule. This leads to 11 MO's, but the number of empty MO's remains fixed at 4. CNDO results for CH_3F oriented with the C–F bond in the $-y$ direction are reproduced in Table IV. The empty MO's may be characterized in order of increasing energy as (8) CH_3 antibonding with some C–F antibonding, (9–10) CH_3 antibonding *via* p_x and p_y AO's of carbon, (11) strongly C–F antibonding, and weakly CH_3 antibonding.

A CNDO calculation was performed for an $F^- \cdots CH_3F$ complex with F^- on the $+y$ axis 5 Å from carbon. (For an *ab initio* study of this system in D_{3h} symmetry, see ref 9 and 10.) The analysis of the MO's of the complex in terms of MO's of CH_3F shows that the highest empty MO (no. 11) contributes about three times more heavily than any of the other empty MO's. The loss of participation by MO 5, which is strongly C–F bonding, exceeds the loss of any other filled MO by a factor of 4. In short, the participation by filled and empty MO's in substrate CH_3F is analogous with that in CH_4.

Attack by a Neutral Base

A CNDO calculation for C_{3v} $H_3N \cdots CH_3F$, with a C–N distance of 5 Å was performed. Here we expect

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(9) G. Berthier, D.-J. David, and A. Veillard, *Theor. Chim. Acta*, **14**, 329 (1969).

(10) A. Dedieu and A. Veillard, *Chem. Phys. Lett.*, **5**, 328 (1970).

an extremely weak covalent interaction to be the dominant perturbation. CH_3F MO's 8 and 11 are both of a nature to respond most strongly to such a perturbation. But now there is no ionic repulsion to favor MO 11 for being large on F, and MO 8 enters more heavily than MO 11. Filled MO 5 is the most lost. Mixing in and out these MO's has the effect of causing charge polarization to fluorine and weakening the C–F bond. The extent of perturbation for neutral base attack at 5 Å is very much smaller than for charged base attack, consistent with the idea that covalent interactions are of shorter range than Coulombic interactions.

Discussion

When a charged base attacks along the back-side of the C–F axis in CH_3F, the major perturbing influence at 5 Å is the charge repulsion due to the base, which induces charge polarization from H_3 to F in the CH_3F substrate. Two of the empty MO's of CH_3F can effect such a polarization. Of these, the lowest in energy (MO 8) has relatively small size on the fluorine. The highest in energy (MO 11) is quite large on fluorine. As a result, MO 11 is mixed in more than MO 8. Both of these MO's (especially MO 11) are C–F antibonding. This result suggests that MO theories of reactivity which focus on only the highest filled or lowest empty MO's are of limited applicability. Inspection of eigenvalues reported in this paper indicates that orbital energies among the empty MO's are not widely different. This further argues against arbitrary neglect of higher members of this set.

When a neutral base replaces the charged base, the perturbation of CH_3F becomes very much smaller. Again, MO's 8 and 11 are of such symmetry as to interact best with the base in a covalent way. But now there is no premium in using an MO which is large on F, so here we find the lower energy MO 8 entering most heavily, followed by 11. Because MO's 8 and 11 are mixed in, some charge polarization to F results. Hence we have the interesting contrast: when a charged base induces polarization, MO's 11 and 8 mix in and the C–F bond weakens, but when a neutral base approaches, MO's 8 and 11 mix in to engage in a covalent interaction with the base, *incidently* causing charge buildup on F and weakening of the C–F bond. It appears that the neutral base must approach closer to the S_N2 center than the charged base for the same extent of CH_3F distortion, C–F (leaving) charge buildup and bond weakening, and C–base bond formation.

Hückel Molecular Orbital π Resonance Energies. A New Approach

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Abstract: Single and double bonds in hydrocarbons have been classified into eight types according to the number of attached hydrogen atoms. Total HMO π energies, calculated in the usual way, have been found to be linear functions of the number of each type of bond. This allows the assignment of an empirical π-bond energy to each bond type, such that the total HMO energy of acyclic polyenes is simply a sum of these bond-energy terms. HMO π energies of cyclic hydrocarbons are not linear functions of the numbers of bonds and hence are not obtainable as a sum of bond-energy terms. Resonance energies are then defined as the difference between HMO π energy and the additive contribution obtained by summing individual bond energies. An excellent correlation between resonance energies calculated in this manner and the observed stability and chemical behavior of a wide range of cyclic polyenes is obtained. This treatment greatly extends the utility of HMO calculations.

The Hückel molecular orbital theory has served for many years as a basis for the explanation of the extraordinary stability or aromaticity of benzene and related compounds.[1] HMO theory indicates that benzenoid systems should have significant delocalization energies in agreement with their high degree of stability and unusual chemical behavior. The resonance stabilization of the acyclic polyenes relative to the benzenoid systems has long been recognized experimentally to be quite small even though HMO calculations predict a significant amount of delocalization in the acyclic polyenes. In spite of this, the HMO delocalization energies of nonbenzenoid cyclic polyenes have been used as a basis for suggesting that many of them should have significant resonance stabilization. This has been largely disproved with the synthesis of compounds such as fulvene (**45**),[2] heptafulvene (**46**),[3] and fulvalene (**55**).[3] All three have large calculated delocalization energies, but none is considered to be in the least aromatic, heptafulvene and fulvalene even being too reactive to be isolated.

There are a number of nonbenzenoid cyclic polyenes which experimentally do appear to have significant resonance stabilization. Azulene (**59**) has stability and chemical behavior closer to those of benzene than to those of a normal acyclic polyolefin; thus it has become

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