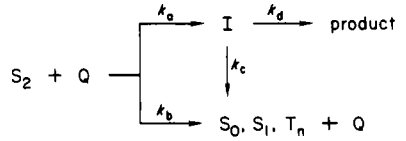
assisted electronic relaxation process, suggests that a bifurcation in the interaction path (leading to a chemically distinct intermediate in one branch and physical quenching in the other) may exist at relatively large S_2–quencher separations. The intermediate, I (vide infra), could be a free radical formed by H abstraction (initially trapped in a solvent cage with a second radical) or a dark excited complex. There is photochemical evidence[31] for both. A simple mechanism which encorporates these ideas follows:



If only one thione molecule is involved in the more detailed path, d, leading to chemical product, then the overall branching ratio, $\phi_d/(1 - \phi_d) = k_{q,chem}/k_{q,phys}$, would be equal to $(k_a k_d)/(k_b k_c)$. Complications requiring an expansion of this minimal set of reactions would occur if any step (e.g., step a) were reversible or if any of the products of electronic relaxation (e.g., T_1) were chemically reactive. No information concerning the magnitudes of the two separate branching ratios, k_a/k_b and k_d/k_c, can be inferred from the present data.[46] Path a followed by path c produces the same net effect as path b. The latter is included as a separate step because the magnitude of the S_2–Q interaction energy apparently required for assisting the radiationless relaxation of S_2 is smaller than that normally needed to stabilize a chemically distinct intermediate such as an exciplex in solution. Thus, relaxation at relatively large intermolecular separation is envisaged.

The overall branching ratio varies with the nature of Q. Small values would appear to be characteristic of aromatics such as benzene and pyridine ($\phi_d < 10^{-3}$), intermediate values ($\phi_d \approx 10^{-2}$) for saturated aliphatics, and perhaps larger values for addends such as ethanol which have readily abstractable hydrogen atoms or for ground-state thione itself in which the quantum yield of dimerization approaches unity at high thione concentration in some systems.[47]

Finally we suggest that the present observations, including the existence of an isotope effect in the overall thione quenching process (if slower than diffusion controlled), may necessitate a reinterpretation of the results of experiments in which mechanistic conclusions have been drawn primarily from the nature of the final products and the rates of their formation. Detailed photochemical studies of thiones **1**, **2**, and **3**, whose second excited singlet states are radiative and for which rate constants for excited state quenching can be determined directly, are currently under way.

Conclusions

Aromatic thiones excited to their second excited singlet, $^1(\pi, \pi^*)$, states are among the most reactive molecular species known in solution. Highly inert perfluoroalkane solvents are therefore needed to eliminate even relatively weak solute–solvent interactions which would otherwise mask the decay properties of the excited thiones themselves. In perfluoroalkane solution at room temperature, the S_2 states of photostable, rigid aromatic thiones decay nonradiatively by $S_2 \rightsquigarrow S_1$ internal conversion according to the predictions of the energy gap law of Englman and Jortner.[36]

When perfluoroalkane solutions of thiones are spiked with addends, the nature of the specific S_2 thione–addend interactions which lead to electronic quenching can be illuminated. Quenching occurs by both "photophysical" and "photochemical" means, although the fraction of encounters leading to chemically distinct end product is apparently small in most cases. The quenching process cannot be characterized by a single parameter mechanism, and the more general approach to understanding molecular interactions, such as the ECDD method developed by Morokuma,[44,45] may be required to interpret thione S_2 quenching.

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Registry No. 1, 74768-62-0; **2**, 6005-15-8; **3**, 492-21-7; **4**, 86399-30-6; **5**, 86399-31-7; **6**, 3591-73-9; C_6H_6, 71-43-2; C_6F_6, 392-56-3; CCl_4, 56-23-5; CS_2, 75-15-0; pyridine, 110-86-1; perfluoropyridine, 700-16-3; acetonitrile, 75-05-8; perfluorooctanonitrile, 647-12-1; cyclohexene, 110-83-8; perfluorocyclopentene, 559-40-0; tetrahydrofuran, 109-99-9; perfluoro-2-butyltetrahydrofuran, 335-36-4; 3-methylpentane, 96-14-0; perfluoro-*n*-hexane, 355-42-0; 1*H*-perfluoro-*n*-heptane, 375-83-7; cyclohexane, 110-82-7; perfluoromethylcyclohexane, 355-02-2; 1,3-cyclohexadiene, 592-57-4; thiacyclohexane, 1613-51-0; ethylenediamine, 107-15-3.

(46) Note that picosecond time-resolved absorption measurements might be used to measure the kinetics of I's formation and decay. Together with knowledge of the rate of product formation, such data could be used to determine k_a/k_b and k_d/k_c individually.

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The Origin of the Barriers to Thermally Allowed, Six-Electron, Pericyclic Reactions: The Effect of HOMO–HOMO Interactions on the Trimerization of Acetylene

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Abstract: The activation barrier to the trimerization of acetylene to form benzene is calculated to be 62 kcal/mol when both polarization functions (HF/3-21G) and electron correlation (MP3/3-21G) are taken into consideration. The electronic contribution to the barrier is dominated by closed-shell repulsions between filled π orbitals. The large favorable change in enthalpy attending this reaction can be attributed to the formation of three new σ bonds since no aromatic stabilization accompanies this six-electron pericyclic reaction at the transition state.

Frontier molecular orbital (FMO) theory has provided the organic chemist with a powerful tool for understanding chemoselectivity.[1,2] The use of quantum calculations in conjunction with FMO theory has been particularly successful in predicting

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the regiochemistry of cycloaddition reactions.[3] The application of HOMO–LUMO (two-electron) interactions to the periselectivity of the Diels–Alder reaction has also been moderately successful. However, certain apparent inconsistencies in FMO theory as applied to the energetics of pericyclic reactions have been noted. For example, Salem[4a] suggested that a good part of the activation barrier for the Diels–Alder reaction could be traced to the energy increase of the filled alkene π orbital which is obligated to mix with the lowest filled butadiene π_1 orbital in an antibonding manner. Another such apparent enigma concerning pericyclic reactions was noted by Houk[5] in a study of the trimerization of acetylene. The in-plane occupied π-MOs of acetylene increased in energy until the transition state was attained, whereupon they were suddenly stabilized. It was suggested that the overlap of nonconjugated π systems resulting in the formation of σ bonds increases the interactions between filled orbitals and exerts a destabilizing influence on the course of the reaction and contributes to an elevated activation barrier. Such closed-shell repulsions (mixing of filled orbitals) have typically been ignored in FMO analyses since the two-electron (HOMO–LUMO) interactions were often adequate to estimate trends in chemical reactivity.[6]

We have recently reported an extended FMO (EFMO) model describing the consequences of the mixing of three fragment orbitals containing four electrons.[7,4b] When the third higher lying empty orbital is of the proper symmetry, a three-orbital, four-electron interaction can be net stabilizing. Our basic premise is that both two- and four-electron interactions should be considered in order to fully comprehend the origin of activation barriers. This is particularly relevant for reactions between molecules with nearly degenerate HOMO levels. In pericyclic reactions, for example, consideration of only the interactions between filled and vacant orbitals leads to the prediction of no activation barrier at all.[5] This reaction has posed a particularly intriguing problem because the formation of benzene is a highly exothermic ($\Delta H°$ = −143 kcal/mol)[5] process with an apparently prohibitive activation energy but yet has no symmetry-imposed barrier. We now provide more quantitative evidence that closed-shell repulsions between filled π orbitals makes a significant contribution to the elusive thermal barrier in the putative trimerization of acetylene. It is also emphasized that the formation of a transition state involving a cyclic array of six π electrons is not always stabilizing relative to starting materials despite the *potential* for aromaticity.

Several recent attempts by Vollhardt to achieve an intramolecular [2 + 2 + 2] cycloaddition of both acyclic and cyclic 1,5,9-dodecatriynes were unsuccessful.[8] Even the reverse reaction involving the thermolysis (400 °C) of the highly strained molecule *endo,exo*-tetracyclo[6.1.0.0,^{3,4} 0^{5,7}]nonane (*trans*-tris-σ-homobenzene) to 1,4,7-cyclononatriyne has an activation barrier of 42 kcal/mol.[9a] A theoretical study of this cycloreversion suggested a barrier of 63 kcal/mol (MINDO/3) for the forward cycloaddition.[9b] In a similar study on acetylene trimerization, a barrier of about 80 kcal/mol was calculated (STO-3G) and about three-fourths of this activation energy was ascribed to the energy required to distort the three acetylenes to their transition-state geometries. The remaining 20 kcal/mol was mainly attributed to the excess of exchange repulsion (four-electron) over charge-transfer stabilization (two-electron) as the transition state was approached.[5]

With an extended basis and including polarization functions, we find an almost identical activation barrier of 81 kcal/mol at the Hartree–Fock level (HF/6-31G*, Table I) but a somewhat lower barrier (62 kcal/mol) when correlation energy is included.[10] The transition structure was fully optimized at HF/3-21G with energy gradients[11] (Table II) followed by single-point calculations with the larger basis. Initially, D_{3h} symmetry was enforced but partial relaxation of this constraint suggested that transition states of lower symmetry should be higher in energy. To confirm this, the full set of vibrational frequencies was calculated by using analytical second derivatives at the HF/3-21G level. Only one imaginary frequency was found, indicating that the D_{3h} structure is a true transition state and that all distortions to lower symmetry yield a higher barrier.[12] The possibility of meaningful contributions from excited configurations of either the in-plane or the incipient aromatic system seemed plausible. A small configuration interaction calculation involving six filled and six virtual orbitals arising from the π and π^* bonds of acetylene did not lower this imposing activation barrier (Table I). However, when all valence and virtual orbitals were included and electron correlation was calculated via Møller–Plesset perturbation theory[13] to third order,

Table I. Total Energies and Relative Energies for the Trimerization of Acetylene[a]

level	reactants[b]	transition structure	E_{rel} (kcal/mol)
HF/3-21G	−229.187 87	−229.068 01	75.2
HF/6-31G*	−230.453 27	−230.324 04	81.1
MP2/3-21G(6π,6π^*)[c]	−229.306 89	−229.155 42	95.0
MP3/3-21G(6π,6π^*)[c]	−229.332 33	−229.173 16	99.9
CISD/3-21G(6π,6π^*)[c]	−229.335 39	−229.171 76	103.1
MP2/3-21G(full)[d]	−229.739 84	−229.664 37	47.4
MP2/3-21G(f.c.)[e]	−229.730 27	−229.654 42	47.6
MP3/3-21G(f.c.)[e]	−229.744 31	−229.655 52	55.7
MP2/6-31G* (estimated)[f]			53.5
MP3/6-31G* (estimated)[f]			61.6

[a] Total energies in au, relative energies in kcal/mol, 1 au = 627.51 kcal/mol. All geometries were fully optimized at HF/3-21G. [b] Three times total energy of acetylene. [c] Included only the six occupied and six empty orbitals arising from the π and π^* orbitals. CI values include size consistency correction. [d] Full Møller–Plesset calculations including all occupied and unoccupied orbitals of acetylene. [e] Frozen-core Møller–Plesset calculations; no excitations from the carbon 1s orbitals. [f] The correlation correction obtained with the 3-21G basis set (e.g., MP2/3-21G(f.c.) − HF/3-21G) was added to the HF/6-31G* energy barrier.

Table II. Optimized Geometries (3-21G) for the Trimerization of Acetylene[a]

structure	$r_{C=C}$	$r_{C\cdots C}$	r_{C-H}	∠CCH
acetylene	1.188	∞	1.051	180.0
transition state	1.217	2.213	1.052	152.0
benzene	1.385	1.385	1.072	120.0

[a] Bond lengths in Å, angles in deg.

(1) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry;" Verlag Chemie: Weinheim, 1970.
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(4) (a) Townshend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190. (b) For an earlier discussion of the consequences of interacting both a subjacent and a superjacent orbital with a third filled orbital see: Salem, L. The Sixth Jerusalem Symposium, Chemical and Biochemical Reactivity, 1974, p 329.
(5) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paqwuette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.
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(10) The calculations were performed with the GAUSSIAN 80 and 82 series of programs with standard MO theory. Binkley, J. F.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, No. 406.
(11) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.
(12) Aside from the single imaginary frequency, the transition structure has three low-frequency vibrations, two at 38 cm^{-1} (E″) and one at 223 cm^{-1} (A″). These three modes are composed of the symmetry-adapted linear combinations of twists of the acetylene moieties about the C_2 axes passing through their midpoints. Distortion along one of the E″ modes leads to acetylene plus HC═CH—CH═CH diradical. The single determinental wave function used in the optimization does not describe diradicals correctly. MCSCF calculations could concievably find this lower symmetry diradical pathway more favorable.

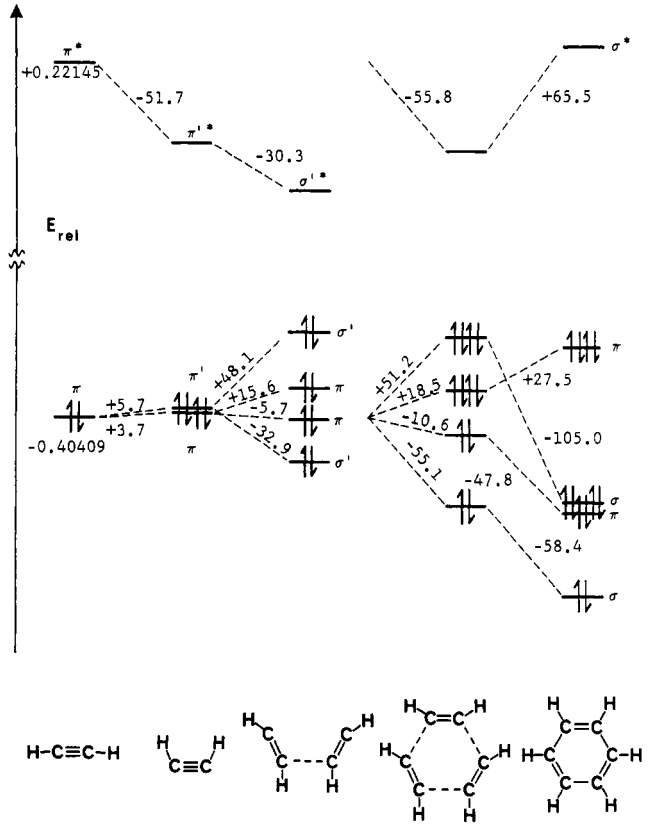
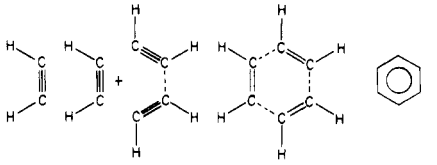


Figure 1. Changes in orbital energies (kcal/mol, 6-31G*) during the trimerization of acetylene.

the barrier to acetylene trimerization was significantly reduced (MP3/3-21G, frozen core approximation). When both polarization functions (HF/6-31G*) and electron correlation (MP3/3-21G) are taken into account, out best estimate of the barrier is 62 kcal/mol (Table I).

An examination of the relative energy levels of the FMO's along the reaction coordinate for this pericyclic reaction is particularly revealing (Figure 1). One is first struck by the enormous HOMO–LUMO energy gap (393 kcal/mol) of acetylene and by the realization that the three degenerate π-MO's must be elevated in energy by four-electron interactions before the transition state can be reached.[7] However, the singularly most important electronic factor that is responsible for this anomalously high barrier is a simple consequence of orbital splitting.[14] In this particular six-electron interaction, when overlap is included, *two occupied orbitals increase in energy by a greater amount than one filled MO is stabilized.* As the three acetylenes approach each other, there is a smooth evolution of the out-of-plane orbitals into the three filled aromatic orbitals of benzene. At the transition structure, the lower π orbital has been stabilized by 10.6 kcal/mol while the degenerate doubly occupied *pair* of MO's have each been elevated in energy by 18.5 kcal/mol. Since all other MO's are orthogonal to the developing aromatic sextet, it is obvious that *no aromatic stabilization accompanies this reaction at the transition state* (Figure 1). In addition, the overall net change in orbital energies of the π bonds of acetylene relative to the aromatic sextet of benzene is at best isothermal and is most likely destabilizing. In addition to the π system, at the transition state two developing in-plane σ orbitals are each increased in energy by 51.2 kcal/mol while only a single σ orbital is stabilized (55.1 kcal/mol). *The large favorable energy change attending this pericyclic reaction can be attributed to the formation of three new σ bonds*, after the barrier has been crossed.

Table III. Relative Energies of Geometrically Distorted Structures Involved in Acetylene Trimerization[a]



HF/3-21G	50.9[b]	71.3[c]	75.2[d]	−145.3[e]
CISD/3-21G-(6π,$6\pi^*$)		49.6	75.5	−98.8
MP2/3-21G(f.c.)[f]	31.4	46.9	47.6	−127.9
MP3/2-21G(f.c.)[f]	34.8	52.7	55.7	−134.0
HF/6-31G*	50.6	73.2	81.1	−156.8

[a] Energy relative to three ground-state acetylene in kcal/mol. [b] Three times the energy of acetylene distorted to the transition-state geometry. [c] Energy of two interacting acetylenes at the transition-state geometry with the third distorted acetylene at infinite distance. [d] Energy of the transition structure. [e] Calculated enthalpy of acetylene trimerization. [f] Frozen-core approximation.

An FMO study of the stepwise formation of benzene serves to simplify the complexity of the orbital interactions involved. Geometrical distortion of the three addends increases the total energy of the system by 51 kcal/mol (6-31G*; MP3/3-21G = 34.8 kcal/mol, Table III). This angular deformation (H–C–C) also has an effect upon the HOMO–LUMO energy separation. The energy of the in-plane distorted π bond is elevated very slightly while its π^* complement is decreased in energy by 52 kcal/mol (Figure 1). Interaction of two of these distorted acetylenes, at their transition-state geometries (with the third molecule at infinite distance), is destablizing by an additional 23 kcal/mol (Table III) but induces a further frontier orbital narrowing (78 kcal/mol) of the developing σ and σ^* orbitals of benzene. The orbital splitting within the dimer does not differ significantly from the trimer (transition state) except for a slightly larger separation in the σ orbitals (Figure 1).

Although an exhaustive electronic rearrangement is required by this pericyclic process, it is offset to some extent by the bond making of a late transition state. When Mulliken overlap population[15] is used as a criteria of bonding, the π contribution to a carbon–carbon bond in benzene is 26%. A similar analysis suggests that each of the newly developing C–C bonds at the transition state are formed to the extent of about 12% of that in benzene. However, the π contribution to that emerging C–C bond is only about 3%. The essential lack of any π bonding at the transition state is a reflection of the relatively long C–C bond distances (2.2 Å) resulting in poor π overlap between the distorted acetylenes. In a synchronous pathway the energy expended at the transition state on angle strain and bond elongation (34.8 kcal/mol) is compensated for to some extent by bond making. We suggest that no more than half of the activation barrier (62 kcal/mol) should be attributed to changes in ground-state geometry. The electronic contribution to the activation barrier is dominated by closed-shell repulsions since the accompanying two-electron interactions are not sufficient to render the ΔH net stabilizing. Although our assessment of the relative importance of bond-angle deformation and closed-shell repulsion differs slightly due to a higher level of calculation, the mechanistic significance of these two contributing factors was clearly delineated by Houk and his co-workers in their earlier study.[5]

One can rationalize the phasing and the amplitude of the wave function at the transition state by being able to identify the basis or fragment orbitals that mix along the reaction coordinate. The compulsory mixing of filled FMO's early on the rection coordinate must precede their interaction with the empty σ^* MO's. The σ framework of two interacting acetylenes is reminiscent of the π orbitals of butadiene. When these orbitals are allowed to interact with a third acetylene, the degenerate frontier MO's of the

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(14) The orbital splitting between the two degenerate π_2 (e) orbitals and the π_1 (a_1) orbital of neutral homoconjugated 1,4,7-cyclononatriene has been experimentally (PES) measured to be 0.9 eV: Martin, H. D.; Mayer, B. *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 283.

(15) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

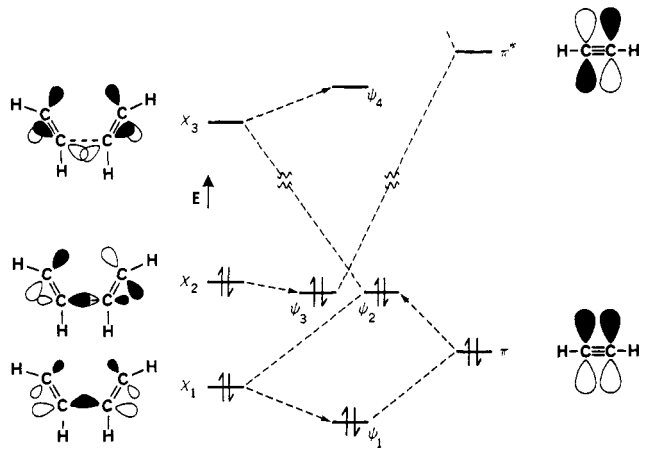
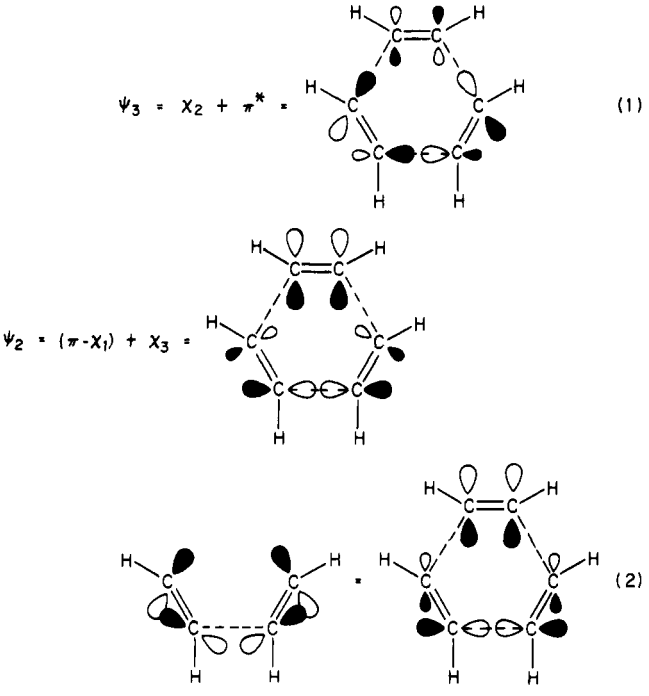


Figure 2. Frontier orbitals in the molecular plane that afford the σ framework.

transition structure may be derived. Interaction of χ_2 with π^* affords ψ_3 (eq 1) while the mixing of π into χ_1 and χ_3 evolves into ψ_2 (eq 2). This analysis is consistent with the four-electron three MO model where ψ_2 is the result of a three-orbital, four-electron interaction and ψ_3 is modestly stabilized by a two-electron interaction (Figure 2).



The splitting pattern in this trimerization reaction is a consequence of symmetry. However, the energy of the two degenerate filled orbitals ψ_2 and ψ_3, relative to ψ_1 (Figure 2), is determined by both the overlap (S_{ij}) and resonance (H_{ij}) intergrals involved in bonding interactions between the filled and virtual orbitals. In the absence of any accompanying two-electron interaction between the upper occupied MO's and high-lying empty orbitals, closed-shell repulsion will cause the interaction of three filled orbitals to be net destabilizing. In those cases where a significant HOMO–LUMO interaction is involved, the occupied orbitals can be sufficiently stabilized to render the overall orbital interaction of the three degenerate orbitals stabilizing. However, if the net elevation in energies of the degenerate orbitals ψ_2 and ψ_3 is greater than the stabilization of ψ_1 then the interaction will be destabilizing. In the case of acetylene trimerization, the initial π–π^* energy gap was large and the closed-shell repulsion between the degenerate π-MO's resulted in a large orbital splitting. Because of the large energy gap, the HOMO–LUMO interaction in the developing σ framework at the transition state is not sufficient to exert a net stabilizing influence on the reaction pathway. In a cyclic six-MO, six-electron system, a net stabilizing interaction can sometimes be difficult to attain since two filled MO's are being elevated in energy and only one is being stabilized. This type of interaction stands in marked contrast to the three-MO, four-electron interaction where only one filled orbital is being elevated and such interactions are typically net stabilizing when the overlap is sufficient to achieve a bonding interaction at the transition state. The above extended FMO treatment provides a method for analyzing the drastic alteration in the composition of the reactant MO's as they ascend to the transition state. It should be pointed out that one may easily arrive at many of these same conclusions by using the more qualitative predictions based upon the valence bond configuration mixing model recently described by Pross and Shaik.[16]

A qualitative estimate of the effects of the balance between the two- and four-electron interactions[4b] can be obtained from an exercise in Hückel theory. There are three possible four-electron interactions ($\pi + \pi'$) and six potantial two-electron interactions ($\pi + \pi^*$) that must be considered for the σ orbitals of the transition structure. The sum of the changes in energies of these valence electrons contained within three filled interactions will equal zero when the destabilizing closed-shell repulsions (four-electron)[17a] are offset by the stabilizing two-electron interactions. For the D_{3h} symmetry transition state

$$3\left[\frac{2(E_a S^2_{aa'} - H_{aa'}S_{aa'})}{(1 - S^2_{aa'})}\right] + 6\left[\frac{-(H_{ab} - E_a S_{ab})^2}{(1 - S^2_{ab})(E_b - E_a)}\right] = 0 \quad (3)$$

where a and a′ refer to occupied in-plane π orbitals of distorted acetylenes and b refers to π^*. Using the qualitative relation $H_{ij} = -kS_{ij}$, we can simplify eq 3; with the approximation that $1 - \frac{S^2_{aa'}}{1 - S^2_{aa'}} = \frac{(k + E_a)S^2_{ab}}{(E_b - E_a)(1 - S^2_{ab})}$ (4)

$S^2_{ij} \simeq 1$, eq 4 reduces to

$$\frac{S^2_{aa'}}{S^2_{ab}} = \frac{E_a + k}{E_b - E_a} \quad (5)$$

The balance between of the two- and four-electron electronic contribution to ΔH can be preserved by adjusting the independent variables in several ways. For example, if the overlap between two filled orbitals $S^2_{aa'}$ is increased, the four-electron repulsion will dominate. However, if the HOMO–LUMO energy gap ($E_b - E_a$) is decreased at the same time, the balance between stabilization and destabilization can be maintained. Conversely, if the energy gap widens, then a larger HOMO–LUMO overlap (S^2_{ab}) is required. For those cases where $E_a + k$ is approximately constant,[18] the energy gap becomes proportional to the ratio of S^2_{ab} to $S^2_{aa'}$ (or $H^2_{ab}/H^2_{aa'}$) and the importance of the HOMO–HOMO interaction becomes immediately evident. This simplified situation is consistent with FMO theory where we have suggested that frontier orbital narrowing should be greatest when the HOMO–HOMO interactions are large.[7]

The potential stabilization energy that may be derived from "aromaticity" at the transition state for the trimerization of benzene may be estimated by comparing the calculated energies of the ground-state FMO's of acetylene to those of the transition structure. For example, the orbital splitting of three acetylene π orbitals (HOMO = −0.40 au) to afford the three occupied π orbitals of the transition structure is endothermic by 26 kcal/mol (Figure 1). Thus, it is not surprising that we did not observe aromatic stabiliziation of the transition state for acetylene trim-

(16) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363.
(17) (a) Epiotis, N. D.; Cherry, W. R.; Shaik, S. S.; Yates, R. L.; Bernardi, F. "Structural Theory of Organic Chemistry"; Springer-Verlag: New York; p 5. (b) Longuet-Higgins, H. C.; Roberts, M. de V. *Proc. R. Soc. London, Ser. A* **1954**, *A224*, 336; **1955**, *A230*, 110.
(18) For example, if $-k$ = 1.46 au and E_a = −0.46 au, the expression $E_a + k \simeq 1$.

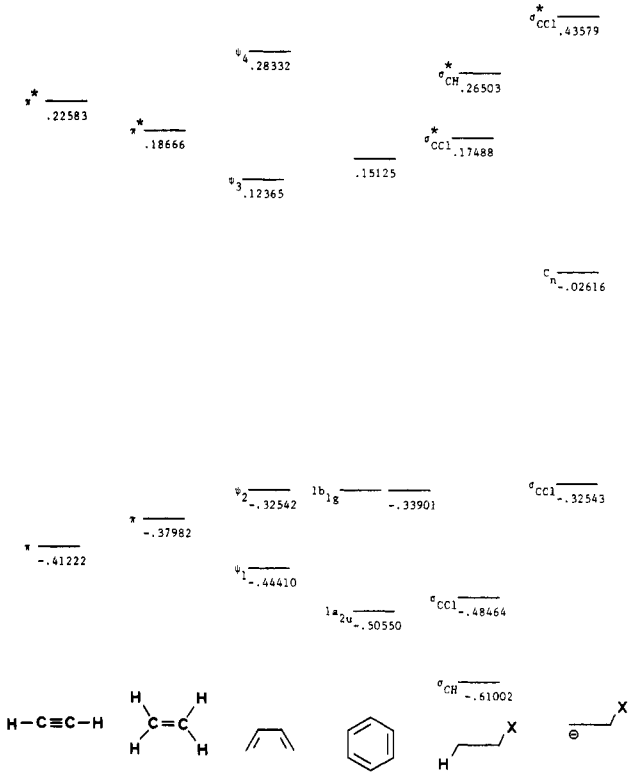


Figure 3. Calculated frontier orbital energies (3-21G, au).

erization. However, if the higher energy HOMO (−0.37 au) of ethylene is used as a refernce fragment orbital, the symmetry-imposed orbital splitting is exothermic by 30 kcal/mol relative to the transition state (Figure 3).[19] With similar arguments, it becomes equally obvious why benzene is so readily formed from substituted cyclohexadienes. If we model the frontier orbitals of 5-chloro-1,3-cyclohexadiene by the π orbitals of butadiene and the antiperiplanar $\sigma_{C\text{-}H}$ bond of ethyl chloride then the relative energy change of the FMO's upon elimination of HCl to afford benzene would be highly endothermic (123 kcal/mol). However, if one first breaks the CH bond to form the cyclohexadienyl carbanion, modeled by butadiene and the β anion of ethyl chloride, the reaction would be very exothermic (243 kcal/mol). The actual E_2 elimination process involves a partially developed β anion and obviously lies between these extremes. It is not difficult to rationalize why such elimination reactions involving "aromatic" transition states proceed with exceptionally low activation barriers.

In conclusion, the HOMO–HOMO interactions incured in the synchronous trimerization of acetylene are not energetically counterbalanced by the stabilization of the lowest lying π orbital ($1a_{2u}$) of benzene. The influence of the accompying stabilizing two-electron interactions is not felt until the transition state, where the phasing of the interacting addends changes from antibonding to net bonding and where *both* of the σ and one of the developing π orbitals rapidly descend in energy. Thus, the large favorable energy change in this pericyclic reaction is due to three new σ bonds formed after the transition state. In view of the combination of adverse geometrical distortions,[5] HOMO–HOMO interactions, and the lack of aromatic stabilization in the transition state, it is not surprising that experimentalists have failed to observe a concerted trimerization of acetylene.

In this most fundamental example involving the prototype aromatic system, the formation of the aromatic sextet is destabilizing. The "magic" of aromaticity that has come to be associated with virtually all "six-electron" processes should not be taken for granted. It is the relative energy of the basis fragment orbitals compared to those of the π-MO's of the aromatic sextet in the transition state that ultimately decides whether a reaction will have a transition structure that is stabilized or "aromatic" in nature.

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(19) The relative energy of the π MOs in benzene is usually compared to three ethylene molecules and the net stabilization is due to the lowering of ψ_1. However, ethylene has a longer C–C bond distance (1.317 Å) and a higher calculated (HF/6-31G*) HOMO level (π = −0.37438 au, π^* = 0.18391) than acetylene (π = −0.40409, π^* = 0.22145 au). Thus, the ground-state HOMO energy in acetylene is 18.64 kcal/mol lower in energy than that in ethylene.