

with the steady-state value. This increase in rate as the chain length increases insures that the synthesis of palmitic acid is greatly favored over hydrolytic cleavage of covalently bound intermediates.

An interesting feature of the synthesis of palmitic acid is that no clear rate-determining step is present during each cycle of chain growth. (The β -ketoacyl reductase reaction is relatively slow but not rate determining.) In terms of evolutionary development, this provides a process of optimal efficiency since there is no evolutionary advantage to having one step in the cycle much slower than all of the others.

Conclusion

Although the molecular details of the action of fatty acid synthase remain to be determined, the remarkable structure and efficiency of the enzyme complex are apparent. With the availability of the gene for fatty acid synthase, the stage is set for some interesting experiments. Individual structural domains can be expressed, their interactions can be studied, and site-specific mutagenesis can be utilized to determine structure-function relationships.

Registry No. Fatty acid synthase, 9045-77-6.

Interactions between Nonconjugated π -Systems

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SCF MO theory predicts that two identical π -systems that are coplanar and are connected by a single bond (e.g., the two ethylene fragments that form the π -system of butadiene, Figure 1) interact strongly due to the overlap of the $2p_x$ AOs at the termini that are connected to each other. As a consequence, the energies of the resulting bonding and antibonding combinations of the two fragment π - and π^* -orbitals will differ: The bonding combinations (π_+ , π_+^*) are stabilized, and the antibonding combinations (π_- , π_-^*) are destabilized. The size of this splitting is a measure of the magnitude of interaction.

Such an interaction is, however, not limited to situations where the π -subunits are directly connected (conjugated). The molecular structure of a number of organic systems can also force π -fragments to overlap through space. This type of interaction has been subdivided into several classes. The most common names that have been introduced are "homoconjugation" and "spiroconjugation". The term homoconjugation¹ is frequently used when both π -fragments (usually olefinic systems) are separated by one or sometimes two CH_2 groups. Prominent examples of this type of through-space interaction are the bicyclo[2.2.*n*] series 1 and 1,4,7-cyclonatriene (trishomobenzene (2)). In spiroconjugation (3) the central atom forces both butadiene

fragments perpendicular to each other and thus they can interact through space, providing an example of spiroconjugation.²



In 1968 R. Hoffmann recognized that the interaction between π -units can also be mediated by the σ -framework of the molecule (through-bond interaction^{3a,b}). Since then several review articles on the interaction between nonconjugated systems have appeared;³ therefore we will concentrate on the most recent work. We will also limit our discussion to neutral systems and to spectroscopic results that demonstrate the interaction between their π -moieties. Finally, we will discuss the consequences for the reactivity of systems where such interactions occur.

Experimental Measurements and Interpretations

The methods of choice to study the interactions in nonconjugated neutral π -systems are He(I) photoelectron (PE)⁴ and electron transmission (ET)⁵ spectroscopy.

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Rolf Gleiter received his Dr. rer. nat. in the field of synthetic organic chemistry from the University of Stuttgart in 1964 with F. Effenberger. After postdoctoral work at Princeton University with P. v. R. Schleyer and at Cornell University with Roald Hoffmann, he went to the University of Basel in 1969, where he worked on his habilitation in the laboratory of E. Heilbronner. In 1973 he joined the faculty of the Technische Hochschule in Darmstadt as Professor of Chemistry, and in 1979 he moved to the University of Heidelberg. His research interest are the synthesis of theoretically interesting molecules and their investigation by spectroscopy and theoretical means.

Wolfgang Schäfer studied chemistry at the University of Heidelberg supported by a scholarship of the Studienstiftung des Deutschen Volkes. In the group of Rolf Gleiter he carried out his doctoral thesis (1984) dealing with interactions between unsaturated systems, especially triple bonds, and a generalization of the through-bond/through-space concept. With a fellowship of the Max Kade foundation he spent a postdoctoral year at the University of Pittsburgh in the group of K. Jordan, followed by work with K. Mislow in Princeton. Since 1986 he has been working in the molecular modelling department of Boehringer Mannheim.

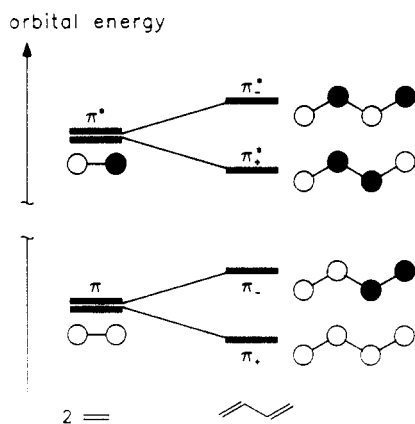


Figure 1. Qualitative interaction diagram between two ethylene π - and π^* -orbitals to yield the MOs of butadiene.

copy. In both experiments the energy difference between the neutral ground state and the different states of the corresponding radical ion (anion in the case of ET, cation in the case of PE spectroscopy) is measured. Although direct calculations of such energy differences are rather complex, it is possible to derive these values from a single calculation of the neutral ground state: According to Koopmans' theorem,⁶ the j th vertical ionization energies $I_{v,j}$ or electron affinities EA_j are equal to the negative value of the energy of the j th canonical molecular orbital (MO) obtained from a SCF calculation of the parent molecule. Conversely, orbital interactions can be calculated by SCF methods, and, via Koopmans' theorem, may be experimentally observed by a split of the corresponding peak in the PE or ET spectrum. Although we will concentrate on experimental results in this Account, it should be noted that all examples listed below have also been studied by theoretical methods and show a good agreement between experiment and theory.

Relations between Through-Space and Through-Bond Interactions

Spatial interactions between π -systems are only possible if the subsystems are forced into close proximity, usually by a σ -framework. Since the orientations of the + and - lobes in the bonding and the antibonding π (or π^*) combinations are different (cf. the example discussed below), the interactions of both combinations with the individual σ orbitals will also be different. This means that in all examples the experimentally observed splitting is a complicated interplay of through-space and through-bond effects and cannot simply be used as a quantitative measure of the spatial interaction. On the basis of model calculations, however, the different interaction terms can be separated, e.g., by the method of Heilbronner and Schmelzer.⁷ Since this Account emphasizes the experimental aspects, we cannot discuss the examples presented below in terms of this theoretical approach. Therefore we will concentrate on systems where one of the two effects is predominant or where the two effects cancel each other as a consequence of the individual molecular topology.

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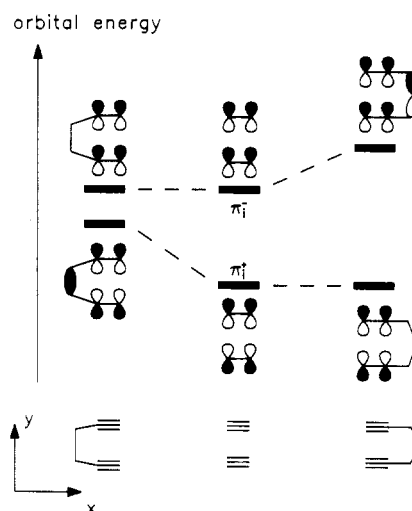


Figure 2. Interaction of the in-plane π -MOs of two acetylene fragments in 1,5-hexadiyne (left) and 1,6-heptadiyne (right) with the σ -frame.

Consider the in-plane π -MOs of two acetylene units (Figure 2). Through-space interaction leads to a stabilization of the bonding (π_1^+) and a destabilization of the antibonding (π_1^-) linear combination. Both wave functions possess different symmetries; π_1^+ is symmetrical, and π_1^- is antisymmetrical relative to the x,z plane. If the unsaturated systems are linked by a hydrocarbon chain, the interactions of both combinations with the σ -framework will depend on the number of CH_2 groups constituting the chain. An ethano bridge (left of Figure 2) destabilizes π_1^+ , thus reducing the through-space split. The σ -skeleton of a propano chain (right of Figure 2) interacts mainly with π_1^- ; consequently the through-space effect is increased. In general, an even-numbered bridge reduces the through-space split, and an odd-numbered bridge is expected to increase the split. The extent of through-space-through-bond coupling depends also on the basis energy of the σ -skeleton. High-lying σ -orbitals—for example, those of silicon compounds—exhibit a stronger interaction with the π -system than those of the carbon analogues. In compounds with σ -orbitals of low basis energy, the amount of π/σ -interaction is reduced, e.g., in fluorine compounds.

Double Bonds

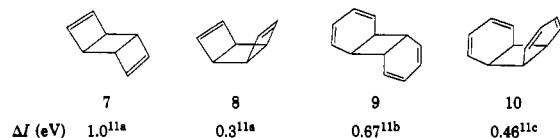
A recent review on proximity effects^{3f} has summarized in an excellent way all kinds of possible through-space interactions. We will therefore limit our discussion to a few examples. The size of the through-space interaction between double bonds should depend on the distance and the orientation of the π -moieties. To demonstrate the dependence on the distance, we list herein the difference of the ionization energies (ΔI) and electron attachment energies (ΔEA) of the first two ionization events together with the shortest distance (d) between the π -units of 4–6. A

	4	5	6
d (Å)	3.1	3.0	2.8
ΔI (eV)	0.2	0.4	1.0
ΔEA^* (eV)	–	–	0.9

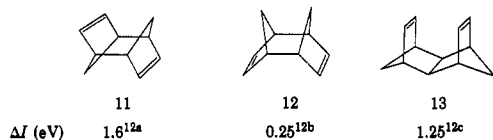
detailed analysis shows that through-space interaction

between both π -fragments in 4-6 is enhanced by the σ -skeleton.⁸ The second factor, the orientation of the π -units, has been demonstrated nicely in an early study on 1.⁹

In systems with high-lying σ -orbitals, the through-bond effect can be predominant. Cyclobutane, for example, provides Walsh-type orbitals¹⁰ that can strongly interact with π -MOs. The amount of this interaction is demonstrated in the series 7-10. In the case of the



anti isomers 7 and 9, we observe large splittings (>0.6 eV) between the π -bonds, while in the corresponding syn isomers the splitting is smaller. The smaller split in 9 as compared to 7 has been ascribed in part to the difference in the dihedral angle between the planes of the π -system and the central four-membered ring. This angle has been estimated to be 121° for 7 and 127° for 9.^{11b} That "normal" σ -bonds are also very efficient can be seen from 11 and 12. The small splitting in the case



of the syn isomers compared to the anti isomers in 7-12 can be rationalized by a balance of through-space and through-bond interaction. In 13 a larger split is observed although the π -units are further apart (2.8 Å) than in 12 (2.6 Å). This supports the rule illustrated in Figure 2, that the uneven chain in 13 enhances the through-space interaction by destabilizing π^- , while the even chain in 12 diminishes the splitting resulting from a pure through-space interaction by destabilizing π^+ .

Spiroconjugation

Most hydrocarbons that qualify for spirointeraction have been studied by UV/vis and PE spectroscopy and have been reviewed already.^{2c} A showpiece for demonstrating the effect of spiroconjugation on spectroscopic properties is 3.¹³ UV and PE investigations carried out on 3 show the same splitting (1.23 eV) for the first two ionic states and the first two excited states (see Figure 6). This coincidence can be traced back to cancellation of the Coulomb and exchange integrals due to symmetry.¹³

In general only in the PE spectra (and probably in the ET spectra) of highly symmetric spiro compounds does one observe a splitting of bands when comparing them with the PE bands of the fragment. In the case of the electronic spectra the effect of spiroconjugation is less striking and leads in most cases to a shift of

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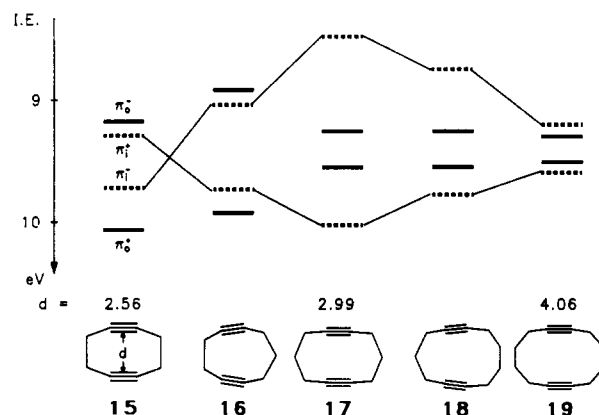
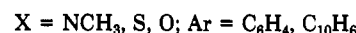
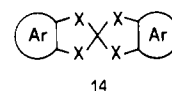


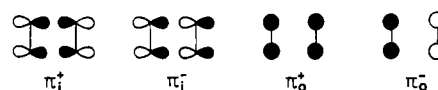
Figure 3. PE results of 15-19 as a function of the mean distance (d) between the triple bonds. Solid lines indicate the out-of-plane π -MOs, and broken lines stand for the in-plane π -MOs.

bands. This has been demonstrated recently also for heterocyclic systems of the type 14.¹⁴



Triple Bonds

The electronic system of acetylenes is more compact than that of ethylenes, and therefore the result of an interaction should be slightly smaller in size. On the other hand, the π -system exhibits cylindrical symmetry; thus, through-space interactions between such fragments should not depend upon the orientation. If two acetylenic systems are arranged in a plane, the four π -orbitals are expected to form two sets of bonding and antibonding linear combinations of the in plane (π_i) and out of plane (π_o) π -MOs, as shown below:



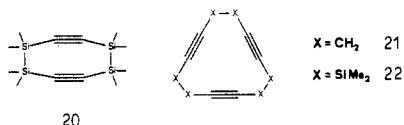
We expect only a small splitting for the π_o set but a sizable one for the π_i linear combinations for distances between 2.5 and 3.5 Å. As shown in Figure 2, the two π_i linear combinations are able to interact with high-lying σ -orbitals localized at the C-C bonds of hydrocarbon chains connecting the triple bonds. Consequently, we expect an interplay of through-space and through-bond effects for cyclic di- and triacetylenes depending on the chain length and distance as discussed above.

Compilation of recent PE measurements on the cyclic diacetylenes 15-19¹⁵ shows an exponential dependence for the π_o set (see Figure 3). For the π_i set, however, the split in 15 is considerably smaller (0.4 eV)^{15a} than in 17 (1.6 eV)^{15b} although the distance in 15 has been determined to be 2.56 Å^{15a} while in 17 both units are separated by 2.99 Å (see Figure 3).^{15b} This discrepancy can be solved on the basis of Figure 2. The two C₂H₄ chains in 15 destabilize π_i^+ and overrule a large

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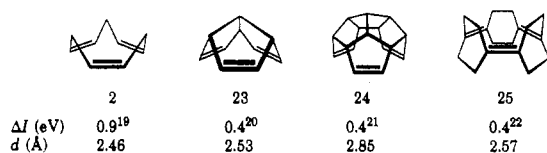
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through-space effect, such that the π_1^+ linear combination is found at lower energy than the π_1^- combination (Figure 3). In **16** a C_2H_4 and a C_3H_6 bridge compete with each other. The observation that π_1^- emerges on top of π_1^+ can be rationalized by assuming that the interaction $\pi-\sigma$ (propano) is stronger than $\pi-\sigma$ (ethano) due to the higher basis orbital energies of the σ -skeleton of the propano bridge as compared to the σ -orbital of the ethano moiety. The importance of the energy of the σ -chain, as encountered in **16**, shows up more strongly when comparing C-C bonds with Si-Si bonds. This has been demonstrated by comparing the PE spectra of **15** and **20**¹⁶ as well as **21**¹⁷ and **22**.¹⁶

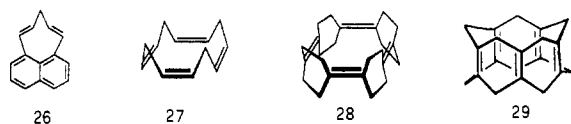


Homoconjugation

Since its postulation by Winstein,¹ the concept of homoconjugation and homoaromaticity has attracted great theoretical and experimental interest.¹ Thermochemical as well as UV and NMR studies on **2** revealed no sign of homoconjugation.¹⁸ By means of PE spectroscopy, however, a definite splitting of the different ionic states of **2** has been found¹⁹ (for the difference between conjugative stabilization and orbital splitting, see the section entitled Consequences for Reactivity). In the case of **23–25**, PE spectroscopy reveals only a



band broadening.^{20–22} This has been ascribed to a difference in the interaction between $\epsilon(\pi)$ and $a_1(\pi)$ with the corresponding σ -MOs. In the case of **26**, the electronic absorption spectra as well as the PE and ¹H NMR data are indicative of homoconjugation.²³ The



two homo- 8π systems **27**²⁴ and **28**²⁵ show no sign of a

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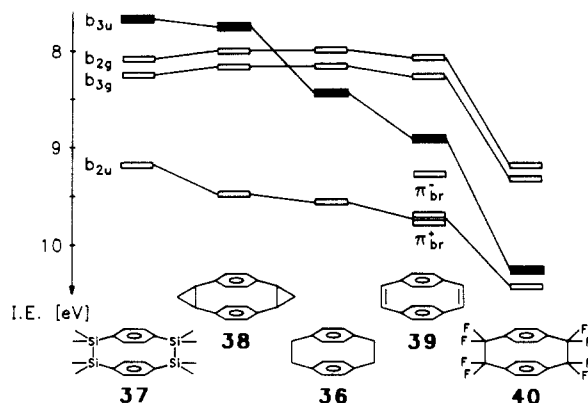
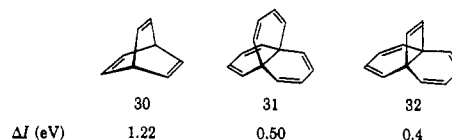
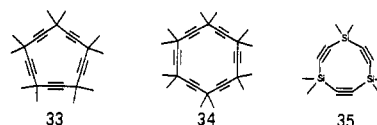


Figure 4. Correlation between the first four PE bands in the PE spectra of **36–40**. Open bars, pure π -orbitals; filled bars, π -orbitals with strong contributions of the ethano σ -orbitals; π_{br} , π -orbitals of the bridges.

sizable interaction between the π -units in their PE spectra. The synthesis of **25** and **28** initiated the theoretical investigation of the “in-plane trishomoaromaticity”.²⁶ Also, systems comprising 1,4-cyclohexadiene units with an overall D_{nh} symmetry like [5]beltene **29** have been theoretically investigated.²⁷ From our investigations on **23–28** it is evident that any $\pi-\pi$ interaction in the beltene will be hard to prove. The larger rings should, however, be of interest with respect to their receptor properties. At this point we should mention barrelene (**30**)²⁸ and the propellanes **31** and **32** for which a definite splitting between the π -bands in the PE spectra has been encountered.²⁹



Examples for the homoconjugation of triple bonds are provided in the pericyclenes. So far data for [5]- to [8]pericyclenes have been reported.³⁰ Spectroscopic (PE and ET) investigations on **33** and **34** reveal a weak



homoconjugation in the cationic and anionic states.³⁰ Also the silicon analogue of [3]pericyclicene (**35**) shows some indication of homoconjugation in its PE spectrum.¹⁶ Although homoaromatic interaction has been detected in some cases, there is no experimental evidence about any stabilization in neutral homoaromatic systems³¹ (for the difference between interaction and

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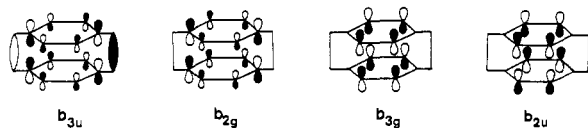
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stabilization, see the section entitled Consequences for Reactivity).

Benzene Rings

There are many ways in which two aromatic rings can interact with each other. We will restrict ourselves to [2.2]paracyclophane (**36**) and its congeners. It should be mentioned that **36** stands for many cyclophanes with different bridges and aromatic units. More recent studies concerning the interaction in these species have been reviewed by Heilbronner and Yang.³² Also mixed cyclophanes with donor and acceptor units have been investigated.³³

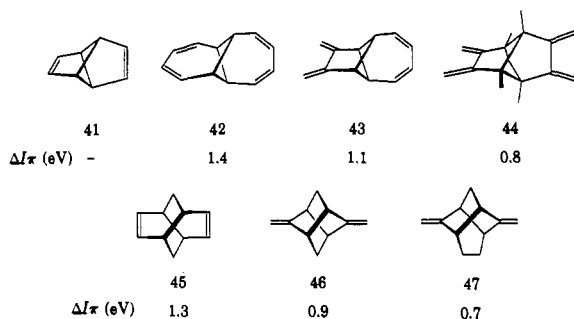
The spatial interaction of benzene rings in **36** is influenced by admixture of σ -orbitals of the ethano fragments connecting the rings. This is demonstrated for **36** and its congeners **37–40** in Figure 4. It is shown that from the four linear combinations of the former benzene $e(\pi)$ MOs (b_{3u} , b_{2g} , b_{3g} , and b_{2u}) the b_{3u} linear combination depends very strongly on the nature of the bridge. In the case of **37**³⁴ and **38**³⁵ the energy of the



σ -bridge is raised with respect to the C_2H_4 bridge of the parent system (**36**); therefore the b_{3u} ionization energy is shifted toward lower energy. In **39** and **40** the opposite is the case.³⁶

Interaction via Rings and Polycyclic Systems

Recently, a series of compounds have been studied in which a central ring system is bridged on both sides such that the double bonds are arranged perpendicularly or nearly perpendicularly to each other. Examples with a central four-membered ring are **41–44**; with a six- and seven-membered ring, **45–47**. In the case of **42–47**



PE investigations reveal a splitting in the range of 0.7–1.4 eV.^{37–39} For **41** the interaction is proven by its

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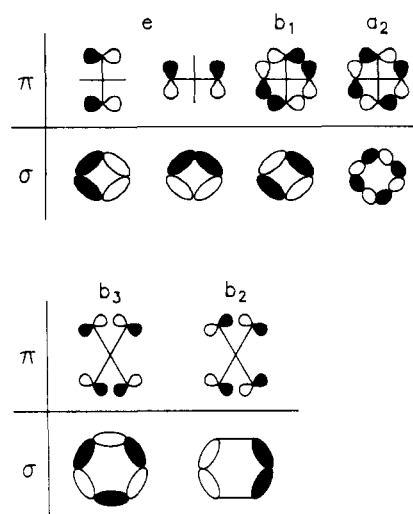


Figure 5. Top: Comparison between the frontier π -MOs of two perpendicular π -systems in **42–44** and the Walsh MOs of a four-membered ring. Bottom: Comparison between π -MOs of b_3 and b_2 symmetry of two olefinic units in **45** and **46** and the corresponding σ -MOs of a twisted six-membered ring.

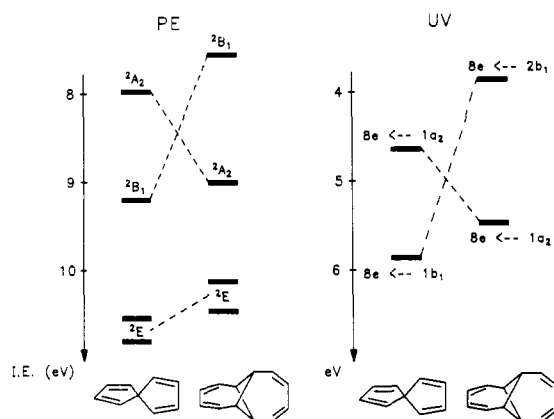


Figure 6. Left: Comparison between the first PE bands of **3** and **42**. Right: Comparison between the first two excited states of **3** and **42**.

long-wavelength absorption (300 nm).⁴⁰ The strong splitting of the first π -bands in the PE spectra of **42–47** can best be understood by comparing the valence orbitals of the π -bridges with those of the central rings. In the case of **42–44** the highest occupied π -MOs of the fragments (a_2 , b_1) ideally match the corresponding Walsh-type $b_1(\sigma)$ and $a_2(\sigma^*)$ MOs of the cyclobutane ring (see Figure 5). As a consequence $a_2(\pi)$ is stabilized and $b_1(\pi)$ is destabilized, so that the first two ionic states of **42–44** are reversed to such an extent that the separation is considerable. The comparison between the first ionic and excited states of **42** with those of **3** reveals a similar energy difference of the first two ionic and excited states of **42** and **3** but a different symmetry of these states (Figure 6). Just as in the case of **3** we notice for **42** a similar value of the splitting of the first two ionic states ($\Delta I(1,2) = 1.4$ eV) and the first two excited states ($\Delta E(1,2) = 1.6$ eV). While in **3** the Coulomb repulsions and exchange contributions cancel each other in a first-order approximation, this is not the case in **42** due to the difference in the interactions b_2 -

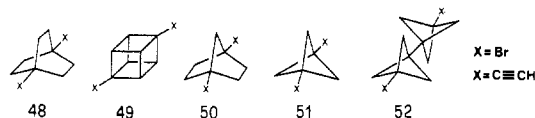
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$(\pi)-b_2(\sigma)$ and $a_2(\pi)-a_2(\sigma^*)$. This difference is, however, small, and therefore the difference between $\Delta I(1,2)$ and $\Delta E(1,2)$ of **42** resides within experimental error. For **45–47** the situation is somewhat different insofar as the two π -MOs (b_2 , b_3) both interact with low-lying σ -MOs of the central ring (Figure 5). The recorded splittings of the first two PE bands of 0.6–1.3 eV³⁹ show that also six- and seven-membered rings can act as good relays.

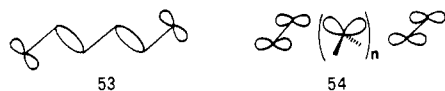
Instead of monocyclic systems like in **41–47** one can also consider polycyclic systems as potential relays (viz., **48–52**). From PE investigations on these species^{41,42}



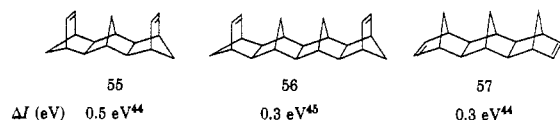
it is evident that only for **51** a sizable splitting is found (0.7 eV). For **48–50** the splitting of the first two PE bands is on the order of 0.2–0.4 eV,⁴¹ a value that has also been found for **52**.⁴² Since in **52** the two substituents are separated by about 8 Å, this splitting is rather remarkable.

Long-Distance Effects

Long-range interactions in rigid molecules have been investigated by means of PE and ET spectroscopy. Since this topic has been reviewed very recently,^{3e} we will keep this paragraph short despite its importance with respect to the intramolecular energy transfer in donor-acceptor systems. For the long-range through-bond interaction, essentially two effects have been invoked, first, π/σ -interaction as discussed for the simpler systems in the preceding paragraphs, e.g., **53**, and sec-



ond, an interaction involving essentially the C-C σ -skeleton and a laticyclic hyperconjugative interaction as indicated in **54**.^{3e,43} This latter effect has been suggested to account for the large splitting in **55** and **56** as compared to **57**.



Consequences for Reactivity

The interaction between π -fragments not directly connected with each other should influence the reactivity in those cases where a net stabilization is encountered. Stabilization should not be confused with energy splitting: Although the energy splitting of the occupied MOs in butadiene is 2.4 eV, the stabilization

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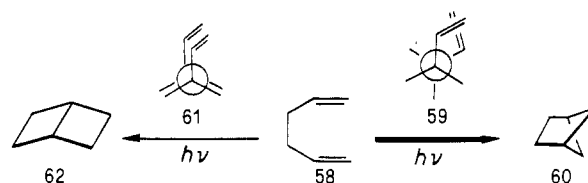
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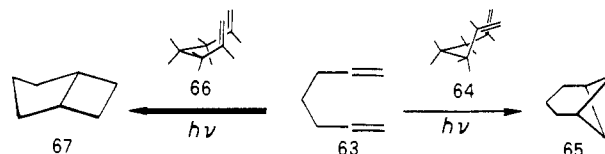
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due to conjugation with respect to two ethylenes is only 4 kcal/mol. From Figure 1 it is also evident that the stabilization due to conjugation would be larger in the radical cation or radical anion case. That means we have to look for those cases where more bonding than antibonding levels are occupied.

As a consequence of this reasoning we expect stabilization effects in those cases where cations, anions, biradicals, or excited states are involved. Since we have restricted this Account to neutral species, we will focus on them. Three examples have been discussed and reviewed⁶ already, the Grob fragmentation,⁴⁶ some aspects of the Birch reduction,⁴⁷ and the concept of σ assistance and σ resistance of the ring closure of radicals and intramolecular hydrogen transfer.⁴⁸ In this Account we point out that through-bond effects are also important for understanding photochemical reactions. To rationalize the "rule of five",⁴⁹ the difference between the interaction of two π -systems and an ethano or propano bridge, as shown in Figure 2, has been invoked.⁵⁰ The strong destabilization of the π^+ linear combination in hexa-1,5-diene (**58**) due to the ethano bridge (e.g., Figure 2) has been made responsible for a considerable electronic activation energy for both modes of photochemical [2 + 2] ring closure.⁵⁰ Thus the "head to tail" transition state **59**, which is sterically more favored than the "head to head" one in **61**, turns the scale toward **60**.



In the case of hepta-1,6-diene (**63**), where the propano bridge enhances the through-space interaction, the electronic contribution to the activation energy for the "head to head" ring closure via **66** to **67** is predicted to be 0, and thus this path is favored over the one via **64** to **65**. A further example is the light-induced ring



closure of the bridged tricyclo[4.2.0.0^{2,5}]octa-3,7-diene derivative **68** to propella[3₄]cubane (**69**).⁵¹ In this connection it is of interest that *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (**70**) and its alkyl derivatives do not lead to cubane upon irradiation.⁵² Apart from the differ-

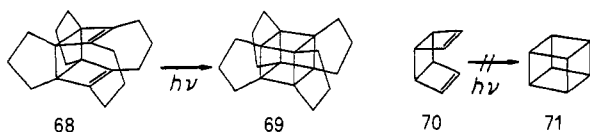
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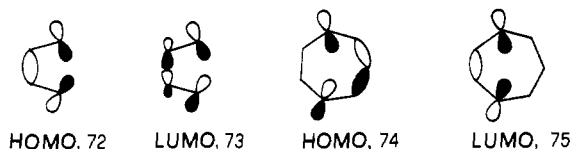
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ences in the strain energies in both systems, electronic factors have been made responsible for this contrasting behavior.⁵¹ Due to the strong π/σ -interactions in 70, the HOMO (72) is found to be bonding (π^+) and the LUMO (73) antibonding with respect to a π/π - and π^*/π^* -interaction^{11a} (see below).



In 68, however, the propano bridges overrule the effect of the ethano bridges as discussed for 16 and thus the phases are reversed, i.e., the HOMO (74) is antibonding and the LUMO (75) is bonding with respect to a π/π - and π^*/π^* -interaction, respectively. Thus the excitation of an electron in 68 from the HOMO (74) to the LUMO (75) increases the bonding between the π -units, and therefore the [2 + 2]cycloaddition in this molecule should be favored.

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Conclusion

The mode of thinking of most chemists with respect to the interaction of π -moieties that are not directly connected with each other is a through-space one and disregards the σ -frame. From this it seems logical that the interaction of π -systems depends on their mutual distance and orientation only. Experimental investigations together with model calculations have revealed that this view is too simple. The σ -frame not only is used to fix the π -units but also contributes considerably. As it turns out, the most important parameters of the σ -frame are its length and the energies of the orbitals associated with the σ -chain. To judge the influence of the length of the σ -frame, a simple rule emerges: a bridge with two carbon atoms narrows the gap between π_+ and π_- , while a bridge with three carbon centers enlarges it (see Figure 2). Usually the effect of a propano bridge overrules that of an ethano bridge. The strong influence of the bridge affects the reactivity considerably. This should be and has been observed in those cases where a switch of the frontier orbitals occurs within a series of similar molecules (e.g., 15-19 or 36-40). Recent experiments in the series of cyclic diacetylenes¹⁵ have demonstrated this prediction.

We are grateful to all the co-workers and colleagues whose names appear in the references. We thank the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the BASF Aktiengesellschaft for continuous support.

The Controversial Heat of Formation of the *t*-C₄H₉ Radical and the Tertiary C-H Bond Energy

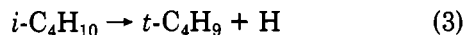
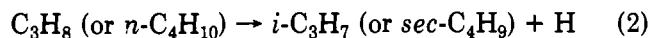
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Introduction

Accurate heats of formation of the alkyl radicals are of value for a number of reasons. For example, they are needed to determine the primary, secondary, and tertiary C-H bond dissociation energies, i.e., DH°_{298} for the following process:¹⁻³



David Gutman attended both UCLA and UC, Berkeley, receiving his B.S. from Berkeley in 1960. It was there, in Harold S. Johnston's physical chemistry class, that he became intrigued with the properties of as well as the chemical kinetics of free radicals, subjects that continue to fascinate him to this date. He studied high-temperature kinetics with a shock tube under the direction of R. Linn Belford at U. Illinois, Urbana, receiving his Ph.D. in 1965. Then he joined the chemistry faculty at the Illinois Institute of Technology, rising to the rank of Professor. In 1988, he moved to The Catholic University of America, where he is chair of the Chemistry Department and continues his studies on the kinetics and thermochemistry of the reactions of polyatomic free radicals, particularly those involved in hydrocarbon combustion, tropospheric processes, industrial synthesis, and most recently, gas-surface catalysis.

These and other bond energies are invaluable in mechanistic chemistry because they provide the means to determine heats of formation of reaction intermediates and transition states (known or postulated).² When this thermochemical information is accurately known, it yields useful enthalpic criteria that, together with laboratory measurements (such as enthalpies of activation), can be used to discriminate between plausible reaction mechanisms.^{2,4-7} When bond energies are inaccurate, their use for this same purpose can lead to erroneous and sometimes unusual conclusions.

A major controversy arose from the use of widely accepted low C-H bond energies to calculate the heats

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