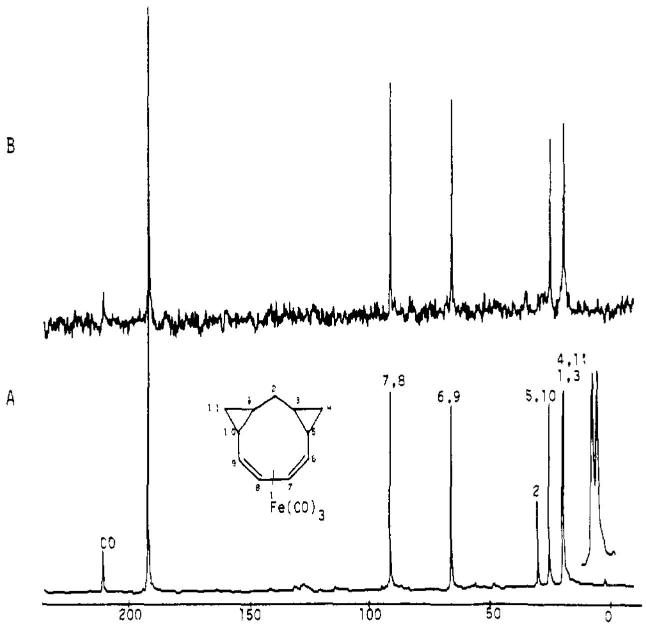

**Figure 1.** Proton decoupled $^{13}C$ NMR spectra: (A) compound **6** with peak assignments and proposed structure (Insert at right is an expansion of the resonances assigned to carbons 1, 3, 4, and 11.); (B) the $d^6$ analog of **6**, deuterated at positions 2, 4, and 11. The resonance at 193 in both is from the $CS_2$ solvent.

of **6** prepared by using $CD_2I_2$ in a Simmons-Smith reaction with **5** as described above. Due to carbon to deuterium coupling, the resonances for the $CD_2$ carbons are not observed. Assignments of resonances can be made as shown in Figure 1 for our proposed structure. The chemical shift of the peak assigned to the cyclopropyl methylene resonance is the same as that of the analogous cyclopropyl methyl resonance in compound **2**, assigned by preparing 8,8′-dideuterio-**2**. Further conformation of the structure comes from the $^1H$ NMR of the $d^6$ analog of **6**. In $CS_2$ solution, it shows complex resonances at $\delta$ 5.16 and 3.76 assigned to a symmetrically metal coordinated diene and an AB pattern centered at $\delta$ 1.18 assigned to the equivalent set of resonances from positions 3,5 and 1,10. The $^2H$ NMR[13] of the $d^6$ derivative of **6** and the $^1H$ NMR of **6** also are consistent with this structure. We are at present attempting to determine the mechanism for the formation of **6**. No mono- or diadducts have been isolated or observed.

The reactions described above show that polycyclic metal complexes can be prepared by the addition of methylene to uncoordinated double bonds present in metal olefin $\pi$ complexes. The conditions of the reaction are mild enough to prevent thermal rearrangement of the products unless a vinylcyclopropane is formed as in the reaction with **5**. Thus, potentially, methylene addition can be directed to desired locations in polyolefins by proper choice of coordinating metal. We are now attempting to cleave from the metal and isolate the tricyclic rings in compounds **4** and **6** (both unknown organic compounds) to show that this approach can be useful in the synthesis of new organic compounds.

**Acknowledgment.** Support of this research by the Research Corporation is gratefully acknowledged.

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## Perturbed Pericyclic Reactions. Electrocyclic Ring Closure of Heteroacycles Isoelectronic with the Allyl Anion

*Sir:*

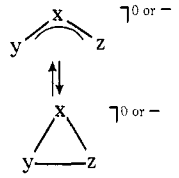
The orbital symmetry conservation principle has proven enormously popular and effective for rationalizing the stereochemistry and relative energies of a host of reactions involving cyclic transition states. Its application, particularly in the form of the Woodward–Hoffmann (W-H) rules,[1,2] usually depends on a knowledge of the behavior of a few critical high-lying molecular orbitals[3] derived from symmetrical hydrocarbons. Nonetheless the rules have been routinely applied to unsymmetrical substances including both highly substituted hydrocarbons as well as hetero derivatives. The justification for this procedure, suggested explicitly by Woodward and Hoffmann,[4] lies partly in the assumption that a small deviation from molecular symmetry is expected to produce an equally small change from the symmetry of the derived molecular orbitals. Consequently the slightly perturbed system is anticipated to lead to the same overall result as for the symmetric analog.[5,6] The question which naturally arises concerns the magnitude of the deviation from symmetry a molecule can withstand before the W-H rules no longer apply in a straightforward fashion.

The present work concerns itself with the heteroacyclic unit **1**, isoelectronic with the allyl anion, and its CNDO-computed[8] ring closure to the corresponding three-membered ring **2**. For the nine cases **3–11** all possible acyclic stereoisomers were transformed stepwise through both conrotatory and disrotatory transition states[9a] to all possible cyclic conformations.[9b] An orbital correlation diagram was constructed for each reaction investigated.

As a test for the predictive ability of this procedure, three cases (**3**, **7**, and **11**) were repeated with an energy-geometry optimization at each of the points along the reaction coordinate. The qualitative result was retained in every essential respect:[10] (i) the relative magnitude of the energy difference between the disrotatory and conrotatory modes; thus (ii) the favored stereochemistry for ring closure, and (iii) the details of the orbital correlation diagrams.

The results of the calculations reveal that heteroatom substitution of **1** leads to three types of ring closures. The first is represented by the least perturbed series **3**, **4**, and **5**. The symmetrical aziridine system **4** has been shown experimentally to conform to the W-H rules.[11] The computed reaction characteristics are in accord with observation and identical in all essentials to the hydrocarbon parent **3**.[12]

**1**



**2**

|  |  | x | y | z |
|---|---|---|---|---|
| I | **3** | CH | $CH_2$ | $CH_2$ |
|  | **4** | NH | $CH_2$ | $CH_2$ |
|  | **5** | CH | $CH_2$ | NH |
| II | **6** | NH | $CH_2$ | NH |
|  | **7** | NH | $CH_2$ | O |
| III | **8** | CH | $CH_2$ | O |
|  | **9** | CH | NH | NH |
|  | **10** | CH | NH | O |
|  | **11** | CH | O | O |

System **5** is devoid of symmetry. Figure 1 indicates, however, that the construction of the key MO strongly resembles the all-carbon case. Correlation diagrams for the conrotatory and disrotatory closure of the 1-azaallyl anion (**5**) are given in Figure 2. The parallel with the symmetrical cases **3** and **4** is complete. Thermal conrotation is "allowed"; disrotation, "forbidden". The latter terms are operationally defined by the absence or presence of a HOMO-LUMO crossing, respectively. In category I ring closure is qualitatively predicted by following the conversion of the $\pi$-HOMO of the open anion to the high-lying occupied $\sigma$-orbital[13a] of the closed anion.

Category II contains the azomethine imine and nitrone moieties, **6** and **7**, respectively. All variations[9a] of the ring closure reactions are found to be "allowed".[14] That is, the corresponding correlation diagrams resemble that depicted in Figure 2A. Furthermore the total energy of the eight isomeric transition states for the closure of **6** is calculated to fall within the narrow range 18.7-22.1 kcal/mole. In complete agreement with these predictions, oxaziridines (**7**-closed) undergo rapid first-order ring cleavage ($t_{1/2}$ ($-8°$) = 17 min) to give a 50:50 mixture of the corresponding cis and trans nitrones.[15] The correlation common to this category is the transformation of the $\pi$-HOMO of the acycle to the highest lying $\sigma$-lone pair MO[13b] of the corresponding ring. It is noteworthy that the $\pi$-HOMO for open **6** (Figure 1) does not differ significantly from that for **5** of category I. The danger inherent in relying on potential surface minima or end point wave functions as predictors of reactivity is evident.

Structures **8-11** include both symmetric and unsymmetric entries. Thermal ring closure and opening for all geometrical variants[9a] are distinguished by a correlation diagram of the type illustrated in Figure 2B. Namely category III cases are thermally "forbidden" but photochemically "allowed". A straightforward consideration of the formate ion (**11**) by construction of a Walsh-diagram[16] for example leads to the same conclusion. Thus if $C_{2v}$ symmetry is preserved, the antisymmetric in-plane oxygen lone pair combination ($b_2$) is transformed to an antibonding ring MO. The highest occupied $\pi$-MO ($a_2$) becomes a filled $\pi$-MO. Four of the 12 isomeric closure pathways of structure **9** follow this pattern, but the most frequently observed fate of the open $\pi$-HOMO in cases **8-10** is connection with an antibonding $\sigma^*$ [13c] of the three-membered ring. Figure 1 illustrates the relevant $\pi$-MO for the unsymmetrical case **10**. Again HOMO constitution provides no clue as to the course of the closure reaction.

In the present analysis we have relied exclusively on the orbital symmetry conservation principle as manifested by following the behavior of high-lying molecular orbitals within a single electronic configuration.[17] Within the simplicity of this framework, it is clear that the W-H rules as well as the notion of orbital isomerism[2a] are inadequate for handling categories II and III. For the symmetric extremes of series **3-11** ("allowed" and "forbidden" respectively), analysis can be made by using symmetry arguments alone. The results imply a gradual transformation from one type of behavior to the other.[18] Nonetheless the overall course of ring closure as well as the details of orbital correlation are complex[13] and dependent on the type of heterosubstitution.

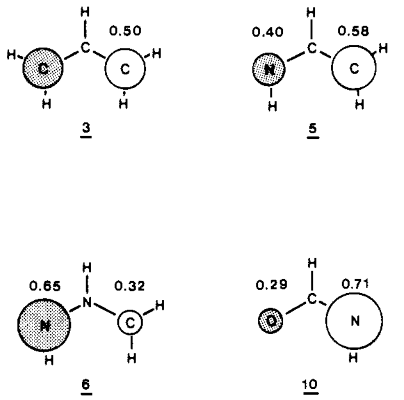


**Figure 1.** The highest occupied $\pi$-molecular orbitals for the energy-geometry optimized acyclic, potential-surface end points **3**, **5**, **6**, and **10**. Decimal values represent the relative AO contributions to the MO pictured, i.e., the square of the AO coefficients.

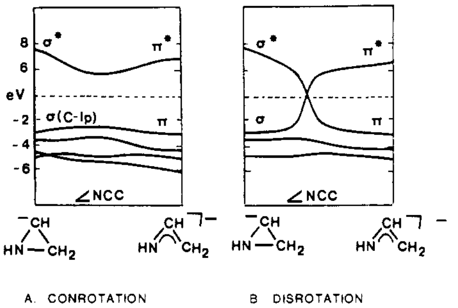


**Figure 2.** Molecular orbital correlation diagrams for the interconversion of the 1-azaallyl anion and the 2-azacyclopropyl anion. Only the lowest-lying virtual orbitals (LUMO's) and the three highest-lying filled MO's are pictured. The uppermost $\sigma$-MO for the three-membered ring corresponds essentially to the lone electron pair on carbon.

The major conclusion to be drawn from the present work is that, for strongly perturbed systems, the mechanistic details of electrocyclic ring closure can be predicted neither from a naive consideration of orbital symmetry, orbital topology, or by end point MO analysis alone.[19] Likewise the bond order criterium[20] appears to be ineffective as an indicator for either the overall energetics of a given reaction or the preferred ring closure mode. Finally reordering of specific MO energies as a function of heteroatom substitution is irregular for structures **3-11** and provides no clearcut rationalization of the computed transformations.[21]

Until more is learned about the nature of heteropericyclic reactions, the construction of an orbital correlation diagram with the aid of the extended Hückel or the CNDO/INDO approximations is recommended as the simplest procedure for avoiding the pitfalls associated with intutitive analysis of unsymmetrical concerted processes.

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(10) For a quantitative and detailed assessment of electrocyclic reactions, geometry optimization throughout the entire reaction is essential.[7] However, for a *qualitative prediction* of "allowedness"/"forbiddeness" and overall stereochemistry, our results indicate that judicious use of geometric constraints is valid. Needless to say, computer expenses are thereby significantly reduced.

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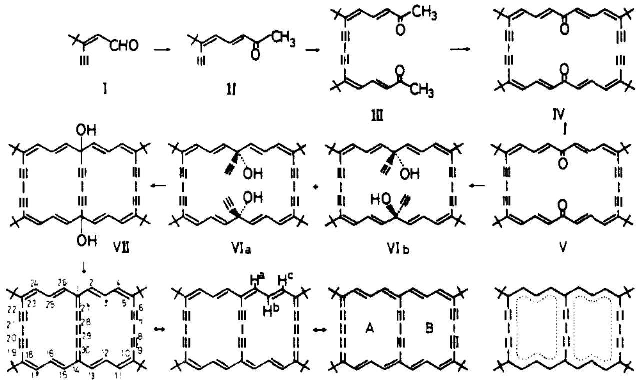
## Synthesis of a Condensed Nonbenzenoid Aromatic System. An Annulenoannulene Consisting of Two 18π-Electron Systems

*Sir:*

In spite of fascinating developments in the chemistry of nonbenzenoid aromatic compounds, condensed systems of aromatic annulenes corresponding to naphthalene still remain unknown. In view of the strong diatropicity and high conformational stability of symmetrical tetradehydro- or didehydro[$4n + 2$]annulenes containing formal acetylenic and cumulenic linkages in the cyclic system,[1] it seemed of considerable interest to synthesize a fused dehydroannulene system of this type. We now describe the preparation of an annulenoannulene (VIII) consisting of two tetradehydro-[18]annulene nuclei.

The ethynyl ketone (II, pale yellow liquid, 56%) obtained by the aldol condensation of I[2] with acetone (NaOH-H$_2$O-EtOH, room temperature, 8 min) was oxidatively coupled by cupric acetate in pyridine to give III (yellow crystals, mp 121.5–123.5°, 71%; Anal. (C$_{24}$H$_{30}$O$_2$) C, H).[3] Treatment of III in benzene with an excess of I in the presence of sodium ethoxide (4°, 2 hr) yielded IV (yellow crystals, mp 128.5–129.0°, 92%; Anal. (C$_{42}$H$_{50}$O$_2$) C, H; ir (KBr) 1659 cm$^{-1}$ (C=O)). Oxidative coupling of IV by cupric acetate in pyridine–ether–methanol under high dilution conditions (46°, 16 hr) resulted in the 26-membered cyclic diketone (V, yellow crystals; mp ca. 183° dec, 97%; Anal. (C$_{42}$H$_{48}$O$_2$) C, H; ir (KBr) 1666 cm$^{-1}$ (C=O)). Bisethynylation of V (2°, 2 hr) using the lithium acetylide-ethylenediamine complex in THF saturated with acetylene gave a mixture (VI$_a$ and VI$_b$) which, upon chromatography on alumina, yielded a high melting isomer (pale yellow crystals; mp 167–170° dec; Anal. (C$_{46}$H$_{52}$O$_2$) C, H) and a low melting isomer (light brown crystals, mp 162–165° dec; Anal. (C$_{46}$H$_{52}$O$_2$) C, H) in ca. 4:1 ratio (total yield 88%). The isomerism can be reasonably ascribed to the differing disposition of the ethynyl and hydroxyl groups. Treatment of the high melting isomer with cupric acetate in pyridine–methanol–ether under high dilution conditions (46°, 6 hr) yielded the bicyclic glycol (VII, yellow crystals, mp 168–170° dec; 61%; Anal. (C$_{46}$H$_{50}$O$_2$) C, H; *m/e* 634 (M$^+$)).[4]



Glycol (VII) in ether was mixed at −60° with a solution of stannous chloride dihydrate in the same solvent saturated with hydrogen chloride. After 10 min, the resulting deep green reaction mixture was quenched with water and worked up in the usual way, and the product was recrystallized from THF to yield 5,10,18,23-tetra-*tert*-butyl-6,8,19,21,27,29-hexadehydro[26]bi[12.12.4]annulene (VIII: dark green crystals; mp 230° dec; 79%; Anal. (C$_{46}$H$_{48}$) C, H; *m/e* 600 (M$^+$)).[5] VIII gave a 1:1 CT complex with 2,4,7-trinitrofluorenone (dark green crystals; mp ca. 250° dec; Anal. (C$_{59}$H$_{53}$N$_3$O$_7$) C, H, N). VIII was found to be a fairly stable and sparingly soluble compound, whose electronic spectrum consists of three main absorption bands ($\lambda_{\max}{}^{\text{THF}}$ 446 nm ($\epsilon$ 630,000), 641 (88,900), 855 (2200)) clearly showing features characteristic of [$4n$ + 2]annulenes; *i.e.*, the spectrum of VIII was found to be closely related with that of tetra-*tert*-butyltetradehydro-[18]annulene (IX) except for bathochromic shift and hy-