

Pericyclines: "Exploded Cycloalkanes" with Unusual Orbital Interactions and Conformational Properties. MM2 and STO-3G Calculations, X-ray Crystal Structures, Photoelectron Spectra, and Electron Transmission Spectra¹

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Abstract: Geometries and electronic structures of [*N*]pericyclines, (C≡CCH₂)_{*N*}, where *N* = 2–6, and some permethylated analogues have been investigated by using Allinger's MM2 force-field and ab initio STO-3G calculations, photoelectron spectroscopy, and electron transmission spectroscopy. The "small-ring" pericyclines, *N* = 3 and 4, are planar, with all the angle strain absorbed by the relatively easily deformable acetylene linkages. The "common-ring" pericyclines, *N* = 5 and 6, behave conformationally like cyclopentane or cyclohexane in which all torsional interactions are eliminated. For example, [6]pericycline has chair, twist-boat, and boat forms of essentially identical energy. Both through-space and through-bond interactions between the acetylenic units are found to be important, with the former dominating in the in-plane orbitals and the latter in the out-of-plane orbitals. The structure of decamethyl[5]pericycline predicted by MM2 compares well with the X-ray crystal structure. The crystal structure of a tetrayne, 5,5,6,6,11,11,12,12-octamethyl-1,3,7,9-cyclododecatetrayne, obtained in the attempted preparation of a [4]pericycline, is also reported.

The conceptual insertion of a —C≡C— unit between each pair of adjacent CH₂ groups in a cycloalkane greatly lengthens the sides of the original ring, while leaving the total number of CH₂ vertices unchanged. Such "exploded cycloalkanes" constitute a novel family of homoconjugated cyclic polyacetylenes which have been referred to as the [*N*]pericyclines,² where *N* indicates both the number of CH₂ groups and the number of —C≡C— units. Molecules of this class are expected to manifest special electronic properties arising from unusual orbital interactions, especially in the first members of the series, and should provide insight into the question of homoconjugation in neutral hydrocarbons.³ In addition, the "exploded" dimensions of a pericycline ring ought to endow these molecules with peculiar conformational properties, since torsional strain and transannular van der Waals repulsions, which play such a crucial role in determining the relative energies of various conformations of cycloalkanes, will be virtually absent. We present here the results of molecular mechanics calculations and ab initio molecular orbital calculations on pericyclines of the order [2], [3], [4], [5], and [6] that allow several interesting conclusions to be drawn about the conformational properties of these molecules and the unusual nature of the orbital interactions therein. The photoelectron spectra and electron transmission spectra of decamethyl[5]pericycline and dodecamethyl[6]pericycline are also presented in detail for the first time and are interpreted with the aid of ab initio calculations. Dewar and Holloway recently reported MNDO calculations on [3]-, [4]-, and [5]pericycline,^{4,5} and our results are compared to theirs. The X-ray crystal structures of decamethyl[5]pericycline and of an isomer obtained in the attempted preparation of octamethyl[4]-pericycline are also reported.

Conformational Analysis

Since pericyclines are nonconjugated alkynes without any electronically idiosyncratic groups, force-field calculations should

provide reliable geometrical predictions and relative energies of different conformations. Allinger's MM2 force field⁶ provides reasonable geometries and strain energies of alkynes and other nonconjugated hydrocarbons and was chosen for the calculations.

The strain energies and geometries of various conformations of the [*N*]pericyclines, *N* = 2–6, are summarized in Table I. The only major geometrical differences between various species were in bond angles and dihedral angles. These are summarized in Table I for each species, while the relatively constant bond lengths are summarized in footnote a of the table.

[2]Pericycline. Primarily for amusement, the highly strained [2]pericycline was calculated. As indicated in Table I, the molecule is very strained. Since all the strain can be released upon CC bond scission, this molecule should not survive under any conditions. Only [1]pericycline (cyclopropyne) will be a more strained member of this series.

[3]Pericycline. The unsubstituted compound is planar *D*_{3h}, with a strain energy of 28 kcal/mol, essentially identical with that of cyclopropane.⁷ As is apparent from Figure 1, the angle strain

(1) Part 5 in the series on "Cyclines". For Parts 3 and 4, see ref 2 and 8, respectively.

(2) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1983**, *105*, 7760–7761.

(3) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106. Warner, P. M. "Topics in Nonbenzenoid Aromatic Chemistry"; Hirokawa Publishing Co.: Tokyo, 1977; p 283.

(4) Dewar, M. J. S.; Holloway, M. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1188.

(5) The original computational studies of [3]pericycline, the isomeric tricyclopropabenzene, and their interconversions were carried out in 1978 by Ruth Wells Gandour at Louisiana State University and James P. Ritchie in Prof. Dewar's laboratories at the University of Texas, using MINDO/3 and MNDO, respectively. These studies were undertaken in collaboration with Prof. Randolph P. Thummel of the University of Houston. [4]Pericycline was studied with a variety of semiempirical computational techniques by Cielo Santiago at Louisiana State University in 1977.

(6) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Quantum Chemistry Program Exchange, No. 395. For an excellent general description of MM2 and force-field calculations, see: Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, DC, 1982; ACS Monograph No. 177.

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Table I. Summary of MM2 Geometries and Strain Energies for [N]Pericyclines^a

pericyclyne	conformation	strain energy ^c	$\angle -C\equiv CC-$	$\angle CCC$	$\angle RCR^d$	ring dihedral angles ^e
[2]	planar	106.7	141	79	117	0.0
[3]	planar	28.0	162	97	113	0.0
Me ₆ -[3]	planar	31.4	162	96	113	0.0
[4]	planar	5.5	173	105	111	0.0
Me ₈ -[4]	planar	11.2	173	103	112	0.0
[5]	planar	-0.3	179	110	109	0.0
[5]	envelope	-0.3	179	110	109	A
Me ₁₀ -[5]	planar	8.2	180	107	111	0.0
Me ₁₀ -[5]	envelope	8.2	180	107	111	B
[6]	planar	1.6	177	113	119	0.0
[6]	chair	-0.5	180	111	109	±55.5 ^f
[6]	boat	-0.6	180	110	109	C
[6]	twist-boat ^b	-0.6	180	110	109	D
[6]	half-chair	0.2	177-180	110-114	109	E
Me ₁₂ -[6]	planar	12.9	175	108	111	0.0
Me ₁₂ -[6]	chair	9.8	179	108	111	±56.3 ^f
Me ₁₂ -[6]	boat	9.5	179	108	111	F
Me ₁₂ -[6]	twist-boat ^b	9.4	179	108	111	G
Me ₁₂ -[6]	half-chair	11.0	175-179	108-111	109-111	H

^aC—C lengths are 1.47–1.48 Å and C≡C lengths are 1.21–1.22 Å in all the molecules studied, except [2]pericyclyne, in which these values are 1.514 and 1.229 Å, respectively. ^bThese structures are actually intermediate between ideal boat and twist-boat conformations. ^cIn kcal/mol. ^dR=H or Me. ^eSince the C—C≡C—C units are all planar to within a few degrees, the "ring dihedral angles" are dihedral angles involving four saturated carbons, that is, the angle between the plane of C₁R₂—C≡C—C₃R₂—C≡C—C₃R₂ and the plane of C₂R₂—C≡C—C₃R₂—C≡C—C₄R₂. ^fThe dihedral angles alternate in sign around the ring. A 10.5, 0.0, -10.5, 17.0, -17.0; B 10.5, 0.0, -10.5, 16.9, -16.9; C 55.0, 0.0, -55.0, 55.0, 0.0, -55.0; D 64.5, -14.8, -46.8, 64.5, -14.8, -46.8; E 30.1, 0.0, 0.0, -30.1, 61.3 -61.3; F 57.1, 0.0, -57.1, 57.1, 0.0, -57.1; G 64.1, -5.6, -57.0, 63.9, -5.3, -57.2; H 30.6, 0.0, 0.0, -30.6, 62.0, -62.0.

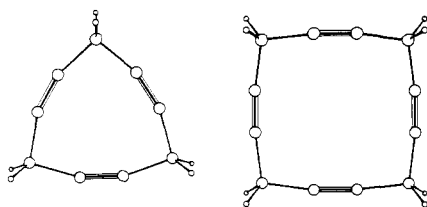


Figure 1. MM2-optimized structures of [3]- and [4]pericyclyne.

is concentrated primarily in the acetylenic carbons, causing them to bow out. The tetrahedral carbon atoms at the vertices deviate less from the normal tetrahedral angle, since bending force constants are smaller for acetylenic carbons than for tetrahedral carbons. Nevertheless, the total angle strain absorbed by six C≡C—C distortions is approximately the same as that absorbed by three CCC angles in cyclopropane. The moderate strain energy indicates that [3]pericyclyne and derivatives should be isolable under ordinary laboratory conditions. The MM2 geometry is very similar to the MNDO geometry,⁴ with bond lengths differing by at most 0.01 Å and angles by 2°.

The permethylated compound, Me₆-[3], was also investigated, since practical synthetic routes to date have led to permethylated derivatives, which are anticipated to be more easily handled than the parent systems.^{2,8} The energy minimum is planar, and the geometry resembles the unmethylated compound in all respects.

[4]Pericyclyne. Both the parent and the octamethyl[4]pericyclyne are planar *D_{4h}* structures. The former is shown in Figure 1. The strain energies of both are very small, and again the greatest deviation from natural angles occurs at the acetylenic carbons. Each acetylenic group bows out slightly in order to permit adoption of natural tetrahedral angles at saturated carbons. Whereas cyclobutane adopts a bent conformation to avoid eclipsing interactions between vicinal hydrogens, even at the expense of angle strain,⁷ such torsional effects are absent in the pericyclines because the 1,4 CH or CC bonds are more than 4 Å apart. Nonplanar starting geometries of [4]pericyclyne relax to the planar geometry upon optimization.

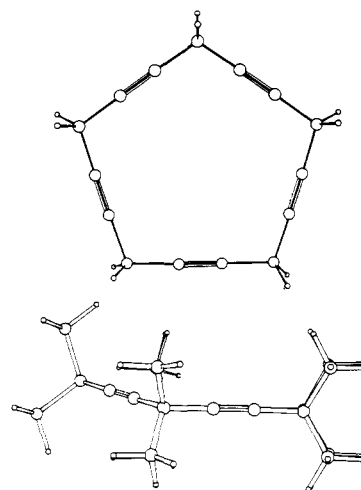


Figure 2. MM2-optimized planar parent and envelope decamethyl[5]pericyclyne.

[5]Pericyclyne. A regular pentagon has internal angles of 108°, very close to the natural tetrahedral angles of saturated carbons. Calculations on the parent and decamethyl[5]pericyclines reveal an extremely flat potential surface, with an envelope conformation which has the same energy as the planar conformation. Figure 2 shows the planar conformation of the parent, and a side view of the envelope conformation of the decamethyl derivative. Cyclopentane adopts nonplanar envelope and half-chair conformations, in order to relieve torsional strain. The envelope of cyclopentane has large torsional angles (25, 0, -25, 40, and -40°)⁷ and is more puckered than the envelope [5]pericyclyne. The MM2 structure of decamethyl[5]pericyclyne is similar to, but considerably flatter than, the X-ray crystal structure, as described later in this paper. Calculations indicate that the molecule should have a freely pseudorotating geometry in the gas phase. Optimizations beginning with different puckering angles tend to end at somewhat different final geometries because of the flat potential surface. Dewar and Holloway reported only the planar *D_{5h}* structure⁴ which is essentially identical with the *D_{5h}* structure obtained by MM2.

[6]Pericyclyne. This species should be capable of adopting chair, boat, and twist-boat conformations analogous to those of its more diminutive cousin, cyclohexane. These three cyclohexane con-

(7) Testa, B. "Principles of Organic Stereochemistry"; Marcel Dekker: New York, 1979.

(8) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.*, preceding paper in this issue.

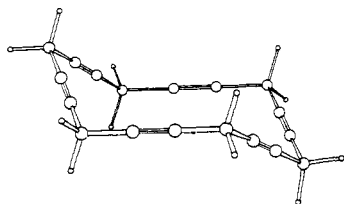


Figure 3. MM2-optimized structures of chair [6]pericyclyne.

formations can be constructed without altering the natural angles of the carbon atoms. Torsional strain and transannular van der Waals repulsions destabilize the boat and twist-boat relative to the chair form of cyclohexane. The relative energies of the chair, twist-boat, and boat conformations of cyclohexane are 0, 5, and 6 kcal/mol,⁷ respectively, and the boat conformation is a transition state for pseudorotation of the twist-boat. The torsional effects which differentiate these conformations are absent in [6]pericyclyne. Indeed, all three conformations of [6]pericyclyne are calculated to be essentially equienergetic. Figure 3 shows the chair conformation. The chair and boat conformations were obtained by optimizing the structures with D_{3d} and C_{2v} symmetry, respectively, while the calculated twist-boat conformation is actually intermediate between idealized C_{2v} boat and D_2 twist-boat. Because of the absence of torsional interactions, the boat and twist-boat forms are equal in energy to the chair form. [6]Pericyclyne should be a freely pseudorotating species, about 2 kcal/mol more stable than the planar form.

The barrier for interconversion of the chair and boat via the half-chair is also extremely low. The angle strain in the half-chair is spread out over all six acetylenic carbons. In the planar conformation, the acetylenes now bow "in" instead of "out" as they did in the planar [3]- and [4]pericyclynes. The deviation from linearity is only 3° at each acetylenic carbon. The conformations of the dodecamethyl derivative are similar to those of the parent. Dodecamethyl[6]pericyclyne has been synthesized,⁸ but the low barriers anticipated and predicted theoretically have discouraged attempts to examine its conformational properties by low-temperature NMR spectroscopy.

Larger Pericyclynes. Calculations have not been performed on larger pericyclynes, but qualitative predictions can still be made about the conformations of such molecules. All should have very flat potential surfaces with large numbers of nearly equienergetic conformations separated by low barriers.

X-ray Crystal Structures

Decamethyl[5]pericyclyne. Figure 4 shows a computer-generated perspective drawing of the final X-ray model for Me_{10} [5]. The internal consistency of the molecular parameters is excellent. The average bond lengths (in Å) were found to be 1.190 (5) for the sp-sp bonds, 1.480 (7) for the sp-sp³ bonds, and 1.533 (8) for the sp²-sp³ bonds. At the quaternary sp³ carbons, the internal angles are 108.0 (8) $^\circ$, and the remaining angles are 109.8 (7) $^\circ$. This compares with a regular pentagon with perfectly straight sides which also has internal angles at the five vertices of 108° ; however, the pentayne does not remain planar in the crystal but adopts an envelope (C_s) conformation with C15 serving as the flap. This deviation from planarity accounts for the slight bending of all five acetylene units; an average C≡C-C angle of 177.3 (1.5) $^\circ$ was found. The torsional angle around the C6-C9 link is 5° , those around the C3-C6 and C9-C12 links are $\pm 24^\circ$, and those around the C12-C15 and C3-C15 links are $\pm 38^\circ$. Atoms C3 through C12 are essentially coplanar (rms deviation 0.05 Å); atoms C2 and C13 lie 0.64 Å away from this plane, and atoms C1 and C14, 1.10 Å, and C15, 1.6 Å. Nonbonded sp atoms separated by an sp³ carbon (C5-C7 type) are 2.4 Å apart, and those separated by one edge of the pentayne (C5-C10 type) are 5.0 Å apart. From this X-ray analysis, it is clear that cyclic homoconjugation in Me_{10} [5] has no dramatic structural consequences. The molecule is virtually devoid of angle strain, torsional strain, and transannular van der Waals repulsions. A comparison of the side views in Figures 4 and 2 show the gross similarities of X-ray and MM2

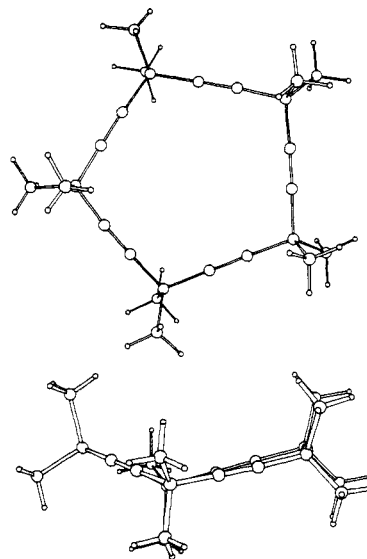


Figure 4. Two perspective drawings of the X-ray structure of decamethyl[5]pericyclyne.

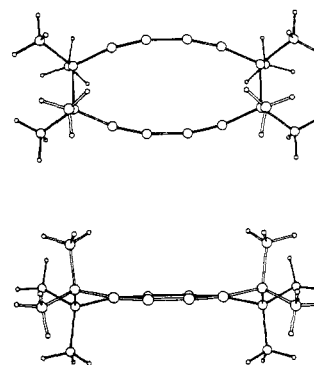


Figure 5. Two perspective drawings of the X-ray structure of octamethyl-1,3,7,9-dodecatetrayne.

structures, although the latter is flatter.

Octamethylcyclododeca-1,3,7,9-tetrayne. Figure 5 shows two computer-generated perspective drawings of the final X-ray model for the doubly conjugated tetrayne obtained in the attempted synthesis of Me_8 [4].^{8,12} In the crystal, the molecule adopts a nonplanar conformation with C_{2h} symmetry. Repulsions between the adjacent pairs of *gem*-dimethyl groups give rise to torsional angles around the sp³-sp³ ring bonds (C4-C5-C6-C7 and C10-C11-C12-C1) of 40.7° and a lengthening of those bonds to 1.602 (3) Å. Around the remainder of the ring, the average bond lengths (in Å) were found to be 1.200 (4) for the triple bonds, 1.387 (3) for the sp-sp single bonds, and 1.482 (3) for the sp-sp³ bonds. All eight acetylenic carbons deviate substantially from linearity, with bond angles ranging between 165.9° and 167.1° . The internal bond angles at the saturated carbons, on the other hand, appear more nearly normal, ranging from 107.7° to 108.2° . Each diacetylene unit forms an essentially planar arch, and the two planes lie parallel to one another, separated by only 0.14 Å.

(9) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.

(10) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. Calculations were performed with GAUSSIAN 82: Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. Carnegie-Mellon University, Pittsburgh, PA. The DEC-10 and Harris 800 versions, converted by Dr. John Yates, were used at Pittsburgh.

(11) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245 and references cited therein.

(12) Santiago, C.; Houk, K. N.; DeCicco, G. J.; Scott, L. T. *J. Am. Chem. Soc.* **1978**, *100*, 692. Houk, K. N.; Strozier, R. W.; Santiago, C.; Gandour, R. W.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1979**, *101*, 5183.

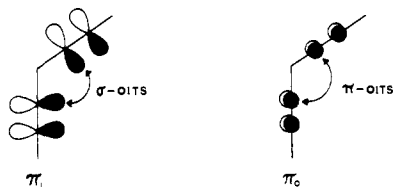


Figure 6. Definitions of π_1 and π_0 orbitals and OITS by σ and π mechanisms.

This tetrayne can be viewed formally as a somewhat flattened chair cyclohexane in which carbons 1 and 4 have each been replaced by an arched diacetylene unit. Thus, the methyl groups on the four sp^3 ring carbons occupy axial and equatorial positions, and a ring inversion should interconvert these. Indeed, the disorder observed in the crystals at room temperature (see Experimental Section) was found to result from precisely such a conformational change. X-ray data for the detailed structural analysis were therefore collected at -160°C . Rapid ring inversion at room temperature in the solution reduces the ^1H NMR spectrum of the tetrayne to a single line; however, two singlets can be resolved at very low temperatures. From the coalescence temperature ($T_c = -148^\circ\text{C}$), a $\Delta G^\ddagger = 5.7$ kcal/mol could be derived for ring inversion of the tetrayne in solution.⁸

Electronic Structures and Orbital Interactions

The conformational analysis described in a previous section made the tacit assumption, based upon the use of MM2, that there are no special electronic interactions between the π systems of the acetylenes in these molecules. We have shown elsewhere that the interactions between acetylenic units arranged in a cyclic array, as in pericyclines, are repulsive and that no special stabilization arises from interaction, even when a total of $4n + 2\pi$ electrons are involved.⁹ In other words, neutral homoaromaticity, such as is doubly feasible in [3]- and [5]pericycylene, will not occur.^{3,9} By the same token, neutral antiaromaticity, formally possible in [4]- and [6]pericycylene should not be significant. Indeed, the near identity of the MM2 and MNDO structures confirms the contention that these molecules are classical polyynes, unaffected structurally by cyclic homoconjugation. Nevertheless, interactions between filled orbitals, and between unfilled orbitals, will occur, and these interactions will influence the spectroscopic properties of the pericyclines.

In order to learn about these orbital interactions and the consequences upon electronic structures, we carried out *ab initio* calculations with the minimal STO-3G basis set.¹⁰ The use of this small basis set was necessary because of the size of the molecules in question. We carried out only single-point calculations on the geometries obtained from the MM2 optimizations, again because of the enormity of these molecules. Finally, only the parent systems were studied, since the methyls are expected to have a relative benign influence on orbital interactions, raising all the orbital energies to a similar extent relative to the energies of the parent species.

General. The high-lying filled and low-lying vacant molecular orbitals (MO) of the pericyclines consist primarily of delocalized combinations of the π (and π^*) orbitals of the acetylenic units. For the planar species, these separate cleanly into out-of-plane and in-plane sets of orbitals, mutually interacting through space in π and σ fashions, respectively. We define these sets as π_0 (out-of-plane π) and π_1 (in-plane π), respectively (Figure 6). To the extent that orbital interactions through space (OITS) dominate the interaction, the orbital symmetries and energies of both of these out-of-plane and in-plane orbitals of [*N*]pericyclines can be deduced from the well-known pattern of orbital symmetries and energies of [*N*]annulenes. For example, mixing of *N* degenerate π_0 orbitals will generate *N* occupied MOs with the same symmetries and energy ordering as the complete manifold of orbitals, occupied and vacant, of the corresponding [*N*]annulene, the orbitals of which are formed from an admixture of *N* *p* orbitals. The [*N*]pericycylene occupied orbitals can be considered to be linear combinations of *N* occupied π molecular orbitals, while the orbitals

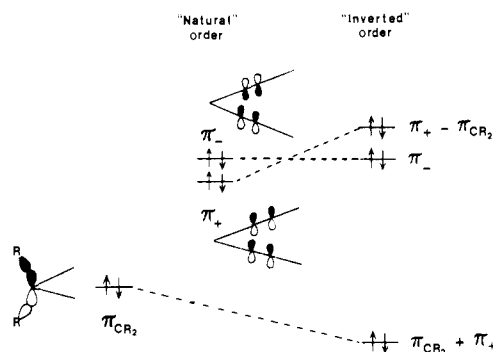


Figure 7. Through-bond mixing (OITB) of adjacent π_0 acetylenic orbitals.

of the [*N*]annulene are linear combinations of *N* *p* atomic orbitals. Mixing of the *N* vacant acetylenic π^* orbitals will similarly generate a set of vacant orbitals, again resembling the *N* orbitals of the [*N*]annulene, but the pericycylene orbitals will be linear combinations of acetylenic π^* MOs. This analogy assumes that an admixture of π and π^* orbitals will be negligible, which is a good approximation for relatively undistorted hydrocarbons, where these orbitals are very far apart in energy.¹⁰

These through-space interactions may be smaller than orbital interactions through bonds (OITB).^{11,12} In the pericyclines, OITB is the admixture of the out-of-plane or in-plane π orbitals of the acetylene units with CH_2 or CMe_2 orbitals of appropriate symmetry on each vertex. This OITB will produce exactly the opposite order of orbital energies as OITS. Figure 7 shows why this occurs. In the center of the figure, adjacent π_0 acetylenic orbitals are sketched, with the π_+ below π_- , or normal order, which is a result of OITS. There will be a lower-lying orbital at the vertex (CH_2 or CMe_2) with the appropriate symmetry (π_{CR_2}) to mix with π_+ . This mixing generates $\pi_+ - \pi_{\text{CR}_2}$, which is destabilized as a consequence of this mixing. The π_{CR_2} orbital does not mix with π_- , since it has a nodal plane passing through CR_2 . Thus, π_- is unchanged in energy. The "unnatural" order, π_+ above π_- , is produced if this OITB is sufficiently large. Because of this mechanism of interaction, OITB causes the energies of the orbitals to increase as the number of nodes between interacting π units increases. That is, the fewer antibonding interactions between interacting units, the higher the energy of the OITB-coupled π orbitals. OITB, however, can only occur at each vertex where there is no node. If there is a node through the vertex, there can be no contribution from a vertex orbital. Thus, if OITB dominates over OITS, the nodeless MO will be the least stable, while the MO with the most nodes between the units will be the most stable, precisely the opposite situation from that when OITS dominates. As demonstrated for the pericyclines below, the pattern of orbital energies is thus an immediate signal as to whether OITB or OITS is more important.

[3]Pericycylene. Large splittings are seen in the molecular orbitals formed from the in-plane acetylenic π_1 orbitals, as shown in Figure 8. The STO-3G orbital energies are generally too high, as judged by comparisons to ionization potentials of various cyclic acetylenes, obtained by photoelectron spectroscopy. We have found that reasonable estimates of ionization potentials can be obtained from STO-3G calculations by the following correction: $\text{IP} = 0.778 (-\epsilon^{\text{STO-3G}}) + 3.40$ (in eV).¹² According to Koopmans' theorem, $\text{IP} = -\epsilon^{\text{SCF}}$, so that the corrected STO-3G orbital energies are obtained from the equation $\epsilon(\text{corrected}) = 0.778(\epsilon^{\text{STO-3G}}) - 3.40$ (in eV).

The splitting of the in-plane orbitals of [3]pericycylene is very large, and a "normal" pattern is observed, indicative of large OITS. The patterns predicted by STO-3G are the same as those predicted by MNDO.⁴ However, the predicted splittings of π_0 and π_1 are very different according to the two types of calculations. The π_1 splitting [$\epsilon(e') - \epsilon(a_1')$] is 1.68 eV by STO-3G, but only 0.57 eV by MNDO.⁴ The π_0 splitting [$\epsilon(a_2'') - \epsilon(e'')$] is 0.14 and 0.39 eV, respectively. Both could be due to an underestimation of OITS by MNDO.⁴ The out-of-plane orbitals give the "unnatural" order,

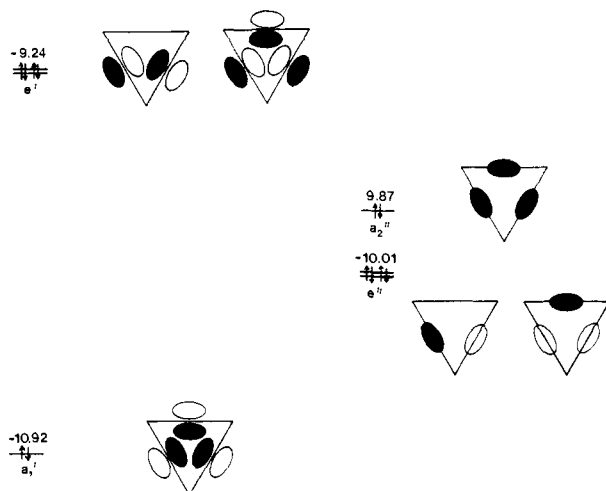


Figure 8. Corrected STO-3G molecular orbital energies and shapes for [3]pericycylene. For the π_o orbitals, only the top lobe of each π orbital is shown.

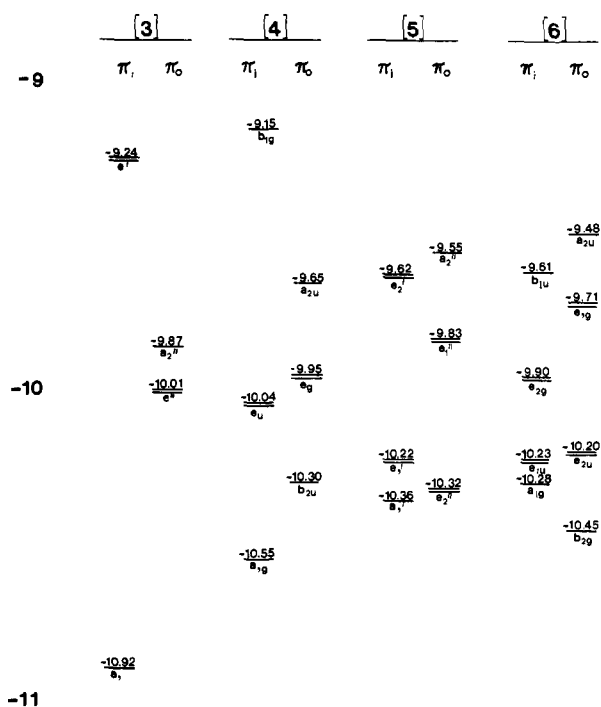


Figure 9. Corrected STO-3G molecular orbital energies and symmetries for planar [3]-, [4]-, [5]-, and [6]pericycylene.

but the splitting is small. Thus, OITB dominates for π_o . The splitting patterns found in the vacant orbitals are the same as for the occupied, but the splittings are substantially larger for antibonding orbitals than for bonding orbitals. This is consistent with the greater diffuseness and consequent more substantial interaction of the π^* orbitals than the π orbitals.

Planar [4]-, [5]-, and [6]Pericycylene. The corrected orbital energies and symmetries for planar [3]- to [6]pericycylene are shown in Figure 9. The trends noted for [3]pericycylene are also found in the other planar species. The splitting between the π_i orbitals decreases in the series from [3]- to [6]pericycylene, as the termini of adjacent acetylenes move apart and OITS decreases. The magnitude of the splitting of the π_o orbitals remains large in the whole series, and the splitting actually increases slightly in the larger pericyclynes. This could be due to a diminution of OITS, resulting in an increase in the OITB-dominated splittings, or to better overlap of σ_{CR_2} orbitals with π_o in the larger, unstrained pericyclynes. As noted for [3]pericycylene, the STO-3G and MNDO patterns of π_i and π_o orbitals are the same in each case, but the OITB is smaller by MNDO than by STO-3G.

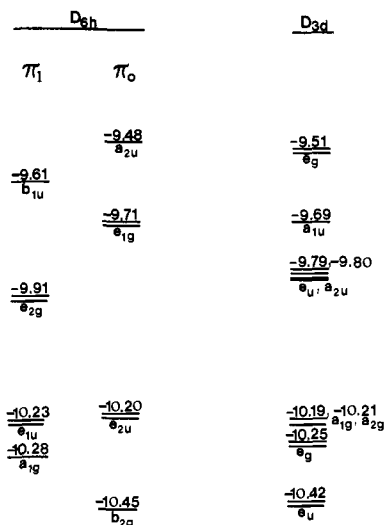


Figure 10. Corrected STO-3G orbital energies and symmetries for planar and chair [6]pericycylene.

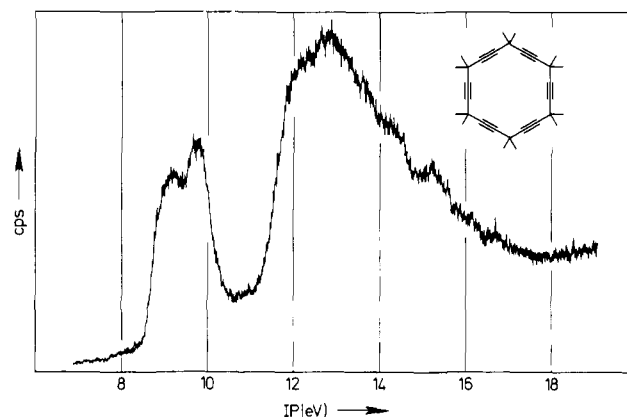


Figure 11. Photoelectron spectrum of dodecamethyl[6]pericycylene.

The corrected STO-3G orbital energies of planar and chair [6]pericycylene are shown in Figure 10. In the chair conformation, the distinction between π_i and π_o orbitals disappears, and the pattern of mixing becomes more complicated. Nevertheless, the changes in orbital energies are rather subtle, and it is unlikely that photoelectron spectroscopy will be capable of distinguishing the difference between these conformations.

Photoelectron Spectra of Decamethyl[5]pericycylene and Dodecamethyl[6]pericycylene

The full spectrum of the photoelectron spectrum of decamethyl[5] are shown in Figures 11 and 12.¹³ Both spectra are relatively broad, with only a few characteristic maxima in the region from 8.1 to 10.5 eV and σ onsets at ~ 11.5 eV. The spectrum of the [5]pericycylene is in reasonable agreement with the calculated spectra, with regard to the overall width of the 8.8–9.8-eV band, but little else can be concluded from it. There is really no detailed information to compare, and any set of random numbers between 8 and 11 eV would fit either spectrum quite well!

The STO-3G calculations were carried out on the parent systems, while the spectra are for the permethylated derivatives. The methyls are expected to lower the IPs of all π ionizations to some extent. For example, the IPs of dimethylacetylene, diethylacetylene, diisopropylacetylene, and di-*tert*-butylacetylene are 9.56, 9.32, 9.17, and 9.05 eV, respectively.¹⁴ Since the IP

(13) Photoelectron spectra were recorded on Perkin-Elmer PS-16 and PS-18 spectrometers at Louisiana State University and Copenhagen. The calibrant gases were xenon and argon, and the reported ionization energies are averages of five determinations.

(14) Carlier, P.; Dubois, J. E.; Masclat, P.; Mouvier, G. *J. Electron Spectros. Rel. Phenom.* **1975**, *7*, 55.

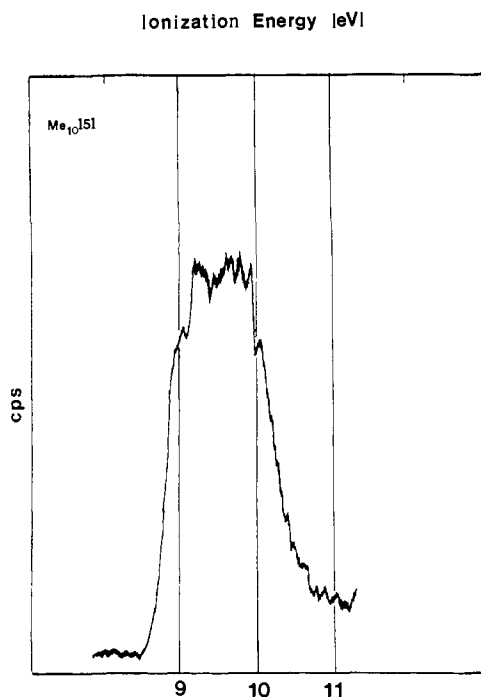


Figure 12. Expanded scale of 8–11-eV region of photoelectron spectrum of decamethyl[5]pericycylene.

of an alkylacetylene is related to the Taft inductive constants, σ^* , of the alkyl groups,¹⁴ the IPs of hypothetical noninteracting π_i and π_o orbitals of the pericyclines are expected to be higher than the 9.05-eV IP of di-*tert*-butylacetylene, perhaps as high as the 9.56-eV IP of dimethylacetylene. Put another way, since substitution of two sets of two α -methyl groups lower the IPs of dimethylacetylene or diethylacetylene by 0.3–0.4 eV, this correction, rather than the 1-eV correction suggested by Dewar,⁴ should be subtracted from calculations of IPs for the parent compounds in order to provide reasonable estimates for the IPs of the permethylated compounds.

The photoelectron spectrum of dodecamethyl[6]pericycylene shows two broad bands with maxima at 9.05 and 9.74 eV. This fits reasonably well (but not overwhelmingly so!) with the pattern predicted for chair [6]pericycylene. The average energies of the two groups of orbitals, corrected by 0.4 eV to take into account the methyl substituent effects, are 9.18 and 9.89 eV. The planar conformation should have a similar spectrum. The widths of the photoelectron bands do indicate, however, that the sizes of the calculated splittings are of the correct order of magnitude.

If the alkyne units are appreciably bent, the π_i and π_o degeneracy can be lifted even before OITB or OITS interactions. However, this effect should be negligible in [5]- and [6]pericyclines, and even for the degree of bending predicted for [3]- and [4]pericyclines, the differences in energies of π_i and π_o orbitals are predicted to be only <0.2 and <0.1 eV, respectively.¹⁵

Electron Transmission Spectra of Decamethyl[5]pericycylene and Dodecamethyl[6]pericycylene

The electron transmission spectra of permethylated [5]- and [6]pericycylene are shown in Figure 13.¹⁶ Each spectrum shows two major peaks due to temporary anion formation which correspond to electron affinities of -1.87 and -3.45 eV for the [5]pericycylene and -2.15 and -3.75 eV for the [6]pericycylene. The shapes of these features suggest that each consists of two or more closely spaced anion states. STO-3G calculations predict that the lowest temporary ion states of both molecules involve occupation of the most OITS bonding combination of π^*_i orbitals. The corresponding OITS bonding combination of π^*_o orbitals is only slightly higher in energy, so that the lowest energy band is most likely due to overlapping resonances due to occupation of these orbitals. The remaining π^* orbitals are calculated to be 0.9–2.0 eV higher in energy, and all should appear, therefore, in the

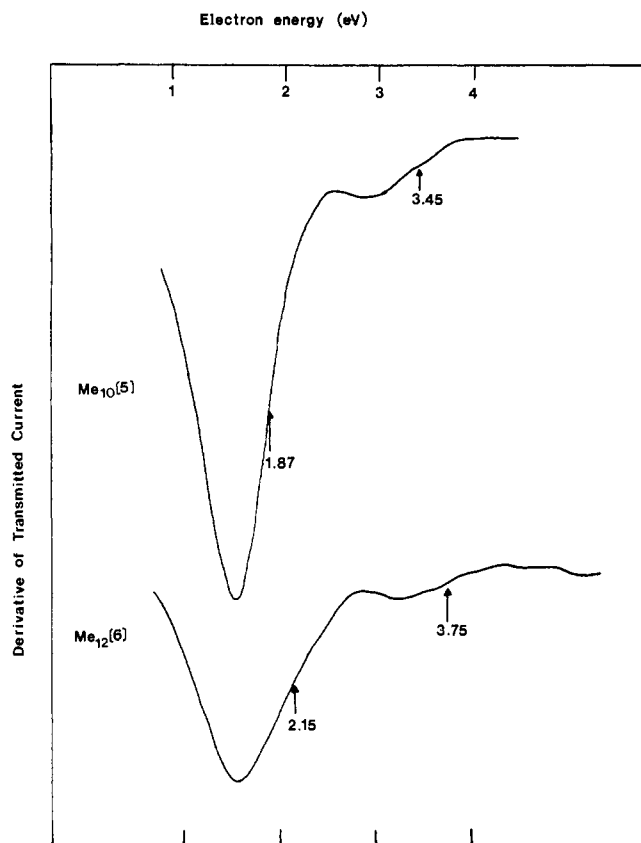


Figure 13. Electron transmission spectra of decamethyl[5]pericycylene and dodecamethyl[6]pericycylene.

2.9–4-eV region of the transmission spectrum. The ETS spectrum gives strong indications of the mixing of π^* orbitals, since the EA of acetylene is -2.6 eV,¹⁷ indicative of a considerably higher LUMO orbital energy for the noninteracting π^* orbitals of this species. Alkyl groups are expected to make the EA of an alkyne even more negative.¹⁷

Summary

The [N]pericyclines constitute an unusual set of homoconjugated cyclic polyacetylenes which have large OITS and OITB. These interactions are manifested in the large splittings in π orbital energies calculated and observed for these molecules. The relatively low IPs and high EAs of these molecules indicate that they should show unusual redox chemistry and might serve as good donor or acceptor "giant ligands" for complexation of metal ions. The conformational trends found for these molecules indicate that they may be considered as "exploded cycloalkanes", having the flexibility expected of cycloalkanes with no torsional interactions present.

Experimental Section

X-ray Crystallography of Decamethylcyclopentadeca-1,4,7,10,13-pentayne. Crystals of the pentayne were grown from ethanol, and preliminary X-ray photographs showed monoclinic symmetry. Accurate lattice constants were $a = 20.457$ (4) Å, $b = 9.512$ (2) Å, $c = 11.313$ (3) Å, and $\beta = 92.68$ (2)°. Systemic extinctions indicated space group $P2_1/c$, and the density suggested an asymmetric unit of $C_{25}H_{30}$. All unique diffraction maxima with $2\theta \geq 114.1^\circ$ were collected by using graphite monochromated Cu $K\alpha$ (1.54178 Å) radiation. After correction for Lorentz polarization and background effects, 2609 (78%) were judged observed ($F_o \geq 3\sigma(F_o)$). All the carbon atoms were easily located in an E synthesis following a multisolution sign-determining procedure.¹⁸

(15) Schmidt, H.; Schweig, A.; Krebs, A. *Tetrahedron Lett.* **1974**, 1471.

(16) The ET spectrum was recorded on the spectrometer at the University of Pittsburgh. The onset of the beam zero was utilized for calibration of the energy scales.

(17) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

Hydrogen atoms were located in a difference synthesis following partial refinement. Block-diagonal least-squares refinements with anisotropic carbons and isotropic hydrogens have converged to a standard crystallographic residual of 0.055 for the observed reflections. Please consult the paragraph headed supplementary material for additional crystallographic data.

X-ray Crystallography of Octamethylcyclododeca-1,3,7,9-tetrayne.

Crystals of the tetrayne grown from ethanol were clear, with many solvent occlusions, and gathered in bunches from which single crystals were cut with a razor blade. Preliminary investigation by rotation and Weissenberg photography showed a primitive monoclinic cell with systematic absences characteristic of space group $P2_1/n$ (OkO , $k = 2n + 1$, and hOl , $h + l = 2n + 1$). Unit-cell parameters determined at room temperature by a least-squares fit to the diffractometer angles of 15 reflections in the range $38^\circ < 2\theta < 84^\circ$ using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) were $a = 6.974 (1) \text{ \AA}$, $b = 10.725 (2) \text{ \AA}$, $c = 11.279 (2) \text{ \AA}$, $\beta = 90.62 (1)^\circ$, and $V = 843.6 (2) \text{ \AA}^3$. The density measured by flotation in aqueous KI was 1.02 g cm^{-3} ; the calculated density for $Z = 2$ is 1.04 g cm^{-3} . Half a molecule comprises the crystal asymmetric unit.

A set of intensity data to a limit of $2\theta = 157^\circ$ was collected on a Syntex P1 diffractometer with $\text{Cu K}\alpha$ radiation. The 1725 unique reflections obtained were corrected for Lorentz and polarization effects. Normalized structure factor magnitudes obtained by use of a Wilson plot were used as input to the program MULTAN,¹⁹ which returned phases sufficient to show the 10 independent carbon atoms in an E map. Some unusual aspects of the molecular geometry after several cycles of least-squares refinement of this model with anisotropic temperature factors led to the introduction of a disorder model, described elsewhere.²⁰

In the hope that the disorder evident at room temperature would decrease at lower temperatures, a new set of data was collected. An irregularly shaped crystal, free of solvent occlusions and with maximum linear dimension 0.25 mm, was cut from the cluster to which it was attached. Before the crystal was mounted on a Syntex P1 diffractometer equipped with a crystal-cooling apparatus,²¹ the temperature at the crystal position was measured with a copper-constantan thermocouple and liquid N_2 reference junction and found to be -160°C . Unit-cell dimensions obtained from a least-squares fit to all diffractometer angles of 15 reflections in the range $14^\circ < 2\theta < 20^\circ$ ($\text{Mo K}\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$) were $a = 7.053 (3) \text{ \AA}$, $b = 10.436 (3) \text{ \AA}$, $c = 10.821 (2) \text{ \AA}$, $\beta = 92.91 (2)^\circ$, and $V = 795.4 (3) \text{ \AA}^3$. Rotation photographs about each of the chosen axes showed no spots corresponding to nonintegral indexes; only rotation about b gave a mirror plane. Examination of all intensities in a hemisphere of reciprocal space to a limit of $2\theta = 20^\circ$ also indicated the preservation of monoclinic symmetry. The lack of intensity in the previously observed systematic absences to a limit of $2\theta = 55^\circ$ implied that the space group remained $P2_1/n$ on cooling.

(18) All crystallographic calculations on decamethyl[5]pericyclyne were done on a PRIME 850 computer, operated by the Cornell Chemistry Computing Facility. Principal programs employed were REDUCE and UNIQUE, data reduction programs: Leonowicz, M. E. Cornell University, 1978. MULTAN 78, "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data," direct methods programs and Fast Fourier Transform routine (locally modified to perform all Fourier calculations including Patterson syntheses): Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. University of York, England, 1978. NQUEST, CYBER 173 version, negative quartets figure of merit calculation: Weeks, C. M. Medical Foundation of Buffalo, Inc., Aug 1976. BLS78A, anisotropic block-diagonal least-squares refinement: Hirotsu, K.; Arnold, E. Cornell University, 1980; ORTEP, crystallographic illustration program: Johnson, C. K. Oak Ridge, ORNL-3794; For a summary description of MULTAN see: Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. B* 1970, B26, 274-285. Woolfson, M. M. *Acta Crystallogr., Sect. A* 1977, A33, 219-225. For a summary of NQUEST, refer to: DeTitta, G. T.; Edmonds, J. W.; Langs, D. A.; Hauptman, H. *Acta Crystallogr., Sect. A* 1975, A31, 472-479.

(19) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* 1971, A27, 368.

(20) Weiss, R. Ph.D. Dissertation, University of California, Los Angeles, CA, 1976.

(21) Strouse, C. E. *Rev. Sci. Instrum.* 1976, 47, 871.

Intensity data were collected in the bisecting mode with crystal-monochromatized $\text{Mo K}\alpha$ radiation. Reciprocal space was scanned with $\theta/2\theta$ movement from $2\theta = 1.2^\circ$ less than the calculated position of the $\text{K}\alpha_1$ ($\lambda = 0.71354 \text{ \AA}$) at a rate of 2° min^{-1} in 2θ . Backgrounds were measured on each side of the scan range for a total time equal to that of the scan. A parabolic coincidence correction using the measured dead time of the counter was applied to the most intense reflections of three standard reflections lying in approximately orthogonal directions of reciprocal space; one decreased in intensity by about 6% during the measurement period, another increased by 3%, and the third changed by less than 1%. All reflections in a quadrant of reciprocal space to a limit of $2\theta = 55^\circ$ ($\sin \theta/\lambda = 0.65$) were measured.

Data reduction involved correction for Lorentz and polarization effects. Absorption corrections ($\mu_{\text{calcd}} = 0.61 \text{ cm}^{-1}$, $\mu_{\text{Tmax}} \sim 0.02$) were not applied. Of the 1841 unique reflections measured, the 1090 with intensity greater than 3 times σ of the background were labeled "observed". Most standard deviations were assigned as

$$\sigma(I) = [\sigma_{\text{statistical}(I)}^2 + 9 \times 10^{-4} I^2]^{1/2}$$

Reflections with measured intensities less than zero were assigned intensities of 0 and σ 's of 50.

The 10 independent carbon atoms were placed at the positions of highest occupancy in the disordered room-temperature structure. Full-matrix least-squares refinement to the weighted F 's of the observed reflections, with first isotropic and then anisotropic temperature factors, converged to an unweighted $R(F) = \sum(F_{\text{obsd}} - F_{\text{calcd}})/\sum F_{\text{obsd}}$ of 0.11. The unsatisfactory aspects of the molecular geometry in the room-temperature structure were no longer apparent.

The 12 independent hydrogen atoms were located in a difference Fourier map, with peak heights of 0.7-1.0 electron \AA^{-3} and at reasonable positions relative to the carbon atoms. They were included in subsequent cycles of least-squares refinement.

The last three cycles of full-matrix least-squares refinement with the program ORFLSE²² used all reflections, including the "unobserved". Weights of the observations were taken as $1/\sigma^2(F)$. All parameters (scale factor, carbon-atom positions and anisotropic temperature factors, and hydrogen-atom positions and isotropic temperature factors) were allowed to vary. The scattering factors of Cromer and Waber²³ for carbon and Steward, Davidson, and Simpson²⁴ for bonded hydrogen were used. Final R values were 0.128 (all reflections, unweighted), 0.064 (all reflections, weighted), and 0.060 (observed reflections, unweighted). The largest parameter shift in the final cycle was 0.14 estimated standard deviations. A difference Fourier map contained no features higher than 0.25 electron \AA^{-3} . Please consult the paragraph headed supplementary material for additional crystallographic data.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for financial support of this research. We thank Prof. K. N. Trueblood (UCLA) for advice on the X-ray analysis of Me_{10} -[5]. We are also indebted to Ruth Wells Gandour, James P. Ritchie, and Cielo Santiago for initial calculations in this area (see ref 5).

Registry No. [2]pericyclyne, 98361-05-8; [3]pericyclyne, 95361-64-1; Me_6 -[3]pericyclyne, 98361-06-9; [4]pericyclyne, 95339-42-7; Me_8 -[4]pericyclyne, 98361-07-0; [5]pericyclyne, 95339-41-6; Me_{10} -[5]pericyclyne, 88057-40-3; [6]pericyclyne, 98361-08-1; Me_{12} -[6]pericyclyne, 98127-90-3; octamethylcyclododeca-1,3,7,9-tetrayne, 61414-48-0.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, bond angles, torsional angles, and observed and calculated structure factor magnitudes (30 pages). Ordering information is given on any current masthead page.

(22) Strouse, C. E. *Acta Crystallogr., Sect. A* 1970, A26, 604.

(23) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* 1965, 18, 104.

(24) Steward, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175.