Evaluation of Through-Space Interaction in 9-Substituted Pentacyclononane Derivatives

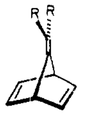
Peter Bischof,[1] Michael Böhm,[1] Rolf Gleiter,*[1] Robert A. Snow,[2]
Christopher W. Doecke,[2] and Leo A. Paquette*[2]

*Institut für Organische Chemie der Technischen Hochschule, D61 Darmstadt, West Germany
and Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210*

Received December 19, 1977

The pentacyclic hydrocarbons 4–7 have been prepared from homocuneone (9) and their photoelectron spectra have been recorded. In each instance, it has proved possible to assign the first five bands, reliance being placed upon a ZDO model and comparison with related compounds. The matrix elements for the through-space interaction between the dicyclopropyl fragment and the structural unit at the 9 position were determined to be the same as in the corresponding norbornadiene compounds. A comparison between experiment and computational results derived from the all-valence-electron methods EH, CNDO/2, MINDO/3, and SPINDO/1 indicates that the first three drastically underestimate through-space interaction.

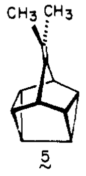
Recent photoelectron (PE) spectroscopic measurements on 7-isopropylidenenorbornadiene (1)[3] and 7-methylenenorbornadiene (2)[4] have shown that considerable through-space interaction exists between the exocyclic π orbital and $b_2(\pi)$ orbital of the norbornadiene moiety. A similar interaction has been detected in 3.[5] In this connection, it was of interest to supplant the double bonds in 1–3 by cyclopropane rings as in 4–7 and to investigate the magnitude of the through-space interaction in such structurally rigid molecules. Accordingly, these hydrocarbons were synthesized and their PE spectra were recorded. The first measured vertical ionization potentials, $I_{V,J}$, are listed in Table I together with our assignments. The relevant spectra are illustrated in Figure 1 and appropriate correlation of the first bands is made in Figure 2. In this work, the validity of Koopmans' theorem ($-\epsilon_J = I_{V,J}$) is assumed.[6] The individual orbital energies (ϵ_J) have been derived by a zero differential overlap (ZDO) treatment as discussed below. A comparison of the ZDO results with those of semiempirical calculations is subsequently provided.



1, R = CH_3
2, R = H

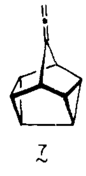
3

4

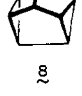


5

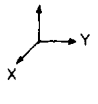
6



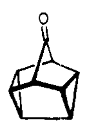
7



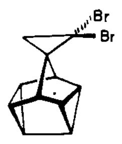
8



Synthesis. The pentacyclononane derivatives 4 and 5 were available by direct condensation of homocuneone (9)[7] with methylene- and isopropylidenetriphenylphosphorane, respectively, in tetrahydrofuran solution. Treatment of 4 with bromoform and potassium *tert*-butoxide in pentane afforded the dibromocarbene adduct **10.** This intermediate gave the spirocyclopropane derivative 6 when reduced with lithium in a combined *tert*-butyl alcohol–tetrahydrofuran solvent system. Allene 7 was obtained when 10 was exposed to the action of methyllithium.



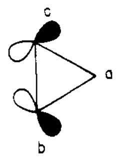
9



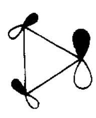
10

ZDO Model for 4, 5, and 6. To derive the orbital energies for 4–6 within a ZDO model, it is necessary to define the wave functions, basis orbital energies, and interaction parameters.

(a) Wave Functions. Wave functions for the highest occupied MO's of 4–6 are constructed from the two basis orbitals e_S and e_A of the cyclopropane ring shown below:

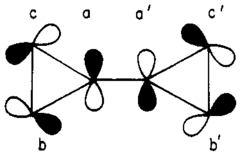


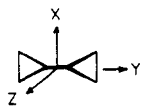
$e_s = 1/\sqrt{2}(\phi_b - \phi_c)$



$e_A = 1/\sqrt{6}\,(2\phi_a - \phi_b - \phi_c)$

The relative phases of the tangential p orbitals, ϕ_μ, of dicyclopropyl are defined as follows:





Assuming C_{2v} symmetry for the dicyclopropyl unit, one obtains the following four linear combinations:

	C_{2v}
$\psi_4 = 0.5\,(\phi_a + \phi_{a'}) - 0.354\,(\phi_b + \phi_c + \phi_{c'} + \phi_{b'})$	a_2
$\psi_3 = 0.5\,(\phi_b - \phi_c + \phi_{c'} - \phi_{b'})$	a_1
$\psi_2 = 0.5\,(\phi_b - \phi_c - \phi_{c'} + \phi_{b'})$	b_2
$\psi_1 = 0.628(\phi_a - \phi_{a'}) - 0.230(\phi_b + \phi_c - \phi_{c'} - \phi_{b'})$	b_1

The irreducible representations according to which these wave functions transform in the point group C_{2v} are listed following the equations. The wave functions are sketched below.

(b) Basis Orbital Energies. The basis orbital energies for the wave functions of the dicyclopropyl unit in 4–6 are derived from **8.**[8] As concerns 4 and 6, an inductive effect of −0.15 eV is assumed for the double bond and the three-membered ring. This assumption is consistent with the results of earlier investigations.[5] In the case of 5, the inductive effect of the iso-

0022-3263/78/1943-2387$01.00/0

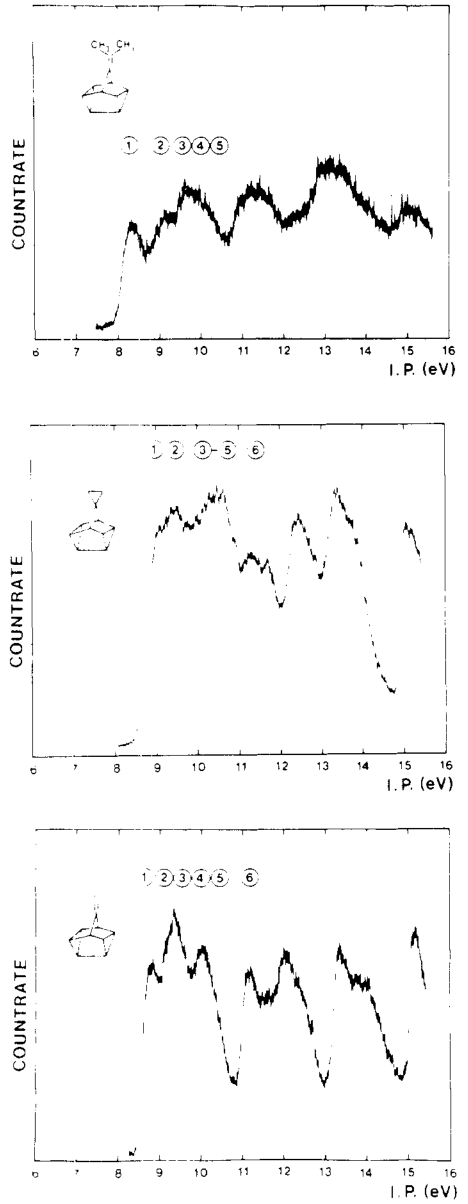
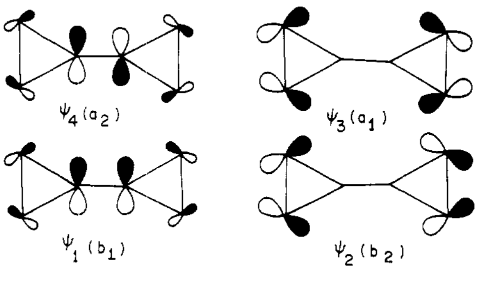


Figure 1. PE spectra of 5–7.

propylidene group is taken to be +0.1 eV.[3]

In these terms, the basis orbital energy for the ethylene moiety in 4 is expected to reside at −9.6 eV. This value is derived from the ionization potential of 7-methylenenorbornane (9.4 eV)[4,5] reduced by the inductive effect (−0.2 eV) of the two



cyclopropane rings. In a similar manner, the basis orbital energy of the π orbital in 5 (−8.7 eV) is derived from the ionization potential of 7-isopropylidenenorbornane (8.5 eV).[5] Since the ionization potentials assigned to the two Walsh orbitals of the three-membered ring in 7-spirocyclopropylnorbornane are 9.6 eV for $b_2(e_A)$ and 10.9 eV for $a_1(e_S)$, the corresponding basis orbitals in 6 are anticipated to be −9.8 and −11.1 eV.

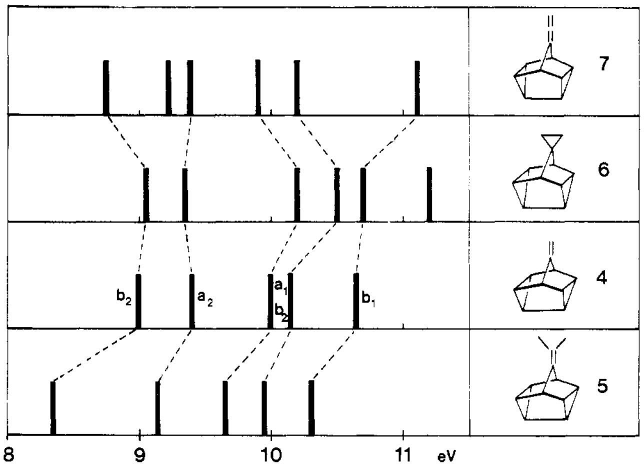


Figure 2. Correlation between the first bands in the PE spectra of 4–7.

(c) Interaction Parameters. The calculated orbital energies for 1 and 2 agree well with experiment[3] by assuming the matrix element

$$\langle \pi_- |H| \pi \rangle = -0.64 \text{ eV}$$

In this expression, π_- represents the antisymmetric linear combination of the π orbitals in the norbornadiene unit and π the ethylene moiety at the 7 position. For 3, the corresponding matrix element has been found[5] to be

$$\langle \pi_- |H| e_A \rangle = -0.66 \text{ eV}$$

If the same matrix element values are adopted for 4 and 5 (H_{ij} = −0.64 eV) as well as for 6 (H_{ij} = −0.66 eV), the following secular determinants and solutions for the eigenvalues corresponding to the orbitals of B_2 symmetry are obtained:

$$\mathbf{4} \quad \begin{vmatrix} -9.6-\epsilon & -0.64 \\ -0.64 & -9.8-\epsilon \end{vmatrix} = 0 \qquad \begin{aligned} \epsilon_1 &= -9.05 \text{ eV} \\ \epsilon_2 &= -10.34 \text{ eV} \end{aligned}$$

$$\mathbf{5} \quad \begin{vmatrix} -8.7-\epsilon & -0.64 \\ -0.64 & -9.5-\epsilon \end{vmatrix} = 0 \qquad \begin{aligned} \epsilon_1 &= -8.42 \text{ eV} \\ \epsilon_2 &= -9.87 \text{ eV} \end{aligned}$$

$$\mathbf{6} \quad \begin{vmatrix} -9.8-\epsilon & -0.66 \\ -0.66 & -9.8-\epsilon \end{vmatrix} = 0 \qquad \begin{aligned} \epsilon_1 &= -9.15 \text{ eV} \\ \epsilon_2 &= -10.48 \text{ eV} \end{aligned}$$

We have not carried out a comparable ZDO based calculation on 7 since PE data on 7-allenylidenenorbornane or 1,1′-diisopropylallene are missing. However, an alternate model for 7-vinylidenenorbornane is 1,1-di-*tert*-butylallene. For this compound, the first two ionization potentials are seen to be located at 8.55 and 9.30 eV.[9] These values lie close to the first two bands of 7. The values for the ionization potentials of bands ③–⑤ of 7 compare closely to the ones observed for 4, as anticipated. The agreement between the calculated orbital energies and the measured band positions for 4–6 is very good.

Semiempirical Calculations. To check the assignments made above, semiempirical calculations of the EH,[10] CNDO/2,[11] MINDO/3,[12] and SPINDO/1 types[13] have been performed for 4–7. Since the detailed structures of these compounds are not known, their geometries were optimized using the MINDO/3 method under the assumption of C_{2v} symmetry. The predicted heats of formation, H_f, together with the orbital sequences are listed in Table II. The MINDO/3, CNDO/2, and EH calculations predict in all cases a much smaller split between the b_2 orbitals than the values provided by the ZDO and SPINDO/1 models. This implies a relatively minute through-space interaction between ψ_2 and the π sys-

Table I. Comparison between Measured Vertical Ionization Potentials ($I_{V,J}$) and ZDO Orbital Energies for 4–7 (all values in eV)

Compd.	Registry no.	Band	$I_{J,V}$	Assignment	ZDO
4	64630-96-2	1	9.00	7 b_2 ($\pi - \psi_2$)	8.05
		2	9.40	3 a_2 (ψ_4)	9.30
		3	10.00	10 a_1 (ψ_3)	10.05
		4	10.15	6 b_2 ($\psi_2 + \pi$)	10.34
		5	10.65	6 b_1 (ψ_1)	10.75
5	65915-87-9	1	8.35	7 b_2 ($\pi - \psi_2$)	8.42
		2	9.14	4 a_2 (ψ_4)	9.05
		3	9.65	12 a_1 (ψ_3)	9.80
		4	9.95	6 b_2 ($\psi_2 + \pi$)	9.87
		5	10.3	7 b_1 (SA)	10.55
6	65915-88-0	1	9.05	6 b_2 ($e_A - \psi_2$)	9.15
		2	9.35	4 a_2 (ψ_4)	9.30
		3	10.2	10 a_1 (ψ_3)	10.05
		4	10.5	5 b_2 ($\psi_2 + e_A$)	10.48
		5	10.7	6 b_1 (ψ_1)	10.8
		6	11.2	9 a_1 (e_S)	11.1
7	65915-89-1	1	8.75	7 b_2 ($\pi - \psi_2$)	
		2	9.22	6 b_1 (π)	
		3	9.38	3 a_2 (ψ_4)	
		4	9.9	11 a_1 (ψ_3)	
		5	10.2	6 b_2 ($\psi_2 + \pi$)	
		6	11.1	5 b_1 (ψ_1)	

tem positioned at C_9. As a consequence, the highest occupied orbitals of **4**–**6** are predicted to belong to the irreducible representations A_2 and A_1 (see Table II). A similar discrepancy has been encountered in the case of spiroconjugated molecules.[14] A detailed analysis of the shortcomings of the CNDO and MINDO methods in reproducing long-range through-space interaction has been given by Heilbronner and Schmelzer.[15] According to their results, the SPINDO/1 model seems at present the most appropriate model for interpreting the PE spectra of hydrocarbons.

The SPINDO/1 results we have obtained on structures derived from MINDO/3 optimization compare very closely to those obtained from ZDO calculations, especially as regards **4**, **5**, and **7**. The only differences are the ordering between 10 a_1 and 6 b_2 in the case of **4** and the corresponding orbitals in **5** and **7**. The main discrepancy is associated with **6** (see Tables I and II). Such differences have previously been observed in other hydrocarbons endowed uniquely with small ring fragments.[16]

Concluding Remarks. The ZDO model predicts the HOMO for **4**–**7** to be $b_2(\pi-\psi_2)$ or $b_2(e_A-\psi_2)$. This prediction is corroborated by the following observations: (i) The first ionization potentials of 7-methylenenorbornane (9.4 eV),[4] 7-isopropylidenenorbornane (8.5 eV),[5] and 7-spirocyclopropylnorbornane (9.6 eV)[5] are close to, but slightly higher than, the corresponding first ionization potentials of **4**–**6**. The lower values for **4**–**6** are due to the larger carbon skeleton and the through-space interaction discussed. (ii) Methyl substitution on a double bond is known to substantially lower the ionization potential of the π orbital. A comparison between the spectra of **4** and **5** shows that an appropriate shift is observed only for the first band.

One of the purposes underlying publication of our semiempirical results at this time is to point out the difficulties and pitfalls encountered with such methods when applied to strained hydrocarbons.

Experimental Section

Proton magnetic resonance spectra were obtained on a Varian A-60A spectrometer; apparent splittings are given in all cases. Carbon spectra were recorded with a Bruker HX-90 instrument. Infrared spectra were obtained with a Perkin-Elmer Model 467 spectrometer, while mass spectra were measured with an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

9-Methylenepentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (4). To a stirred suspension of methyltriphenylphosphonium bromide (4.20 g, 11.76 mmol) in 30 mL of dry tetrahydrofuran was added under nitrogen at 25 °C 5.0 mL of a 2.35 M solution of *n*-butyllithium in hexane (11.75 mmol). After 2 h, a solution of **9**[7] (1.50 g, 11.35 mmol) in 20 mL of dry tetrahydrofuran was introduced dropwise via syringe. The reaction mixture was stirred for an additional 2 h at 25 °C, heated to a gentle reflux for 30 min, cooled, poured into ice water (300 mL), and filtered. The precipitate was washed with 75 mL of pentane which was used to extract the aqueous filtrate. The pentane layer was washed with water (3 × 100 mL), dried, filtered, and distilled at ambient pressure through a 1 × 13 cm Vigreux column to remove solvent. The residual oil was vacuum transferred at 50 °C (0.2 mm) into an

Table II. Calculated Heats of Formation and Orbital Energies for 4–7 According to EH, CNDO/2, MINDO/3, and SPINDO/1 Methods (orbital energies are given in eV)

Compd	H_f, kcal/mol	EH	CNDO/2[a]	MINDO/3	SPINDO/1
4	121.74	−12.27 (a_2)	−11.80 (a_2)	−9.07 (a_2)	−10.14 (b_2)
		−12.35 (a_1)	−11.91 (a_1)	−9.31 (a_1)	−10.45 (a_2)
		−12.56 (b_2)	−13.77 (b_2)	−9.35 (b_2)	−10.58 (b_2)
		−12.70 (b_2)	−14.00 (b_2)	−9.51 (b_2)	−10.76 (a_1)
		−12.96 (b_1)	−15.34 (b_1)	−9.76 (b_1)	−10.87 (b_1)
5	109.34	−12.18 (b_2)	−11.59 (b_2)	−8.87 (b_2)	−9.71 (b_2)
		−12.28 (a_2)	−11.73 (a_2)	−9.09 (a_2)	−10.52 (a_2)
		−12.33 (a_1)	−11.89 (a_1)	−9.31 (a_1)	−10.66 (b_2)
		−12.59 (b_2)	−13.07 (b_2)	−9.49 (b_2)	−10.73 (a_1)
		−12.83 (b_1)	−15.13 (b_1)	−9.70 (b_1)	−11.07 (b_1)
6	122.76	−12.26 (a_2)	−11.65 (a_2)	−9.05 (a_2)	−10.48 (a_2)
		−12.30 (a_1)	−11.83 (a_1)	−9.15 (a_1)	−10.58 (b_2)
		−12.50 (b_2)	−12.49 (b_2)	−9.35 (b_2)	−10.61 (a_1)
		−12.62 (b_2)	−13.53 (b_2)	−9.49 (b_2)	−10.95 (b_2)
		−13.00 (b_1)	−14.61 (a_1)	−9.87 (b_1)	−11.07 (b_1)
		−12.15 (a_1)	−15.20 (b_1)	−10.23 (a_1)	−11.36 (a_1)
7	144.37	−12.27 (a_2)	−11.78 (b_2)	−8.85 (b_2)	−9.57 (b_2)
		−12.34 (b_2)	−11.82 (a_2)	−8.99 (b_1)	−9.90 (b_1)
		−12.36 (a_1)	−12.00 (a_1)	−9.09 (a_2)	−10.44 (a_2)
		−12.58 (b_1)	−13.02 (b_1)	−9.36 (a_1)	−10.56 (b_2)
		−12.59 (b_2)	−13.18 (b_2)	−9.47 (b_2)	−10.68 (a_1)
		−13.36 (b_1)	−15.38 (b_1)	−10.66 (b_1)	−11.42 (b_1)

[a] Several σ levels in the region between 12 and 15 eV have been omitted.

ice-cooled receiver to give 1.09 g (73.7%) of **4:** ν_{max} (neat) 3045, 2985, 1669, 1283, 810, 777, and 728 cm^{-1}; ^{1}H NMR (CCl_4) δ 4.03 (s, 2 H), 2.61 (m, 2 H), 2.18 (m, 2 H), and 1.94 (m, 4 H); ^{13}C NMR ($CDCl_3$) 172.54, 89.10, 44.13, 37.23, and 36.93 ppm; *m/e* calcd 130.0782, obsd 130.0785.

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.23; H, 7.83.

9-Isopropylidenepentacyclo$[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]$nonane (5). To a magnetically stirred suspension of anhydrous isopropyltriphenylphosphonium bromide (1.40 g, 3.63 mmol) in 6.0 mL of anhydrous tetrahydrofuran was added dropwise under nitrogen at 25 °C a solution of *n*-butyllithium (1.64 mL of 2.08 M) in hexane. After 1 h, a solution of 9[7] (0.450 g, 3.41 mmol) in 4.0 mL of tetrahydrofuran was introduced dropwise via syringe. After 2.5 h the reaction mixture was heated at gentle reflux for an additional 2.5 h, cooled to ambient temperature, and processed as above. Vacuum transfer at 70 °C (0.1 mm) of the residual oil after removal of solvent gave 0.435 g (80.7%) of **5:** ν_{max} (neat 3045, 3000, 2915, 1283, 788, and 715 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.86 (m, 2 H), 2.13 (m, 2 H), 1.88 (m, 4 H), and 1.55 (m, 6 H); ^{13}C NMR ($CDCl_3$) 159.43, 105.59, 40.76, 37.74, 36.55, and 20.18 ppm; *m/e* calcd 158.1095, obsd 158.1098.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.09; H, 8.99.

Dibromocarbene Addition to 4. A solution of bromoform (1.30 g, 5.14 mmol) in 3.0 mL of pentane was added dropwise to a vigorously stirred suspension of potassium *tert*-butoxide (0.480 g, 4.28 mmol) and **4** (0.550 g, 4.22 mmol) in 10 mL of pentane under nitrogen at 15 °C. The reaction mixture was stirred at 25 °C for 12 h, poured into 15 mL of water, and extracted with 2 × 10-mL portions of ether. The combined extracts were washed with 3 × 20 mL of water, dried, filtered, and evaporated to leave a semisolid suspended in a small amount of oil. This material was taken up in 4 mL of 5% benzene in pentane and washed down a 1 × 5-cm column of neutral alumina (activity grade 1) using an additional 20 mL of solvent. Evaporation left 0.94 g of a white semisolid which was recrystallized from pentane to give 0.583 g (45.5%) of **10:** mp 98.5–99.5 °C; ν_{max} (KBr) 3050, 1185, 1032, 1017, 789, 764, and 684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.44 (br s, 2 H), 2.32 (br s, 4 H), 2.11 (br s, 4 H), and 1.76 (s, 2 H); *m/e* calcd 299.9150, obsd 299.9157.

9-Spirocyclopropylpentacyclo$[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]$nonane (6). To a magnetically stirred solution of **10** (0.298 g, 0.987 mmol) and anhydrous *tert*-butyl alcohol (0.50 g, 6.75 mmol) in 10 mL of dry tetrahydrofuran was added at 25 °C under nitrogen finely cut lithium wire (0.22 g, 31.7 mg). The reaction mixture was stirred for 10 h at ambient temperature and excess lithium was removed by filtration (with ether washing). Twenty milliliters of 10% ammonium chloride solution was added, the layers were separated, and the aqueous layer was extracted with pentane (2 × 10 mL). The combined organic layers were washed with three 20-mL portions of water, dried, filtered, and freed of solvent by distillation at ambient pressure. The residual oil was vacuum transferred at 80 °C (0.1 mm) into an ice-cooled receiver to give 0.1143 g (80.5%) of **6:** mp 28 °C; ν_{max} (neat) 3040, 2965, 1288, 781, and 760 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.02 (br s with shoulder at 1.97, 8 H) and 0.46 (s, 4 H); *m/e* calcd 144.0939, obsd 144.0942.

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.62; H, 8.43.

9-Allenylidenepentacyclo$[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]$nonane (7). To a magnetically stirred solution of **10** (0.2319 g, 0.768 mmol) in 10 mL of anhydrous ether was added under nitrogen at −24 °C 0.6 mL of a 1.84 M solution of methyllithium in ether via syringe. After 40 min at −24 °C, 3.0 mL of water was introduced, the layers were separated, the aqueous layer was extracted with 2 mL of ether, and the combined ether layers were washed three times with 5-mL portions of water, dried, and freed of solvent by distillation at ambient pressure. The residual material was vacuum transferred at 0.3 mm into a receiver cooled to −24 °C to give 0.103 g (94.5%) of **7** as a crystalline solid; mp 27 °C; ν_{max} (neat) 3045, 1277, 846, 787, and 720 cm^{-1}; ^{1}H NMR (CCl_4 δ 4.64 (s, 2 H), 2.96 (m, 2 H), and 2.12 (m, 6 H); *m/e* calcd 142.0782, obsd 142.0785.

Anal. Calcd for $C_{11}H_{10}$: C, 92.91; H, 7.09. Found: C, 93.01; H, 7.14.

Photoelectron Spectroscopy. The PE spectra were recorded on a Perkin-Elmer PS 18 instrument (Beaconsfield, England) and calibrated with argon. A resolution of about 20 meV on the argon line was observed.

Calculations. The semiempirical calculations have been carried out with standard programs. All calculations were based upon the geometrical parameters obtained by the MINDO/3 method.

Acknowledgment. The work at Darmstadt has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Financial support for the research conducted in Columbus was provided by the National Science Foundation.

Registry No.—**9**, 20682-66-0; **10**, 65915-90-4; methyltrisphenylphosphonium bromide, 1779-49-3; isopropyltriphenylphosphonium bromide, 1530-33-2.

References and Notes

(1) Institut für Organische Chemie der Technischen Hochschule Darmstadt.

(2) The Ohio State University.

(3) E. Heilbronner and H.-D. Martin, *Helv. Chim. Acta*, **55**, 1490 (1972).

(4) R. W. Hoffmann, R. Schüttler, W. Schäfer, and A. Schweig, *Angew. Chem.*, **84**, 533 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 512 (1972).

(5) F. Brogli, E. Heilbronner, and J. Ipaktschi, *Helv. Chim. Acta*, **55**, 2447 (1972).

(6) T. Koopmans, *Physica*, **1**, 104 (1934).

(7) W. G. Dauben and R. J. Twieg, *Tetrahedron Lett.*, 531 (1974); R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **90**, 4162 (1968).

(8) H.-D. Martin, C. Heller, R. Haider, R. W. Hoffman, J. Becherer, and H. R. Kurz, *Chem. Ber.*, **110**, 3010 (1977).

(9) F. Brogli, J. K. Crandall, E. Heilbronner, E. Kloster-Jensen, and S. Sojka, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 455 (1973).

(10) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).

(11) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.

(12) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).

(13) C. Fridh, L. Åsbrink, and E. Lindholm, *Chem. Phys. Lett.*, **15**, 282 (1972); L. Åsbrink, C. Fridh, and E. Lindholm, *J. Am. Chem. Soc.*, **94**, 5501 (1972).

(14) M. D. Gordon, T. Fukunaga, and H. E. Simmons, *J. Am. Chem. Soc.*, **98**, 8401 (1976).

(15) E. Heilbronner and A. Schmelzer, *Helv. Chim. Acta*, **58**, 936 (1975).

(16) J. Spanget-Larsen, unpublished results.