Photoelectron Spectra of Molecules. III.[1] Ionization Potentials of Some Cyclic Hydrocarbons and Their Derivatives, and Heats of Formation and Ionization Potentials Calculated by the MINDO SCF MO Method[2]

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Abstract: The ionization potentials of 28 cyclic hydrocarbons, including adamantane and several of its derivatives, have been measured from photoelectron spectra. Few of the molecules in this series have been studied previously. The first ionization potentials for adamantane and all of its derivatives except adamantanone and congressane are approximately the same. The MINDO method, a recently developed semiempirical SCF MO procedure, has been employed in predicting ionization potentials and heats of formation for all of the cyclic molecules.

Photoelectron spectroscopy (PS) provides a relatively new and extremely versatile technique for determining ionization potentials. Not only are first ionization potentials (I_1) derived accurately (*ca.* ±0.01 eV), but also higher ionization potentials (I_i $(i > 1)$) are obtained. Thus the method provides a stringent test of theoretical procedures which predict ionization potentials or orbital energies[5] for molecules. The PS method measures adiabatic ionization potentials, but for small molecules for which high resolution can be obtained, vertical ionization potentials are also accessible.[6] Ionization potentials predicted by any theoretical method which employs Koopmans' theorem should really be compared with vertical ionization potentials, since Koopmans' theorem does not allow for changes in geometry or wave functions upon ionization. However, since vertical ionization potentials are commonly only 0–0.3 eV higher than the corresponding adiabatic ones, and since this is within the limits of error of all current theoretical procedures, a comparison of values calculated from Koopmans' theorem with PS adiabatic ones is quite useful.[7]

Because there are many closely spaced energy levels in a large organic molecule, particularly one with low symmetry containing only σ electrons, resolution in the photoelectron spectra can be poor (*e.g.*, most alkanes[9]). In large molecules of high symmetry, however, many of the energy levels should be degenerate; in this case it may be possible to resolve them. Adamantane provides an example of a molecule with high (threefold) symmetry; many of its energy levels are expected to be degenerate, and the photoelectron spectrum should be therefore better resolved than that for most other σ-electron systems. We therefore undertook a PS study of a series of adamantane derivatives and a number of other interesting cyclic systems having various degrees of symmetry, in the hope of obtaining accurate ionization potentials which could serve as a test of semiempirical valence shell methods for calculating the properties of large molecules. This paper reports the PS ionization potentials and the orbital energies predicted by the MINDO SCF MO method for many cyclic hydrocarbons and their derivatives; the calculated heats of formation are also reported.

Experimental Section

The photoelectron spectrometer employed in this investigation was of the retarding potential-grid type and has been recently described.[9] It was necessary to heat the ionization chamber (to *ca.* 100°) only in the case of congressane, the other compounds being sufficiently volatile at room temperature. At least 12 runs were made for each compound studied. The purity of all of the samples except barrelene (bicyclo[2.2.2]octatriene) was checked by glpc. When necessary, the compounds were purified by several recrystallizations from appropriate solvents, followed by sublimation. The sample of barrelene available to us was too small to risk purification. All samples were subjected to cycles of freezing, evacuation, vaporization, etc., on a high-vacuum line immediately before use.

Theoretical

A. Methods of Calculation. The calculations reported in this paper were carried out by two versions of the MINDO method.[8] The MINDO method is a semiempirical SCF MO procedure in which all valence electrons, both σ and π, are included, and ionization potentials are estimated from the σ and π orbital energies (Koopmans' theorem). The two versions of MINDO (1 and 2) differ only in the expressions for nuclear repulsions. In MINDO/1[8] the core–core repulsions are set equal to the electron–electron repulsions, and the energy minimum at the calculated equilibrium geometry does not correspond to the experimental molecular geometry. MINDO/1 is parameterized to give accurate heats of formation for a large variety of mole-

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[1] Paper II: M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **51**, 263 (1969).

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[3] Robert A. Welch Postdoctoral Fellow; on leave of absence from The Chemical-Pharmaceutical Research Institute, Cluj, Romania.

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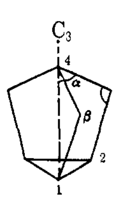
[5] Ionization potentials are commonly equated to minus the corresponding calculated orbital energies (Koopmans' theorem).

[6] An adiabatic ionization potential is the difference in energy between the ground vibrational levels of the molecule and the ion, while a vertical ionization potential is the difference in energy between the ground vibrational level of the molecule and some vibrational level of the ion, the nature of which is dictated by the Franck–Condon principle.

[7] Relative magnitudes of I_i predicted by the MINDO method[8] (Koopmans' theorem used) generally agree quite well with the PS values[9] for a molecular series.

[8] (a) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); (b) N. C. Baird, M. J. S. Dewar, and R. Sustman, *ibid.*, **50**, 1275 (1969).

[9] (a) M. J. S. Dewar and S. D. Worley, *ibid.*, **50**, 654 (1969); (b) M. J. S. Dewar, M. Shanshal, and S. D. Worley, *J. Am. Chem. Soc.*, **91**, 3590 (1969).



C_1–C_2: 1.558Å, $\alpha = 59.95°$
C_2–C_3: 1.480Å, $\beta = 103.58°$
C_3–C_4: 1.524Å

Figure 1. Optimum geometry for nortricyclene from the MINDO/2 method.

cules, the molecular geometries used being the standard ones of Baird and Dewar.[8] In MINDO/2 the more realistic core–core repulsion term introduced by Dewar and Klopman[10] in their PNDO treatment is used, and the predicted geometries are consequently close to the experimental ones. Here experimental bond lengths and angles, rather than standard ones, should be used in calculations.

The MINDO/2 method was recently parameterized separately for hydrocarbons[11] and compounds containing oxygen.[12] However, the initial set of parameters for carbon and hydrogen[11] were not the optimum ones for compounds containing nitrogen.[13] Therefore MINDO/2 was parameterized for a set of 40 compounds containing carbon, hydrogen, oxygen, and nitrogen and various types of bonds.[14] The latter set of parameters was used in this study.

Since the values of the resonance integrals (treated as empirical parameters) are different for the two versions of MINDO, orbital energies predicted by the two versions are usually somewhat different.[15] Of course heats of formation predicted by the two versions of MINDO, being dependent on the nature of the core–core repulsion expression as well as the empirical parameters, usually differ.

B, Molecular Geometries. The molecular geometries chosen for the MINDO/1 calculations for this series of molecules were the standard ones of Baird and Dewar.[8] For the MINDO/2 calculations experimental geometries were used where accurate data were available.[16] For key molecules for which no geometries have been reported, the energy was minimized by simultaneous variation of the bond lengths and bond angles. For example, the optimum C–C bond lengths and angles for bicyclo[2.2.2]octane were 1.534 Å and 109.5°, respectively, while for bicyclo[2.2.2]octatriene the C–C sp^2–sp^3 length was 1.496 Å, the C–C sp^2–sp^2 length was 1.338 Å, and the bridge angles were 120°. These bond lengths and angles were used for bicyclo[2.2.2]octene and bicyclo[2.2.2]octadiene and for the bicyclo[2.2.1] systems, the bond angles being optimized for the latter.

For the adamantane derivatives and bicyclohexyl the C–C bond lengths used were obtained by optimizing the structures of cyclohexane (the cyclic C–C bond length was 1.524 Å) and methylcyclohexane (the equatorial exocyclic C–C bond length was 1.528 Å). The value found for the cyclic C–C bond length is in excellent agreement with the recent experimental value (1.528 Å)[16c] for cyclohexane.

A complete optimization of the structure of nortricyclene was carried out with the results at the energy minimum shown in Figure 1. The bond lengths of Figure 1 are not in satisfactory agreement with the experimental ones[16e] obtained in 1951, *i.e.*, $r_{34} = r_{23} = 1.54 \pm 0.02$; $r_{12} = 1.50 \pm 0.02$ Å, which seem to be supported by a recent study[16f] of 4-chloronortricyclene (r_{12}, 1.510; r_{23}, 1.535; r_{34}, 1.537 Å), but it is difficult to see why the bonds in the cyclopropane ring should be so much shorter than the corresponding ones in bullvalene (1.544 Å[16a]). The optimized geometry was used in the present calculations.

The structure of cyclooctatetraene was also optimized, the tub conformation being most stable; the calculated "double bond lengths" were 1.355 Å, and the "single bond lengths" were 1.473 Å, the bond angles being 125.3°. For cycloheptatriene the same "double" and "single" bond lengths as for cyclooctatetraene were used except for the sp^2–sp^3 "single" bonds which were chosen to be 1.517 Å, the experimental value[16a] for the similar bonds in bullvalene, and the bond angles were optimized.

For the calculations involving the four isomers of spiroheptadiene, the experimental geometries[16d] given for cyclobutene, cyclopentadiene, cyclopentene, cyclopropane, and cyclopropene were used. For cubane the bond lengths given for cyclobutane[16d] were employed.

Results

A typical photoelectron spectrum (for adamantane, I) given by our retarding potential grid-type spectrometer is shown in Figure 2. The resolution in this spectrum is significantly better than for most other molecules[9] containing only σ electrons. Although the peaks in the first derivative plot do not return to the base line,[17] the "breaks" in the spectra furnish adiabatic ionization potentials which agree well with those obtained by the highly accurate spectroscopic technique.[9]

Table I lists first ionization potentials (I_1) in eV for a number of cyclic hydrocarbons and their derivatives, measured from photoelectron spectra and calculated by the two versions of the MINDO SCF MO method mentioned in the theoretical section. Calculations by MINDO/1 are reported only in some cases for comparison, since MINDO/2 seems clearly superior to the earlier version. The numbers in parentheses following the calculated orbital energies are the orbital degeneracies. Structures for the molecules included in this study (see numbering in Table I) are shown in Figure 3.

There have been few reliable ionization potentials reported for the molecules studied here. We have previously pointed out[9] that the electron impact first ionization potentials of Gohlke[18] for adamantane (8.0 eV) and congressane (7.3 eV) must be too low, probably due

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(10) M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967).

(11) M. J. S. Dewar and E. Haselbach, submitted for publication.

(12) N. Bodor, M. J. S. Dewar, and E. Haselbach, submitted for publication.

(13) M. J. S. Dewar and A. Harget, unpublished results.

(14) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, submitted for publication.

(15) Orbital energies are *not* dependent on the core–core repulsion energy.

(16) (a) B. Andersen and A. Marstrander, *Acta Chem. Scand.*, **21**, 1676 (1967); (b) O. Bastiansen and A. de Meijere, *ibid.*, **20**, 516 (1966); (c) M. I. Davis and O. Hassel, *ibid.*, **18**, 813 (1964); (d) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London: Special Publication No. 11, 1958; Special Publication No. 18, 1965; (e) E. Heilbronner and V. Schomaker, *Helv. Chim. Acta*, **35**, 1385 (1951); (f) J. F. Chiang, C. F. Wilcox, and S. H. Bauer, *Tetrahedron*, **25**, 369 (1969).

(17) Tailing occurs because not all photoelectrons travel in paths perpendicular to the grids (parallel to the retarding potential field).

(18) R. S. Gohlke, private communication to M. D. Newton, F. P. Boer, and W. N. Lipscomb (see M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2367 (1966)).

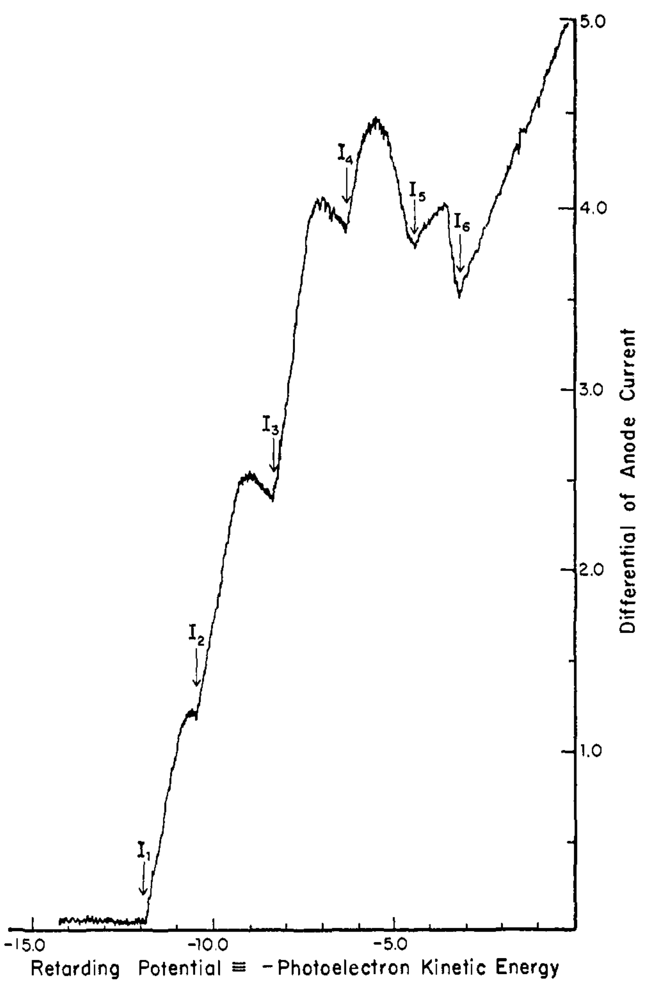

Figure 2. Photoelectron spectrum of adamantane (p = 0.032 mm) excited by the resonance line (21.22 eV) of helium.

to internal rupture of the molecules in the mass spectrometer; there were no indications of breaks in the photoelectron spectra below our I_1 values. The present values of I_1 for cubane (8.74 eV) and cycloheptatriene (8.40 eV) are in reasonable agreement with recent electron impact results (8.74 ± 0.15[19] and 8.52 eV,[20] respectively).

The electron impact value for cubane seems a bit low, given that it should be a vertical ionization potential, while the PS value is adiabatic. The present PS value of I_1 for cyclooctatetraene (8.21 eV) is 0.2 eV higher than the previous PS value reported by Al-Joboury and Turner (8.04 eV)[21] and the value (7.99 eV) measured from photoionization yield curves by Watanabe, *et al.*[22] This is peculiar because our results usually agree well with those obtained by Turner and Watanabe. However, Price, *et al.*, have also reported an adiabatic first ionization potential for this molecule of 8.6 eV.[23]

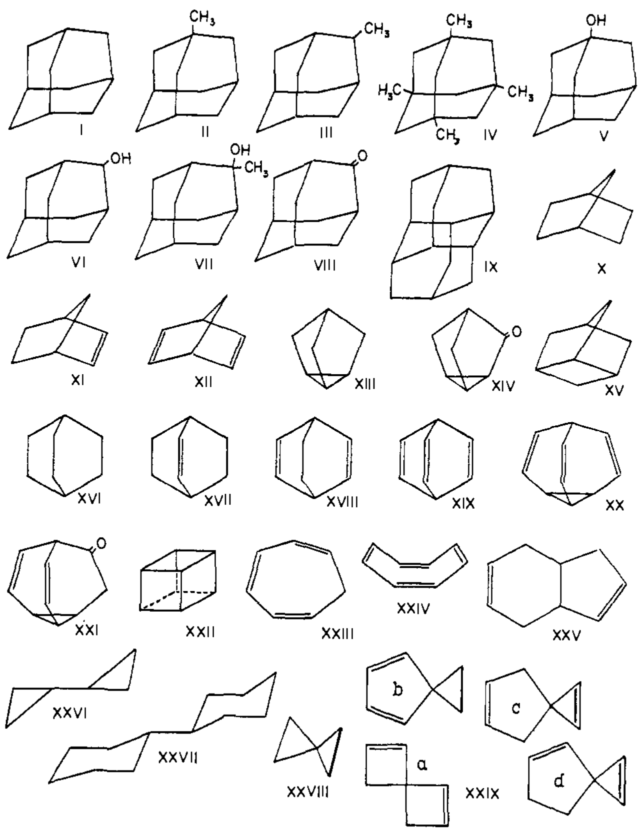

Figure 3. Structures for the molecules listed in Table I.

Table II lists higher ionization potentials deduced from breaks in the photoelectron spectra together with calculated orbital energies. Only orbital energies below *ca.* −15 eV are listed, to save space. The PS values in parentheses are uncertain but correspond to reproducible changes of slope in the spectra. The uncertain values above 18 eV may have been caused by ionization by hydrogen Lyman α radiation,[24] due to traces of hydrogen present as impurity in the helium. It should also be pointed out that, as indicated in Table II, several of the breaks in the photoelectron spectrum of barrelene correspond to, and resemble closely, those in the spectrum of benzene. We suspect that they were in fact due to benzene, either present in traces as an impurity in XIX, or conceivably formed from XIX by photochemical reaction in the spectrometer.

Discussion

A, Ionization Potentials. 1. Adamantane Derivatives, The first set of compounds studied were derivatives of adamantane. This is an interesting ring system in view of its symmetry and some earlier indications that it might show peculiarities in its electronic structure. The results in Table I lead to the surprising conclusion that substituents have little effect on the ionization potential, the I_1 values for I–VII varying only from 9.22 to 9.25 eV. In small molecules substitution leads to large changes in I_1, due to the inductive/field effect of the substituent; thus introduction of methyl into ethane to give propane lowers I_1 by 0.45 eV.[9] However, Watanabe[22] has reported a similar insensitivity to methyl substitution in the case of cyclohexane (I_1, 9.88 eV; I_1 for methylcyclohexane, 9.85 eV), and the effect in the case of n-hexane is also small (I_1, 10.27

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(19) B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave, and J. L. Franklin, *J. Am. Chem. Soc.*, 88, 626 (1966).

(20) S. Meyerson, J. D. McCollum, and P. N. Rylander, *ibid.*, 83, 1401 (1961).

(21) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964).

(22) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiative Transfer*, 2, 369 (1962).

(23) L. D. Isaacs, W. C. Price, and R. G. Ridley, in "The Threshold of Space," M. Zelikoff, Ed., Pergamon Press Ltd., London, 1957, pp 143–151.

(24) We are grateful to Dr. D. W. Turner for pointing out this possibility.

Table I. First Ionization Potentials and Heats of Formation for Some Cyclic Molecules

Molecule	First ionization potentials, eV Obsd	MINDO/2	MINDO/1	$\Delta H_f°$ (298°K), kcal/mole MINDO/2	MINDO/1	Estd[a]	Estd[b]
I. Adamantane	9.25	9.66 (3)[c]	10.07 (3)[c]	−34.8	−27.4	−33.9	−33.9
II. 1-Methyladamantane	9.24	9.61	9.84	−32.8	−35.6	−42.2	−42.1
III. 2-Methyladamantane	9.24	9.33	9.88	−29.4	−35.5	−40.2	−40.2
IV. 1,3,5,7-Tetramethyladamantane	9.23	9.55 (3)	9.79 (3)	−26.2	−60.3	−66.8	−66.7
V. 1-Adamantanol	9.23	9.62	10.11	−81.4	−65.4	−81.2	−77.4
VI. 2-Adamantanol	9.25	9.64	10.16	−69.5	−66.4	−75.0	−76.5
VII. 2-Methyl-2-adamantanol	9.22	9.39	9.97	−67.4	−76.5	−83.2	−83.9
VIII. Adamantanone	8.76	9.38	9.96	−70.3	−37.9	−60.6	−52.4
IX. Congressane	8.93	9.20	9.54	−41.7	−27.2	−38.3	−38.3
X. Bicyclo[2.2.1]heptane	9.80	9.64		5.4		−26.8	−26.8
XI. Bicyclo[2.2.1]heptene	8.83	8.91		32.0		1.9	−0.2
XII. Bicyclo[2.2.1]heptadiene	8.62	8.78		59.8		30.7	28.5
XIII. Nortricyclene	9.02	9.46 (2)		−7.5		−19.1	−19.2
XIV. Nortricyclone	9.01	9.34		−48.0		−45.8	−38.8
XV. Tricyclo[3.2.1.$0^{3,6}$]octane	8.75	8.56		36.7		−24.0	−24.1
XVI. Bicyclo[2.2.2]octane	9.53	9.68 (2)		−25.4		−31.7	−31.7
XVII. Bicyclo[2.2.2]octene	8.92	9.34		5.7		−3.0	−4.0
XVIII. Bicyclo[2.2.2]octadiene		9.07		26.6		25.7	24.1
XIX. Bicyclo[2.2.2]octatriene	8.24	8.88		49.0		54.5	51.2
XX. Bullvalene	8.13	8.54 (2)		42.0		52.3	49.0
XXI. Bullvalone	8.72	8.78		−9.7		−3.1	2.0
XXII. Cubane	8.74	9.17 (3)	9.68 (3)	19.9	116.9	−8.7	−8.8
XXIII. Cycloheptatriene	8.40	8.45		41.2		51.7	40.9
XXIV. Cyclooctatetraene	8.21	9.00		71.5		75.5	56.0
XXV. Bicyclo[4.3.0]nona-3,7-diene	8.78	9.16		17.0		20.8	18.6
XXVI. Bicyclopropyl	9.04	9.07	9.46	13.6	39.5	−21.9	−21.9
XXVII. Bicyclohexyl	9.41	9.19		−35.9		−51.4	−51.3
XXVIII. Spiropentane	9.45	9.55 (2)	9.59	13.8	42.2	−16.9	−18.7
XXIX. Spiroheptadiene (a)	9.02	9.03		61.3		28.7	26.7
Spiroheptadiene (b)		9.19		26.2		28.7	22.9
Spiroheptadiene (c)		8.98		42.9		28.7	26.7
Spiroheptadiene (d)		8.68		44.2		28.7	26.7

[a] Franklin's group method for strain-free molecules (see J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949)). [b] The bond energy scheme of Cox (see J. D. Cox, *Tetrahedron*, **19**, 1175 (1963)). [c] Orbital degeneracies are given in parentheses.

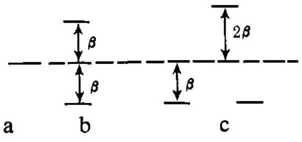

Figure 4. Effect of mutual interactions on π orbital energies: (a) isolated double bond; (b) two interacting double bonds, (c) three double bonds interacting symmetrically, as in barrelene (XIX).

eV[9]; I_1 for *n*-heptane, 10.20 eV[21]). Thus the effect of substituents on I_1 for saturated molecules seems to decrease rapidly with molecular size. Note that this conclusion holds only for substituents that do not alter the connectivity of the carbon skeleton or its geometry. Thus additional annelation of four carbon atoms to the diamondoid skeleton of I to form congressane (IX) leads to a decrease of 0.32 eV in I_1, while conversion of I to adamantanone (VIII) leads to an even greater decrease (0.49 eV). The latter change is particularly noteworthy since the $+I$ effect of the carbonyl group in VIII might have been expected to increase I_1.

The I_1 values given by MINDO/2 are uniformly too high, for reasons that have been discussed previously,[9] but otherwise, with one exception, the calculated and observed values correspond well. Note in particular the correct prediction that I_1 for adamantanone (VIII) should be less than that for adamantane (I). The exception concerns the effect of a 2-methyl substituent (III and VII) which is erroneously predicted to lower I_1 by *ca.* 0.3 eV. The reason for this is not clear, given that a 2-hydroxyl is correctly predicted to have virtually no effect on I_1. The values given by MINDO/1 are much less satisfactory, as expected from previous studies.

2, "Propeller" Molecules. Measurements were carried out for a number of "propeller-shaped" molecules in order to assess the effect of longitudinal interactions between the π electrons of isolated double bonds, a problem of some topical interest. Assuming the highest occupied MO's in bicyclo[2.2.1]heptadiene (XII), bicyclo[2.2.2]octadiene (XVIII), and bicyclo[2.2.2]octatriene (XIX) (*i.e.*, barrelene) to arise from such interactions between adjacent double bonds, one can predict the relationship to be expected between the corresponding orbital energies and those for the single occupied π MO's in the corresponding monoolefins. The relationships are indicated in Figure 4, β being the interaction energy between two adjacent double bonds. In the symmetrical case with threefold symmetry, the expected orbital pattern is that indicated in Figure 4c.

The calculated orbital patterns for XVII, XVIII, and XIX follow the predicted pattern. The energy of the highest occupied MO in XVII (9.34 eV) is close to the mean (9.28 eV) of the two corresponding perturbed MO's in XVIII, and reasonably close to the weighted mean (9.21 eV) of the three corresponding perturbed MO's in XIX. The decrease along the series can reasonably be attributed to ring strain. On this basis, the value of β, the interaction parameter in Figure 4, is *ca.* 0.2 eV, and a similar value follows from the orbital energies of XI and XII. Unfortunately, these values cannot be reliably checked against the ionization potentials reported here since the resolution of our spectrometer

Table II. Higher Ionization Potentials for Some Cyclic Molecules

Molecule	Observed, eV	MINDO/2,[a] eV
I. Adamantane	10.69, 12.90, 14.94, 16.79, (18.01)	10.56 (3), 10.79 (2), 13.11 (3), 13.18 (3), 14.94, 14.94 (3)
II. 1-Methyladamantane	10.68, 12.37, 14.44, (16.95), (18.02)	9.66 (2), 10.38 (2), 10.57, 10.81 (2), 12.08 (2), 12.23, 13.12, 13.19 (2), 14.10 (2), 14.62, 14.99 (2), 15.03
III. 2-Methyladamantane	10.51, 12.42, 12.97, 14.78, (18.26)	9.64, 9.65, 10.29, 10.38, 10.55, 10.66, 10.78, 11.64, 12.07, 12.67, 13.09, 13.17, 13.35, 13.41, 14.08, 14.64, 14.94, 15.03
IV. 1,3,5,7-Tetramethyladamantane	10.34, 12.07, 14.51, (17.67)	10.09 (3), 10.83 (2), 11.81 (3), 11.99 (3), 12.79 (2), 12.86 (3), 13.46, 14.69 (3), 15.24 (3)
V. 1-Adamantanol	(12.62), 13.13, 14.60, (15.18), (18.27)	9.70, 10.29, 10.36, 10.48, 10.66, 10.88, 10.89, 11.90, 12.16, 13.14, 13.20, 13.28, 13.30, 13.76, 14.21, 14.95, 15.05, 15.06, 15.61
VI. 2-Adamantanol	10.88, 12.90, (13.97), (15.35), (18.68)	9.78, 9.83, 10.39, 10.52, 10.75, 10.98, 11.13, 11.90, 12.59, 12.86, 13.29, 13.33, 13.50, 13.71, 13.83, 14.92, 15.11, 15.15
VII. 2-Methyl-2-adamantanol	10.75, 12.52, (18.36)	9.59, 9.80, 10.26, 10.28, 10.71, 10.94, 10.99, 11.77, 11.84, 12.13, 12.65, 12.93, 13.03, 13.30, 13.52, 14.12, 14.32, 14.72, 15.08
VIII. Adamantanone	9.99, 11.50, 13.41, 15.16, (18.20)	10.09, 10.11, 10.35, 10.95, 11.18, 11.44, 11.46, 12.29, 13.09, 13.29, 13.48, 13.54, 13.59, 14.32, 14.43, 15.02, 15.27, 15.32
IX. Congressane	10.20, 11.59, (12.50), (14.30), 14.84, (15.52), (18.20)	9.66 (2), 9.98 (2), 10.09, 10.27 (2), 11.06, 11.37 (2), 11.97, 12.42 (2), 13.27, 13.67, 13.70 (2), 13.93 (2), 14.86, 14.88 (2), 15.61
X. Bicyclo[2.2.1]heptane	(10.15), (11.26), 13.36, 15.42, (19.13)	9.82, 9.89, 10.63, 10.92, 11.29, 11.58, 11.80, 12.98, 13.06, 15.50
XI. Bicyclo[2.2.1]heptene	10.32, 11.47, 13.08, (19.04)	9.71, 10.32, 10.48, 10.70, 11.17, 11.71, 12.14, 12.69, 14.36
XII. Bicyclo[2.2.1]heptadiene	9.42, 11.11, 12.38, 14.01, (15.41), (16.73)	9.20, 10.18, 10.62, 10.66, 10.93, 12.30, 12.37, 12.43, 15.90
XIII. Nortricyclene	10.71, 12.06, 14.14, 15.08, 16.96, (19.35)	10.29 (2), 11.33, 11.41 (2), 11.60, 12.59, 15.29 (2)
XIV. Nortricyclone	9.98, (10.33), 12.60, 14.90, (16.93)	10.16, 10.33, 10.92, 11.53, 11.79, 11.94, 12.56, 12.93, 13.37, 15.01, 15.04
XV. Tricyclo[3.2.1.0^{3,6}]octane	9.40, (10.05), 15.00, 16.75	9.07, 9.68, 10.69, 10.80, 10.85, 11.80, 11.84, 12.17, 12.47, 13.68, 14.03, 16.28
XVI. Bicyclo[2.2.2]octane	11.08, 11.98, (12.60), 15.65, (18.80)	9.72, 10.45, 11.36 (2), 12.34 (2), 12.35, 12.38 (2), 13.46, 16.05
XVII. Bicyclo[2.2.2]octene	9.87, 11.93, (18.75)	9.35, 9.69, 10.19, 11.26, 11.30, 11.80, 12.30, 12.35, 12.43, 13.20, 15.22
XVIII. Bicyclo[2.2.2]octadiene		9.37, 9.49, 10.23, 10.27, 11.48, 11.91, 12.07, 12.64, 13.23, 13.91, 15.13
XIX. Bicyclo[2.2.2]octatriene	9.22,[b] 9.63, 11.11, 11.49,[b] 13.05, 13.79,[b] 14.51, 16.89,[b] (18.11), (19.24), (20.20)[b]	9.37 (2), 10.13 (2), 10.36, 12.25 (2), 13.23, 14.17 (2), 14.83
XX. Bullvalene	(9.16), 11.12, (11.33), 12.87, 14.68, 16.32, 16.65, (18.51)	10.06, 10.31, 10.58 (2), 11.27 (2), 11.40, 11.93 (2), 14.50 (2), 14.62, 16.40
XXI. Bullvalone	10.85,(12.46),(14.49),(15.32), 16.98	9.23, 10.14, 10.66, 10.78, 11.02, 11.14, 11.36, 11.89, 12.25, 12.90, 13.17, 13.41, 14.46, 14.92, 15.18
XXII. Cubane	13.62, 15.34, (16.87), (17.26)	9.69 (3), 13.18 (3), 13.99 (2), 15.63
XXIII. Cycloheptatriene	9.31, 10.73, 11.51, (12.27), 14.00, 14.65, 16.52	10.04, 10.23, 10.65, 10.84, 10.89, 11.77, 13.59, 14.11, 14.73, 16.09
XXIV. Cyclooctatetraene	9.62, 10.91, 12.22, 14.28, 14.50, 16.46, (17.79), (19.29)	9.39, 9.69, 10.09, 10.12, 10.74, 10.93, 12.38, 13.96, 14.09, 14.51, 15.33
XXV. Bicyclo[4.3.0]nona-3,7-diene	10.39, 12.28, 15.79, (18.45), (19.56)	9.48, 9.76, 10.19, 10.65, 10.95, 11.09, 11.56, 11.76, 12.39, 12.73, 13.79, 14.85, 15.76
XXVI. Bicyclopropyl	11.72, 12.43, 13.97, 15.32, 15.59, (19.05), (19.51)	9.57, 10.49, 11.11, 11.17, 11.86, 11.89, 12.73, 13.28, 15.80
XXVII. Bicyclohexyl	10.73, (12.46), 14.04, 14.53, (18.72)	9.25, 9.99, 10.35, 10.75, 11.00, 11.14, 11.25, 11.29, 11.37, 11.76, 11.91, 12.04, 12.23, 13.07, 13.18, 13.62, 14.48, 14.65, 14.78, 14.99
XXVIII. Spiropentane	11.89, 15.50, 18.04, (18.69), (19.17)	9.73, 11.29, 11.54, 12.09, 13.44, 16.17 (2)
XXIX. Spiroheptadiene (a)	10.30, 11.26, 12.41, 14.18, (14.50), 16.23, (19.26)	9.64, 9.95, 10.28, 10.69, 11.71, 11.91, 12.50, 12.92, 15.04

[a] Orbital degeneracies are given in parentheses. [b] These ionization potentials could be those of a benzene impurity (see PS data for benzene in ref 9).

was insufficient; we hope to repeat some of these measurements presently at higher resolution.

In the case of bullvalene (XX), the calculations indicate that the highest occupied MO should be doubly degenerate, in contrast to the situation in barrelene. The reason for this is that the double bonds in XX can undergo pseudo π interactions with the bonds in the cyclopropane ring. In the MO description of cyclopropane,[25] the highest occupied MO is one derived from a cyclic interaction of p AO's of the three carbon atoms, analogous to the lower degenerate pair of olefinic MO's in barrelene; the corresponding nondegenerate upper MO is antibonding and empty. The energy of the degenerate cyclopropane MO's in nortricyclene (XIII) is moreover very similar to that of the degenerate olefinic level in barrelene (calculated orbital energies, 9.46 and 9.37 eV; ionization potentials 9.02 and (estimated) *ca.* 8.9 eV). There should therefore be very strong interaction in bullvalene between the degenerate pair of cyclopropane MO's and the degenerate pair of olefinic MO's. The highest occupied MO's in bullvalene arise from that interaction, being composed almost equally of 2p AO's of the cyclopropane and olefinic carbon atoms.

3. Miscellaneous Cyclic Systems. Tables I and II list ionization potentials for a number of other cyclic

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paraffins and olefins together with orbital energies; the results follow the earlier general pattern, showing in particular a marked decrease in I_1 with increasing ring strain. Thus bicyclopropyl (XXVI) has a lower I_1, 9.04 eV, than bicyclohexyl (XXVII), 9.41 eV; and nortricyclene (XIII), 9.02 eV, than adamantane (I), 9.25 eV; while I_1 for cubane is not only very low (8.74 eV) but similar to that (8.75 eV) for the structurally similar homolog (XV). It will be seen from Table I that these trends are well reproduced by the MINDO/2 orbital energies.

Note also the remarkable decrease in I_1 in passing from cyclopropane (10.06 eV[9]) to bicyclopropyl (9.04 eV); this presumably indicates a strong first-order conjugative interaction between the cyclopropane rings (*cf.* Figure 4b). The difference is about two-thirds that on passing from ethylene (I_1, 10.50 eV[9]) to 1,3-butadiene (I_1, 9.07 eV[9]), and, as expected, much greater than the corresponding difference between cyclohexane (I_1, 9.81 eV[9]) and bicyclohexyl (I_1, 9.41 eV). These results emphasize once more the distinction between collective and one-electron properties.[26] There is little or no chemical evidence for conjugation in XXVI or its derivatives; the first-order interactions indicated in Figure 4b have a large first-order effect on orbital energies, but not on the total energy of the molecule.[26]

The ionization potential for spiroheptadiene (XXIXa), 9.02 eV, is somewhat greater than the values observed for other cyclic olefins and unconjugated cyclic dienes (*e.g.*, cyclohexene, 8.72[27]; XI, 8.83; XVII, 8.92; XXV, 8.78 eV), although one might have expected that of XXIXa to be lowered by ring strain (see ref 9a). It therefore seems unlikely that there can be any significant spiroconjugative interaction[28] between the double bonds in XXIXa since this would also be expected to lower I_1 (*cf.* cyclopentadiene, $I_1 = 8.55$ eV[9a]). Possibly cyclobutenyl may exert a weak $+I$ effect due to changes in the electronegativity of carbon with hybridization.[29] In view of the current interest in spirenes, we have included calculations for four isomers (XXIXa–d) of spiroheptadiene in Table I.

B, Heats of Formation. The heats of formation predicted by MINDO/2 for the 29 cyclic molecules in this study are listed in Table I. Table I also gives the heats of formation predicted by MINDO/1 for a few of the molecules and those predicted by the Franklin group method[30] and the bond energy scheme of Cox[31] for all of the strain-free analogs.[32] Unfortunately the available experimental data for this series of molecules are very limited. The MINDO/2 predictions for adamantane (−34.8 kcal/mole) and cyclooctatetraene (71.5 kcal/mole) are in excellent agreement with the experimental values of −33.0 kcal/mole[33] and 71.1 kcal/mole,[19] respectively. The remaining experimental data (kcal/mole) are for molecules which have considerable strain energies, *i.e.*, bicyclo[2.2.1]heptane (−11 ± 2.5),[34] cubane (148.7),[19] bicyclopropyl (31.0),[35] and spiropentane (44.2).[36] As observed previously,[11,14] MINDO/2 does not predict strain energies[32] nearly as well as does MINDO/1; this is evident once again from the data in Table I. However, for molecules having little strain, MINDO/2 gives quite reasonable predictions of heats of formation.

It should be mentioned that MINDO/2 predicts XXIXb (see Figure 3) to be the most stable isomer of spiroheptadiene.

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