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Electronic and Molecular Structure of Simple Bicyclopropyls. Photoelectron Spectroscopy and Model Calculations

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The electronic and molecular structure of bicyclopropyl (**1**), 1,1′-dimethylbicyclopropyl (**2**), dispiro[2.0.2.3]nonane (**3**), dispiro[2.0.2.4]decane (**4**), dispiro[2.0.2.5]undecane (**5**), dispiro[2.0.2.6]dodecane (**6**), dispiro[cyclopropane-1,2′-bicyclo[2.2.1]heptane-3′,1″-cyclopropane] (**7**), dispiro[cyclopropane-1,2′-bicyclo[2.2.2]octane-3′,1″-cyclopropane] (**8**), *cis*- and *trans*-tricyclo[5.1.0.0^{2,4}]octane (**9** and **10**), *cis*- and *trans*-tricyclo[6.1.0.0^{2,4}]nonane (**11** and **12**), and *trans*-tricyclo[7.1.0.0^{2,4}]decane (**13**) have been investigated by means of photoelectron (PE) spectroscopy (**2**–**6** and **11**–**13**), model calculations, and empirical correlation procedures. Low-energy PE bands of **1**–**13** can be assigned to ejection of electrons from the bicyclopropyl *Walsh* orbital system and are conveniently discussed in terms of a simplified "Linear Combination of *Walsh* Orbitals" (LCWO) model, allowing tentative prediction of conformational features from the PE data. In the case of the mobile species **1** and **2**, the PE spectra are best understood under the assumption that the observed maxima in the low-energy region correspond to the gauche conformer, implying that contributions from the trans conformer are either weak or broad and featureless. This assumption is at variance with previous interpretations but is supported by a consideration of torsional amplitudes and the results of LCWO and all-valence-electrons calculations.

Introduction

The unusual structural, spectroscopic, and chemical properties of cyclopropane and its derivatives have fascinated chemists and theoreticians for many years.[1,2] A number of theoretical bonding models for cyclopropane have been proposed in order to account for its puzzling behavior,[3-5] the most popular being the so-called *Walsh* orbital model.[4] According to this model, the highest occupied molecular orbitals (HOMOs) of cyclopropane consist of a degenerate pair of Walsh orbitals, w_S and w_A (Chart I), composed of "tangentially" oriented carbon 2p atomic orbitals. The Walsh orbitals can be considered as a simplified representation of the 3e′ orbitals of cyclopropane,[6] corresponding to the characteristic Jahn–Teller split band close to 11 eV in the photoelectron (PE) spectrum.[7-9]

The primitive Walsh orbital picture accounts admirably well for many of the peculiar properties of cyclopropane and the cyclopropyl group.[1] However, application of the model to bicyclopropyl (**1**) and its homologues (Chart II) raises a number of problems. The simple tangential model does not, in general, qualitatively explain the orbital energy level pattern for this class of compound.[10-12] On the other hand, the results of more sophisticated MO calculations are very sensitive to the choice of method, frequently leading to divergent predictions (vide infra). A further complicating factor is the torsional mobility of simple

Chart I

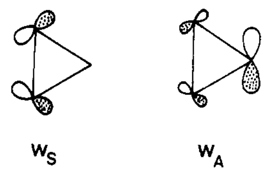

Chart II

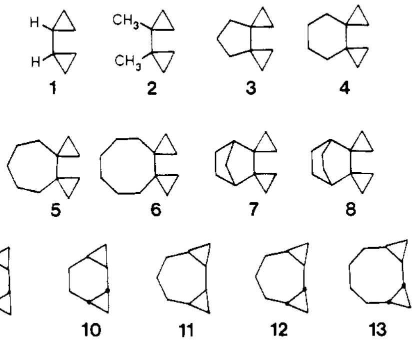

Table I. Vertical Ionization Energies for 1-13, with Indication of Observed (1,[14] 9, 10[31]) or Estimated Torsional Angles (θ)[a]

no.	θ	ionization energies, eV			
1	48[b]	9.5	10.1	11.0	11.7
2	~50[b]	9.3	9.9	10.4_5	10.9
3	<40	9.0_5	10.0		
4	60	9.2	9.7	10.2	10.8
5		~9.2	~9.7		
6		9.1	9.6		
7	0	8.76	9.82	~10.3	~10.6
8	0	8.67	9.58	9.99	10.6
9	18	8.95	9.66	10.14	11.34
10	56	9.39	9.82	10.14	11.24
11	<30	8.9_5	9.7_0	10.0	10.8
12	~120	9.0_0	9.4_5	~10.5	
13	⩾90	9.1_0	9.5_5	10.2_5	10.60

[a] The PE data for 7, 8,[18] 9, and 10[19] are taken from the literature. [b] Gauche conformer.

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bicyclopropyls. For example, **1** is known to exist in the gas phase as a mixture of almost equal parts of gauche and trans conformers[13-15] and a similar situation is expected for the 1,1′-dimethyl derivative **2**.[15] As a consequence, the interpretation of the PE spectra in this area is not straightforward, and there is disagreement in the literature concerning the assignments of the PE bands of **1**.[10,12,16]

In an attempt to clarify some of these questions, we have undertaken a PE spectroscopic investigation of bicyclopropyl (**1**) and some of its simple alkyl derivatives, including 1,1′-dimethylbicyclopropyl (**2**), the dispiro compounds **3–6**, and the tricyclic systems **11–13**. Two slightly different versions of the PE spectrum of **1** have been published recently.[12,16] We have presently remeasured the spectrum of **1**, obtaining a curve closely similar to the one published by Klessinger et al.;[16] probably the spectrum published by Gleiter[12] was influenced by the presence of an impurity. PE data for **4** have been reported previously,[17] however, since the spectral curve was not published, we have redetermined it. The PE spectra of **1–6** and **11–13** are shown in Figure 1, and the relevant ionization energies are listed in Table I. Previously published PE data for **7**, **8**,[18] **9**, and **10**[19] are included in Table I for comparison.

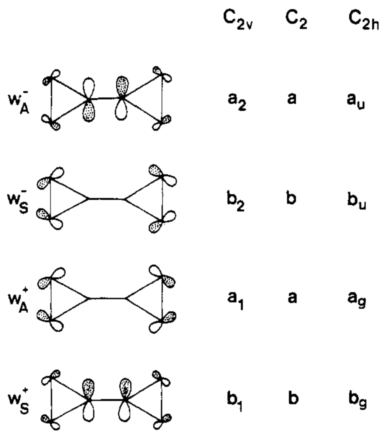
Our interpretation of the PE spectra is based on Koopmans' approximation;[20] i.e., $I_{V,J} = -\epsilon_J$ (where ϵ_J is the orbital energy of the MO Ψ_J vacated in the ionization process giving rise to the PE band at position $I_{V,J}$). In the following section, orbital energy diagrams derived by means of a "Linear Combination of Walsh Orbitals" (LCWO) model[10] are presented. These qualitative results are substantiated by the results of more sophisticated MO methods, which are critically discussed under "All-Valence-Electrons Calculations on 1 and 2". Finally, suitable assignment of the PE spectra in terms of the results of the preceding sections is made under "Discussion and Assignment of the PE Spectra". Particular emphasis is given to possible interpretations of the spectra of **1** and **2**; as concerns the remaining compounds **3–13**, the emphasis is placed upon application of the general analysis presented in the following section and an estimate of its implications, relative to the molecular conformations.

LCWO Model for Bicyclopropyl[10]

The linear combination of Walsh orbitals (LCWO) model for bicyclopropyl has been previously described in detail,[10] and we give here only a very brief outline in order to present some results that are useful in the ensuing study.

The occupied Walsh orbitals of bicyclopropyl are frequently represented in terms of linear combinations of cyclopropane w_S and w_A orbitals (Chart I).[10,12,16,18,19] In Chart III, the resulting symmetry-adapted orbitals are indicated for the C_{2v} syn conformation (torsional angle θ = 0°). Rotating one cyclopropyl group by 180° generates the C_{2h} anti conformation (θ = 180°). For intermediate conformations, the symmetry is reduced to C_2. The dependence of the orbital energies on the torsional angle θ for the assumption of pure tangential Walsh orbitals is indicated in Figure 2a.

Chart III



The simple tangential model predicts that w_S^+ and w_S^- are degenerate with a constant energy independent of θ and that all levels become degenerate for θ = 90°. This situation is artificial and results because the w_S combinations within this model have zero amplitude on the linked centers. Introduction of "radially" oriented contributions is seen to lift the degeneracy of w_S^+ and w_S^- and enable w_S^+ (w_S^-) to interact with w_A^- (w_A^+) for conformations of C_2 symmetry. The symmetry-forbidden crossings for θ = 90° are thereby avoided. This is shown in Figure 2b for 20% admixture of "radial" components.[10]

It is also necessary to consider interactions which occur within the remaining σ frame of bicyclopropane. In particular, "through-bond" interaction with σ and σ^* type orbitals of the central bond tends to destabilize w_S^+ and stabilize w_S^-, while w_A^+ and w_A^- remain unaffected because they have a node on the central bond axis. Simulating this effect by appropriate shifts of the w_S^+ and w_S^- basis orbital energies leads to the picture indicated in Figure 2c.[10]

Comparison of Figure 2a,c indicates that the simple tangential model can be expected to be a reasonably good model only for θ values close to zero. This can be explained by noticing that contributions due to radial components and through-bond effects tend to cancel for small torsional angles but add for large values. It is particularly relevant that the tangential model has served satisfactorily for several di- and tricyclopropyl compounds with small torsional angles[10,11,18,19] but not for compounds with strongly twisted bicyclopropyl units.[10,11]

The tangential picture is particularly misleading when torsional angles close to 90° are involved. In this region, the interaction between w_S^+ (w_S^-) and w_A^- (w_A^+) becomes first order simultaneously with maximization of the interaction integral (approximately proportional to sin θ[10]). The result is strong avoidance of symmetry-forbidden crossings. For θ values between, say, 60° and 120°, the mixing of w_S and w_A type orbitals is profound, rendering the identification of w_A^-, w_A^+, w_S^- and w_S^+ levels impossible or highly approximative.

In the case of the alkyl-substituted bicyclopropyls **2–13**, inductive effect contributions from the alkyl groups must be considered. Here we distinguish between the 1,1′-disubstituted compounds **2–8** and the 2,2′- or 2,3′-disubstituted compounds **9–13**. In the first case, the w_A orbitals should be destabilized relative to the w_S orbitals, because of the larger amplitude of the former in the substituted positions. In the second case, the situation is reversed, and

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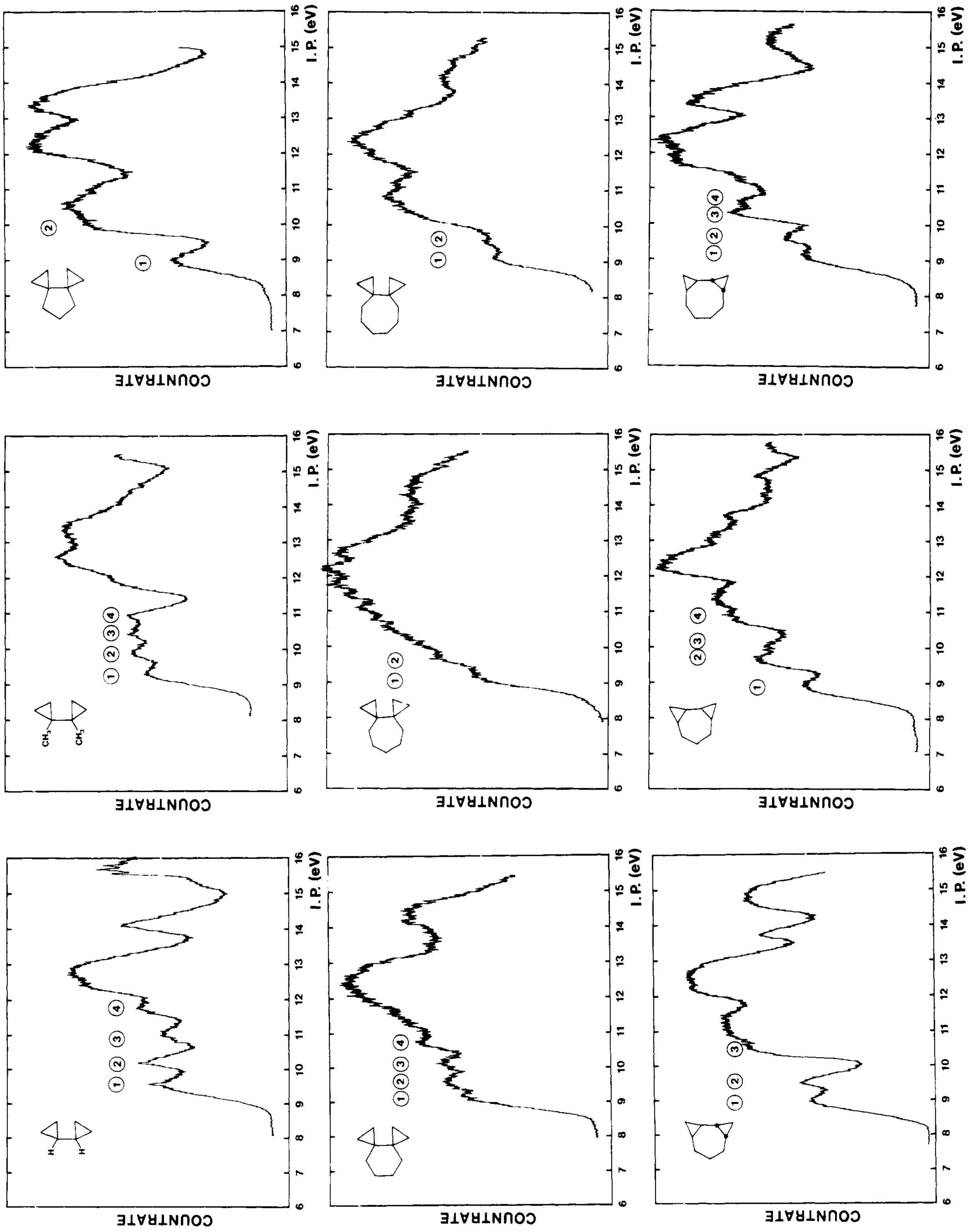

Figure 1. PE spectra of 1–6 and 11–13.

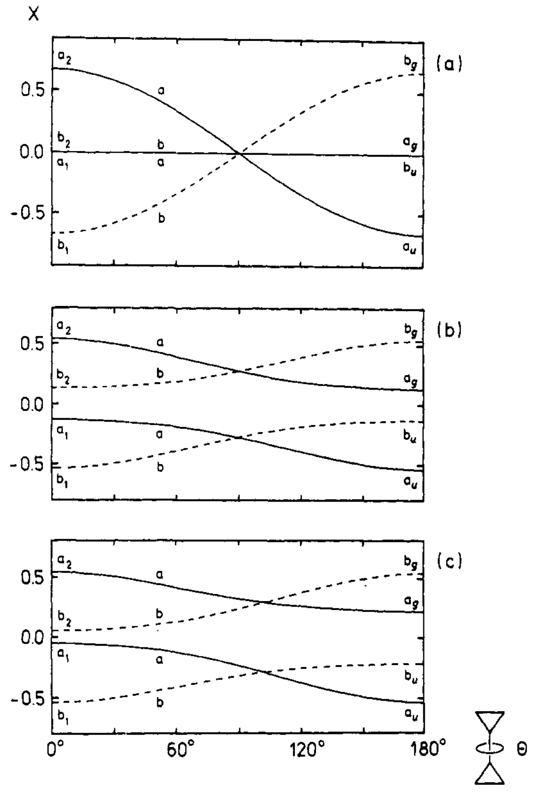

Figure 2. LCWO orbital energies, $X = (\alpha - E)/\beta$, for bicyclopropyl (1) as a function of the twist angle θ. (a) Results corresponding to the assumption of purely tangential Walsh orbitals; (b) results with inclusion of 20% radial character; (c) results of a calculation with inclusion of radial components and consideration of through-bond interaction via the central CC bond. For designation of levels, see Chart III.

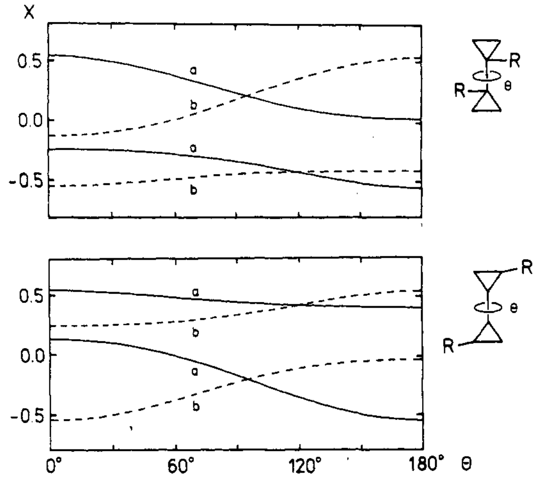

Figure 3. LCWO energies corresponding to Figure 2c but with simulation of inductive effects caused by alkyl substitution. Results relevant for 1,1′-disubstituted bicyclopropyls, such as **2–8** (top) and 2,2′- or 2,3′-disubstituted bicyclopropyls, such as **9–13** (bottom).

the w_S orbitals are destabilized relative to the w_A orbitals. These effects can be represented by simple shifts of the relative basis orbital energies. The results of such a treatment are visualized in Figure 3. It is clearly apparent that alkyl substitution can have a significant impact on the Walsh orbital level pattern, particularly for θ values close to 0° and 180°. For θ values in the intermediate region, the impact is much less striking because of the profound mixing of w_A and w_S type orbitals as noted above.

Apart from the inductive effect, the Walsh orbital systems in **2–13** are influenced by strong "hyperconjugative" interactions. A detailed account of this effect is complicated by the complexity of the σ orbital structures of these compounds. As far as the relative spacing of the Walsh-type levels are concerned, we shall assume that hyperconjugative interactions in **2–13** can be represented by interactions within the bicyclopropyl moiety (which we have already accounted for in a qualitative sense). However, an important effect of hyperconjugative interactions in these compounds is dilution of the Walsh orbital amplitudes at the substituted centers. The impact of this effect should be particularly marked in the case of the 1,1′-disubstituted bicyclopropyls **2–8**, leading to a reduction of the interaction between the Walsh orbitals of the two three-membered rings. Within the framework of the LCWO model, this effect can be represented by appropriate reduction of the effective resonance integral β, corresponding to a reduction of the "energy unit" in Figures 2 and 3.

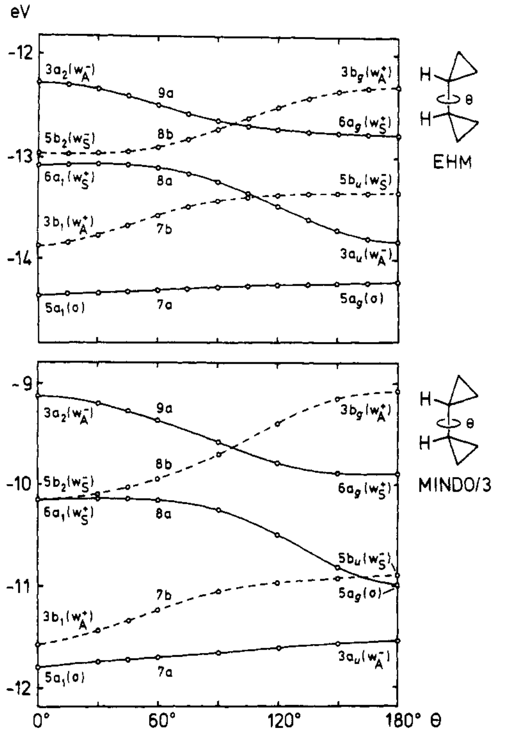

Figure 4. Orbital energies calculated by Extended Hückel (EHM) and MINDO/3 for bicyclopropyl (1) as a function of the torsional angle θ.

All-Valence-Electrons Calculations on 1 and 2

To substantiate the qualitative analysis in the preceding section, we have carried out semiempirical all-valence-electrons calculations of the Extended Hückel (EHM),[21] MINDO/3,[22,23] and/or MNDO/1[24,25] type for **1** and **2**. The computed Walsh orbital and highest occupied σ orbital energies are indicated in Figures 4 and 5 as a function of the torsional angle θ. Whereas an otherwise rigid structure[10,13] was assumed in the EHM calculations, the geometrical parameters in the MINDO/3 and MNDO/1 calculations were optimized under the constraint of C_2

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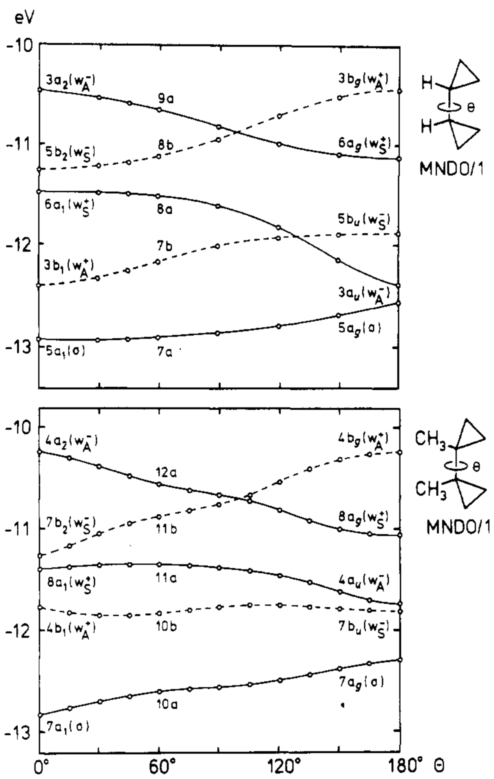

Figure 5. Orbital energies calculated by MNDO/1 for bicyclopropyl (1) and 1,1′-dimethylbicyclopropyl (2) as a function of the torsional angle θ.

symmetry. The methyl groups in 2 were assumed to possess local C_{3v} symmetry and were fixed in the staggered conformation with respect to the central bond axis, in agreement with the results of a force-field investigation.[15]

Comparison of the diagrams indicates that the calculational results for 1 are sensitive to the choice of method. The EHM results displayed in Figure 4 are very similar to the results of the LCWO method shown in Figure 2c, while the MINDO/3 method yields a markedly different diagram. The MNDO/1 data for 1 displayed in Figure 5 are again reasonably consistent with the trends of the LCWO diagram. Although we shall not attempt a detailed analysis of the results in Figures 4 and 5, it is immediately apparent that the MINDO/3 prediction is affected by profound mixing of Walsh and σ orbitals. This is obvious from an inspection of the 8a and 7a orbitals and from the intermingling of Walsh and σ levels for the anti conformation (Figure 4, bottom). We explain this behavior as a result of the tendency of MINDO/3 to place σ orbitals at unrealistically low binding energies relative to orbitals of Walsh (or π) character,[26,27] leading to a first-order interaction between Walsh and σ orbitals and distortion of the Walsh orbital picture.

This situation strongly emphasizes the dangers involved when an analysis or an assignment is based uncritically on the results of a single approximate theory. However, we consider the similarity of the Walsh orbital level diagrams predicted by such fundamentally different procedures as LCWO, EHM, and MNDO/1 as strong evidence for the reliability of the predicted trends, thereby also supporting the qualitative analysis underlying the LCWO model. There are of course minor differences between the curves produced by the three methods. Thus, the crossing of the third and fourth Walsh-type levels (8a and 7b in Figure 4 and 5) is predicted by LCWO, EHM, and MNDO/1 to occur for θ values close to 100°, 110°, and 130°, respectively. The main reason for this can be traced back to small variations in the extent of through-bond interaction with bonding σ orbitals in the three models, but these variations do not destroy the essential consistency of the predictions.

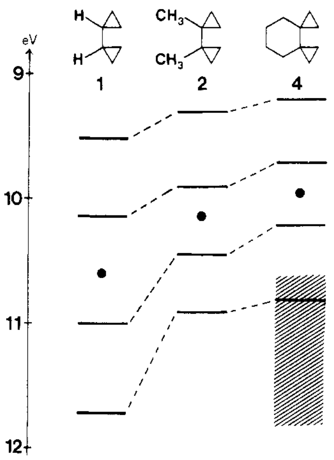

Figure 6. Correlation of the four lowest ionization energies for 1, 2, and 4. The dots indicate centers of gravity.

The MNDO/1 results for 2 are shown in the lower panel of Figure 5. Compared with the curves in the upper panel and with the LCWO curves in Figure 3, the curves for 2 exhibit weak oscillatory perturbations, mainly originating from a dependence of geometrical parameters on the torsional angle. This is understandable in view of the steric interference of the methyl groups in the case of 2. A number of trends predicted by the analysis contained in the preceding section are verified by the MNDO/1 results; e.g., the impact of the methyl groups on the relative spacing of the Walsh levels is particularly marked for θ values close to 0° or 180°, but is insignificant in the intermediary region with θ values between 60° and 120°, and the hyperconjugative effect leads to an overall reduction of the total width of the Walsh orbital spectrum by about 20%. The total width is also affected by an increase of the predicted 1,1′ bond length by about 2% relative to 1.

All things considered, the results of the sophisticated MO calculations support the qualitative picture outlined under "LCWO Model for Bicyclopropyl". In the remaining part of the paper, we discuss the PE spectra of bicyclopropyls 1–13 in terms of the general trends displayed in Figures 2 and 3.

Discussion and Assignment of the PE Spectra

PE Spectra of 1 and 2. The PE spectrum of the parent compound 1 has been the subject of several investigations.[10,12,16,28] The low-energy region of the spectrum is characterized by four almost equally spaced bands of comparable intensities. Apart from a shift toward lower energies and a somewhat narrower spacing of the peaks, the spectrum of 2 is very similar to that of 1. The position of the band maxima are indicated in Figure 6.

As mentioned under Introduction, 1 exists chiefly as a mixture of gauche and trans conformers.[13-15] The trans conformer and the gauche conformer with a torsional angle close to 50° have very similar energies, and at room temperature the mixture contains almost equal parts of the

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two conformers.[14] According to the results of force-field calculations, very similar data are expected for 2.[15] For 1 and probably also for 2, the PE spectrum should thus represent a superposition of two spectra due to gauche and trans conformers, and we would expect a total of eight ionizations in the low-energy region, corresponding to four levels (a, b, a, b) for the gauche and four levels (b_g, a_g, b_u, a_u) for the trans conformer. However, only four bands are clearly observed, and the assignment of these to the eight expected transitions is problematic.

Asmus and Kleśsinger[16] attempted an analysis of the PE spectrum of 1 on the basis of MINDO/2[29] calculations. Under the assumption of Lorentzian line shapes with half-height widths equal to 0.5 eV, they superimposed the two spectra calculated for the gauche and the trans conformer and compared the resulting curve with the measured spectrum. On the basis of this comparison, they suggested for the first four PE bands the assignment of two, three, one, and two individual ionization events, respectively. However, according to this assignment, band 2 with a maximum at 10.1 eV should be at least three times as intense as band 3 at 11.0 eV, which seems to be in poor agreement with the measured relative intensities. However, as previously suggested,[10,12] the PE spectrum of 1 can easily be interpreted under the assumption of two individual transitions per band, an assumption which seems more consistent with the rather similar intensities of the four PE bands.

A relevant factor which has so far not been taken into consideration is the different torsional distribution characteristics for the two conformers. Detailed investigations[13-15] show that the gauche conformer exhibits a well-defined equilibrium angle, corresponding to a fairly rigid molecular structure. In contrast, the trans angle is distributed in a large region (±100°)[14] around the equilibrium value with a governing potential approximating a square well. The trans conformer is by no means a rigid species—there is essentially free rotation around the central carbon–carbon bond within an angle interval between 100° and 260°. Hence, the PE spectrum of this conformer would be expected to exhibit broad bands, approaching a structureless continuum, particularly in the region of the conformationally dependent Walsh-type levels. The assumption by Asmus and Klessinger[16] of identical line widths for the two conformers is thus hardly justified, and their assignment of the third PE band of 1 exclusively to the trans conformer seems highly unlikely. We propose that the four well-defined maxima close to 9.5, 10.1, 11.0, and 11.7 eV indicate PE bands of the relatively rigid gauche conformer, superimposed on a more or less smooth "background continuum" corresponding to the trans conformer. We base this assumption on the essentially different torsional amplitudes characterizing the two conformers, but further investigations, including detailed line-shape analysis and probably temperature-dependent PE spectroscopy, are needed to throw more light on this problem. Nevertheless, the assumption leads to a nice consistency with the PE data for 2 and 4 (Figure 6).

An experimental investigation of the torsional potential for 2 has so far not been published, but data very similar to those for 1 have been predicted, indicating a torsional angle close to 50° for the gauche conformer and a large torsional amplitude for the trans conformer.[15] Somewhat in contrast to the case of 1, essentially different Walsh orbital level patterns are expected for the gauche and trans conformers of 2. In this instance, the system should be characterized by four almost equidistant levels for the gauche conformer ($\theta \approx 50°$) in contrast to a pattern of widely spaced first, second, and third, but near-degenerate third and fourth, levels for the trans conformer ($\theta = 180°$). This prediction is evident from the MNDO/1 results indicated in Figure 5 and is consistent with the tendency of the LCWO results in Figure 3. The PE spectrum of 2 features four peaks close to 9.3, 9.9, 10.4$_5$, and 10.9 eV, very well separated from the onset of compact regions (Figure 1). This spectrum is consistent only with that expected for the gauche conformer and shows no indication of significant contributions from the trans conformer. This indicates to us, firstly, that the gauche conformer forms a significant or dominating part of the conformational equilibrium at room temperature. Secondly, if the trans conformer is present to a significant degree, its PE spectrum must be of such a nature that it does not influence the general shape of the superimposed gauche spectrum (i.e., approaching a structureless continuum as discussed in the case of 1).

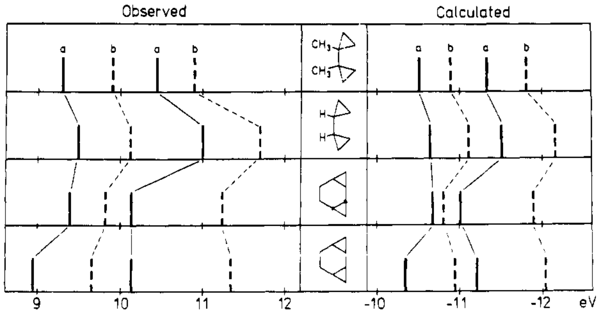
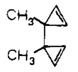


Figure 7. Observed ionization energies and calculated orbital energies (MNDO/1) for 2, 1, 10, and 9. The calculated results for 1 and 2 correspond to those given in Figure 5 for torsional angle $\theta = 60°$.

Under the assumption that the four low-energy PE peaks of 1 and 2 can all be assigned to the gauche conformer, we have correlated the levels in the diagram in Figure 6. The shifts observed are consistent with what would be expected on the basis of the discussion in the two preceding sections and compare well with the MNDO/1 results for the gauche conformers of 1 and 2 (Figure 7). Moreover, the fact that the low-energy region of the PE spectrum of 2 is very similar to the corresponding region of the spectrum of 4 (Figure 6) lends further support to our assignment of the spectrum of 2 to the gauche conformer, since a trans conformation is impossible for 4. This situation closely parallels the one observed for the corresponding bicyclopropenyls 14 and 15.[30]



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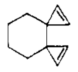

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PE Spectra of 3–8. The dispiro compounds 3–8 can be divided into two groups: compounds 3, 7, and 8 where the bicyclopropyl moieties have equilibrium torsional angles close to zero, compounds 4–6 where the torsional angle is expected to deviate significantly from zero.

Inspection of Figure 3 (upper panel) indicates that for torsional angles close to zero the PE spectrum should be characterized by a single band at low energies, well separated from closely spaced, probably strongly overlapping bands at higher energies. This prediction is verified by the PE data; the PE spectra of 3, 7, and 8 each exhibit a

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[29] M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, 92, 590 (1970).

[30] J. Spanget-Larsen, C. de Korswagen, M. Eckert-Maksić, and R. Gleiter, *Helv. Chim. Acta*, 65, 968 (1982).

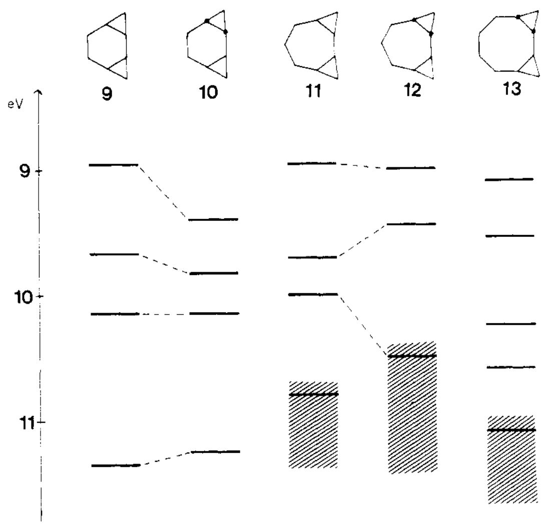

Figure 8. Indication of observed ionization energies for the tricyclic compounds **9–13**.

well-resolved band with maximum close to 9.0 eV, separated by about 1 eV from those which are more complex. In the case of **3**, only the first Walsh band is resolved; the remaining ones seem to overlap strongly with one or more σ bands, forming a compact region between 10.0 and 11.5 eV (Figure 1). The spectra of **7** and **8** show higher resolution; two and three low-energy peaks, respectively, are clearly discernible.[18]

For **4**, a bicyclopropyl torsional angle close to 60° would be expected. Four bands close to 9.2, 9.7, 10.2, and 10.8 eV are observed, which correlate nicely with the data for **1** and **2**, as indicated above (Figure 6). The spectrum of **5** is very poorly resolved; we suspect that the structure of this ring system is not rigid. Two peaks at 9.1 and 9.6 eV can be singled out in the case of **6**, indicating the existence of a preferred molecular geometry and a torsional angle different from zero, but more definite conclusions cannot be derived from the limited PE data.

PE Spectra of 9–13. In contrast to some of the compounds considered in the preceding paragraph, the tricyclic compounds **9–13** are expected to be rigid, strained species. This is consistent with the fact that the PE spectra of **9–13** are generally better resolved, allowing more interesting conclusions from the PE data.

According to an electron-diffraction investigation, the bicyclopropyl torsional angle is 18° in the case of cis isomer **9** and 56° in the case of the preferred conformation of the trans isomer **10**.[31] The PE data (Figure 8) are consistent with what would be expected from the diagram in Figure 3 (lower panel), but minor discrepancies are apparent when the individual shifts of the two intermediate levels are considered.[19] The results of MNDO/1 calculations on **9** and **10** indicated in Figure 7 are in fair agreement with the relative spacing of the observed PE bands, but the shifts of the second and third PE bands observed when passing from **9** to **10** are not well reproduced. The discrepancy seems to originate in difficulties with the treatment of through-bond effects in these compounds, involving orbitals of the distorted (twist shaped) six-membered ring.

The low-energy regions of the PE spectra of isomers **11** and **12** are strikingly different, as indicated in Figure 8. The spectrum of cis isomer **11** starts with a single peak close to 9.0 eV which is well separated from two strongly overlapping bands close to 10 eV, followed by the onset of compact structures around 11 eV. According to the diagram in Figure 3, this level pattern is strongly indicative of a torsional angle of the bicyclopropyl moiety close to 0°. In the case of trans isomer **12**, two PE peaks are observed at 9.0 and 9.5 eV separated by a fairly large gap from the complex region starting around 10.5 eV. Inspection of Figure 3 indicates that this pattern is consistent only with a large bicyclopropyl torsional angle, probably close to or above 90°. *Dreiding* and other molecular models seem to favor a torsional angle close to 120°, in pleasing consistency with the PE spectroscopic evidence.

In the case of **13**, we are able to locate four PE peaks below 11 eV, as indicated in Figure 8. This spectral region provides a pattern which is most consistent with the assumption of a bicyclopropyl torsional angle close to 90°, provided that all four bands can be assigned to Walsh orbitals. Dreiding models indicate an angle considerably larger than 90°, which may be taken either to question the assignment of Walsh orbitals or to indicate the inadequacy of Dreiding models for this class of strained species.

Conclusion

The most significant results of this investigation can be summarized as follows: (a) The PE spectra of bicyclopropyl and its simple alkyl derivatives can be conveniently interpreted in terms of a simplified LCWO model, allowing tentative prediction of conformational features from the PE data. (b) The PE spectra of the conformationally labile species bicyclopropyl and 1,1′-dimethylbicyclopropyl are best understood under the assumption that the observed maxima correspond to the gauche conformer, implying that contributions from the trans conformer are broad and featureless as the result of an exceptionally large torsional amplitude.

Experimental Section

The He(Iα) gas-phase PE spectra shown in Figure 1 were measured at room temperature on a PS 18 instrument (Perkin-Elmer Ltd., England) and calibrated with reference to the Ar line at 15.76 eV. Samples of **1** and **2** were kindly provided by Professors W. Lüttke and A. de Meijere, respectively. Hydrocarbons **3–6** were prepared by exhaustive dichlorocyclopropanation of the corresponding 1,2-dimethylenecycloalkane, followed by reductive dechlorination. For steric reasons, the synthesis of **6** was most efficiently carried out in two stages as outlined below.

Dispiro[2.0.2.3]nonane (3). A solution of 1,2-dimethylenecyclopentane (5.0 g)[32] in 50 mL of benzene was stirred with 60 mL of chloroform, 100 mL of 50% aqueous potassium hydroxide, and 1 g of benzyltriethylammonium chloride at room temperature for 36 h. The resulting mixture was poured into water (250 mL) and extracted with dichloromethane (3 × 75 mL). The combined extracts were washed with water (100 mL), dried, and concentrated. Distillation of the residue afforded 11.8 g (85%) of bisadduct: bp 70 °C (0.1 mm); IR (film) 2949, 2863, 1443, 1414, 1326, 1077, 1034, 1014, 878, 748 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.35–1.85 (m, 6 H), 1.65 and 1.42 (AB q, J_{AB} = 9 Hz, 4 H); mass spectrum, *m/e* (M$^+$) calcd, 257.9537; found, 257.9541.

To a refluxing solution of the bisadduct (2.0 g, 7.69 mmol) in ethanol (50 mL) was cautiously added sodium metal (8.64 g, 0.37 mg-atom) in small pieces over a 2-h period. The reaction mixture was heated at reflux for an additional hour before water (80 mL) was carefully added. The product was extracted into pentane (3 × 20 mL), washed with water (30 mL), dried, and carefully evaporated. Pure **3** was obtained by preparative VPC (12 ft × 0.25 in., 15% SE-30, 150 °C); IR (film) 3060, 2990, 2940, 2850, 1450, 1438, 1415, 1005, 956, 930 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.85–1.60 (m, 6 H), 0.30–0.01 (m, 8 H); mass spectrum, *m/e* (M$^+$) calcd, 122.1095; found, 122.1099.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.22; H, 11.52.

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Dispiro[2.0.2.4]decane (4). Reaction of 1,2-dimethylenecyclohexane (910 mg, 8.43 mmol)[33] with dichlorocarbene under phase-transfer conditions as described above afforded a crystalline product, which was twice recrystallized from ether–hexane to give 2.0 g (87%) of bisadduct, mp 94–95 °C; IR (KBr) 2950, 2860, 1445, 1435, 1050, 1030, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3–1.6 (m, 8 H), 1.3 (s, 4 H); mass spectrum, *m/e* (M^+) calcd, 271.9693; found, 271.9698.

Reduction of 2.0 g (7.3 mmol) of this bisadduct as predescribed furnished 4, which was purified by preparative VPC (15% SE-30, 150 °C): IR (neat) 3075, 3000, 2920, 2852, 1460, 1444, 1420, 1260, 1200, 1100, 954, 900, 855 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75–1.15 (m, 8 H), 0.25–0.0 (m, 8 H); mass spectrum, *m/e* (M^+) calcd, 136.1252; found, 136.1256.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.33; H, 11.81.

Dispiro[2.0.2.5]undecane (5). Reaction of 1,2-dimethylenecycloheptane (1.48 g, 12.1 mmol)[33] with dichlorocarbene under phase-transfer conditions as described above afforded 1 g (29%) of bisadduct as a colorless oil: bp 98–100 °C (0.15 mm); IR (neat) 2940, 2863, 1450, 1243, 1140, 1095, 1040, 895, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05–1.55 (m, 10 H), 1.36–1.16 (m, 4 H); mass spectrum, *m/e* (M^+) calcd, 285.9850; found, 285.9841.

Reduction of the bisadduct (1.0 g, 3.47 mmol) as described above gave 5, which was purified by preparative VPC (15% SE-30, 150 °C): IR (neat) 3072, 2993, 2920, 2852, 1450, 1414, 1037, 1002 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76–1.35 (m, 10 H), 0.40–0.13 (m, 8 H); mass spectrum, *m/e* (M^+) calcd, 150.1408; found, 150.1404.

Anal. Calcd for $C_{11}H_{18}$: C, 87.43; H, 12.08. Found: C, 88.04; H, 11.83.

Dispiro[2.0.2.6]dodecane (6). From 1.27 g (9.34 mmol) of 1,2-dimethylenecyclooctane,[33] 27.5 g (0.23 mol) of chloroform, 242 mg (1.13 mmol) of benzyltriethylammonium chloride, benzene (11 mL), and a solution of sodium hydroxide (12 g, 0.30 mol) in water (24 mL) there was isolated 1.5 g (73%) of monoadduct, bp 76–78 °C (0.05 mm); IR (neat) 3080, 2925, 2855, 1635, 1445, 1200, 1048, 905, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.12 (s, 1 H), 4.95 (s, 1 H), and 2.45–1.28 (series of m, 14 H); mass spectrum, *m/e* (M^+) 219.

This monoadduct (1.0 g, 4.60 mmol) was reduced with sodium (2.8 g, 0.121 g-atom) in ethanol (16 mL) to give the vinylcyclopropane, which was purified by VPC (5% SE-30, 155 °C); IR (neat) 3071, 2990, 2917, 2850, 1627, 1435, 1002, 867 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.71 (s, 2 H), 2.4–2.1 (m, 2 H), 1.56 (br s, 10 H), 0.60 (s, 2 H), 0.50 (s, 2 H); *m/e* (M^+) calcd, 150.1408; found, 150.1404.

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.56; H, 12.02.

Treatment of the vinylcyclopropane (667 mg, 4.50 mmol) with dichlorocarbene in the usual manner gave a yellow oil, which was used without purification. The following spectra were obtained on material that had been subjected to preparative VPC (5% SE-30, 155 °C); IR (KBr) 2920, 2848, 1440, 1374, 1020, 738, 683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.72–1.46 (series of m, 12 H), 1.28–0.96 (m, 2 H), 0.85–0.19 (m, 4 H); mass spectrum, *m/e* (M^+) calcd, 232.0785; found, 232.0779.

Reduction of the preceding dichlorocyclopropane (1.04 g, 4.5 mmol) gave 6 as a colorless oil after VPC purification (5% SE-30, 140 °C); IR (neat) 3065, 2990, 2900, 1440, 1415, 1005 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.79–1.22 (m, 12 H), 0.47–0.19 (m, 8 H); mass spectrum, *m/e* (M^+) calcd, 164.1565; found, 164.1559.

Anal. Calcd for $C_{12}H_{20}$: C, 87.80; H, 12.20. Found: C, 87.71; H, 12.36.

Hydrocarbons 11 and 12 were prepared by Wolff–Kishner reduction[34] of known ketone precursors. Hydrocarbon 13 was obtained by exhaustive dichlorocyclopropanation of *cis,cis*-1,3-cyclooctadiene, followed by reductive dechlorination.

***cis*-Trichloro[6.1.0.0^{2,4}]nonane (11).** A mixture of *syn*-3,5-bishomocycloheptadienone (900 mg),[35] potassium carbonate (4.2 g), hydrazine hydrate (4.5 mL), and diethylene glycol (25 mL) was heated at the reflux temperature for 1.5 h. A small distillation head was attached atop the flask, and the temperature was raised to 200 °C. After 1.5 h, the collected distillate was taken up in ether. The flask residue was heated at 230 °C for 3 h, cooled, diluted with water, and extracted with ether. The combined etheral extracts were washed with 3 N hydrochloric acid, dried, and carefully evaporated. The desired hydrocarbon 11, obtained in 47% yield, was purified by preparative VPC (5% SE-30, 150 °C): IR (CCl_4) 3070, 3005, 2925, 2850, 1465, 1450, 1385, 1355, 1020, 1005, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.15–1.58 (m, 4 H), 1.58–0.75 (m, 6 H), 0.75–0.25 (m, 2 H), 0.25 to −0.05 (m, 2 H); mass spectrum, *m/e* (M^+) calcd, 122.1095; found, 122.1100.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.58; H, 11.52.

***trans*-Tricyclo[6.1.0.0^{2,4}]nonane (12).** Comparable reduction of *anti*-3,5-bishomocycloheptadienone (229 mg)[35] afforded 117 mg (57%) of 12, which was also purified by VPC (5% SE-30, 150 °C): IR (CCl_4) 3070, 3000, 2935, 2865, 1449, 1020, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0 (m, 2 H), 1.55 (m, 2 H), 1.18 (m, 2 H), 0.68 (m, 6 H), −0.10 (m, 2 H); mass spectrum, *m/e* (M^+) calcd, 122.1095; found, 122.1092.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.51; H, 11.47.

***trans*-Tricyclo[7.1.0.0^{2,4}]decane (13).** Exhaustive dichlorocyclopropanation of *cis,cis*-1,3-cyclooctadiene (54 g, 0.5 mol) as described above furnished 60 g of the bisadduct as a crystalline solid (from ether–pentane): mass spectrum, *m/e* (M^+) calcd, 271.9693; found, 271.9700. Without further purification, a 13.7 g (0.05 mol) sample of this material was heated with lithium wire (7.0 g, 1 g-atom) and *tert*-butyl alcohol (22.2 g, 0.6 mol) in anhydrous tetrahydrofuran (600 mL) at the reflux temperature for 12 h. While being ice cooled, the reaction mixture was treated dropwise with water (900 mL), transferred to a separatory funnel, and extracted with pentane (4 × 150 mL). The combined organic layers were washed with water (2 × 100 mL) and brine, dried, and carefully evaporated. Hydrocarbon 13 was initially obtained by distillation [bp 65–68 °C (20 mm)] and further purified by VPC (5% Carbowax 20M, 100 °C): IR (film) 3040, 2990, 2920, 2860, 1450, 1440, 1350, 1320, 1295, 1210, 1160, 1015, 970, 885, 825, 820, 740 cm^{-1}; ^1H NMR (CCl_4) δ 2.2–0.2 (series of m, 14 H) and −0.2 (m, 2 H); ^{13}C NMR ($CDCl_3$) 29.97, 29.54, 29.12, 18.98, 15.22, 14.13, 4.30 ppm; mass spectrum, *m/e* (M^+) calcd, 136.1252; found, 136.1256.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.22; H, 11.83.

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Registry No. 1, 5685-46-1; 2, 59020-33-6; 3, 24973-90-8; 4, 24029-74-1; 5, 52879-54-6; 6, 64601-40-7; 11, 81969-71-3; 12, 81969-72-4; 13, 81969-73-5; 1,2-dimethylenecyclopentane, 20968-70-1; 1,2-dimethylenecyclohexane, 2819-48-9; 1,2-dimethylenecycloheptane, 58738-52-6; 1,2-dimethylenecyclooctane, 64306-16-7; *syn*-3,5-bishomocycloheptadienone, 62163-68-2; *anti*-3,5-bishomocycloheptadienone, 62279-37-2; *cis,cis*-1,3-cyclooctadiene, 3806-59-5.

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