(30) For further discussion of benzenediazonium stabilization, see (a) H. G. Richey, Jr., and J. M. Richey, "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1970, Chapter 21; (b) J. F. Chlebowski, *ibid.*, Chapter 16, p 770; (c) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1959, p 457; (d) H. Zollinger, *Acc. Chem. Res.*, **6**, 335 (1974); (e) H. Zollinger, "Azo and Diazo Chemistry", Interscience, New York, N.Y., 1961, pp 39–44 and 137–142.

(31) STO-3G energies (hartrees) at standard geometries are as follows: $C_6H_5N_2^+ = -334.547\ 91$; *o*-$H_2NC_6H_4N_2^+ = -388.870\ 99$; *m*-$H_2NC_6H_4N_2^+ = -388.867\ 97$; *p*-$H_2NC_6H_4N_2^+ = -388.879\ 40$. All NH_2 groups are coplanar with the ring. The corresponding $C_6H_5NH_2$ energy is $-282.204\ 58$ (ref 18).

(32) Sources for heats of formation for neutral species involved in reaction 1 are given in S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969), unless noted otherwise.

(33) To estimated heats of formation of C_6H_5X for X = Li, BeH, and BH_2, we have employed the reactions $C_6H_5X + CH_4 \rightarrow CH_3X + C_6H_6$. Heats of formation of the CH_3X species are not known; they are estimated at the 6-31G* level[23] to be 35.8 ($LiCH_3$), 22.1 ($HBeCH_3$), and 18.2 kcal mol^{-1} (H_2BCH_3).

(34) T. B. McMahon, Ph.D. Thesis, California Institute of Technology, 1974.

(35) J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034 (1968).

Conjugative Interaction between Π and Cyclobutane Orbitals. The Synthesis and Electronic Structure of Bicyclo[4.1.1]octa-2,4-diene

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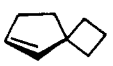
Abstract: The photoelectron (pe) spectra of bicyclo[4.1.1]octa-2,4-diene (**4**), bicyclo[4.1.1]oct-3-ene (**5**), and bicyclo[4.1.1]octane (**6**) have been recorded. Based upon assignment of the first bands in the pe spectrum of **4**, it is concluded that the interaction between the Walsh orbitals of the cyclobutane ring and the olefinic moiety can be described by a resonance integral $\beta = -1.9$ eV. This analysis is based on a simple ZDO model and substantiated by semiempirical calculations. The theoretical results are in reasonable agreement with experiment. Synthetic access to **4–6** was gained in several steps from diethyl *cis*-1,3-cyclobutanediacetate (**8**).

The study of conjugative interactions between a cyclobutane ring and an adjacent vinyl group or sp^2-hybridized center has attracted increasing interest in recent years.[3-9] A method very well suited to the investigation of such interactions is provided by photoelectron (pe) spectroscopy. The experimentally observed band positions in various pe spectra were shown to be satisfactorily reproduced within the framework of a ZDO model by adopting a resonance integral for the interaction between a 2p atomic orbital on the double bond (p_π) and a 2p atomic orbital on the cyclobutane ring (p_w) separated by one carbon–carbon single bond.

$$\beta = \langle p_\pi | H | p_w \rangle = -1.9\ \text{eV} \qquad (1)$$

Recently we reported[7,8] pe spectroscopic evidence concerning the direct conjugation of the Walsh orbitals in a cyclobutane ring with the π orbitals of adjacent double bonds. The systems studied so far have been rigid 1,1- and 1,3-disubstituted cyclobutanes such as spiro[3.4]oct-5-ene (**1**), spiro[3.4]octa-5,7-diene (**2**),[7] and tricyclo[3.3.0.0^{2,6}]octene (**3**).[8] In the case of **1** and **2**, analysis of the interaction between the π and Walsh orbitals was complicated because two Walsh orbitals (ϕ_1 and ϕ_3, see below) had to be considered. Furthermore, in the region below 10 eV, interpretation of the pe spectra was difficult due to strongly overlapping bands. As regards **3**, a simpler pattern was seen,[8] but only the interaction between π and one Walsh orbital (ϕ_1) could be studied. These uncertainties and difficulties gave rise to different assignments[7,9] and as a result different interaction parameters were obtained.

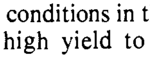


1

2

3

Given these shortcomings, bicyclo[4.1.1]octa-2,4-diene (**4**) deserves special interest. For reasons of symmetry, we considered that it should be possible to study separately the interaction between ψ_1 and ϕ_1 (defined below) and between ψ_2 and ϕ_3 and thus to check our previous assignments.[7,8] In this paper, we also provide details of the synthesis of **4**, bicyclo[4.1.1]oct-3-ene (**5**), and bicyclo[4.1.1]octane (**6**).



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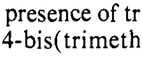

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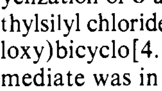


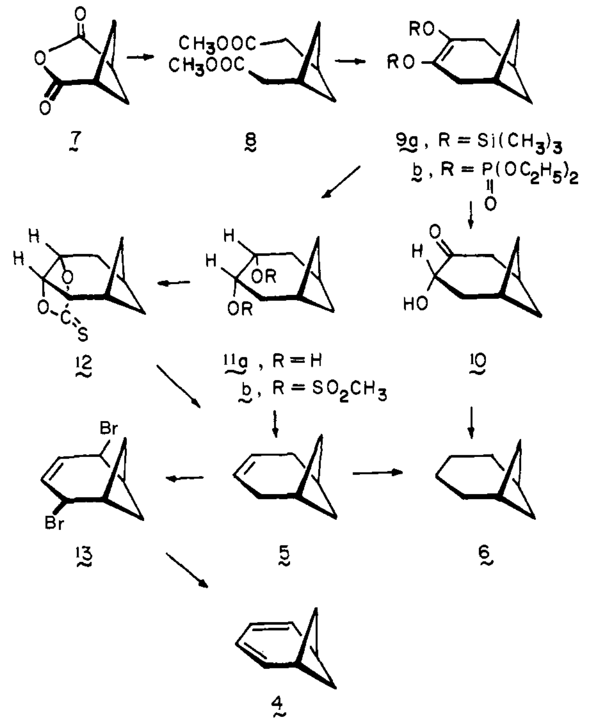
6

Synthetic Considerations

1,3-Cyclobutanedicarboxylic anhydride (**7**), which can readily be prepared from pentaerythritol in several steps,[10] was bishomologated to dimethyl *cis*-1,3-cyclobutanediacetate (**8**) according to the published procedure.[11] Cyclization of **8** under acyloin conditions in the presence of trimethylsilyl chloride[11,12] led in high yield to 3,4-bis(trimethylsiloxy)bicyclo[4.1.1]oct-3-ene (**9a**, Scheme I). This key intermediate was in turn hydrolyzed[12] to provide α-hydroxy ketone **10** and reduced directly with sodium borohydride in ethanol to deliver the crystalline cis diol **11a**. Stereochemical assignment to **11** followed principally from its ^{13}C NMR spectrum which exhibits the five signals required by a plane of symmetry (point group C_s); its trans counterpart which possesses axial symmetry (point group C_2) should display only four peaks.

In our development of a convenient route to **5**, several methods were examined for their efficiency. The reductive elimination of dimesylate **11b** with sodium anthracenide in

Scheme I



tetrahydrofuran[13] was immediately abandoned, for it gave **5** in only 4% isolated yield. With sodium iodide and activated zinc in HMPA at 100 °C,[14] the conversion of **11b** to **5** was increased somewhat (10%). A similar low level of improvement was noted upon conversion of **9a** to **9b** (75%) and reductive cleavage[15] of this substance with lithium in ammonia at −78 °C (8% of **5**). The preferred procedure consisted of preliminary conversion of diol **11a** to cyclic thionocarbonate **12** and decomposition of the latter in triethyl phosphite at 150 °C (18%).[16] This hydrocarbon is characterized by four carbon signals at 125.8, 35.6, 31.8, and 30.3 ppm and a ^{1}H NMR spectrum consisting of an ill-defined series of multiplets. Catalytic hydrogenation of **5** gave the fully saturated system **6** as did the Clemmensen reduction of **10**.

Synthesized by conversion of **5** to dibromide **13** with 2 equiv of NBS and subsequent reduction with zinc-copper couple, potassium iodide, and iodine in dimethylformamide,[17] bicyclo[4.1.1]octa-2,4-diene (**4**) was isolated as a colorless oil. Its spectral features (see Experimental Section) were fully compatible with those expected of a fully symmetrical planar diene system.

Photoelectron Spectroscopy

The pe spectra of **4–6** are shown in Figure 1 and the relevant pe data are listed in Tables I and II together with results of molecular orbital calculations. In this study, use was made of Koopmans' theorem.[18] In this approximation the orbital energy ϵ_J is set equal to minus the measured vertical ionization potential $I_{V,J}$.

$$\epsilon_J = -I_{V,J} \qquad (2)$$

This allows correlation of the bands of the pe spectra with orbital energies obtained from model calculations. A ZDO model and semiempirical methods of the Extended Hückel (EH)[19] and MINDO/3 type[20] have been used for the interpretation of the pe spectra.

The ZDO Model

For this model, the wave functions and basis orbital energies of the butadiene and cyclobutane fragments are needed. Although these have previously been given in our earlier publications,[7,8] they are briefly repeated here for clarity. The relevant π and Walsh orbitals[4,21] are illustrated below.

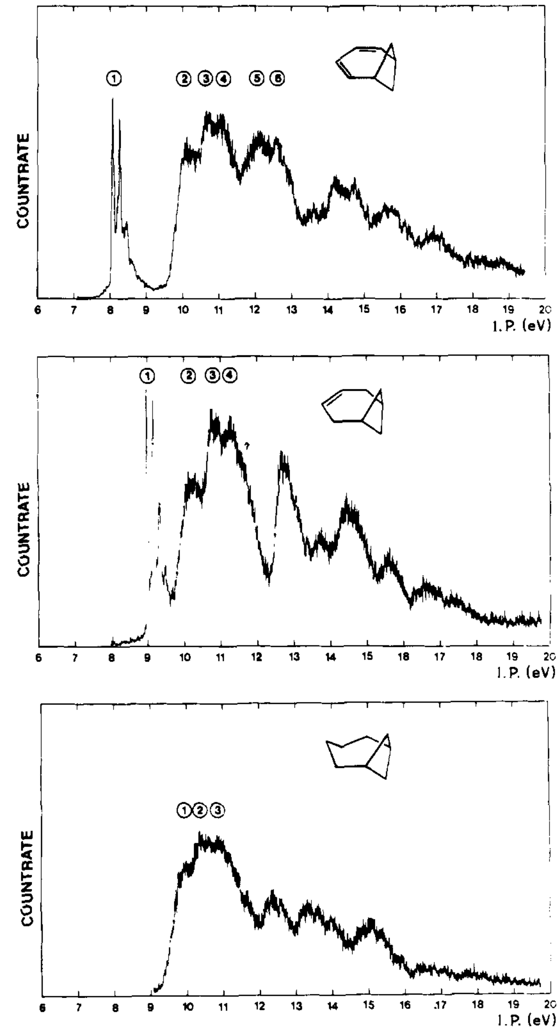
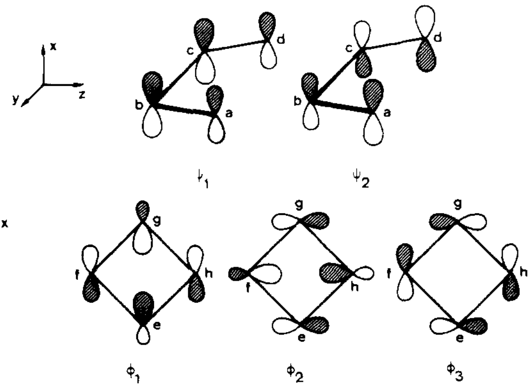


Figure 1. The pe spectra of **4**, **5**, and **6**.



The corresponding wave functions are:

$$\psi_1 = 0.372(p_{xa} + p_{xd}) + 0.602(p_{xb} + p_{xc}) \qquad B_1 \qquad (3)$$

$$\psi_2 = 0.602(p_{xa} - p_{xd}) + 0.372(p_{xb} - p_{xc}) \qquad A_2 \qquad (4)$$

$$\phi_1 = 0.5(\varphi_{xe} - p_{xf} + \varphi_{xg} - p_{xh}) \qquad B_1 \qquad (5)$$

$$\phi_2 = 0.5(p_{ye} - \varphi_{yf} + p_{yg} - \varphi_{yh}) \qquad A_1 \qquad (6)$$

$$\phi_3 = 0.5(p_{ye} + p_{xf} - p_{yg} - p_{xh}) \qquad A_2 \qquad (7)$$

In these equations the $p_{\mu i}$'s are pure p_μ atomic orbitals, while the $\varphi_{\mu i}$'s are $sp^n{}_\mu$ hybrid atomic orbitals parallel to the μ axis. The irreducible representations according to which these wave

Table I. Comparison between Vertical Ionization Potentials $I_{V,J}$ and Orbital Energies ϵ_J of **4** (C_{2v}) (All Values are in eV)

Band	$I_{V,J}$	Assignment	Orbital energies ZDO	MINDO/3	EH
1	8.11 8.29 8.48	$2a_2$ (π-σ)	−8.10	−8.54	−12.05
2	10.15	$5b_1$ (π-w)	−10.14	−10.06	−12.99
3	10.72	$5b_2$ (w)	−10.6	−10.08	−12.93
4	11.13	$4b_1$ (π + w)	−11.56	−11.65	−13.97
5	12.1	$13a_1$ (σ)		−10.41	−13.40
6	12.5	$1a_2$ (π + σ)	−12.6	−12.61	−14.30

functions transform in the point group C_{2v} are listed following these equations. It is important to note that only the π and Walsh orbitals are being considered. In the case of cyclobutane, the lowest occupied Walsh orbital (a_{1g} in D_{2h})[4,21] is omitted since, for reasons of symmetry, it does not interact with any one of the occupied π orbitals of the butadiene moiety.

To construct the corresponding wave functions of **4**, the atomic orbitals at centers a and d of the butadiene moiety have to be combined with those at centers f and h of the cyclobutane ring. The choice of a unique wave function in the cases of ϕ_1 to ϕ_3 is difficult. Semiempirical calculations, however, suggest that the orbital density is equally distributed over all four centers. This implies that alkyl substitution should only slightly remove the degeneracy of ϕ_1 and ϕ_2. If it is assumed that the first two ionization potentials in **6** are due to the removal of an electron from the Walsh orbitals corresponding to ϕ_1 and ϕ_2, this hypothesis receives experimental verification. The split ΔI = 0.6 eV is in line with that found in cyclobutane (0.55),[22] methylcyclobutane (0.57),[8] and tricyclo[3.3.0.0^{2,6}]octane (0.67).[8]

Basis Orbital Energies and Interaction Parameters

The basis orbital energies for *cis*-butadiene have already been discussed.[7,8]

$$\epsilon(\psi_2) = -8.40 \text{ eV} \qquad (8)$$

$$\epsilon(\psi_1) = -10.90 \text{ eV} \qquad (9)$$

We assume, as previously,[7] that the inductive shift of the Walsh orbitals realized upon introduction of a butadiene unit amounts to 0.2 eV. The following basis orbital energies are thereby obtained.

$$\epsilon(\phi_1) = \epsilon(\phi_2) = -10.8 \text{ eV} \qquad (10)$$

$$\epsilon(\phi_3) = -12.3 \text{ eV} \qquad (11)$$

In order to set up the interaction matrix, values for the resonance integrals H_{ij} must be estimated. From eq 3 and 5 we obtain

$$H_{\pi w} = \langle\psi_1|H|\phi_1\rangle = 2(0.5)(0.372)\langle p_{xa}|H|p_{xf}\rangle \qquad (12)$$

Equations 4 and 6 yield

$$H_{\pi\sigma} = \langle\psi_2|H|\phi_3\rangle = 2(0.5)(0.602)\langle p_{xa}|H|p_{xf}\rangle \qquad (13)$$

while substitution of eq 1 into (12) and (13) provides

$$H_{\pi w} = -0.707 \text{ eV} \qquad (14)$$

$$H_{\pi\sigma} = -1.144 \text{ eV} \qquad (15)$$

This treatment leads to the following secular equations for the interacting basis orbitals belonging to the irreducible representations B_1 and A_2.

Table II. Comparison between Vertical Ionization Potentials $I_{V,J}$ and Orbital Energies ϵ_J of **5** and **6** (All Values are in eV)

Band	$I_{V,J}$	Assignment	Orbital energies MINDO/3	EH
		5 (C_{2v})		
1	8.90 9.08 9.24 9.40	$6b_1$ (π)	−9.42 ($6b_1$)	−12.54 ($6b_1$)
2	10.15	$9b_2$ (w)	−10.07 ($9b_2$)	−12.88 ($9b_2$)
3	10.75	$5b_1$ (w)	−10.37 ($5b_1$)	−13.08 ($5b_1$)
4	11.15	$13a_1$ (σ)	−10.61 ($13a_1$)	−13.40 ($13a_1$)
		6 (C_2)		
1	10.0	16b (w)	−10.08 (16b)	−12.86 (16b)
2	10.5	15b (w)	−10.19 (15b)	−12.91 (15b)
3	11.0	15a (σ)	−10.53 (15a)	−13.30 (15a)

$$\begin{vmatrix} -84 - \epsilon & -1.144 \\ -1.144 & -12.3 - \epsilon \end{vmatrix} = 0$$

$$\begin{vmatrix} -10.9 - \epsilon & -0.707 \\ -0.707 & -10.8 - \epsilon \end{vmatrix} = 0$$

By solving these secular determinants, the following eigenvalues are obtained:

$$\epsilon_1(a_2) = -8.1 \text{ eV} \qquad \epsilon_3(b_1) = -10.1 \text{ eV}$$

$$\epsilon_2(a_2) = -12.6 \text{ eV} \qquad \epsilon_4(b_1) = -11.6 \text{ eV}$$

As can be seen from Table I, these values compare very well with those measured for bands 1, 2, 4, and 6. The chosen basis orbital energy for the highest occupied Walsh orbital of the cyclobutane ring (ϵ = −10.6 eV) corresponds very well to the value measured for band 3. The vibrational fine structure encountered in band 1 (see Table I) is very similar to that seen in cycloheptadiene. In the latter compound, the vibrational spacing is reported to be 0.19 eV;[23] in **4**, a value of 0.18 eV is observed.

The only large difference between the ZDO results and the experimental values is found for $\epsilon_4(b_1)$, which differs by 0.43 eV from $-I_{V,4}$ (see Table I). This discrepancy could be due to the interaction of this orbital with a lower lying C–H σ orbital of B_1 symmetry which leads to the observed destabilization. The results of the ZDO calculations are summarized in Figure 2. In this figure an interaction diagram has been constructed between the occupied π orbitals of butadiene on the left and the three highest occupied Walsh orbitals of cyclobutane on the right. The orbital energies are taken from the ZDO calculations. The wave functions have been drawn schematically. This diagram nicely illustrates that **4** is an ideal molecule for the study of interactions between π systems and highest occupied Walsh orbitals of cyclobutane.

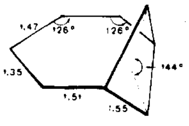
In hydrocarbons **5** and **6**, no conjugative interaction with π orbitals is possible and thus interpretation of the first bands of the pe spectra is straightforward. As mentioned above, the assignment given for bands 1 and 2 in the pe spectrum of **6** interlocks very nicely with data from a series of other alkyl substituted cyclobutane derivatives.[8]

The assignment of the first three bands of **5** on the basis of Koopmans' assumption[18] is also straightforward. The value of its first ionization potential (8.90 eV) is close to the first ionization potential of cycloheptene (9.04 eV)[23] and cyclooctene (8.98 eV).[23] The vibrational spacing of 0.16 eV observed in its first band is also identical with that observed for cycloheptene[23] and cyclooctene.[23]

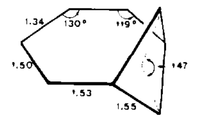
The ionization potentials for bands 2 and 3 of **5**, which are due to the ejection of an electron out of the highest occupied Walsh orbitals, are lowered by about 0.2 eV compared with the Walsh orbitals of **6**. This is due to a dominance of the inductive effect of the double bond over the hyperconjugative effect of the CH_2 groups. A similar lowering (−0.18 eV) is observed by comparing the center of gravities of the π-orbital energies for cyclohexene (9.12 eV)[24] with cyclohexadiene ($\bar{I}_V$ = 9.3 eV).[24]

Semiempirical Calculations

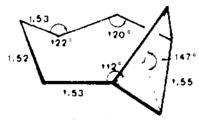
To test the analysis given above, we have compared the experimental results with extended Hückel[19] and MINDO/3[20] calculations. Since the detailed structures of **4** to **6** are not known, we have optimized their geometries within the MINDO/3 scheme.[20] For this optimization a modified Fletcher-Powell search procedure was used.[25] The heats of formation so calculated are: **4**, 49.09 kcal/mol; **5**, 18.74 kcal/mol; and **6**, −6.06 kcal/mol. Below we have indicated the geometrical parameters obtained for the carbon skeletons. For **4**, **5**, and **6**, C_{2v}, C_s, and C_2 symmetry, respectively, was assumed throughout the geometry optimization procedure in order to reduce the large number of variables. Molecular model studies indicated this choice to be reasonable. Although **5** was assumed to have one plane of symmetry only, the structure converged to the higher symmetry C_{2v}. This result was quite unexpected. However, it is in line with the known tendency of MINDO/3 to underestimate puckering amplitudes of hydrocarbon rings.[26] In the case of **6**, centers 3 and 4 are situated 0.23 Å above and below the plane defined by carbons 1, 2, 5, and 6.



4(C_{2v})



5(C_{2v})



6(C_2)

The structural parameters realized for the cyclobutane segments in **4** to **6** closely parallel those derived from electron diffraction and x-ray experiments on cyclobutane,[27] bicyclo[2.1.1]hexane,[28] bicyclo[2.1.1]hexene,[29] and tricyclo[3.3.0.0^{2,6}]octane.[30]

Conclusion

The aim of this study has been to elucidate the orbital interactions taking place between the butadiene and cyclobutane units in **4**. A measure of the magnitude of this interaction is given by the atomic resonance integral in eq 1. Interestingly, the value found for this parameter not only confirms our previous results[7,8] but is seen to be identical with the β value found for the interaction between a cyclopropane ring and a double bond.[7-9,31] The interaction integrals, $H_{\pi w}$, between a double bond and a cyclopropane or a cyclobutane ring, however, are quite different due to the wide numerical divergence in the coefficients of the atomic orbitals in the corresponding wave functions. This gap in the interaction integrals should be a measure of the difference in the ability of the particular ring to stabilize a π system.

$$H_{\pi w}(\text{cyclopropane}) = \beta c_\pi c_w = -1.9 \frac{2}{\sqrt{6}} 0.707 = -1.1 \text{ eV}$$

$$H_{\pi w}(\text{cyclobutane}) = \beta c_\pi c_w = (-1.9)(0.5)(0.707) = -0.67 \text{ eV}$$

The numbers are entirely consistent with the outcome of semiempirical calculations on the cyclobutylcarbinyl system[4] and agree with experimental results.[32]

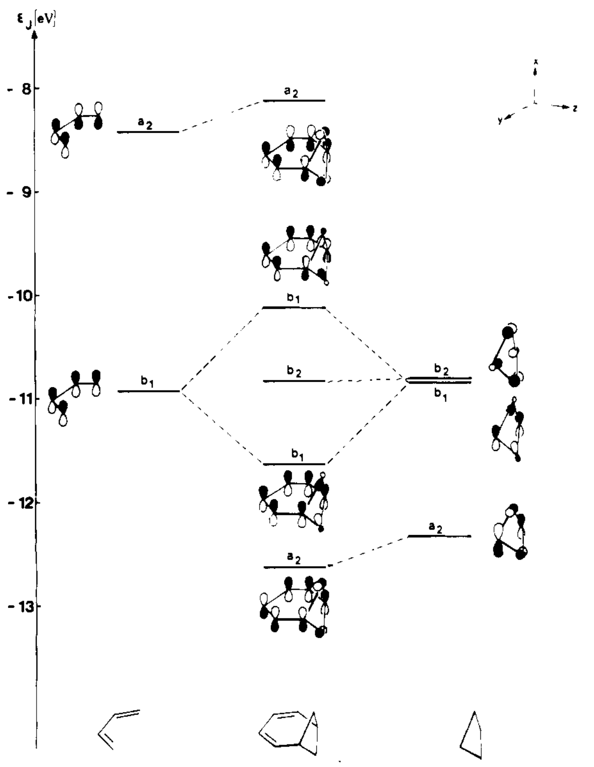


Figure 2. Orbital interaction diagram for **4** based upon perturbation theory.

Experimental Section

The pe spectra have been measured with a PS8 Photoelectron Spectrometer (Perkin-Elmer Ltd., Beaconsfield, England). Proton magnetic resonance spectra were recorded with a Varian A-60A spectrometer, while the carbon magnetic resonance spectra were obtained with a Bruker 90 instrument. Apparent splittings are given in all cases. Infrared spectra were recorded on Perkin-Elmer Model 137 and 467 spectrometers, whereas the mass spectra were obtained with an AEI-MS9 instrument at an ionizing potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

3,4-Bis(trimethylsiloxy)bicyclo[4.1.1]oct-3-ene (9a). A solution of **8**[11] (2.00 g, 10 mmol) and chlorotrimethylsilane (6.5 ml, 50 mmol) in 200 ml of anhydrous ether was added dropwise during 30 min to a rapidly stirred mixture of sodium-potassium alloy (1:1, 3.0 g, 100 mmol) in 100 ml of dry benzene at room temperature under nitrogen. This mixture was refluxed for 20 h, cooled, filtered through glass wool, and evaporated to leave 2.37 g (83.5%) of **9a** as a pale yellow oil. This substance which could be molecularly distilled (70 °C (0.01 mm)) or more extensively purified by VPC (6 ft × 0.25 in. 10% QF-1 on Chromosorb G, 150 °C) was identical with that previously described:[11] $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.8-2.1 (m, 10 H) and 0.18 (s, 18 H).

3,4-Bis(diethylphosphonyl)bicyclo[4.1.1]oct-3-ene (9b). To a solution of **9a** (1.00 g, 3.51 mmol) in 10 ml of anhydrous tetrahydrofuran was added 5.6 ml (8.4 mmol) of 1.5 M methyllithium in ether at ambient temperature. The resulting bright yellow solution was stirred for 1 h and 1.51 g (8.74 mmol) of diethyl chlorophosphate dissolved in 10 ml of tetrahydrofuran was added. The clear solution was stirred overnight and evaporated to leave an oily solid which was partitioned between ether (100 ml) and water (50 ml). The aqueous layer was extracted with chloroform (2 × 50 ml) and the combined organic layers were dried, filtered, and evaporated. There remained 1.09 g (75%) of **9b** as a pale yellow oil which was not further purified: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.4-3.7 (m, 8 H), 2.8-1.0 (m, 10 H), and 1.33 (m, 12 H); the molecular ion was too weak to mass measure.

Bicyclo[4.1.1]octan-3-on-4-ol (10). A 1.35-g (6.74 mmol) sample of **8** was subjected to the acyloin conditions previously described. The crude **9a** so obtained was dissolved in tetrahydrofuran (15 ml) and treated with nitrogen (gas diffusion tube) while stirred with 5 ml of 5% hydrochloric acid. After 1 h at the reflux temperature, the solution was neutralized by the addition of calcium carbonate (1 g). Filtration and solvent evaporation left 2.3 g of oil which was partitioned between water (50 ml) and ether (200 ml). From the dried organic layer, there was obtained 800 mg (84.6%) of **10** which was further purified by chromatography on Florisil (elution with 1:1 ether-petroleum ether): $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 3495 (br) and 1704 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.70 (dd, J = 10.5 and 7.5 Hz, 1 H), 3.5 (br s, OH), and a broad continuum of peaks from 3.07 to 0.08 (10 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.96; H, 8.86.

***cis*-Bicyclo[4.1.1]octane-3,4-diol (11a).** A mixture of **9a** (530 mg, 1.86 mmol), absolute ethanol (10 ml), and sodium borohydride (150 mg, 4.0 mmol) was stirred for 2 h at room temperature and for 2 h at the reflux temperature. The cloudy solution was evaporated and the residual white solid was dissolved in 5% hydrochloric acid (40 ml) and ether (50 ml). The aqueous phase was extracted with ether (2 × 100 ml) and dichloromethane (100 ml). The organic phases were combined, dried, filtered, and evaporated to give 206 mg (78%) of **11a** as a white solid, mp 129.5-130.5 °C, after crystallization from ether-hexane: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.26 (t of m, J = 5.5 Hz, 2 H), 3.6 (br s, OH, 2), 2.38 (br s, 2 H), 2.62-2.02 (m, 3 H), 2.02-1.82 (dd, J = 6.0 and 5.5 Hz, 4 H), and 1.55-1.23 (q of m, J = 9.5 and 5.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 74.2 (d), 35.6 (t), 32.4 (d), 31.1 (t), and 29.9 (t) ppm; *m/e* calcd 142.0996, found 142.0996. Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.45; H, 9.74.

The dimesylate **11b**, prepared by the usual treatment of **11a** with methanesulfonyl chloride in pyridine, was isolated as a colorless crystalline solid, mp 133.5-134.5 °C, from hexane-dichloromethane; *m/e* 298.

Bicyclo[4.1.1]oct-3-ene (5). A solution of **11a** (710 mg, 5.0 mmol) in 75 ml of xylene was dried by azeotropic distillation (removal of 15 ml) prior to addition of thiocarbonyldiimidoazole (1.25 g, 7.0 mmol). A cloudy distillate (5 ml) was removed prior to a reflux period of 8 h under nitrogen. The volume was reduced to 20 ml by rotary evaporation. Dichloromethane (10 ml) was added and the desired ester was obtained pure by chromatography on Florisil (elution with 40-80% CH_2Cl_2 in hexane); white needles, mp 73.8-74.5 °C (from ether-hexane); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.28 (t with additional coupling, J = 4.2 Hz, 2 H), 2.53 (m, 3 H), 2.28 (m, 5 H), and 1.73-1.03 (br m, 2 H). Anal. Calcd for $C_9H_{12}O_2S$: C, 58.67; H, 6.56. Found: C, 58.82; H, 6.53.

A solution of **12** (450 mg, 2.44 mmol) in 5 ml (24 mmol) of distilled triethyl phosphite was heated to 150 °C under nitrogen for 90 h, cooled, diluted with pentane, and applied to a column of neutral, activity I alumina (50 g). Pentane elution gave a mixture containing **5** and the phosphite. VPC purification (6 ft × 0.25 in. 10% QF-1 on Chromosorb G, 80 °C) afforded 48 mg (18%) of **5** as a colorless liquid: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.57 (m, J = 2 Hz, 2 H), 2.48 (m, 3 H), 2.26 (m, 4 H), and 1.57-1.03 (m, 3 H); ^{13}C NMR ($CDCl_3$) 125.8 (d), 35.6 (t), 31.8 (d), and 30.3 (t) ppm. Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.64; H, 11.63.

Bicyclo[4.1.1]octane (6). (A) Hydrogenation of 5. A mixture of **5** (16 mg), ether (20 ml), and 10% palladium on carbon (100 mg) was hydrogenated at atmospheric pressure for 3 h. Filtration through silica gel (5 g, pentane elution) and vpc isolation (6 ft × 0.25 in. 5% OV-11 on Chromosorb G, 80 °C) gave 12 mg (75%) of **6** as a colorless low-melting solid: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.80-1.95 (m, 4 H) and 1.95-1.00 (m, 10 H); ^{13}C NMR ($CDCl_3$) 34.0, 31.6, 29.9, and 25.5 ppm; *m/e* calcd 110.1095, found 110.1098.

(B) **Clemmensen Reduction of 10.** To a mixture of **10** (700 mg, 5.0 mmol), water (2 ml), and concentrated hydrochloric acid (3 ml) was added 5.0 g of amalgamated zinc. Heating at 100 °C was maintained for 5 h with hourly addition of acid (1 ml). The reaction mixture was cooled, diluted with ether (50 ml) and water (20 ml), and filtered. The aqueous phase was diluted with brine (20 ml) prior to further ether extraction (25 ml). The combined organic layers were washed with sodium bicarbonate solution, dried, and concentrated. VPC analysis indicated that both **5** and **6** had been formed. Preparative scale techniques furnished 95 mg (15%) of **6** which was identical in all respects with the sample isolated above.

Bicyclo[4.1.1]octa-2,4-diene (4). A solution of 41 mg (0.38 mmol) of **5** in 4 ml of carbon tetrachloride containing 75 mg (0.42 mmol) of *N*-bromosuccinimide and 5 mg of azobisisobutyronitrile was refluxed for 2 h. VPC analysis at this time showed **5** to still be present. Additional NBS (100 mg) and AIBN were added and heating was continued for an additional 2 h before filtration and evaporation. The resulting dark yellow oil was applied in pentane to a column of silica gel (pentane elution). Fractions 8-12 when combined afforded 85 mg (84%) of **13** as a colorless oil: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.73 (m, 2 H), 4.93 (m, 2 H), 3.20-2.67 (m, 2 H), and 2.67-1.18 (series of m, 4 **H**); *m/e* calcd 184.9966, found 184.9970.

A mixture of **13** (150 mg, 0.56 mmol), zinc-copper couple (300 mg, 4.6 mmol), potassium iodide (100 mg, 0.60 mmol), and sublimed iodine (50 mg, 0.20 mmol) in 2 ml of dimethylformamide was stirred under nitrogen for 12 h. Ten milliliters each of pentane and ether were added and the suspension was filtered through 10 g of alumina (act. *I*, neutral). Following elution with 50 ml of pentane and 10 ml of ether, the eluate was fractionally distilled and the residue was subjected to preparative VPC purification (6 ft × 0.25 in. 20% Carbowax 20M on Chromosorb P, 110 °C). There was obtained 18 mg (18%) of **4** as a colorless oil: $\lambda_{\mathrm{max}}^{\mathrm{hexane}}$ 266 (ϵ 2800), 277 (3800), 288 (3750), and 301 nm (2000); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.53-5.67 (AA′BB′, 4 H), 3.28-2.73 (m, 2 H), 2.73-2.12 (m, 2 H), and 1.63-1.08 (m, 2 H); ^{13}C NMR ($CDCl_3$) 138.6, 123.7, 34.8, and 21.4 ppm; *m/e* calcd 106.0782, found 106.0784.

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