Trimethylsilyl 2,2-Dimethyl-3-(trimethylsiloxy)-4-(trimethylsilyl)-4-butenoate (12). A 17.5-mmol (2-g) portion of 1 was added dropwise to a stirred solution of 17.5 mmol (4.07 g) of dimethylketene bis(trimethylsilyl) acetal at 110 °C under a nitrogen atmosphere. The reaction solution was stirred at this temperature until the ketene had been consumed as evidenced by the disappearance of the ketene band in the IR (~36 h). Vacuum distillation resulted in 4.5 g (75%) of **12**: bp 68 °C at 0.025 mm; IR 1615 (C=C), 1720 (C=O) cm^{-1}; NMR (CCl_4 with $CHCl_3$ as a reference) δ 0.15 (s, 9 H), 0.27 (s, 9 H), 0.33 (s, 9 H), 1.35 (s, 6 H), 4.45 (s, 1 H); mass spectrum, parent peak at *m/e* 346, found *m/e* 346.

Anal. Calcd for $C_{15}H_{34}O_3Si_3$: C, 52.02; H, 9.83. Found: C, 51.92; H, 9.83.

Acknowledgments. The authors would like to express appreciation to the Robert A. Welch Foundation and to the North Texas State University Faculty Research Fund for support of this investigation.

Registry No.—**1**, 4071-85-6; **2a**, 67354-22-7; **2b**, 67354-14-7; **3a**, 67354-23-8; **3b**, 67354-15-8; **4a**, 67354-24-9; **4b**, 67354-16-9; **5a**, 68781-92-0; **6c**, 68781-93-1; **6d**, 68781-94-2; **7c**, 68781-95-3; **7d**, 68781-96-4; **8c**, 68781-97-5; **8d**, 68781-98-6; **9**, 56772-77-1; **10**, 68781-99-7; **11**, 18720-11-1; **12**, 68782-00-3; trimethylsilyl 5-phenylpentanoate, 68782-01-4; trimethylsilyl hexanoate, 14246-15-2; (*E,Z*)-trimethylsilyl 4-methyl-5-phenyl-2,4-pentadienoate, 68782-02-5; (*E,E*)-trimethylsilyl 4-methyl-5-phenyl-2,4-pentadienoate, 68782-03-6; (*Z,E*)-trimethylsilyl 4-methyl-5-phenyl-2,4-pentadienoate, 68782-04-7; (*Z,Z*)-trimethylsilyl 4-methyl-5-phenyl-2,4-pentadienoate, 68782-05-8; trimethylsilyl 4-methyl-5-phenylpentanoate, 68782-06-9; propionaldehyde, 123-38-6; *n*-butyraldehyde, 123-72-8; isobutyraldehyde, 78-84-2; 3-cylohexenecarboxaldehyde, 100-50-5; (*E*)-cinnamaldehyde, 14371-10-9; (*E*)-crotonaldehyde, 123-73-9; furfural, 98-01-1; (*E*)-α-methylcinnamaldehyde, 15174-47-7; (*Z*)-α-methylcinnamaldehyde, 66051-14-7; dichloroketene, 4591-28-0; trichloroacetyl chloride, 76-02-8; diphenylketene, 525-06-4; dimethylketene bis(trimethylsilyl) acetal, 31469-25-7; ethoxyacetylene, 927-80-0; trimethylchlorosilane, 75-77-4.

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Photoelectron Spectra of the 1,2,5,6-Tetramethyl-3,4,7,8-tetramethylene Derivatives of Tricyclo[3.3.0.0^{2,6}]octane and Tricyclo[4.2.0.0^{2,5}]octane

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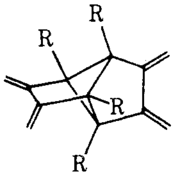
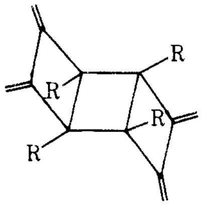
Received July 11, 1978

The photoelectron spectra of the title compounds, 4 and 5, are reported, along with assignments of the first three bands in each. Analysis within a ZDO model of the splitting between the first two bands in the spectrum of 4 requires that the b_1 orbital of the tetramethylcyclobutane ring have an energy of −9.3 eV. This finding is discussed in light of calculations on the effect of tetramethylation of cyclobutane and the approximations inherent in the ZDO model.

The magnitude of the through-bond splitting between different symmetry combinations of π orbitals localized on unsaturated groups depends on the extent to which one combination is destabilized relative to the other by interaction with adjacent σ orbitals of appropriate symmetry.[2] The bonds of small rings, by virtue of their high energy and large amounts of p character, are ideal candidates for producing substantial through-bond splittings.[3] In particular, cyclobutane rings have been shown by a variety of spectroscopic,[4] chemical,[5] and theoretical[6] studies to interact strongly with unsaturated bridging groups. Therefore, the through-bond splittings in 3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (**1**) and *anti*-3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane (**2**) are expected to be significant.



1, R = H
4, R = CH_3



2, R = H
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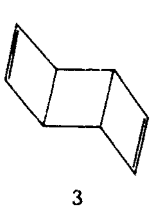

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More specifically, in **1** the b_1 and a_2 combinations of the butadiene highest occupied molecular orbitals (HOMO's) should be significantly split by their interactions with b_1 and a_2 orbitals of the cyclobutane ring.[7] The b_1 orbital of the ring

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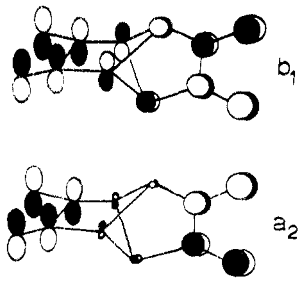


Figure 1. Schematic drawing of the two highest occupied MO's of 1.

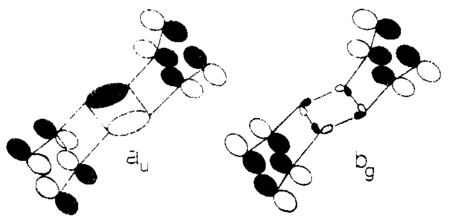


Figure 2. Schematic drawing of the two highest occupied MO's of 2.

is filled and lies slightly below the degenerate (e) pair of cyclobutane HOMO's.[6] Interaction of the b_1 combination of butadiene π HOMO's with the ring orbital of the same symmetry effects a destabilization of the former. The highest lying MO in 1 results from this mixing and is shown schematically in Figure 1. Also shown is the orbital that arises from mixing of the a_2 butadiene combination with the cyclobutane ring. There are no filled a_2 ring orbitals, but there is an antibonding cyclobutane orbital of this symmetry. Consequently, the mixing of the a_2 butadiene π MO combination with the ring should be weaker than that of the b_1 combination and, in addition, should be stabilizing rather than destabilizing. Unlike the HOMO's of the butadiene groups, there is no splitting between combinations of the lowest π orbitals for they belong to the e representation.[8] These π orbitals can interact with the degenerate pair of HOMO's of the cyclobutane ring to give two pairs of relatively low-lying orbitals with e symmetry in 1.

In 2 the 1,2 bridging of the cyclobutane ring by the butadiene units not only lowers the molecular symmetry from D_{2d} in 1 to C_{2h}, but also changes the ring orbitals with which the butadiene π-orbital combinations can interact. The a_u combination of butadiene HOMO's in 2 can interact with one of the cyclobutane HOMO's which also has this symmetry in C_{2h}. This differentiates 2 from not only 1 but also from *anti*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (3), whose photoelectron spectrum has been analyzed by Heilbronner and co-workers[4g] in terms of through-bond splitting between the two symmetry combinations (a_g and b_u) of the ethylene π bonds. In 3, because of the difference in symmetry between the HOMO's of ethylene and butadiene, neither of the bonding ethylene π combinations interacts strongly with either of the HOMO's of the ring. Instead, the a_g combination of π bonds interacts with the ring orbital that lies just below the HOMO's in energy, and the b_u mixes with an antibonding ring orbital. Similarly, the b_g π combination in 2 mixes only with an antibonding ring orbital since it also is antisymmetric to the twofold axis which passes through two σ bonds of the ring. The MO's of 2 that result from the mixing of the highest occupied butadiene π-orbital combinations with the orbitals of the four-membered ring are shown schematically in Figure 2.

Although 1 and 2 are both unknown molecules, we have previously described the preparation of their 1,2,5,6-tetramethyl derivatives, 4 and 5.[9] In this paper we report the photoelectron spectra of these molecules and discuss the assignments and positions of the bands.

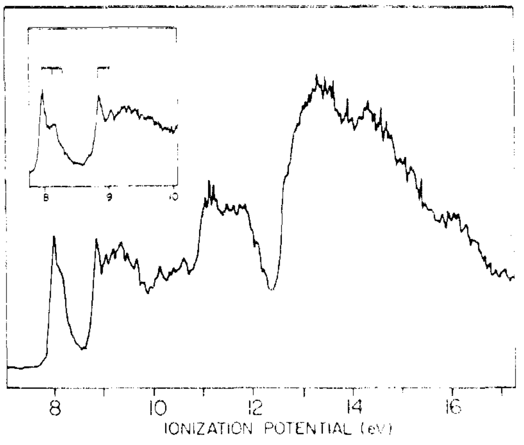


Figure 3. Photoelectron spectrum of 4. The inset shows the 8–10 eV region at higher resolution.

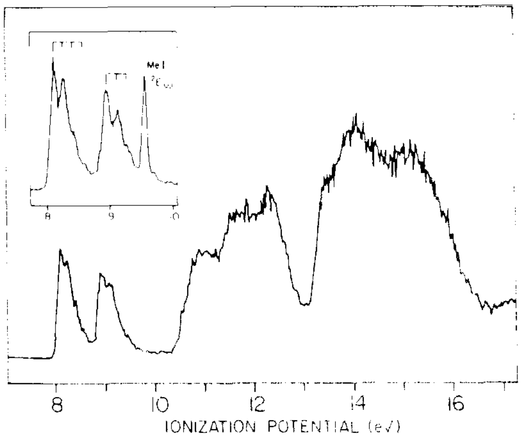


Figure 4. Photoelectron spectrum of 5. The inset shows the 8–10 eV region at higher resolution.

Experimental Section

anti-1,2,5,6-Tetramethyl-3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane (5) was prepared by sensitized photodimerization of 1,2-dimethyl-3,4-dimethylenecyclobutene, as described previously.[9] 1,2,5,6-Tetramethyl-3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (4) was also synthesized by the literature procedure[9] involving pyrolysis of 5 to 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenecycloocta-1,5-diene, followed by sensitized photochemical ring closure to 4. Both 4 and 5 were stored under an inert atmosphere at −78 °C prior to sublimation at room temperature under high vacuum into the inlet of the ionization chamber of the photoelectron spectrometer.[10] He I excitation was used, and the spectra were calibrated with the known ionization potentials of N_2 and CH_3I.

Results and Discussion

The photoelectron spectra of 4 and 5 are shown in Figures 3 and 4. The first three bands in the spectrum of 4 are assigned as ionizations from, respectively, the uppermost b_1, a_2, and e orbitals. These assignments are supported by the results of EH[11] and MINDO/3[12] calculations. Because of the size limitations in the MINDO/3 program, calculations were carried out on 1 and 2 instead of 4 and 5. The geometry for both molecules was obtained by complete MINDO/3 optimization, assuming D_{2d} symmetry for 1 and C_{2h} for 2. Although, as shown in Table I, both EH and MINDO/3 find the b_1 orbital to be the HOMO of 1, the relative energies of a_2 and e are interchanged in the two calculations. However, both calculations indicate that the separation between the a_2 and e should be small, as is observed in the spectrum. Confirmatory evidence for the assignment of the first three bands as ionizations from, respectively, the b_1, a_2, and e MO's is provided by the sharp,

Table I. Calculated Orbital Energies in 1 and 2 and Observed Ionization Potentials in 4 and 5

molecule	orbital	MINDO/3[a]	EH[a]	observed[a]	vibrational spacing[b]
1,4	b_1	−8.61	−12.23	7.97	1350
	a_2	−9.38	−12.68	8.80	1420
	e	−9.58	−12.67	9.3	
2,5	a_u	−8.77	−12.23	8.10	1220
	b_g	−9.21	−12.57	8.92	1350
	b_u	−9.16	−12.08	10.9	

[a] Energies in eV (±0.02). [b] In cm^{-1} (±50).

structured Franck–Condon envelopes of the first two, indicative of ionization from orbitals primarily π butadiene in character. The third band, in contrast, is broad, its shape being characteristic of the Jahn–Teller effect expected in the ^2E state of the ion formed by removal of an electron from an MO of e symmetry.

The assignment of the first three bands in the photoelectron spectrum of **5** is also shown in Table I. Both sets of calculations predict a high-lying orbital of b_u symmetry, consisting of one of the HOMO's of the cyclobutane ring interacting in an antibonding fashion with the central σ bond of each of the two unsaturated bridges. This b_u orbital is predicted to be the HOMO of **2** by the EH calculation and the second highest orbital by MINDO/3. We have assigned the third band in the spectrum of **5** as corresponding to ionization from this orbital for three reasons. First, the bands at 8.10 and 8.92 eV, like the first two bands in the spectrum of **4** and like the first bands in the spectra of other conjugated dienes that have been studied,[4f] both show a vibrational progression with a splitting of 0.15 and 0.17 eV, respectively. This suggests that the first two bands correspond to ionizations from MO's that are predominantly butadiene π HOMO in character, which results in the observed reduction in the C=C vibrational frequencies in the ions. Second, Heilbronner[4g] has identified the ionization from the b_u orbital in **3** with a band at 10.57 eV in the photoelectron spectrum of this molecule, in fair agreement with the assignment of this band at 10.89 eV in **5**. Finally, the calculations both predict that the through-bond splitting between a_u and b_g in **2** should be smaller than that between b_1 and a_2 in **1**. If either of the first two bands in the tetramethyl derivative of **2** (**5**) were assigned to ionization from b_u, the splitting between the bands then assigned to a_u and b_g would be more than twice as large as that between the bands assigned to removal of electrons from b_1 and a_2 in the tetramethyl derivative of **1** (**4**).

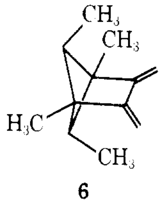
With the assignment of the first three bands in the photoelectron spectra of **4** and **5** apparently secure, it is tempting to try to fit the observed splittings with simple models for through-bond interactions. For instance, Gleiter and coworkers have used a semiempirical zero-differential overlap (ZDO) model to fit the photoelectron spectra of other molecules containing unsaturatively bridged cyclobutane rings.[4d–f] In the ZDO calculations, energies were assumed for the σ orbitals of the ring and the π orbitals of the bridges. Knowing the approximate form of these orbitals and taking $\beta = -1.9$ eV between p orbitals of the ring and bridge, the matrix elements for interactions between the filled orbitals of the ring and bridge could be computed. Matrix diagonalization then gave calculated band positions, which were generally in very good agreement with experiment.

We have not attempted such calculations for **5**, because the MINDO/3 and EH results for **2** show significant mixing between the σ and π orbitals of the butadiene bridging group. The problem is that in **2** and **5** there are no elements of symmetry that distinguish the σ from the π orbitals of the bridges. Consequently, the contribution of the unsaturated bridges to the a_u and b_g MO's consists not of pure π orbitals, but of σ–π mixtures. This fact renders pointless any attempt to fit the observed spectrum of **5** with a model that involves mixing between only the σ MO's of the ring and pure π orbitals on the bridges. For the same reason, the 0.8-eV splitting between the first two bands in the spectrum of **5** should not be strictly interpreted as an experimental measure of the through-bond splitting between a_u and b_g combinations of pure butadiene π orbitals.

The higher symmetry of **1** and **4** does differentiate between the σ and π orbitals of the bridges, and we have attempted to fit the observed spectrum of **4** within a ZDO model. Since in the ZDO model interactions between filled and unfilled orbitals are not included, the stabilization of the a_2 combination of butadiene HOMO's by the small admixture of the antibonding ring MO is ignored. Therefore, within the ZDO model the energy of both combinations of butadiene HOMO's before interaction with the ring is established as −8.8 eV by the spectrum of **4**. This compares fairly well with a value of −8.4 eV employed by Gleiter and co-workers for the HOMO of endocyclic dienes.[4e,f] Following Gleiter, we use 0.5 for the coefficients of the b_1 ring orbital and 0.372 for those of the butadiene HOMO at the atoms adjacent to the ring. The matrix element mixing the b_1 combination of bridge HOMO's with the b_1 ring orbital is then equal to $0.5 \times 0.372 \times (-1.9) \times 4/\sqrt{2} = -1.0$ eV. The factor of $1/\sqrt{2}$ comes from the normalization of the bridge orbital combination. Since it is not clear what energy to employ for the b_1 ring orbital in **4**, perturbed as it is by four methyl groups, we instead use the band observed at 8.0 eV in the spectrum to calculate it. Substituting $\epsilon = -8.0$ eV in the secular determinant,

$$\begin{vmatrix} -8.8-\epsilon & -1.0 \\ -1.0 & x-\epsilon \end{vmatrix} = 0$$

x, the energy of the b_1 ring orbital, is found to be −9.3 eV. Using this value, the position of the first band in the spectrum of the monobridged compound 1,2,5,6-tetramethyl-3,4-dimethylenebicyclo[2.1.1]hexane (**6**),[13] can be predicted as 8.3 eV, in good agreement with the observed[14] position at 8.22 eV.



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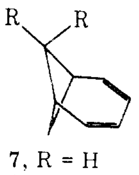

7, R = H
8, R = CH_3

In their ZDO analysis of the photoelectron spectrum of bicyclo[4.1.1]octa-2,4-diene (**7**),[4f] Gleiter et al. assumed energies for the orbitals of the four-membered ring based on an inductive shift from the corresponding energies in cyclobutane itself of 0.1 eV for each attached vinyl group. Using their prescription and the resulting value of −12.1 eV for the b_1 ring orbital in **1**, the first band in the photoelectron spectrum of this molecule is expected to appear at 8.5 eV, if the second band is found at 8.8 eV, as it is in **4**.

Because **1**, as yet, has not been synthesized, it cannot be determined how well basis orbital energies of −8.8 and −12.1 eV fit the photoelectron spectrum of this molecule. Nevertheless, there is good precedent for methylation of **1**, to give **4**, resulting in a reduction of the first ionization potential. All of the bands in the photoelectron spectrum[15] of 7,7-dimethylbicyclo[4.1.1]octadiene (**8**)[16] are shifted to lower energy by 0.3–0.5 eV from the corresponding bands in the spectrum of the parent hydrocarbon (**7**).[4f] Within the ZDO model these lowered ionization potentials must be accounted for by destabilization of the ring orbitals upon methylation, and the bands in the photoelectron spectra of alkylated cyclobutane derivatives are, in fact, shifted to lower energy, compared to those in the parent molecule.[4d]

Could the shift from −12.1 to −9.3 eV in the b_1 cyclobutane MO energy, which is required to fit the spectrum of **4**, be due entirely to destabilization of this ring orbital by the methyl groups present in **4**? MINDO/3 and EH calculations for cyclobutane and for its all-trans 1,2,3,4-tetramethyl derivative[17] do show destabilization of the b_1 ring orbital on tetramethylation,[18] amounting to 1.02 eV in the MINDO/3 and 0.62 eV in the EH calculations. However, the highest occupied b_1 orbital in tetramethylcyclobutane (ϵ = −9.90 eV in the MINDO/3 and −12.95 eV in the EH calculation) is found by both methods to have smaller coefficients on the ring carbons than the b_1 orbital in cyclobutane itself. Apparently, the destabilization of the b_1 ring orbital of cyclobutane on tetramethylation is due primarily to hyperconjugative mixing, in an antibonding fashion, with the pseudo π orbitals of the methyl groups. Consequently, the matrix element, used in the ZDO treatment of **4**, for the interaction of the highest occupied b_1 orbital of tetramethylcyclobutane with the b_1 combination of butadiene HOMO's should be reduced in magnitude from the corresponding matrix element in **1**. Thus, if coefficients of 0.5 for the ring carbon atoms in **4** are used for computing the off-diagonal matrix element within the ZDO model, −9.3 eV represents a fictitious effective energy for "the b_1 ring orbital". The actual energy of the upper of the *two* orbitals resulting from the interaction between the b_1 combination of methyl group pseudo π orbitals and the cyclobutane ring orbital of b_1 symmetry would have to be greater than −9.3 eV to give the pair of b_1 MO's in tetramethylcyclobutane this effective energy.

It seems probable, therefore, that the value of −9.3 eV for the effective b_1 ring orbital energy in **4**, which must be assumed in order to fit the observed spectrum, is an artifact. We suggest that it results from the breakdown of Koopmans' theorem in **4**. Koopmans' theorem equates ionization potentials with the negative of orbital energies,[19] whereas an ionization potential actually represents the difference in energy between a neutral molecule and a particular state of the derived positive molecular ion. Application of Koopmans' theorem neglects possible electronic reorganization in going from the neutral molecule to the positive ion. For instance, electron donation from the methyl groups in **4** is expected to be greater in the positive ion states than in the neutral molecule. If the electronic reorganization energy is the same for two states of an ion, the Koopmans' theorem prediction of the energy difference between them should be satisfactory. However, in the two lowest states of the positive ion formed from **4**, there is ample cause to question whether the electronic reorganization energies can reasonably be expected to be the same.

Since the b_1 MO of **1** has substantially larger coefficients at the cyclobutane ring atoms than does the a_2 MO, the $^2B_1$ state of the positive ion, formed by removal of an electron from the b_1 MO, is anticipated to have more positive charge localized in the ring than the $^2A_2$ state. Consequently, the enhanced electron donation expected from the methyl groups in the positive ion states of **4** should have a greater stabilizing effect on the $^2B_1$ state than on $^2A_2$.[20] Therefore, the 0.8-eV difference between these states, observed experimentally, is not expected to be fully mirrored in the difference between the ZDO energies of the highest occupied b_1 and a_2 MO's of **4**.[22] Thus, we believe that the energy of −9.3 eV for the b_1 cyclobutane ring orbital, which is required to reproduce within the ZDO model the splitting between the first two bands in the spectrum of **4**, does not represent an effective average energy of the two b_1 orbitals in tetramethylcyclobutane, but is instead merely an artifact, resulting from the assumption of Koopmans' theorem.

Acknowledgments. The financial support of the National Science Foundation, the Alfred P. Sloan Foundation, the National Research Council of Canada, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank Professor C. A. McDowell for his interest in this work.

Registry No.—**4**, 34106-16-6; **5**, 34101-24-1.

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(6) (a) R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, **93**, 5699 (1971); (b) R. Gleiter and T. Kobayashi, *Helv. Chim. Acta*, **54**, 1081 (1971); (c) W. L. Jorgensen and W. T. Borden, *J. Am. Chem. Soc.*, **95**, 6649 (1973); (d) W. L. Jorgensen, *ibid.*, **97**, 3082 (1975); (e) W. L. Jorgensen and W. T. Borden, *Tetrahedron Lett.*, 223 (1975); (f) see also ref 4d-g and 5.

(7) This has previously been discussed by P. Bischof, R. Gleiter, and R. Haider, *Angew. Chem., Int. Ed. Engl.*, **16**, 110 (1977), and *J. Am. Chem. Soc.*, **100**, 1036 (1978).

(8) For the same reason there is no splitting between combinations of the ethylene π orbitals in tricyclo[3.3.0.0^{2,6}]octadiene.[6a,b]

(9) W. T. Borden, A. Gold, and S. D. Young, *J. Org. Chem.*, **43**, 486 (1978).

(10) D. C. Frost, S. T. Lee, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, **12**, 95 (1977).

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(14) A. Schweig, private communication. We wish to thank Professor Schweig for communicating this result to us in advance of publication.

(15) We are indebted to Professor R. Gleiter for obtaining this spectrum for us.

(16) W. T. Borden and S. D. Young, *Tetrahedron Lett*., 4019 (1976).

(17) For these calculations, the geometry of the ring was taken as that of the cyclobutane ring in **1**.

(18) The calculations also reveal a destabilization of the degenerate pair of e orbitals. On tetramethylation of cyclobutane these orbitals move from −10.22 to −9.31 eV in the MINDO/3 and from −13.22 to −12.39 eV in the EH calculations. Both methods again reveal hyperconjugative interaction between the pseudo π orbitals of the methyl groups and the ring orbitals, although it appears smaller in size than in the b_1 manifold.

(19) T. Koopmans, *Physica* (*Utrecht*), **1**, 104 (1934).

(20) Within the ZDO model, which assumes Koopmans' theorem and no interaction between filled and unfilled orbitals, ionization from the a_2 orbital in **1** and **4** should require exactly the same energy since the a_2 orbital is assumed to be localized completely on the butadiene bridges in both molecules. However, for reasons discussed by Heilbronner,[21] the breakdown of Koopmans' theorem should cause the ionization from a_2 to appear at higher energy in the spectrum of **1** than in that of **4**. In addition, since we believe that the methyl groups in **4** stabilize the $^2B_1$ ion much more than the $^2A_2$, we predict a smaller splitting between these bands in the spectrum of **1**.

(21) F. Brogli, P. A. Clark, E. Heilbronner, and M. Neuenschwander, *Angew. Chem., Int. Ed. Engl.*, **12**, 422 (1973).

(22) A similar situation is expected in **5**.