Photoelectron Spectra and Electronic Structures of Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes[1]

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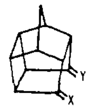
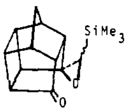
Contribution from the Department of Chemistry, North Texas State University, Denton, Texas 76203, the Department of Chemistry, City University of New York, Queens College, Flushing, New York 11367, the School of Chemistry, University of Hyderabad, Hyderabad 500 134, India, and the Central Research and Development Department, Experimental Station E328, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19898. Received March 25, 1987

Abstract: Syntheses of several new substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (PCUDs, i.e., compounds **4–8**) are described. Photoelectron (PE) spectra have been obtained for compounds **1–10**. Molecular orbital calculations on systems **1–3** were performed by using a minimum STO-3G basis set. Infrared vibrational frequencies and absorption intensities were calculated for **1–3**. Extended Hückel theory (EHT) calculations were performed on a model geometry derived from that of 1-methylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione. The PE spectroscopic results, together with the results of ab initio and EHT calculations, support the following conclusions: (i) oxygen lone pair interactions in **1** are mainly through-bond, where π and π^* C=O bond interactions in **1** occur via a mixture of through-space and through-bond mechanisms; (ii) mixing with the σ-framework orbitals plays an important role in delocalizing the oxygen lone pair in **2**; (iii) lone pair delocalization in **1** and **2** occurs primarily via 1,3- rather than 1,2-interactions; and (iv) both through-bond and through-space mechanisms play a role in **3**.

Substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (PCUDs) recently have received considerable attention as intermediates in the synthesis of tricyclopentanoid natural products.[2,3] In our studies of the synthesis and chemistry of new substituted PCUDs,[4-10] we have sought to synthesize novel cage alkenes that might serve as useful precursors to new, substituted, linearly fused cis,syn,cis triquinanes.[3] The PCUD cage system is also of interest in terms of the degree of interaction that can take place between substituents in the 8- and 11-positions. Such "proximity effects"[11] can significantly influence chemical and spectroscopic properties. We report here the syntheses and the results of a photoelectron (PE) spectroscopic investigation of several substituted PCUDs. The through-bond and through-space components of the proximity effect depend upon the nature of the substituents present at the 8- and 11-positions. The effects observed in the PE spectra are analyzed in terms of ab initio and semiempirical molecular orbital calculations.

Syntheses. Recently, we reported the syntheses of compounds **2** and **3** via Peterson reaction[12,13] of (trimethylsilyl)magnesium chloride with **1** and **2**, respectively.[9] We now report the syntheses of four new alkene-substituted PCUDs, **4–7**, and a closely related oxirane, **8**. Compounds **9** and **10** also were prepared in connection with this study.[9]





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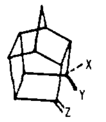
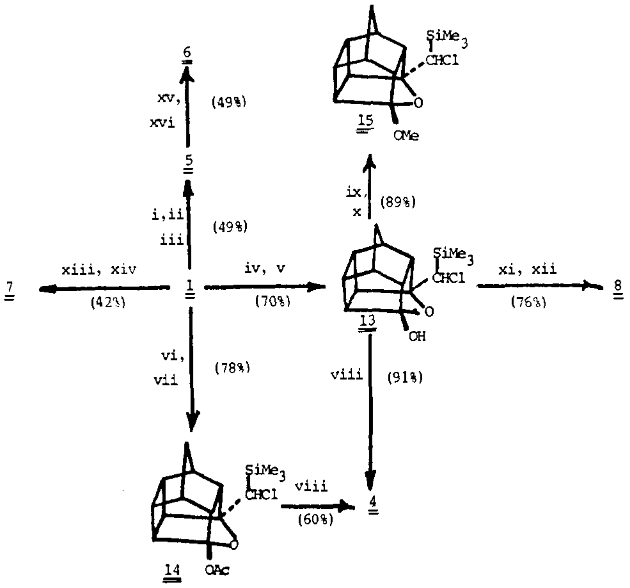


1: X = Y = O
2: X = O, Y = CH$_2$
3: X = Y = CH$_2$
4: X = O, Y = CHCl
5: X = O, Y = CHSiMe$_3$
6: X = CH$_2$, Y = CHSiMe$_3$
7: X = Y = CHSiMe$_3$
9: X = Y = H, Z = O
10: X = Y = H, Z = CH$_2$

Scheme I[a]



[a] (i) LiCH(SiMe$_3$)$_2$, THF–HMPA (4:1), −60 °C; (ii) CH$_3$COCl, reflux 3 h; (iii) CF$_3$CO$_2$H, reflux 2 h; (iv) Me$_3$SiCH(Cl)Li, −70 °C; (v) aqueous NH$_4$Cl, −60 °C; (vi) Me$_3$SiCH(Cl)Li, −70 °C; (vii) CH$_3$COCl, dry THF; (viii) F$_3$B·OEt$_2$, CH$_2$Cl$_2$; (ix) KH, dry THF, −60 °C; (x) (MeO)$_2$SO$_2$; (xi) KH, dry THF, −5 °C; (xii) 5% aqueous NH$_4$Cl solution; (xiii) 2LiCH(SiMe$_3$)$_2$, −60 °C; (xiv) saturated aqueous NH$_4$Cl solution; (xv) Me$_3$SiCH$_2$MgCl, dry THF; (xvi) SOCl$_2$, reflux.

Peterson olefination of diketone **1** with (bis(trimethylsilyl)methyl)lithium (**11**)[14] provided a means for synthesizing **5** and **7** (Scheme I). Reaction of **1** with **11** at −60 °C followed by treatment of the reaction mixture first with acetyl chloride and then with trifluoroacetic acid afforded **5** in 49% yield. Reaction of **1** with 2 mol of (bis(trimethylsilyl)methyl)lithium at −60 °C followed by quenching with aqueous ammonium chloride solution afforded diene **7** as a mixture of diastereoisomers (syn,sym, syn,anti, and anti,anti; 42%).

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[1] This paper constitutes part 2 of the series "Synthesis of Alkene-Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes". For part 1, see ref **9**.

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Table I. Summary of Photoelectron Spectroscopic Results

compd	vertical IP's measured from spectra, eV
1	9.1, 9.65 (n_- and n_+)
2	8.95 (n_0), 9.55 (π)
3	8.95 (π_+), 9.40 (π_-)
4	9.0–9.1 ($n_0 + \pi_{CC}$), 11.4 (n_{Cl}), 11.75 (n_{Cl})
5	8.7–8.9 ($n_0 + \pi_{CC}$)
6	8.6–9.1 (broad band, $\pi_+ + \pi_-$)
7	8.85 ($\pi_+ + \pi_-$)
8	9.75 (n_0 or C=O), 8.6–8.7 (n_0 of epoxide)
9	8.8 (n_0)
10	9.0 (π)

In addition, reaction of **1** with ((trimethylsilyl)chloromethyl)lithium (**12**)[15] at −70 °C followed by quenching with aqueous ammonium chloride solution at −60 °C afforded hemiketal **13** (70%). Upon treatment with boron trifluoride etherate, **13** eliminated the elements of Me_3SiOH to afford **4** as a mixture of syn and anti isomers (91%). Alternatively, **4** could be synthesized via the corresponding hemiketal acetate **14** (60% overall yield; see Scheme I and Experimental Section).

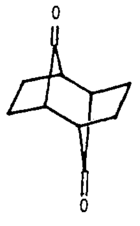
Interestingly, **13** could be further elaborated into monomethyl ketal **15** and into oxirane **8** via reaction with potassium hydride. When this reaction was performed at −60 °C and then quenched by addition of dimethyl sulfate, **15** was formed in 89% overall yield. However, when **13** instead was reacted with potassium hydride at room temperature, oxirane **8** was formed (mixture of diastereoisomers, 76%).[16]

One feature of the reactions depicted in Scheme I merits comment. It should be noted that these reactions result in selective conversion of only *one* of the two chemically identical carbonyl groups in symmetrical dione **1**; two new unsymmetrical enone systems (**4** and **5**) and an unsymmetrical keto oxirane (**8**) are thereby produced.

Finally, Peterson reaction of enone **5** with (bis(trimethylsilyl)methyl)lithium followed by treatment of the reaction mixture with thionyl chloride[9] afforded the corresponding monotrimethylsilylated diene **6** (49%).

PE Spectra. Vertical ionization potentials (IPs) obtained for compounds **1**–**10** are presented in Table I. Their PE spectra provide straightforward evidence for the operation of a proximity effect in this family of compounds.

The PE spectrum of diketone **1** displays a significant splitting of the oxygen lone pair n_0 levels (0.55 eV). Earlier examples of the operation of a 1,6-n,n interaction in 1,4-diketones have been reported.[11,18,19,28] Splittings of only 0.15–0.16 eV are observed for the n_0 levels of 1,4-cyclohexanedione and of 2,5-norbornanedione. A somewhat larger splitting (ca. 0.4 eV) has been reported by Martin[11] for **16**, while a splitting of almost 1 eV has been reported for **18** (vide infra).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The relative orderings of the n_+ and n_- orbital levels in these 1,4-diketones cannot be ascertained by experiment in a straightforward way. However, we observe that the shapes of the two n_0 bands differ in the PE spectrum of **1**, the higher IP band being the sharper of the two. The contribution from the through-space interaction between the oxygen atoms to the splitting undoubtedly is very small, simply because the oxygen atoms in **1** are relatively far apart (i.e., 4.05 Å; vide infra). Also, literature precedent suggests that through-space interactions between n_0 lone pairs in diketones generally are quite small even in molecules which possess optimal geometries.[20] Thus, in cyclic α-diketones (e.g., 2,3-norbornanedione), the large n_+/n_- splittings that are encountered (>1.5 eV) result chiefly from a strong through-bond effect relayed via the σ-orbital associated with the carbon–carbon bond linking the keto functionalities.

The mean of the n_0 IPs of diketone **1** is 9.38 eV, which is 0.58 eV higher than the n_0 IP of monoketone **9**. This value coincides with that reported by Houk and co-workers[21] for the inductive shift of the second keto group that occurs upon proceeding from cyclohexanone to 1,4-cyclohexanedione. Slightly smaller inductive shifts have been reported for bridged 1,4-cyclohexanediones,[18] whereas somewhat larger values (by ca. 0.8 eV) have been reported in the case of α-diketones.[20]

PE spectroscopy has been utilized extensively for the study of 1,4-π,π interactions in 1,5-dienes.[11] Diene **3** is a particularly interesting example in this regard since the p-orbitals on C-8 and C-11 are so oriented that the operation of a significant through-space interaction is possible. Such a through-space interaction could also affect the energies of the C=O π molecular orbital levels of diketone **1**, but these bands are not visible in the PE spectrum of **1** (i.e., they merge with the bands due to the σ-framework in this compound; vide infra).

The observed π–π splitting for **3** (i.e., ca. 0.45 eV) is similar to that observed in 1,5-hexadiene.[22] It has been suggested previously by other investigators[23] that the through-bond interaction mechanism is dominant in **3**. However, as we pointed out in a preliminary communication,[24] the experimental basis for the earlier claim is suspect, since our measured IPs do not agree with the earlier reported[23] values. In particular, we find that the two π IPs of diene **3** are *not* both lower than that of the corresponding model monoene (**10** in the present study).

Comparison of the PE spectra of enone **2** with those of **4** and **5** indicated that the HOMO of **2** is of n_0-type and not of π-type. Substitution on the carbon–carbon double bond by either chloro or trimethylsilyl groups results in the second band in the PE spectrum of **3** becoming shifted to lower IP. Thus, it is this band that must be associated with an orbital that is predominantly carbon–carbon π-bonding. It should be noted that the second IP of **2** (which corresponds to the highest π molecular orbital in this compound) is almost 0.6 eV higher than the first IP of diene **3**. This result reflects the operation of a significant proximity effect in this compound which involves both the electron-withdrawing carbonyl groups and the proximate alkene functionality.

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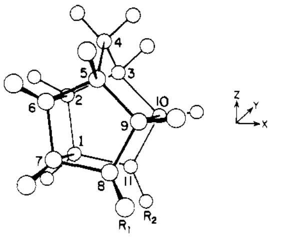
Table II. Calculated Heavy-Atom Bond Lengths (Å) for **1**, **2**, and **3**



parameter	**1** (calcd) $R_1 = R_2 = O$	**1** (exptl) $R_1 = R_1 = O$	**3** (calcd) $R_1 = R_2 = CH_2$	**2** (calcd) $R_1 = O$, $R_2 = CH_2$
$r(C_1-C_7)$	1.572	1.589	1.575	1.573
$r(C_7-C_8)$	1.542	1.510	1.523	1.543
$r(C_1-C_{11})$	1.542	1.510	1.523	1.523
$r(C_6-C_7)$	1.557	1.563	1.561	1.557
$r(C_1-C_2)$	1.557	1.559	1.561	1.561
$r(C_8-C_9)$	1.547	1.518	1.527	1.547
$r(C_9-C_{10})$	1.547	1.515	1.527	1.527
$r(C_8-R_1)$	1.214	1.213	1.308	1.213
$r(C_{11}-R_2)$	1.214	1.212	1.308	1.308
$r(C_9-C_{10})$	1.579	1.589	1.585	1.583
$r(C_5-C_9)$	1.555	1.551	1.558	1.555
$r(C_3-C_{10})$	1.555	1.557	1.558	1.560
$r(C_5-C_6)$	1.559	1.557	1.556	1.559
$r(C_2-C_3)$	1.559	1.562	1.556	1.556
$r(C_4-C_5)$	1.540	1.524	1.539	1.539
$r(C_3-C_4)$	1.540	1.532	1.539	1.538
$r(C_2-C_6)$	1.556	1.553	1.556	1.555

The PE spectra of trimethylsilyl-substituted dienes **6** and **7** also were studied. These compounds were synthesized as mixtures of *Z* and *E* diastereoisomers, so the spectrum obtained for each of these compounds does not correspond to that of a single, pure compound. We observed that trimethylsilyl substitution results in a lower mean π IP for **7** vis-à-vis that of **3** (by ca. 0.3 eV). This result is a predictable consequence of introducing electron-donating groups onto a carbon–carbon double bond. No clear splitting of the π-levels is observed in the PE spectrum, probably because the diastereoisomers present each display slightly different PE spectra, resulting in overlapping spectra wherein the small valley between the two π-bands becomes obscured. Similarly, since **6** also was synthesized as a diastereoisomeric mixture, again it was not possible to resolve the separate π-bands in its PE spectrum.

Finally, we note that the PE spectrum of **8** indicates that there is little or no interaction between the epoxide oxygen lone pair and the carbonyl oxygen lone pair in this compound. Note that the first IP of **8** almost coincides with that of monoketone **9**.

MO Calculations. The geometries of **1**–**3** have been optimized by using a minimal STO-3G basis set. The heavy-atom bond distances for the optimized geometries are given in Table II. Molecular coordinates are given as Supplementary Material. The crystal structure of the 1-methyl derivative of **1** has been determined,[10] and we compare our calculated values to those for the unsubstituted side of the molecule as appropriate. The agreement between the calculated and experimental structures is excellent, especially considering our use of a minimum basis set. The only major differences between the two structures are that the calculated C(7)–C(8) [C(1)–C(11)] and C(8)–C(9) [C(10)–C(11)] bond lengths are longer by 0.03 Å than the corresponding experimental values. However, all of the trends, including the long C(9)–C(10) and C(1)–C(7) bonds, are reproduced by theory.

Substitution of the carbonyl oxygen atoms in **1** by methylene groups (i.e., CH_2 groups, to form **3**) only leads to small changes in the overall structural framework. The C(7)–C(8) [C(2)–C(11)] and C(8)–C(9) [C(10)–C(11)] bond distances decrease by 0.02 Å in **3** as compared to **1**. The only other significant change is the increase of 0.006 Å in r[C(9)–C(10)] in **3**.

Table III. Molecular Orbital Levels and Populations

1, $R_1 = R_2 = O^a$

	HOMO	NHOMO		
		n_+	π_+	π_-
eigenvalue, eV	7.90	8.91	10.23	11.44
$q(R_1,R_2)$	0.47	0.52	0.38	0.32
$q(C_1,C_7)$	0.16	0.18	0.18	
$q(C_9,C_{10})$	0.14	0.14	0.13	
$q(C_8,C_{11})$	0.11	0.04	0.14	0.22
q(other)				0.17 (C_3, C_5) 0.23 (C_4)

2, $R_1 = O$, $R_2 = CH_2{}^b$

	HOMO n_O	NHOMO π_{CC}
eigenvalue, eV	8.02	8.28
q	0.90 (R_1)	0.88 (R_2)
q	0.30 (C_7)	0.64 (C_{11})
q	0.26 (C_9)	0.08 (C_7)
q	0.14 (C_8)	0.08 (C_9)
q	0.06 (C_1)	
q	0.06 (C_{11})	

3, $R_1 = R_2 = CH_2{}^c$

	HOMO π_+	HOMO π_-
eigenvalue, eV	7.78	8.38
$q(R_1,R_2)$	0.46	0.50
$q(C_8,C_{11})$	0.29	0.41
$q(C_1,C_7)$	0.09	
$q(C_9,C_{10})$	0.07	

[a] σ orbitals at 10.68 (a″), 10.99 (a′), and 11.20 (a″) eV. LUMO at −7.64 (a′) eV ($\pi_+{}^*$) and NLUMO at −7.68 (a″) eV ($\pi_-{}^*$). [b] σ orbitals at 10.00 eV, π_{CO} at 10.44 eV. LUMO at −7.95 eV ($\pi_{CO}{}^*$) and NLUMO at −8.56 eV ($\pi_{CC}{}^*$). [c] σ orbitals at 9.57 (a″), 9.91 (a′), 10.40 (a″), 10.77 (a″), and 11.03 (a′) eV. LUMO at −8.73 eV (a″) ($\pi_-{}^*$) and NLUMO at −8.88 (a′) eV ($\pi_+{}^*$).

Substitution of one of the carbonyl oxygen atoms in **1** by CH_2 (to afford **2**) destroys the symmetry of the molecule. The carbon–carbon bond distances in each of the five-membered rings [C(5)–C(6)–C(7)–C(8)–C(9) and C(1)–C(2)–C(3)–C(10)–C(11)] are essentially the same as were found for each such ring in the corresponding symmetric structures (i.e., **1** and **3**, respectively).

The force fields show that the calculated structures are minima. Here, we present the corresponding results for the stretching frequencies of the double bonds. (The total set of calculated frequencies is given as Supplementary Material.) The calculated stretching frequencies are too high by ca. 20%[25] due to (i) our neglect of anharmonic and correlation effects (ca. 10%) and (ii) our use of a small basis set (ca. 10%). We calculate the carbonyl stretching frequencies in **1** at 2165 cm^{-1}, I = 60 km/mol[26] and 2159 cm^{-1}, I = 37 km/mol as compared to experimental values of 1742 and 1720 cm^{-1}, respectively. (This result gives a scale factor of 0.804.) The higher frequency vibration is due to the symmetric coupling of the C=O stretches, while the lower value is due to the corresponding asymmetric coupling. We note that the theoretical splitting is somewhat smaller than the experimental value.

The C=C stretches for **3** are calculated to be slightly split at 2110 cm^{-1}, I = 0.9 km/mol and 2108 cm^{-1}, I = 0.2 km/mol, respectively. Only one band is observed experimentally for the C=C stretching vibration (i.e., at 1675 cm^{-1}), consistent with the small splitting and low predicted intensities. (Here, a scale factor of 0.794 is required.) Again, the symmetric coupling of the two double-bond stretches is at higher frequency.

For **2**, the C=O stretch is calculated to be 2164 cm^{-1}, I = 52 km/mol, and the C=C stretch is calculated to be 2108 cm^{-1}, I = 0.2 km/mol. The corresponding experimental values are 1740 and 1668 cm^{-1}, respectively. The calculated splitting is slightly

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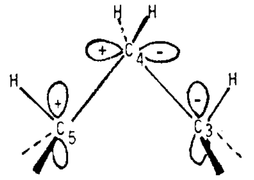
(25) Dixon, D. A.; Miller, J. S. *J. Am. Chem. Soc.*, in press.

(26) The calculated infrared intensities are not meant to be quantitative. The values are reported for qualitative trends in the spirit of the strong, medium, weak terminology employed in the spectroscopic literature.

smaller than the observed splitting, consistent with the scale factors for C=O and C=C stretches differing by 1%. Comparison of the values for **2** with those for **1** and for **3** reveals little effect of asymmetry on the calculated frequency values.

The population and symmetry analyses of various high-lying MOs are given in Table III. The HOMO of **1** is the n_- orbital (i.e., the asymmetric combination of oxygen lone pairs, a″) while the NHOMO is the n_+ orbital (i.e., the symmetric combination of oxygen lone pairs, a′). The calculated splitting, 1.0 eV, is larger than the experimental splitting of 0.55 eV. Both the HOMO and NHOMO are highly delocalized to the σ-framework with only 0.47 e on each oxygen in the HOMO and 0.52 e on each oxygen in the NHOMO. Thus, only 0.99 e is localized on oxygen in the top two orbitals. For both orbitals, the next largest population is found at C(1) [C(7)], 0.16 e, while there is 0.14 e on C(9) [C(10)]. Note that these both involve 1,3-interactions with the oxygen. The largest interaction that involves the oxygen lone pairs, thus, is with the C(1)–C(7) bond. This result is not surprising, since the C(1)–C(7) bond (which forms part of a four-membered ring) is more strained than the C(9)–C(10) bond (which forms part of a five-membered ring). The next highest lying orbital (10.23 eV) corresponds to the highly delocalized symmetric combination (a′) of the C=O π-orbitals (π_+). In fact, C(1) [C(7)] have larger populations than do C(8) [C(11)]. There is also a significant delocalization to C(9) [C(10)]. The next three highest lying orbitals involve the σ-framework; they lie at 10.68 (a″), 10.99 (a′), and 11.20 eV (a″). The delocalized asymmetric combination of C=O π-orbitals, π_-, lies at 11.40 eV. Delocalization of this orbital involves the antisymmetric combination of the C(4)–C(5) and C(3)–C(4) σ-bonds with a significant amount of electron density on C(4) (i.e., 0.23 eV):



The LUMO for **1** is the $\pi_+{}^*$-orbital, while the NLUMO is the $\pi_-{}^*$-orbital. The orbital splitting is predicted to be very small (i.e., 0.04 eV). The above results are all consistent with a through-bond interaction dominating the splitting of the two lone pair orbitals on oxygen in **1**.

The HOMO for **3** is the π_+-combination of the C=C bonds, while the NHOMO is the π_--orbital. The calculated splitting, 0.6 eV, agrees well with the experimental value of 0.45 eV. The HOMO in **3** is more highly localized in the C=C bond (i.e., 0.75 e per bond) as compared to the degree of localization of the lone pair on the oxygen atom in the HOMO of **1**. Consequently, there is only a population of 0.09 e on C(1) [C(7)] and of 0.07 e on C(9) [C(10)] in the HOMO of **3**. However, the HOMO is delocalized beyond the double bonds, thereby suggesting the existence of some through-bond interactions (this point is addressed further, below). The NHOMO for **3** is even more highly localized (i.e., 0.91 e in each C=C bond). The next five orbitals involve the σ-framework and range in energy from 9.57 (a″) to 11.03 eV (a′). The LUMO for **3** is the π_--orbital; the π_+-orbital (NLUMO) is 0.15 eV higher in energy.

The presence of through-bond coupling in **3** (a 1,4-diene) is consistent with predictions based upon STO-3G calculations for 1,5-dienes.[27] The results of these calculations indicate that through-bond interactions are dominant when the torsion angle about the C(3)–C(4) bond is greater than 30°; this leads to $IP(\pi_+) < IP(\pi_-)$, as is the case for **3**.

Although the calculated absolute values for the IPs of **1** and of **3** are lower than the experimental value by ca. 1.0 eV, the IP of **3** is predicted to be 0.12 eV lower than the IP of **1**. This latter result is in good agreement with the observed difference, 0.15 eV. The similarity of the two IPs is consistent with our measurements and is not consistent with the experimental results. The HOMO for **2** is calculated to be the lone pair on oxygen, n_0, as is observed experimentally. Again, the calculations predict the orbital to be quite highly delocalized, as is indeed observed for **1** (for which only 0.90 e resides on the carbonyl oxygen atom). Significant delocalizations occur to C(7) (0.30 e) and to C(9) (0.26 e), a result which again demonstrates the importance of 1,3-interactions (as was the case for **1**). Only 0.14 e is delocalized to C(8), and there are small populations (i.e., 0.06 e) on C(1) and on C(10), the other carbon atoms that are involved in the single bonds to C(7) and to C(9), respectively. The NHOMO is calculated to be 0.26 eV lower in energy as compared to an experimental splitting of 0.6 eV and is best described as being the C=C π-orbital. As found in **3**, this π_{CC}-orbital is more highly localized in the C=C double bond (i.e., 1.52 e), yet there is still a delocalization of almost 0.5 e. Surprisingly, the largest delocalizations are 0.08 e to C(7) and to C(9), which are not in the 1,3-interaction pathway. There is also a small contribution of 0.06 e from the oxygen atom. The carbonyl π-bond is at 10.44 eV but is highly delocalized, only 0.30 e remaining on oxygen and 0.15 e on C(8), just as was observed in **1**.

The electronic structure of **2** provides some interesting insights into the interactions that occur in **1** and in **3**. The lone pair on oxygen in **2** is delocalized, even though there is no possibility for mixing with another lone pair. This result demonstrates that mixing with the σ-framework orbitals plays an important role in delocalizing the oxygen lone pair. The importance of lone pair delocalization in **1** and **2** via 1,3-interactions and *not* to the adjacent carbon atoms is consistent with a model that minimizes electron repulsion between C(8) and C(11). If electron density accumulates at C(8) and C(11), then the through-space interaction will be both large and repulsive, since occupied orbitals on one atom must interact with occupied orbitals on the other. Thus, the 1,2-interactions will be small. This conclusion is consistent with the results of Mulliken charge analysis in **1** and in **2**; here, C(8) and C(11) in **1** bear a positive charge (i.e., +0.19 e), and C(8) in **2** also bears a positive charge (i.e., 0.20 e). Again, to minimize the repulsive interaction between C(8) and C(11), the π-orbitals in **3** are polarized toward the exocyclic methylene carbon atom. Of course, this polarization will tend to decrease the importance of through-space interactions and to increase the effect of through-bond interactions in this system.

Additional insight into the importance of through-space vs through-bond interactions can be obtained from calculations where matrix elements that correspond to through-space or to through-bond interactions have been deleted at the extended Hückel theory (EHT) level. When matrix elements that correspond to through-space interactions were deleted, small changes resulted in the IPs of the n_-- and n_+-orbitals on **1**. However, when matrix elements that correspond to through-bond interactions were deleted, the ordering of n_- and n_+ was reversed. Considerable through-space interactions in **1** might be expected between the carbonyl π-orbitals, since these would be σ-type interactions between the π-bonds. The occupied π MOs have small electron populations on the carbon atoms and large populations on the oxygen atoms, as discussed above. Thus, the through-space interaction again may not be significant in the occupied π-orbitals. However, the coefficients should be reversed in the unoccupied π^*-orbitals, and the larger coefficients should exist on the carbon atoms that lead to the maximum through-space interaction. When the (through-space) overlap between the orbitals on C(8) and C(11) was deleted, significantly enhanced splitting of the $\pi_-{}^*$- and $\pi_+{}^*$-orbitals resulted. The through-bond interactions that affect the energies of the HOMO and NHOMO do not have a corresponding effect upon those of the $\pi_-{}^*$- and $\pi_+{}^*$-orbitals. By way of contrast, σ-type through-bond interactions do, in fact, affect the energies of the $\pi_-{}^*$- and $\pi_+{}^*$-orbitals. Thus, the π^*-orbitals are capable of interacting via a mixture of through-space and through-bond mechanisms.

Similar EHT calculations were carried out for the dimethylene derivative, **3**. The largest through-space interactions in **3** would be expected to occur between atoms C(8) and C(11). When

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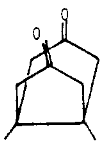
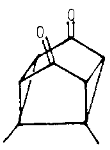
overlap between orbitals on atoms C(8) and C(11) is deleted, increased splitting between π_- and π_+ occurs along with an even larger splitting between π_-^* and π_+^*. Although through-space interactions play a role in **3**, through-bond interactions also may be important. When through-bond interactions are deleted in **3**, π_- and π_+ become essentially degenerate. The corresponding effect upon π_-^* and π_+^* is even more pronounced; their relative ordering becomes reversed when through-bond interactions are deleted. The foregoing results suggest that both through-bond and through-space interaction mechanisms play a role in **3**.

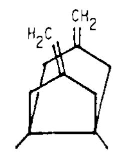
Photoelectron spectroscopy[28] and electron transmission spectroscopy[29] have been utilized to study the orbital interactions in systems **17–20**. The HOMO, NHOMO, LUMO, and NLUMO assignments were based upon the results of MINDO/3,[30] HAM/3,[31] or STO-3G[32] calculations on MINDO/3 or scaled MINDO/3 geometries. The n_- (HOMO)–n_+ (NHOMO) split in **17** is 0.27 eV; this splitting increases to 0.94 eV in **18**. This observation is consistent with the results of the present study; the strained 1,3-interactions that are present in **18** but not in **17** should lead to increased splitting, as is, in fact, observed. For **19**, the HOMO is the π_--orbital and the NHOMO (i.e., π_+) is only lower in energy by 0.2 eV. In **20**, not only as the IP decreased, but the HOMO is the π_+-orbital, and the π_--orbital (with one σ-orbital interleaved) is 1.16 eV lower in energy. Again, the presence of the strained 1,3-interactions leads to the π_+-orbital becoming the HOMO in **20**, as was observed to be the case in **3**.



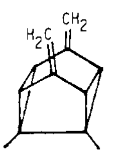
17



18



19



20

The results for the unoccupied molecular orbitals in **18** and **20** could be quite different from our results in **1** and **3**, respectively. The LUMO and NLUMO in **1** and **3** are predicted to be nearly degenerate, whereas a large splitting is predicted for the corresponding orbitals in **18** and **20**. Structural features, i.e., the increased strain in the 1,3-interactions in **18** and in **20**, could render through-bond interactions more pronounced than through-space interactions for the π^*-orbitals, in contrast with our results.

Experimental Section

General. Melting points and boiling points are uncorrected. Proton NMR spectra (90 MHz) and ^{13}C NMR spectra were recorded on a JEOL FX-90-Q NMR spectrometer. In all cases, signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer Model 1330 infrared spectrophotometer. Mass spectra were obtained with a Hewlett-Packard Model 5790A GC-MS (70 eV). High-resolution mass spectra were obtained on an AEI MS-9 double-focusing high-resolution mass spectrometer. Tetrahydrofuran (THF) was dried via distillation from sodium–potassium alloy. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and by Midwest Microlab, Ltd., Indianapolis, IN.

UV PE spectra were obtained with a modified Perkin-Elmer PS-16 PE spectrometer equipped with a He I light source. Calibration of spectra was accomplished by adding traces of argon to provide marker peaks. The scale linearity was checked by measurement of the anthracene spectrum, which provides a number of sharp peaks over the IP range of particular interest to the present study. Repetitive spectra were obtained for all samples over a period of 1 day or longer to ensure that all traces of volatile impurities (e.g., water, solvents used in preparations and/or during workup, and the like) were removed and therefore would not interfere with the measurements.

Calculations. Molecular orbital calculations on systems **1–3** were performed with an STO-3G basis set.[32] The geometries were gradient optimized[33] with the program HONDO[34] on an IBM-3081 computer. The molecular force fields, infrared intensities, and MP-2 correlation corrections were calculated with the program GRADSCF[36] on a Cray-1A computer by using analytic methods.[37] Ionization potentials were calculated by using Koopmans' theorem. Extended-Hückel calculations[38] were performed on a model geometry derived from experiment.[10] In order to examine the effect of through-space and through-bond interactions in **1** and **3**, various overlap contributions were neglected in the overlap matrix. For example, in **1**, through-space interactions between C(8) and C(11) were examined by deleting overlap between orbitals on C(8) and C(11). Through-bond interactions in **1** were examined, e.g., by deleting the overlap between appropriate p_x- and p_y-orbitals on C(1) and on C(7) with minimal disruption of the C(1)–C(7) bond. The data thereby obtained are presented in Figures 1 and 2 in the Supplementary Material.

8-((Trimethylsilyl)methylene)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-11-one (5). To a solution of bis(trimethylsilyl)methane (4.82 g, 0.03 mol) in 4:1 tetrahydrofuran–hexamethylphosphoric triamide (THF–HMPA) mixed solvent (60 mL) was added *tert*-butyllithium (15 mL of a 2 M solution in pentane, 0.03 mol) at −80 °C during 20 min.[14] The resulting solution was stirred at −60 °C under argon (10 h). The reaction mixture was then transferred (double-ended needle) into a solution of **1** (5.226 g, 0.03 mol) in dry THF (30 mL) which has maintained at −60 °C; the transfer was completed in 1 h. The resulting mixture was stirred at −60 °C (5 h) and then was allowed to warm slowly to room temperature and stirred overnight. Acetyl chloride (2.353 g, 0.03 mol) was then added to the reaction mixture, and the resulting solution was refluxed (3 h). Trifluoroacetic acid (3.42 g, 0.03 mol) was then added, and refluxing was continued (2 h). The reaction mixture was then allowed to cool to room temperature and stirred overnight. The resulting mixture was poured into water (150 mL), stirred (10 min), and then extracted with ether. The combined organic layers were washed with brine and then dried (anhydrous magnesium sulfate). The ethereal solution was then filtered, and the filtrate was concentrated in vacuo to afford an oil (5.85 g). This material was found by GC analysis to consist of **5** and **7** (ratio 4:1). The mixture of products was separated by careful elution chromatography on silica gel adsorbent. Initial elution with pentane afforded **7**; further elution with methylene chloride–pentane mixed solvent (1:1) afforded **5** (4.03 g). An analytical sample of **5** was obtained via vacuum distillation; pure **5** (a single diastereoisomer of unknown configuration, 3.59 g, 49%) was obtained as a colorless oil: bp 92–93 °C (0.01 mm); ^{1}H NMR (CDCl$_3$) δ −0.10 (s, 9 H), 1.47 (A*B*, J_{AB} = 11 Hz, 1 H), 1.75 (*A*B, J_{AB} = 11 Hz, 1 H), 2.11–3.30 (m, 8 H), 5.20 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ −0.20 (q, 3 C), 36.5. (d), 38.43 (t), 41.36 (d), 43.31 (d), 43.96 (d), 45.85 (d), 47.20 (d), 54.96 (d), 57.28 (d), 120.56 (d), 158.48 (s), 215.47 (s); IR (film) 2955 (vs), 2870 (m), 1740 (vs), 1637 (s), 1525 (s), 1073 (m), 880 (vs), 850 (vs), 768 (m), 700 cm^{-1} (m); mass spectrum (70 eV), *m/e* (relative intensity) 244.2 (molecular ion, 1.3), 229.1 (49.7), 156.1 (13.7), 155.1 (100.0), 154.2 (9.6), 153.1 (15.2), 128.1 (9.2), 115.0 (11.6), 77.0 (9.7), 75.0 (13.4), 73.0 (21.5), 59.0 (12.7), 45.0 (21.5), 43.0 (20.5).

Anal. Calcd for $C_{15}H_{20}OSi$: C, 73.71; H, 8.25. Found: C, 73.53; H, 8.40.

8-((Trimethylsilyl)methylene)-11-methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (6). A solution of [(trimethylsilyl)methyl]magnesium chloride in dry THF was prepared by reacting (trimethylsilyl)chloromethane (0.53 g, 4.5 mmol) and Mg (0.12 g, 4.9 mmol) in dry THF (10 mL). To this solution under argon was added a solution of **5** (1.05 g, 4.3 mmol) in dry THF (5 mL). The resulting mixture was refluxed (5.5 h) and then cooled by external application of an ice bath. To the cooled reaction mixture was added thionyl chloride

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(0.512 g, 4.3 mmol), and the resulting mixture was stirred at room temperature (2 h) and then refluxed (1 h). The reaction mixture was then poured into water (75 mL), and the layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried (anhydrous magnesium sulfate), and filtered. The filtrate was concentrated in vacuo to afford crude **6**. The crude product was purified via column chromatography on silica gel (pentane eluent); pure **6** (mixture of *Z* and *E* diastereoisomers, 0.51 g, 49%) was thereby obtained as a colorless oil: bp 55 °C (0.01 mm); ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 1.39 (A*B*, J_{AB} = 11 Hz, 1 H), 1.74 (*A*B, J_{AB} = 11 Hz, 1 H), 2.27–3.25 (m, 8 H), 4.52–4.64 (m, 2 H), 5.09–5.20 (singlets, total 1 H); ^{13}C NMR ($CDCl_3$) δ 0.46 (q, 3 C), 36.59 (t), 36.86 (t), 41.46 (d), 42.55 (d), 42.71 (d), 42.98 (d), 44.61 (d), 44.93 (d), 46.23 (d), 47.20 (d), 50.94 (d), 52.46 (d), 52.84 (d), 53.11 (d), 56.41 (d), 102.73 (t), 117.74 (d), 153.44 (s), 163.30 (s); IR (film) 3037 (w), 2960 (s), 2875 (w), 1666 (w), 1640 (m), 1252 (s), 872 cm^{-1} (s); mass spectrum (70 eV), *m/e* (relative intensity) 242.1490 (molecular ion, 2.80), 171.1133 ($C_{13}H_{15}$, 14.52), 170.1096 ($C_{13}H_{14}$, 100.00), 169.1015 ($C_{13}H_{13}$, 28.68), 155.0864 ($C_{12}H_{11}$, 53.33), 154.0781 ($C_{12}H_{10}$, 11.76), 142.0780 ($C_{11}H_{10}$, 27.00), 141.0706 ($C_{11}H_9$, 27.75), 129.0703 ($C_{10}H_9$, 33.76), 128.0627 ($C_{10}H_8$, 25.31), 116.0620 (C_9H_8, 13.00), 115.0549 (C_9H_7, 22.62), 105.0707 (C_8H_9, 30.76), 92.0622 (C_7H_8, 46.77), 91.0550 (C_7H_7, 89.12), 79.0549 (C_6H_7, 95.82), 78.0470 (C_6H_6, 31.39), 77.0393 (C_6H_5, 20.41), 73.0477 (C_3H_9Si, 11.79), 65.0404 (C_5H_5, 14.04).

Anal. Calcd for $C_{16}H_{22}Si$: M_r 242.1495. Found (high-resolution mass spectrometry): M_r 242.1490.

1-Hydroxy-12-oxa-6-(chloro(trimethylsilyl)methyl)hexacyclo-[5.4.1.0^{2,5}.0^{3,10}.0^{4,8}.0^{7,11}]dodecane (13). To a precooled solution (−70 °C) of *sec*-butyllithium (23 mL of a 1.35 M solution in cyclohexane, 0.03 mol) under argon in dry THF (30 mL) was added (chloromethyl)trimethylsilane (3.681 g, 0.03 mol).[15] The resulting solution was stirred at −70 °C (1 h), at which time a solution of **1** (5.226 g, 0.03 mol) in dry THF (25 mL) was added. The reaction mixture was then stirred at −70 °C (5 h). Saturated aqueous ammonium chloride solution (100 mL) was then added to the reaction mixture at −60 °C, and the resulting mixture was stirred at −50 °C (30 min). The mixture was then warmed slowly to room temperature, and the layers were separated. The aqueous layer was extracted with ether, and the ether extracts were added to the organic layer. The combined organic layers were washed with brine, dried (anhydrous magnesium sulfate), and filtered. The filtrate was concentrated in vacuo to afford a solid residue (8.02 g). This material was recrystallized from carbon tetrachloride–hexane mixed solvent (2:3), affording pure **13** (mixture of diastereoisomers) as a colorless microcrystalline solid (6.23 g, 70%): mp 138.5–139.8 °C; ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 1.34 (A*B*, J_{AB} = 10 Hz, 1 H), 1.70 (*A*B, J_{AB} = 10 Hz, 1 H), 2.16–2.81 (m, 8 H), 3.53 (s, 1 H), 5.10 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ −1.71 (q, 3 C), −1.50 (q, 3 C), 38.59 (d), 40.33 (d), 41.63 (d), 42.06 (d), 43.0. (t), 43.63 (d), 43.79 (d), 44.50 (d), 44.82 (d), 45.26 (d), 47.42 (d), 47.75 (d), 51.32 (d), 54.57 (d), 57.06 (d), 57.44 (d), 57.66 (d), 94.12 (s), 117.52 (s); IR (film) 3354 (s, br), 2973 (s), 1352 (s), 1298 (m), 1258 (s), 1221 (m), 1156 (s), 1031 (m), 852 cm^{-1} (s); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 245.1 (30.7), 155.0 (37.7), 151.1 (49.1), 77.0 (34.2), 74.9 (43.9), 73.0 (100.0), 45.0 (49.1), 44.0 (31.6), 42.9 (30.7), 40.0 (34.2).

Anal. Calcd for $C_{17}H_{23}ClO_3Si$: C, 60.69; H, 7.13. Found: C, 60.41; H, 7.20.

1-Acetoxy-12-oxa-6-(chloro(trimethylsilyl)methyl)hexacyclo-[5.4.1.0^{2,5}.0^{3,10}.0^{4,8}.0^{7,11}]dodecane (14). To a precooled (−70 °C) solution of *sec*-butyllithium (111.5 mL of a 1.35 M solution in cyclohexane, 0.15 mol) in dry THF (120 mL) under argon was added (chloromethyl)trimethylsilane (18.41 g, 0.15 mol).[15] The resulting mixture was stirred at −70 °C (1 h), at which time a solution of **1** (26.13 g, 0.15 mol) in dry THF (75 mL) was added. The reaction mixture was then stirred at −70 °C (5 h), at which time a cooled solution of acetyl chloride (11.78 g, 0.15 mol) in dry THF (20 mL) was added. The resulting mixture was stirred at −70 °C (5 h) and then allowed to warm to room temperature, at which time stirring was continued (5 h). The reaction mixture was then poured into water (300 mL) and stirred (10 min), and the layers were then separated. The aqueous layer was extracted with ether, and the ethereal extracts were combined with the organic layer. The combined organic layers were washed with brine, dried (anhydrous magnesium sulfate), and filtered. The filtrate was concentrated in vacuo to afford a yellow oil (47.34 g). The crude oil was distilled in vacuo to afford pure **14** (mixture of diastereoisomers, 39.6 g, 78%) as a colorless oil: bp 115–120 °C (0.02 mm); ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 1.31 (A*B*, J_{AB} = 10 Hz, 1 H), 1.65 (*A*B, J_{AB} = 10 Hz, 1 H), 1.99 (s, 3 H), 2.18–2.90 (m, 8 H), 3.53–3.58 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ −1.78 (q, 3 C), −1.60 (q, 3 C), 21.16 (d), 36.66 (d), 41.25 (d), 41.90 (d), 42.08 (d), 42.32 (t), 42.50 (t), 43.27 (d), 44.76 (d), 44.88 (d), 45.24 (d), 46.67 (d), 47.20 (q), 47.38 (q), 48.69 (d), 50.48 (d), 50.66 (d), 51.85 (d), 54.36 (d), 57.16 (d), 57.40 (d), 58.35 (d), 93.98 (s), 94.10 (s), 119.13 (s), 168.06 (s); IR (film) 2972 (s), 2872 (m), 1748 (s), 1374 (m), 1337 (m), 1297 (m), 1253 (s), 1208 (s), 1172 (m), 1109 (s), 926 (m), 848 cm^{-1} (s).

Anal. Calcd for $C_{17}H_{23}ClO_3Si$: C, 60.25; H, 6.84. Found: C, 60.16; H, 7.05.

8-(Chloromethylene)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-11-one (4). Method A. To a solution of **13** (2.97 g, 0.01 mol) in dry methylene chloride (15 mL) was added freshly distilled boron trifluoride etherate (1.4 mL, 11 mmol),[17] and the resulting mixture was stirred under argon at room temperature (24 h). The mixture was then poured slowly into 5% aqueous sodium bicarbonate solution (100 mL) and stirred vigorously (25 min). The layers were then separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford crude **4** (mixture of *Z* and *E* diastereoisomers, 1.88 g, 91%). Recrystallization of the crude product from carbon tetrachloride–hexane mixed solvent (1:1) afforded pure **4** (single diastereoisomer of unknown configuration) as a colorless microcrystalline solid: mp 106.5–107.8 °C; ^{1}H NMR, ^{13}C NMR, and IR spectral data, along with microanalytical data for **4**, have been reported elsewhere;[25] mass spectrum (70 eV), *m/e* (relative intensity) 208.1 (molecular ion, 24.4), 207.1 (10.4), 206.2 (67.9), 171.1 (49.7), 153.1 (11.7), 144.1 (10.4), 143.1 (80.5), 142.1 (21.1), 141.1 (41.5), 129.1 (30.0), 128.1 (100.0), 127.1 (27.7), 126.1 (27.7), 125.1 (19.0), 116.1 (13.3), 115.1 (55.1), 112.0 (29.2), 91.1 (28.8), 79.1 (35.6), 77.1 (36.9), 75.0 (12.5), 70.1 (10.5), 66.1 (53.6).

Method B. To a solution of **14** (4.69 g, 0.013 mol) in dry methylene chloride (50 mL) was added freshly distilled boron trifluoride etherate (2.2 mL, 18 mmol),[17] and the resulting mixture was stirred under argon at room temperature (24 h). The mixture was then poured slowly into 5% aqueous sodium bicarbonate solution (250 mL) and stirred vigorously (30 min). The layers were then separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford crude **4** (mixture of *Z* and *E* diastereoisomers). Recrystallization of the crude product from carbon tetrachloride–hexane mixed solvent (1:1) afforded pure **4** (single stereoisomer of unknown configuration, 1.61 g, 60%).

1-Methoxy-12-oxa-6-(chloro(trimethylsilyl)methyl)hexacyclo-[5.4.1.0^{2,5}.0^{3,10}.0^{4,8}.0^{7,11}]dodecane (15). A 35% dispersion of potassium hydride in mineral oil (1.40 g, 12.3 mmol) under argon was washed with hexane three times to remove the mineral oil. The remaining dry potassium hydride was then suspended in dry THF (10 mL), and a cooled (−78 °C) solution of **13** (2.52 g, 8.5 mmol) in dry THF (15 mL) was added. The resulting mixture was stirred at −78 °C (45 min), and dimethyl sulfate (1.13 g, 8.9 mmol) was then added to the reaction mixture. The resulting mixture was stirred at −60 °C (2 h) and then warmed slowly to room temperature and stirred overnight. The reaction mixture was then poured into water (100 mL) and stirred (5 min). The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, dried (anhydrous magnesium sulfate), and filtered. The filtrate was concentrated in vacuo to afford crude **15** (2.48 g). The crude product was distilled under reduced pressure to afford pure **15** (mixture of diastereoisomers, 2.35 g, 89%) as a colorless oil: bp 105–109 °C (0.01 mm); ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 1.42 (A*B*, J_{AB} = 11 Hz, 1 H), 1.79 (*A*B, J_{AB} = 11 Hz, 1 H), 2.24–2.42 (m, 8 H), 3.22 (s, 3 H), 3.39 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −1.98 (q, 3 C), −1.82 (q, 3 C), 40.92 (d), 41.73 (d), 41.95 (d), 42.82 (t), 43.03 (t), 44.71 (d), 45.09 (d), 46.72 (d), 48.94 (d), 50.62 (d), 50.73 (d), 52.46 (d), 53.81 (q), 54.14 (q), 56.58 (d), 59.01 (d), 93.04 (d), 120.72 (d), 120.88 (d); IR (film) 2968 (s), 2869 (m), 1452 (m), 1358 (s), 1297 (m), 1253 (s), 1221 (m), 1138 (s), 1033 (m), 986 (m), 918 (s), 868 (s), 850 cm^{-1} (s); mass spectrum (70 eV), *m/e* (relative intensity) 311.0 (molecular ion, 1.5), 308.9 (20.7), 306.9 (10.5), 275.1 (18.9), 179.1 (16.6), 171.1 (11.7), 151.1 (13.0), 143.1 (22.8), 129.0 (12.7), 128.1 (19.9), 121.1 (9.5), 115.0 (20.3), 109.1 (18.5), 95.0 (14.0), 93.0 (15.8), 91.0 (18.4), 89.0 (15.4), 79.0 (16.7), 78.0 (10.3), 77.0 (21.7), 75.0 (22.7), 74.0 (9.2), 73.0 (100.0), 65.0 (24.4), 45.0 (50.9).

Anal. Calcd for $C_{16}H_{23}ClO_2Si$: C, 61.81; H, 7.46. Found: C, 61.64; H, 7.29.

Epoxidation of 5.[16] A 35% dispersion of potassium hydride in mineral oil (1.70 g, 14.7 mmol) under argon was washed with hexane three times to remove the mineral oil. The remaining dry potassium hydride was suspended in dry THF (15 mL), and a cooled (−5 °C) solution of **13** (2.97 g, 0.01 mol) in dry THF (25 mL) was added. The resulting mixture was stirred at room temperature (15 h) and then poured into 5% aqueous ammonium chloride solution (100 mL). The resulting mixture was stirred (10 min), and the layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried (anhydrous magnesium sulfate), and filtered. The filtrate was concentrated in vacuo to afford crude **8** (mixture of syn and anti diastereoisomers, 2.48 g, 95%). The crude product was purified via recrystallization from methylene chloride–pentane mixed solvent to afford pure **8** (a single diastereoisomer of unknown configuration, 1.89 g, 76%) as a colorless microcrystalline solid, mp 104.5–105.8 °C; ^{1}H NMR ($CDCl_3$) δ -0.11 (s, 9 H), 1.42 (AB, J_{AB} = 11 Hz, 1 H), 1.75 (AB, J_{AB} = 11 Hz, 1 H), 2.11–3.04 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ -2.85 (q, 3 C), 36.80 (d), 38.38 (t), 39.40 (d), 41.35 (d), 42.01 (d), 42.71 (d), 44.55 (d), 52.08 (d), 53.92 (d), 56.79 (d), 67.63 (s), 215.74 (s); IR (film) 3055 (w), 2968 (s), 2905 (w), 1735 (s), 1426 (m), 1267 (s), 1252 (s), 1104 (w), 924 (w), 908 (m), 890 (m), 862 (m), 844 cm^{-1} (m); mass spectrum (70 eV), *m/e* (relative intensity) 260.2 (molecular ion, 2.7), 176.1 (20.6), 155.1 (6.2), 151.2 (6.7), 129.1 (8.7), 128.1 (7.7), 115.1 (11.2), 91.1 (10.1), 77.1 (9.4), 75.1 (20.9), 74.1 (9.4), 73.1 (100.0), 45.1 (24.3), 43.0 (13.5).

Anal. Calcd for $C_{15}H_{20}O_2Si$: C, 69.19; H, 7.74. Found: C, 69.42; H, 7.79

8,11-Bis((trimethylsilyl)methylene)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (7). To a solution of bis(trimethylsilyl)methane (6.42 g, 0.04 mol) in 4:1 THF–HMPA mixed solvent (80 mL) under argon maintained between -90 and -78 °C was added *tert*-butyllithium (20 mL of a 2 M solution in pentane, 0.04 mol). The resulting solution was stirred (10 h) while the temperature was maintained between -60 and -50 °C. A solution of **1** (3.484 g, 0.02 mol) in dry THF (20 mL) was then added to the reaction mixture during 10 min; the temperature was maintained at -60 °C throughout the time of addition. The reaction mixture was stirred at -60 °C (2.5 h) and then allowed to warm slowly to room temperature overnight with stirring. The reaction mixture was then poured into saturated aqueous ammonium chloride solution (200 mL) and then stirred (10 min). The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with water several times to remove the last traces of HMPA. The organic layer was then dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford crude **7** (mixture of diastereoisomers, 3.73 g, 59%). The crude product was purified by column chromatography on silica gel (pentane eluent); pure **7** (mixture of diastereoisomers, 2.61 g, 42%) was thereby obtained as a colorless oil: bp 103–106 °C (0.02 mm); ^{1}H NMR ($CDCl_3$) δ 0.06–0.11 (overlapping singlets, 9 H), 1.61 (AB, J_{AB} = 11 Hz, 1 H), 1.93 (AB, J_{AB} = 11 Hz, 1 H), 2.24–3.28 (m, 8 H), 5.06, 5.17 (singlets, total 1 H); ^{13}C NMR ($CDCl_3$) δ 0.51 (q), 0.73 (q), 35.59 (t), 37.02 (t), 41.46 (d), 41.63 (d), 42.50 (d), 42.66 (d), 43.40 (d), 43.69 (d), 46.34 (d), 46.61 (d), 47.31 (d), 47.53 (d), 47.75 (d), 48.78 (d), 49.05 (d), 50.40 (d), 51.75 (d), 57.06 (d), 57.17 (d), 117.74 (d), 117.90 (d), 118.01 (d), 162.16 (s), 162.87 (s), 163.08 (s); IR (film) 2948 (vs), 2900 (s), 2870 (s), 1624 (vs), 1458 (m), 1405 (m), 1290 (m), 1244 (vs), 1109 (w), 868 (vs), 840 (vs), 758 (s), 692 cm^{-1} (s); mass spectrum (70 eV), *m/e* (relative intensity) 314.2 (molecular ion, 4.4), 241.2 (15.2), 240.2 (14.1), 211.1 (7.4), 167.1 (11.9), 166.1 (10.2), 74.1 (7.6), 73.0 (100.0), 59.0 (15.4), 45.0 (19.3), 43.0 (10.1).

Anal. Calcd for $C_{19}H_{30}Si_2$: C, 72.54; H, 9.61. Found: C, 72.45; H, 9.75.

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Supplementary Material Available: A listing of coordinates and vibrational frequencies for **1**, **2**, and **3** and two figures showing the variations in HOMO, NHOMO, LUMO, and NLUMO energies for **1** and **3** that occur when various overlap matrix elements are deleted (7 pages). Ordering information is given on any current masthead page.

Photochemical Transformations. 46. Photophysics and Photochemistry of Some Compounds Undergoing Light-Induced Solvolysis and Wagner–Meerwein Rearrangement[1]

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Abstract: Absorption maxima, fluorescence maxima, and fluorescence quantum yields are reported for a variety of 7-substituted and 7,8-disubstituted dibenzobicyclo[2.2.2]octadienes and veratrolobenzobicyclo[2.2.2]octadienes in cyclohexane and/or acetonitrile. Singlet lifetimes have been computed from these data. Those compounds that are reactive toward photosolvolysis and/or Wagner–Meerwin photorearrangement have fluorescence yields (and lifetimes) 10^{-2}–10^{-4} times those of the corresponding compounds containing only hydrogens on the saturated bridges. Compounds that are photoinert but have an electron-attracting group on the bridge have lifetimes about one-tenth those of unsubstituted compounds. These results and the variations in fluorescence maximum wavelengths are rationalized by assumptions that there is some degree of charge transfer from aromatic ring to C–X bond in the photoexcited state and that this favors decay to the ground state. When more or less complete intramolecular electron transfer to a zwitterionic biradical intermediate is exergonic, lifetimes in the 4–80-ps range are computed.

For some time, members of our research group have been studying photosolvolysis and Wagner–Meerwein photorearrangements. Recently, we reported[2] results on photochemical yields of [3.2.1] products from the cis and trans isomers of 7,8-dichloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-dienes **1** and **2**, irradiated in acetonitrile or in acetic acid. Similar results were reported previously[3] on the corresponding veratrolo–benzo systems **3–5**, irradiated in acetic acid. In addition, results on a variety of species **6–10**, irradiated in acetic acid, have been reported.[4] All

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