

# Transannular Interactions in Polycyclic Hydrocarbons. The System of Cage-Shaped Hexacyclo[6.6.0.0<sup>2,6</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>]tetradecane Derivatives

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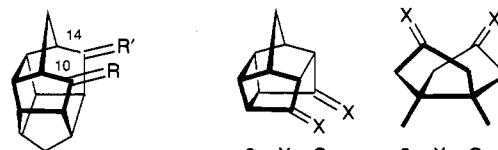
The gas phase He(I $\alpha$ ) photoelectron spectra (PES) of several ketone and olefinic derivatives of the titled compound are measured. The high energy  $\pi$ -orbitals (HOMO and SHOMO) of **1e** show an unusually large energy splitting of 0.90 eV, while the corresponding n-orbitals of **1d** appear to be nearly degenerate (<0.1 eV). The difference between these observations is analyzed with the aid of theoretical models. It is concluded in this work that the  $\pi$ - $\pi$  energy splitting of **1e** is derived mainly from an orbital interaction transmitted through-space (TS) across the ring. Since such a nonbonded interaction is sensitive to distance, a conformational analysis of the cyclooctane ring moiety of **1e** is also performed. As compared to the result of PES, it seems that the ab initio (STO-3G) method is more reliable than AM1, in which the TS interaction is somewhat underestimated.

## Introduction

In our previous analysis of the transannular orbital interactions in the cage system heptacyclo[6.6.0.0<sup>2,6</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>]tetradecane<sup>1</sup> (**1a**), a series of ketones and olefinic derivatives functionalized at C(10) and C(14) have been prepared.<sup>2</sup> A comparison between the <sup>13</sup>C chemical shifts of the ketone **1b** and the dione **1d** indicated the presence of electronic delocalization across the ring.<sup>3</sup> As a consequence, the photolysis of **1d** resulted in a high yield of reductive coupling between the carbonyls.<sup>4</sup> The photoelectron spectrum (PES) of **1d** has also been recorded; however, in the spectrum there is no apparent energy splitting between the nonbonded orbitals.<sup>5</sup> The frontier n-orbitals of **1d** are thus almost degenerate, a phenomenon which is contrary to that expected if mixing of the orbitals is significant. The absence of mixing between the n-orbitals has been rationalized by an improper alignment of geometries.<sup>5</sup>

It is therefore of interest to analyze the PES of the methylene derivatives, i.e., **1e**, in which the  $\pi$  lobes of the olefin moieties are pointing toward each other. The distance between the quaternary carbons of **1d** was measured to be 2.88 Å by crystallography,<sup>5</sup> and that of **1e** is estimated by a force field model (MM2) to be ca.

2.9–3.2 Å. Within such short distances an overlap of the  $\pi$  orbitals is unavoidable and should consequently result in the splitting of  $\pi$  ionization bands in PES. Since the cyclooctane ring moiety is slightly flexible, the  $\pi$ , $\pi$  repulsive energy in the molecular ground state can be reduced by stretching out the ring. In this report a conformational analysis of the diene **1e** is thus included.



- 1a: R = H, H; R' = H, H  
 b: R = H, H; R' = O  
 c: R = H, H; R' = CH<sub>2</sub>  
 d: R = R' = O  
 e: R = R' = CH<sub>2</sub>  
 f: R = O; R' = CH<sub>2</sub>  
 g: R = H, OH; R' = O  
 h: R = H, OH; R' = CH<sub>2</sub>

- 2a: X = O  
 b: X = CH<sub>2</sub>
- 3a: X = O  
 b: X = CH<sub>2</sub>

## Results and Discussion

**Synthetic Studies.** The methylene derivatives **1c**, **1e**, and **1f** are prepared in good yields from the corresponding ketones by treatments with Nozaki–Lombardo reagent.<sup>6</sup> This reagent was prepared from TiCl<sub>4</sub>/Zn/CH<sub>2</sub>-Br<sub>2</sub> in THF, and the reactive slurry can be stored at low temperature for an extended period of time. For certain types of ketones it is regarded to be more effective than both Wittig and Peterson reagents. For example, in a previous report the double methylenation of an analogous compound, pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane-8,11-dione (**2a**), gave a reproducible yield of ca. 10% using the Wittig reagent.<sup>7</sup> The two carbonyl groups in **2a** are

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**Table 1. Comparison of Experimental Ionization Energies  $I_{m,j}$  with Calculated Orbital Energies  $\epsilon_j$  of 1b–1f (Energy Values in eV)<sup>a</sup>**

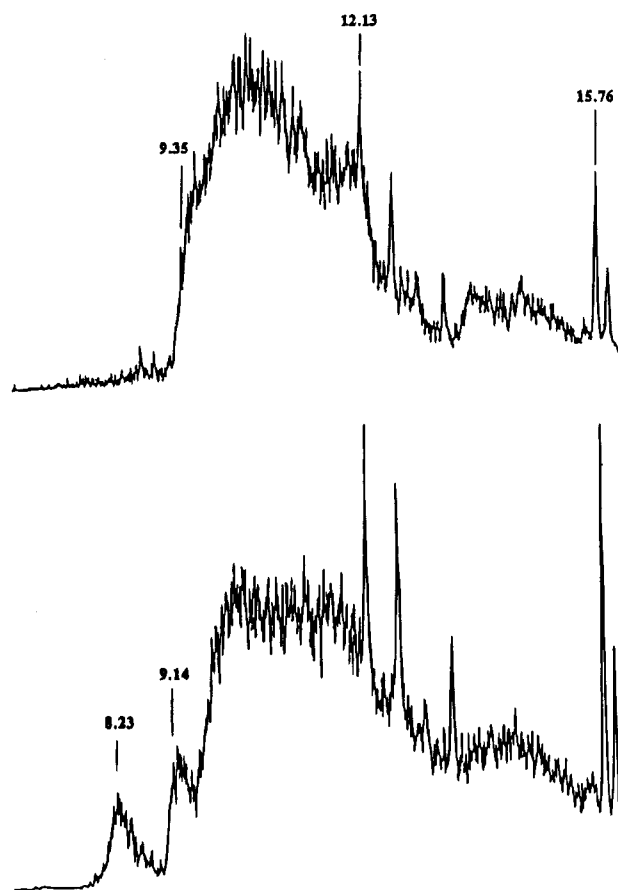
compd		1b	1c	1d	1e	1f
STO-3G	$-\epsilon_1$	8.19	7.58	8.28	7.26	7.78
	$-\epsilon_2$			8.56	8.12	8.21
	$\Delta\epsilon$			0.28	0.86	0.53
MNDO	$-\epsilon_1$	10.40	9.74	10.54	9.58	9.92
	$-\epsilon_2$			10.73	9.88	10.37
	$\Delta\epsilon$			0.19	0.30	0.45
AM1	$-\epsilon_1$	10.09	9.51	10.20	9.31	9.76
	$-\epsilon_2$			10.48	9.87	10.08
	$\Delta\epsilon$			0.28	0.56	0.33
HAM3	$-\epsilon_1$	8.99	8.83	9.00	8.65	8.91
	$-\epsilon_2$			9.14	9.11	8.97
	$\Delta\epsilon$			0.14	0.46	0.06
exptl	$I_{m,1}$	8.65	9.35 <sup>b</sup>	8.90	8.23	8.65
	$I_{m,2}$			8.90	9.14	8.76
	$\Delta I_m$			<0.1	0.91	0.11

<sup>a</sup> All geometries of the molecules are fully optimized by using the model AM1 (MOPAC 6.0), which are subsequently used for the ab initio (GAUSSIAN 90) and HAM3 calculations. <sup>b</sup> "Onset" of ionization potential.

located so close to each other that a transannular nucleophilic attack proceeds readily which leads to undesired side products. A revised procedure using Peterson reagent has been applied for the synthesis of **2b**, which went through three major steps involving the isolation of two intermediate compounds.<sup>7a,8</sup> However, when **2a** was treated with Nozaki–Lombardo reagent in a trial operation, **2b** could be collected in 38% yield in one step,<sup>9</sup> and the yield may be further optimized.

The unsymmetrical enone **1f** was prepared by oxidation of the alcohol **1h** which was made by methylenation of **1g** using Nozaki–Lombardo reagent. The yield of **1h** was 88%; protection of the hydroxy group of **1g** is not required.<sup>9</sup>

**The Photoelectron Spectra.** The gas-phase He(I $\alpha$ ) photoelectron spectra of **1b–f** were measured, and their ionization energies  $I_{m,j}$  and the calculated energies  $\epsilon_j$  are listed in Table 1. Assuming the validity of Koopmans' theorem, the first one or two bands, which are well-separated from those of the  $\sigma$ -region, can be assigned to the ionization energies of either n- or  $\pi$ -electrons.<sup>10–12</sup> The spectrum of **1c** is remarkable in as much as there is no isolated band observed in the  $\pi$ -ionization region (Figure 1). The  $\pi$  ionization band is probably hidden below the  $\sigma$  ionization onset (cf. ionization energies of isobutene, 9.2 eV, and 7-methylene norbornane, 9.4 eV, respectively<sup>12e</sup>). The results of some semiempirical and ab initio calculations are also listed in Table 1. It is not unusual that MNDO<sup>13</sup> overestimates the ionization energies by



**Figure 1.** Gas-phase He(I $\alpha$ ) photoelectron spectra of **1c** (top) and **1e** (bottom), where the peaks at 12.13 and 15.76 eV are internal standards. In the lower energy region of **1e**, the two  $\pi$ -ionization bands are shown at 8.23 and 9.14 eV.

about 1 eV, whereas STO-3G<sup>14</sup> underestimates them by about 1 eV.<sup>15</sup> After a careful examination of these values, there are certain noticeable features worthy of comment. First, for carbonyl derivatives the magnitude of interaction involving the n-orbitals, either through-bond (TB) or through-space (TS),<sup>12</sup> can be negligibly small. Theoretical models predict an energy splitting of 0.14–0.29 eV (Table 1) for the dione **1d**, but experiment showed only one band with no apparent separation apart from vibrational fine structure.<sup>5</sup> It has been suggested in the literature that TS interactions between n<sub>0</sub> lone pairs in diketones generally are quite weak even in molecules which possess optimal geometries. In some cases large n<sub>+</sub>/n<sub>-</sub> splittings<sup>5</sup> result chiefly from strong TB effects associated with the intervening  $\sigma$ -orbitals.<sup>16</sup> For enone **1f** the TB interaction between the C=O and the C=C moieties also seems to be insignificant as indicated by a low degree of perturbation when the  $I_{m,1}$  value of **1f** (8.65 eV) is compared with that of **1b** (8.65 eV). In the case of **1d** the lowering of the observed n-bonding energy ( $I_{m,1} = 8.90$  eV) with respect to that of **1b** ( $I_{m,1} = 8.65$  eV) is due to the mixing of n- and  $\sigma$ -orbitals, i.e., a result of a

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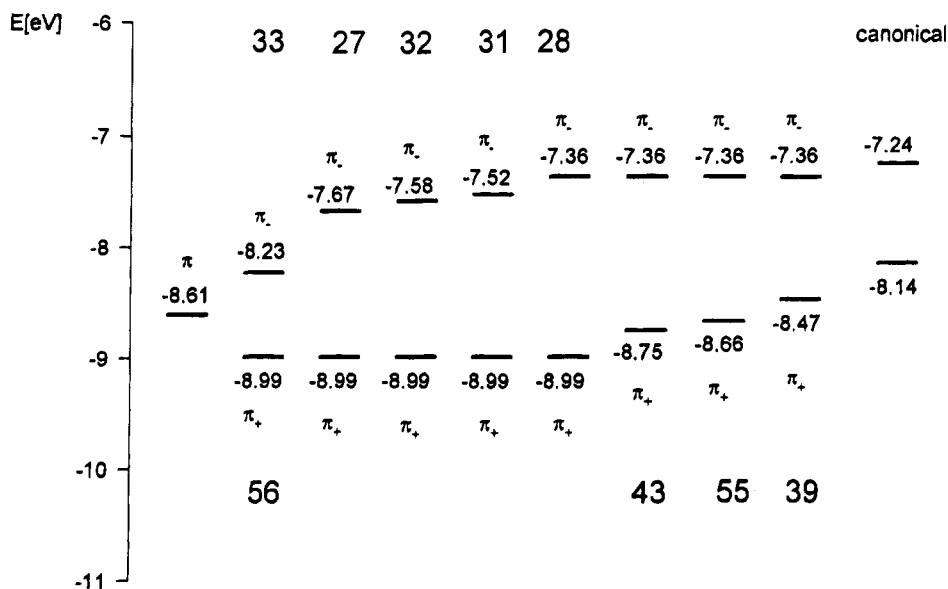
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**Figure 2.** Mixing of localized  $\pi$  orbitals of **1e** with themselves ( $\pi_{+/-}$ , column 2) and with various symmetry-adapted semilocalized  $\sigma$  combinations of precanonical MOs.

$\sigma$ -induction effect derived from the high polarity of the C=O groups.

The situation is different, however, for the olefinic derivatives. Due to a coplanar alignment of the  $\pi$ -lobes of C=C, a strong TS interaction is expected which should be observable in PES. As shown in Table 1 and Figure 1, it is found that the  $\Delta I_m$  of **1e** is indeed much larger than what is expected from semiempirical models; e.g., the experimental value of 0.91 eV is twice that which is predicted by the HAM3<sup>17</sup> model ( $\Delta\epsilon = 0.46$  eV), but it is in harmony with results given by ab initio STO-3G calculations ( $\Delta\epsilon = 0.86$  eV). This large value of  $\Delta I_m$  confirms the significance of a through-space overlap of  $\pi$ -orbitals across the ring. Although such a coplanar arrangement is also true for the  $\pi$ -lobes of the carbonyl groups, the  $\pi$ -ionization bands of C=O can not be seen in PES due to its overlapping with the  $\sigma$ -ionization bands.

The mixing of  $\sigma$ -orbitals with the  $\pi$ -orbital of a C=C group is generally somewhat different from the mixing style with either n- or  $\pi$ -orbitals of a C=O group. The usual reason is due to the larger difference in basis orbital energies between  $\pi_{C=C}$  and  $\sigma$  orbitals and also due to the different spatial topology of  $\pi$  and n orbitals. As a result, the interaction mechanism between a pair of remotely located C=C groups in a molecule is different from that of a corresponding pair of C=O groups substituted in the same structure. This can be evidenced in an earlier analysis of **2a** and **2b**, in which the TB interaction between the n-orbitals of **2a** is larger than that between the  $\pi$ -orbitals of **2b**.<sup>16a</sup> For both compounds an equal value of  $\Delta I_m$  is observed, i.e., 0.55 eV, but in the former it is based purely on through-bond interactions, whereas in the latter it appears as a combination of both TB and TS interactions. In another study of compounds **3a** and **3b**, the situation with respect to  $\Delta I_m$  is similar (0.27 eV in **3a** and 0.20 eV in **3b**).<sup>18</sup> The argument should also be true in the present case so that both the TB interactions of the n-orbitals in **1d** and the  $\pi$ -bonds in **1e** are small. Therefore, the abnormally large

energy splitting for the  $\pi_{+}/\pi_{-}$  combinations of **1e** may be ascribed mostly to an overlapping of orbitals through-space.

In order to assess the relative contributions of TS and TB interaction pathways in compounds **1e** and **1d** the procedure proposed by Heilbronner and Schmelzer is applied,<sup>19</sup> where the details of treatment can be compared with those previously described.<sup>5</sup> The mixing of localized  $\pi$  orbitals with themselves and with various symmetry-adapted semilocalized  $\sigma$  combinations is shown in Figure 2. As can be seen from the second column, the TS interactions between localized  $\pi$  orbitals amount to  $\Delta\epsilon(\pi_{+/-}) = 0.76$  eV, which is in surprisingly good agreement with the final result 0.9 eV (last column) after successive inclusion of relevant  $\sigma$  orbitals. It may be noted that approximately the same number of  $\sigma$  combinations mix into the  $\pi_{-}$  combination (numbered 27, 32, 31, 28) as into the  $\pi_{+}$  combination (numbered 43, 55, 39). The result is that, although  $\sigma$  coupling occurs, the TB interaction does not contribute much to the final splitting which is given in the last column by the full canonical calculation. The original TS splitting between localized  $\pi$  orbitals (second column) is largely retained in the splitting of  $\sigma$  coupled  $\pi$  combinations (last column).

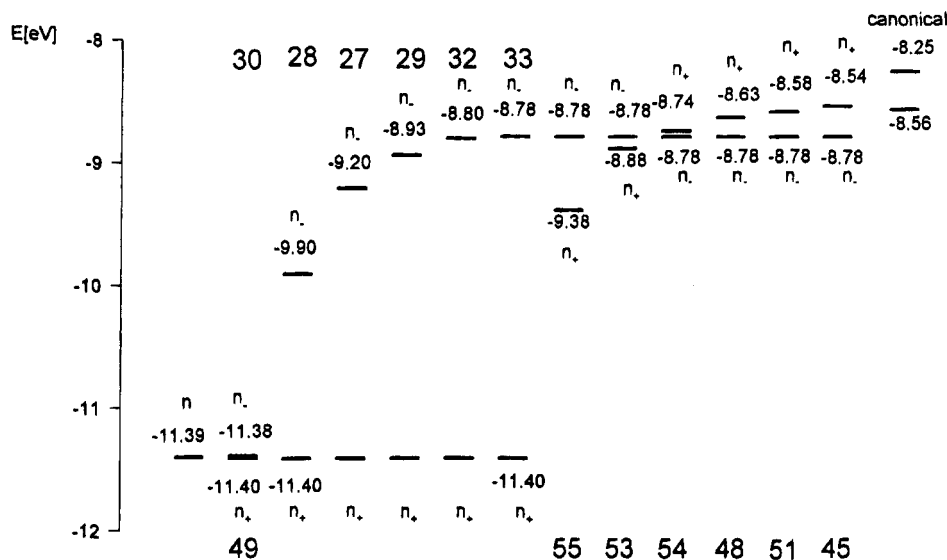
In diketone **1d** the TS splitting is obviously negligible (Figure 3), and the intensive TB mixing with appropriate  $\sigma$  combinations (27, 28, 29, 32, 33, 45, 48, 51, 53, 54, 55) leads finally to a calculated moderate splitting of 0.31 eV which is somewhat larger than the experimentally observed energy difference (ca. 0.1 eV).

**Conformational Analysis.** The cyclooctane ring moiety of compound **1** is not totally rigid. Bending the ring would change the distance between atoms C(10) and C(14) slightly. A variation of 0.3–0.4 Å between the two carbons could result in a ca. 1.0 eV energy difference in the above-mentioned TS type of interaction. The introduction of the R and R' substituents (e.g., **1e**) does not significantly increase the strain of the system (cf. **1a**) since the positions of the groups are directed outward.

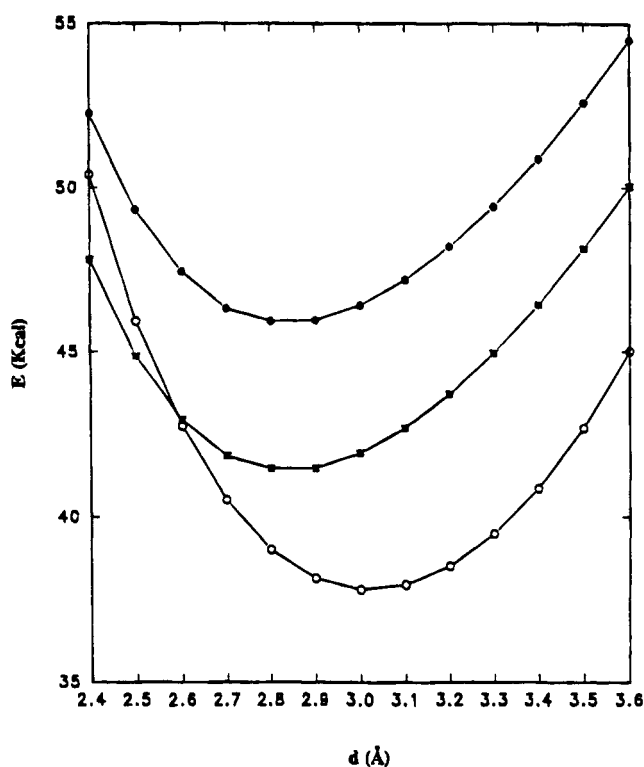
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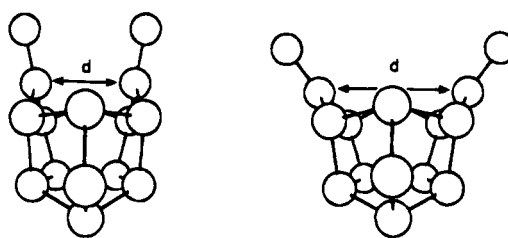
**Figure 3.** Mixing of localized  $n$  orbitals of **1d** with themselves ( $n_{+/-}$ , column 2) and with relevant semilocalized precanonical MOs.



**Figure 4.** Variation of strain energy (●, kcal) and the heat of formation (HF) of **1e** with respect to the distance ( $d$ , Å) between the quaternary carbons. The estimation of HF is done by both the models MM2 (■) and AM1 (○).

The strain of the structure will be increased, however, by either stretching the ring outward or squeezing inward from its equilibrium position. The increased strain by squeezing the ring inward derives from electronic repulsions, while stretching the ring outward increases the  $\sigma$ -bonding strain. The most stable conformation can be estimated by molecular modeling. The TS energy component can thus be estimated by *ab initio* and semiempirical calculations.

In Figure 4 the heat of formation (HF) of **1e** is plotted against the distance of C(10)–C(14). The distance optimized by AM1<sup>13b</sup> (3.00 Å) is ca. 0.15 Å longer than that



**Figure 5.** Molecular drawing of **1e** at two extreme conformations referring to the plots of Figures 4, 6, and 7. Top: a conformation with  $d = 2.40$  Å. Bottom:  $d = 3.60$  Å. Hydrogens are omitted for clarity.

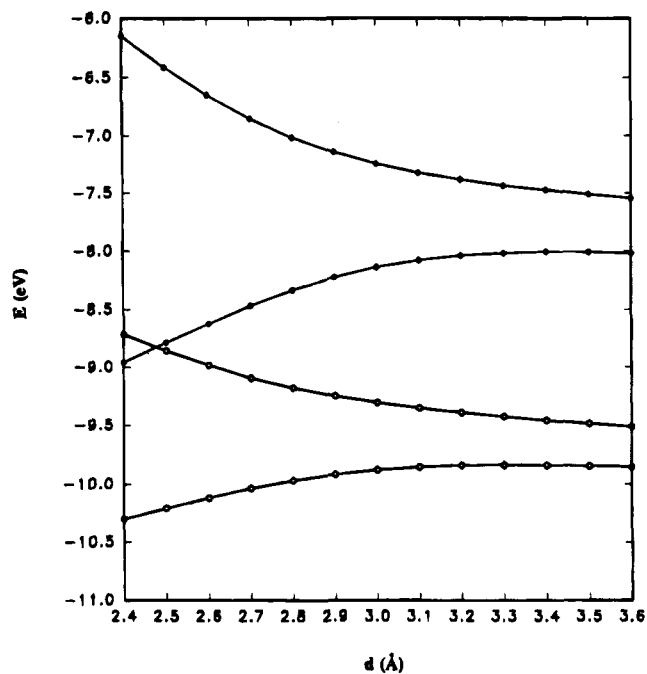
optimized by MM2<sup>20</sup> (2.85 Å). In this case, the latter gave a more accurate estimation in comparison with the experimental value of 2.88 Å measured for dione **1d**.<sup>5</sup> The variation of strain energy (SE) of **1e** is also shown in Figure 4. It appears that the curves of HF are aligned parallel to that of SE, indicating that SE is the dominating factor influencing the conformation of the molecule. The conformations of **1e** at its two extreme conformations, i.e., at  $d = 2.40$  and 3.60 Å, are shown in Figure 5.

The energies of HOMO and SHOMO of **1e** versus the distance between C(10) and C(14) in the range of 2.40–3.60 Å are plotted in Figure 6. As shown in Figure 6, when the distance is shorter than 3.00 Å the repulsive interaction increases sharply, yet when it is longer, the difference in energy gradually levels to a constant gap (cf. 0.47 eV at  $d = 3.60$  Å estimated by STO-3G or 0.34 eV by AM1). This latter amount of energy difference may be ascribed purely to TB interactions.

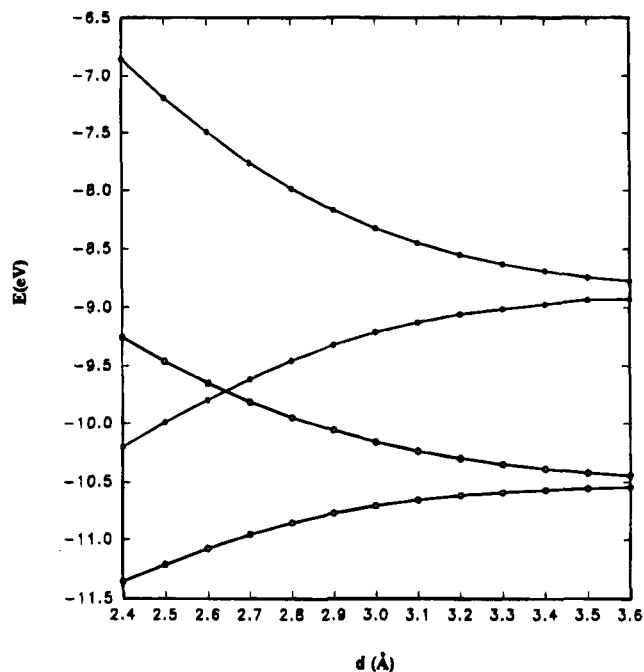
A quantitative estimation of the TS interaction between two isolated C=C bonds in a compound has been successfully performed by a method called the "cluster" approach, where the orbital effects are compared with two independent ethylene molecules affixed at identical positions.<sup>21</sup> The calculated energies of  $\pi_+$  and  $\pi_-$  based on two types of models, i.e., the STO-3G basis set of GAUSSIAN and AM1, are plotted in Figure 7. Here it

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**Figure 6.** Calculated  $\epsilon_1$  (eV) and  $\epsilon_2$  of **1e** with respect to  $d$  (Å) using both the ab initio (STO-3G, ●) and the semiempirical (AM1, ○) methods.



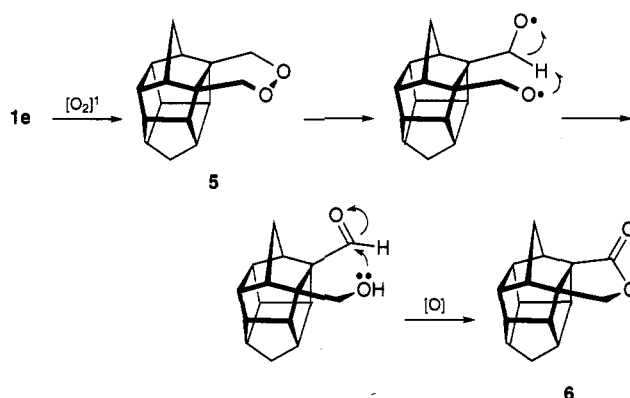
**Figure 7.** Calculated  $\epsilon_1$  (eV) and  $\epsilon_2$  of two independent ethylene molecules positioned at identical geometry as the corresponding carbons of **1e**. The calculations are performed on both the ab initio (STO-3G, ●) and semiempirical (AM1, ○) levels.

is shown that within the range of  $d = 2.85\text{--}3.00$  Å the estimated energy splitting of  $\pi_+/\pi_-$  is consistent with the experimental value of **1e**. By comparison of the data presented in Figures 6 and 7 it may be concluded that the interaction between the  $\pi$ -orbitals of **1e** is mostly transmitted through-space, and this is borne out by the results of Figures 2 and 3. As compared to the result of PES, it seems that the ab initio (STO-3G) method is more reliable than AM1, in which the TS interaction is somewhat underestimated.

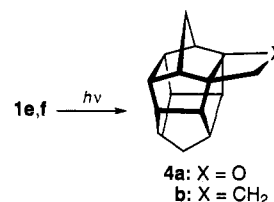
**Table 2.** Comparison of the Strain Energies and the Heats of Formation (kcal/mol) for Compounds **1f/4a** and **1e/4b**, Calculated by MM2 (91)

	<b>1f</b>	<b>4a</b>	<b>1e</b>	<b>4b</b>
strain energy	42.33	77.24	45.87	78.43
$H_f$	-8.50	4.41	41.41	32.95

**Scheme 1**



**Photochemical Reactions.** The alignment of the two  $\pi$ -orbitals in **1f** and **1e** is appropriate for a suprafacial  $[2\pi + 2\pi]$  addition. Upon direct UV irradiation with a medium-pressure Hg lamp, four-membered rings form readily to yield **4a** and **4b**. The connectivities at the



quaternary bridgeheads of **4a** and **4b** are analogous to those of a [3.3.2]propellane. The photocyclizations of **1f**  $\rightarrow$  **4a** and **1e**  $\rightarrow$  **4b** increase the strains of the molecules by ca. 33–35 kcal/mol. Yet, taking into account the different heats of formation, the estimated variations in energy are slight, i.e., 8–12 kcal/mol as shown in Table 2. In a similar photolysis the dione **1d** results in a high yield of a vicinal  $\alpha$ -diol instead of forming a stable dioxetane.

The thermally allowed  $[s2\pi + s2\pi + s2\pi]$  mode of addition does not happen for **1e** in the presence of ordinary olefins. However, the reaction does proceed with singlet oxygen. In a solution containing a small amount of rose bengal, **1e** was irradiated with UV light in an oxygen atmosphere. The products examined with a ferrous indicator immediately following the photolysis show an appearance of peroxides, probably **5** as proposed, but the peroxide disappears after the workup procedures. At the end of purification the lactone **6** is collected in 45% yield, which is most likely to have derived from **5** upon air oxidation (Scheme 1).

### Conclusion

The transannular interactions of the  $\pi$ -orbitals across the cyclooctane ring moiety in the cage molecules **1b–e** are mainly through-space controlled. The TB interaction in **1d** measured by PES is much weaker than that expected from theoretical models. The experimental value of  $\pi_+/\pi_-$  splitting of **1e** is quite consistent with the

value calculated by either the ab initio method or the "cluster approach".

### Experimental Section

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained either on a Bruker MSL-200 FT spectrometer or on a Bruker AW 80 CW spectrometer. Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrophotometer. Melting points were determined using a Yanaco Model MP micro melting point apparatus and were uncorrected. Elemental analyses were obtained on a Perkin-Elmer 240 EA instrument. High-resolution mass spectra were carried out on a Jeol JMS-HX110 mass spectrometer, while low-resolution ones (70 eV) were recorded on a Hewlett-Packard HP 5995B GC/MS system by direct injections. PE spectra were obtained on a Leybold Heraeus UPG 200 photoelectron spectrometer.

**Preparation of the Nozaki-Lombardo Reagent.** Both reagents  $\text{CH}_2\text{Br}_2$  and  $\text{TiCl}_4$  are distilled over  $\text{CaCl}_2$  before use. Zinc powder (12.5 g) was added to a 250-mL three-necked round bottom flask fitted with a dropping funnel, a thermometer, and a gas inlet and outlet under nitrogen atmosphere. The system was evacuated under vacuum and then purged with nitrogen. The flask was cooled to  $-40^\circ\text{C}$  (dry ice in chlorobenzene) and was filled with freshly distilled THF (125 mL) and dibromomethane (5.5 mL). The mixture was stirred magnetically, and to it was added slowly titanium tetrachloride (5.0 mL) through the dropping funnel. The resulting mixture was allowed to warm gradually to  $-5^\circ\text{C}$  and stirred for 3 d. The gray slurry thus produced may be stored in refrigerator ( $-20^\circ\text{C}$ ) for an extended period of time before use.

**Hexacyclo[6.6.0.0<sup>2,6</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>]tetradecan-10-one (1b).** To a round-bottom flask containing 15 mL of toluene was added 14-iodoheptacyclo[6.6.0.0<sup>2,6</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>]tetradecan-10-one<sup>1a</sup> (170 mg, 0.51 mmol), followed by tri-*n*-butyltin hydride (150 mg, 0.51 mmol) and a catalytic amount of azoisobutyronitrile (AIBN). The solution was stirred for 1 h and quenched by addition of saturated  $\text{NaHCO}_3$ . The resulting mixture was extracted several times with ether, dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. The product was purified by silica gel chromatography eluted with *n*-hexane/ethyl acetate (v/v 4/1) and then was crystallized to give a white solid (99 mg, 0.495 mmol, 97% yield):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.14 (1H, dd,  $J = 3.5$  and 15 Hz), 1.67 (2H, s), 1.90–2.00 (2H, m), 2.25 (1H, d,  $J = 12$  Hz), 2.38 (2H, m), 2.52–2.78 (6H, m), 2.95–3.03 (2H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  34.8 (t), 45.3 (t), 46.4 (t), 47.2 (d), 48.0 (d), 48.5 (d), 49.9 (d), 51.9 (d), 53.8 (d), 54.2 (d), 56.5 (d), 56.8 (d), 57.2 (d), 229.4 (s); MS (70 eV)  $m/z$  200 ( $\text{M}^+$ , 100), 182 (2.3), 172 ( $\text{M}^+ - \text{CO}$ , 8.8), 159 (3.9), 143 (6.8), 133 (10), 129 (16); IR ( $\text{CDCl}_3$ ) 3017 (sh), 2995 (s), 2872 (sh), 1721 (s), 1462 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{O}$ : C, 83.96; H, 8.85. Found: C, 84.12; H, 8.16.

**10-Methylenehexacyclo[6.6.0.0<sup>2,6</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>]tetradecane (1c).** To a 25-mL round bottom flask fitted with a magnetic stirrer was added THF (2 mL) and the ketone 1b (46 mg, 0.23 mmol). A small amount of Nozaki-Lombardo reagent (ca. 1.0 mL) was added dropwise to the above solution until all the starting materials were consumed as indicated by TLC. The reaction was quenched by pouring it into a water/ether solution, and the products were extracted with ether (3  $\times$  10 mL). The ether layer was dried over anhydrous  $\text{MgSO}_4$  and evaporated *in vacuo*. The white solid of 1c (42 mg, 0.22 mmol, 93%) was purified by passing it through a silica gel chromatographic column eluted with *n*-hexane. Compound 1c:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.61 (2H, m), 1.75–1.84 (3H, m), 1.92–2.03 (2H, m), 2.40 (1H, m), 2.60 (4H, m), 2.80 (2H, m), 2.95 (1H, m), 3.00 (1H, m), 4.85 (1H, m), 4.90 (1H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  34.1 (t), 46.0 (t), 46.5 (d), 47.0 (t), 48.5 (d), 50.5 (d), 52.3 (d), 52.8 (d), 53.2 (d), 54.5 (d), 55.0 (d), 56.1 (d), 57.5 (d), 106.8 (t), 161.2 (s); HRMS calcd for  $\text{C}_{15}\text{H}_{18}$  198.1409, found 198.1405. Anal. Calcd for  $\text{C}_{15}\text{H}_{18}$ : C, 90.85; H, 9.15. Found: C, 90.62; H, 9.12.

**10,14-Dimethylenehexacyclo[6.6.0.0<sup>2,6</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>]tetradecane (1e).** In a 25-mL round bottom flask the diketone 1d (98 mg, 0.46 mmol) was dissolved in 2.0 mL of dry THF, and

to the solution was added dropwise the Nozaki-Lombardo reagent (ca. 2.0 mL) until all the starting materials were reacted. The reaction was worked up as previously described for the preparation of 1c. The yield of 1e (78 mg, 0.37 mmol) was 81%;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.65 (2H, s), 2.10–2.30 (3H, m), 2.60 (3H, m), 2.83 (2H, m), 2.90 (2H, m), 2.96 (2H, m), 4.77 (4H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  46.0 (t), 48.9 (d), 49.3 (t), 52.3 (d, 2C), 53.0 (d, 2C), 53.1 (d), 55.0 (d, 2C), 56.1 (d, 2C), 108.1 (t, 2C), 159.7 (s, 2C); IR ( $\text{CHCl}_3$ ) 3026 (s), 2949 (s), 1645 (w), 1517 (w), 1420 (w)  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  210 ( $\text{M}^+$ , 67), 182 (29), 167 (16), 153 (10), 144 (15), 129 (46), 117 (100); HRMS calcd 210.1409, found 210.1418. Anal. Calcd for  $\text{C}_{16}\text{H}_{18}$ : C, 91.37; H, 8.63. Found: C, 91.02; H, 8.90.

**14-Methylenehexacyclo[6.6.0.0<sup>2,6</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>]tetradecan-10-ol (1h).** The ketone 1g (126 mg, 0.58 mmol) was dissolved in dry THF (3.0 mL), and to this solution was added dropwise the Nozaki-Lombardo reagent (ca. 7.5 mL) until the reaction was completed. The product 1h (110 mg, 0.51 mmol, 88%) was obtained following the procedures described for the preparation of 1c:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.58–1.60 (2H, m), 1.95–2.05 (2H, m), 2.17–2.27 (3H, m), 2.41–2.48 (1H, t,  $J = 7$  Hz), 2.63 (2H, m), 2.77–3.00 (5H, m), 4.33 (1H, s), 4.85 (1H, s), 4.92 (1H, s);  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  44.8 (d), 44.9 (t), 45.7 (t), 52.0 (d), 52.2 (d), 52.7 (d), 53.2 (d), 54.6 (d), 55.7 (d), 57.3 (d), 60.1 (d), 60.8 (d), 80.6 (d), 108.5 (t), 159.5 (s); IR ( $\text{CHCl}_3$ ) 3605 (m), 3400 (br), 3033 (sh), 2943 (s), 2872 (sh), 1645 (m); MS (70 eV)  $m/z$  214 ( $\text{M}^+$ , 100), 196 (21), 185 (6.2), 171 (6.1), 159 (6.5), 147 (9.5), 133 (17), 130 (21); HRMS calcd 214.1358, found 214.1360. Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{O}$ : C, 84.07; H, 8.47. Found: C, 83.82; H, 8.50.

**14-Methylenehexacyclo[6.6.0.0<sup>2,6</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>]tetradecan-10-one (1f).** The alcohol 1h (77 mg, 0.36 mmol) was dissolved in a minimum amount of DMSO to form a solution which was diluted with 2.0 mL of methylene chloride. The solution was quickly injected through a syringe into a 25-mL round bottom flask containing a methylene chloride (3.0 mL) solution of pyridinium chlorochromate (215 mg, 1.87 mmol). The orange color of the solution immediately turned to dark brown. The solution was stirred overnight at room temperature and then quenched by the addition of water. The organic products were extracted with ether (3  $\times$  10 mL), dried over anhydrous  $\text{MgSO}_4$ , and evaporated *in vacuo*. The colorless compound 1f (70 mg, 0.33 mmol, 92%) was purified by passing it through a silica gel chromatographic column eluted with *n*-hexane/ethyl acetate (v/v 4/1):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.75 (1H, d,  $J = 11$  Hz), 1.84 (1H, d,  $J = 11$  Hz), 2.17–2.26 (1H, m), 2.54–2.66 (4H, m), 2.82–2.88 (3H, m), 3.02 (1H, m), 3.05–3.12 (3H, m), 5.00 (2H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  46.2 (t), 46.8 (t), 47.8 (d, 2C), 51.8 (d), 51.9 (d), 53.2 (d), 53.6 (d), 54.2 (d), 56.0 (d), 56.4 (d), 56.8 (d), 112.0 (t), 157.1 (s), 226.9 (s); IR ( $\text{CHCl}_3$ ) 3019 (s), 2955 (s), 1716 (s)  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  212 ( $\text{M}^+$ , 100), 184 (30), 169 (23), 155 (12), 141 (14), 128 (21), 117 (70), 104 (67), 91 (49), 77 (28), 64 (23); HRMS calcd for  $\text{C}_{15}\text{H}_{16}\text{O}$  212.1201, found 212.1207.

**Direct Photolyses of 1e and 1f.** To a 50-mL round bottom quartz flask fitted with a nitrogen inlet was added freshly distilled *n*-hexane and the enone 1f (83 mg, 0.39 mmol). The solution was irradiated with ultrasound while being purged with nitrogen for 30 min to degas the oxygen. The flask was then exposed under a medium pressure Hg lamp (Hanovia 450 W) for 18 h. The solvent was evaporated *in vacuo*, and the residue was applied onto a silica gel chromatographic column eluted with *n*-hexane/ethyl acetate (v/v 4/1). The oxetane 4a was obtained in 75% yield (62 mg, 0.29 mmol):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.85 (2H, d,  $J = 1.4$  Hz), 2.06 (1H, dt,  $J = 1.3$ , 11 Hz), 2.43 (8H, m), 2.49 (1H, m), 2.60 (1H, dd,  $J = 1.3$ , 11 Hz), 3.21 (1H, m), 4.50 (1H, d,  $J = 7$  Hz), 4.59 (1H, d,  $J = 7$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  40.5 (t), 42.1 (t), 48.6 (d), 48.8 (d), 49.2 (d), 49.7 (d), 51.1 (d, 2C), 51.5 (d), 51.7 (d), 51.8 (d), 53.0 (d), 62.5 (d), 73.0 (t), 110.8 (s); MS (70 eV)  $m/z$  212 ( $\text{M}^+$ , 100), 184 (25), 117 (51), 104 (51), 91 (34); HRMS calcd for  $\text{C}_{15}\text{H}_{16}\text{O}$  212.1202, found 212.1197.

The photolysis of diene 1e (24 mg, 0.11 mmol) was performed similarly to yield the cyclobutane 4b in 88% yield (21 mg, 0.10 mmole):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.69–1.97 (7H, m), 2.15–2.22 (5H, m), 2.27–2.37 (5H, m), 2.92 (1H, m);  $^{13}\text{C}$  NMR

(CDCl<sub>3</sub>)  $\delta$  21.1 (t, 2C), 40.8 (t), 42.1 (t), 51.0 (d), 51.4 (d, 2C), 51.5 (d, 2C), 52.0 (d), 52.3 (d, 2C), 56.1 (d, 2C), 63.1 (s, 2C); MS (70 eV)  $m/z$  210 (M<sup>+</sup>, 100), 182 (19), 167 (9), 153 (5), 143 (8); HRMS calcd for C<sub>16</sub>H<sub>18</sub> 210.1409, found 210.1411.

**Sensitized Photolysis of 1e.** To a 25 mL round bottom quartz flask fitted with gas inlet was added *n*-hexane (10 mL), **1e** (35 mg, 0.17 mmol), and rose bengal (1.5 mg). The system was flushed with nitrogen three times, evacuated, and saturated with oxygen gas. The resulting mixture was irradiated with a medium pressure Hg lamp (Hanovia 450 W) for 18 h. The products were immediately tested by spraying them with a ferrous indicator solution on a TLC plate,<sup>22</sup> and a positive response was observed indicating the presence of peroxides. The solution was concentrated and was eluted through a silica

gel chromatographic column with *n*-hexane/ethyl acetate (v/v 9/1). The peroxide disappeared after the treatment, and a white solid (**6**) was collected (18 mg, 0.075 mmol, 45%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.85 (2H, m), 1.90 (2H, m), 2.45–2.70 (8H, m), 2.80 (1H, m), 2.95 (1H, m), 4.14 (1H, d,  $J = 10$  Hz), 4.28 (1H, d,  $J = 10$  Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  40.58, 42.31, 49.72, 51.29, 51.73, 52.44, 53.19, 53.77, 54.96 (2C), 57.48, 58.34, 66.32, 71.07, 73.37, 180.46; MS (70 eV)  $m/z$  240 (M<sup>+</sup>, 100), 212 (M<sup>+</sup> – CO, 10), 196 (M<sup>+</sup> – CO<sub>2</sub>, 61), 182 (27).

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