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Stabilized Koopmans' Theorem Calculations on the π^* Anion States of 1,4,5,8-Tetrahydronaphthalene

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The exponent stabilized Koopmans' theorem is used to calculate the energies of the π^* anion states of 1,4,5,8-tetrahydronaphthalene. The results indicate that the ordering of π^* anion states is $2\ {}^2B_{3g} < 2\ {}^2A_u < 3\ {}^2B_{3g}$. This order of anion states is the same as that which would prevail were only through-space (TS) interactions present. The through-bond (TB) interactions destabilize all the π^* orbitals; however, they do not change the order.

1. Introduction

The determination of energies of temporary anion states is very important in the study of many chemical properties such as chemical reactivity, electronegativity, nonlinear optical activity, and long-range through-bond (TB) and through-space (TS) interactions.[1] For cases in which the emphasis is on relative energies, a Koopmans' theorem (KT)[2] approach would often suffice except for the problem that when adopting a basis set with diffuse functions, the temporary anion states are prone to collapse onto continuum solutions, called orthogonalized discrete continuum (ODC)[3−6] solutions.

The stabilized Koopmans' theorem (SKT) method[6] (i.e., the stabilization method proposed by Taylor and co-workers[7] coupled with KT), has been much more successful than KT alone at predicting relative energies of temporary anion states,[3−5,6a,6b] that is, relative attachment energies (AEs). Actually, two variants of the stabilization method have been applied in conjunction with KT. One method is the so-called exponent stabilization method and the other is the sphere stabilization method.[6c,6d] Both approaches are able to yield accurate resonance energies for the model potential problems with relatively small basis sets. The eigenvalues are determined as a function of scale parameters that are the exponents of the appropriate diffuse functions in the exponent-stabilized Koopmans' theorem (ESKT) method, and the sphere parameters in the sphere-stabilized Koopmans' theorem (SSKT) method, respectively.

Detailed studies of the ESKT method on the π^* anion states of 1,4-cyclohexadiene (CHD) and a series of substituted benzenes by Cheng et al.[6a,6b] indicate that provided sufficiently flexible basis sets are used, the method gives relative energies between the stabilized π^* orbitals in good agreement with experimental results. In the present study, the ESKT method is used to calculate the π^* orbital energies of 1,4,5,8-tetrahydronaphthalene (isotetralin), which contains one more carbon−carbon double bond and two more CH_2 bridge units than CHD. The results obtained from both ESKT and KT approaches are then compared. To study the π^* TB and TS interactions in isotetralin, the energies of the π^* levels of ethylene and the model ethylene "trimer"[8] are computed via the ESKT method.

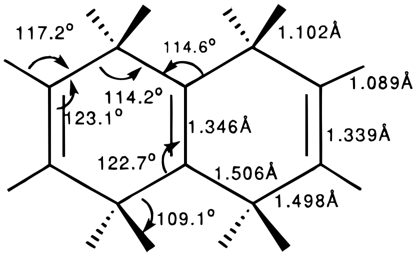

Figure 1. The geometry of isotetralin utilized for the calculations.

2. Methodology and Computational Details

In the present study, the ESKT is employed to distinguish the π^* orbitals from the ODC solutions. Three different Gaussian-type basis sets are employed for the ESKT calculations. The 6-31G+αp_1 basis set is formed by augmenting the 6-31G basis set with the inner diffuse p_1 function multiplied by a scale factor α (denoted by αp_1) on the C atoms. For the C atoms, the p_1 functions denoted by the "+" (i.e., *sp*) in the 6-31+G* basis set[9] have exponents of 0.0438. The 6-31+G+αp_2 and 6-31+G*+αp_2 basis sets[10] are formed by augmenting the 6-31+G, 6-31+G* basis sets with the outer diffuse p_2 functions multiplied by α (i.e., αp_2) on the C atoms. The p_2 functions have the exponents of 0.0146 for the C atoms.

The stabilization graphs are obtained by plotting the calculated energies as a function of the scale factor, α. As α decreases, the ODC solutions may approach the π^* orbital solutions in energy and lead to avoided crossings between two types of solutions. In such cases, the energy of the stabilized π^* orbital is taken as the mean value of the two eigenvalues involved in the avoided crossing at their point of closest approach, α_{ac}.[5,6a,6b]

All calculations were performed using the Gaussian-94 program.[11] The isotetralin geometry used for the calculations is assumed to be planar to exploit D_{2h} symmetry. The calculation was carried out at the MP2/6-31G* optimized geometry as the same procedure employed in our previous CHD calculations.[6a] The isotetralin geometry used for the calculations is shown in Figure 1. The C−C distances and the C−H bond lengths of the ethylene trimer are the same as in isotetralin. The CCH angles are set to be 140° to keep the internal hydrogen atoms of two ethylene molecules from being too close.[12]

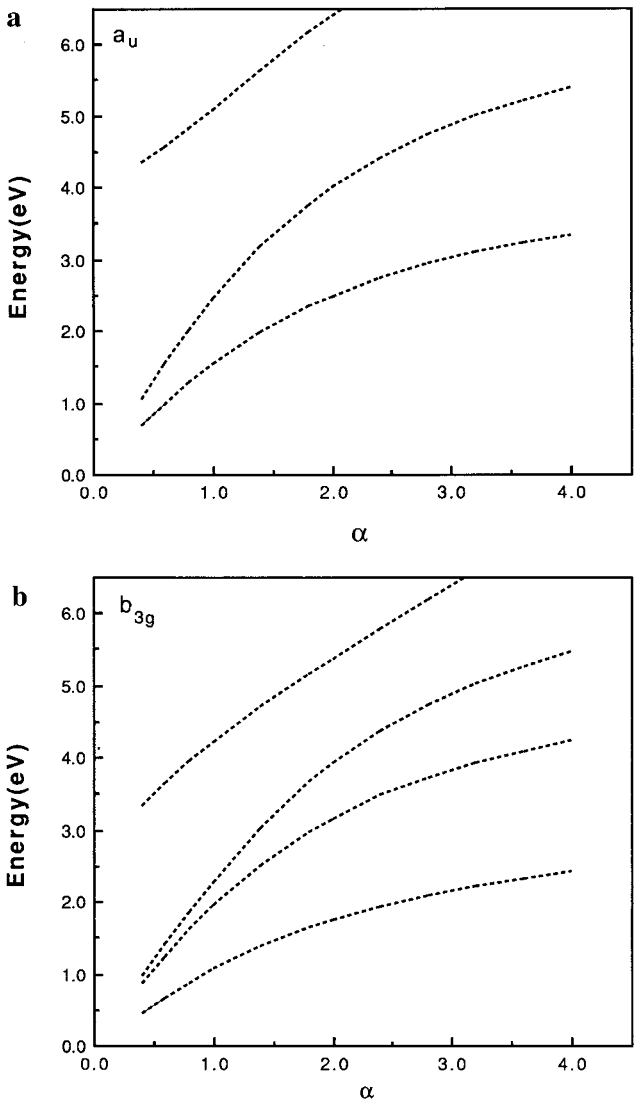

Figure 2. The eigenvalues of (a) a_u virtual orbitals and (b) b_{3g} virtual orbitals as a function of the scaling factor α for a free electron in the absence of potentials obtained with the 6-31+G+αp_2 basis set.

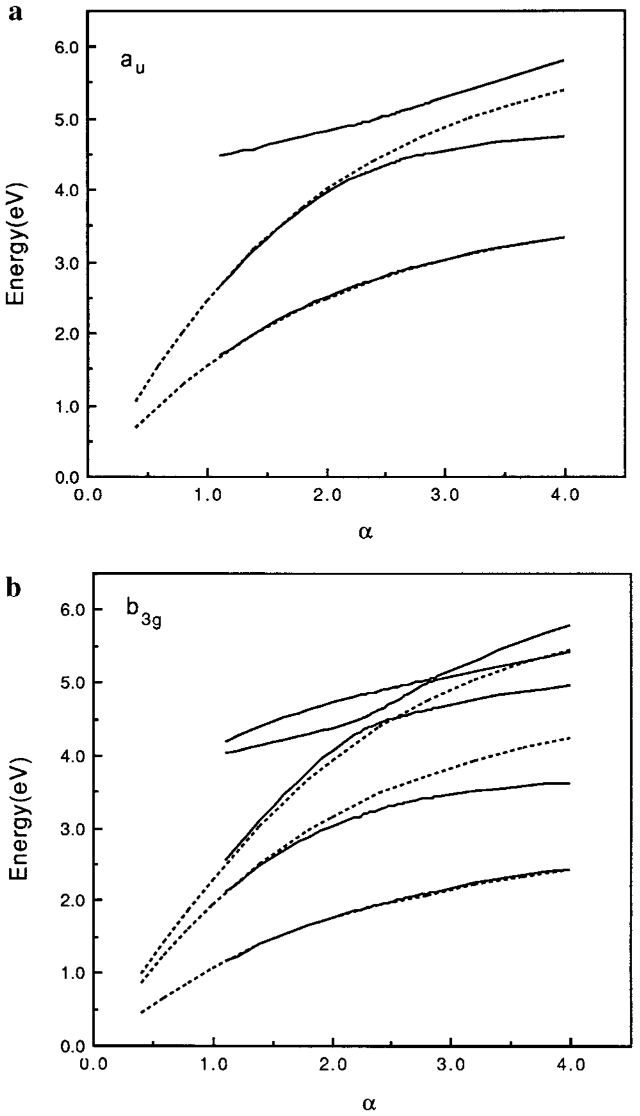

Figure 3. Stabilization graphs of eigenvalues of (a) a_u virtual orbitals, (b) b_{3g} virtual orbitals as a function of the scaling factor α for isotetralin and free electron obtained with the 6-31+G+αp_2 basis set. The eigenvalues for the molecular and the free electron problem are represented by the solid and dashed curves, respectively.

3. Results and Discussion

a. Isotetralin π* Virtual States. The eigenvalues of the discrete continuum (DC)[3] solutions are obtained by solving the SchrÖdinger equation for a free electron in the absence of potentials. Figures 2a and 2b give the eigenvalues of the DC solutions as a function of α for the a_u and b_{3g} virtual orbitals obtained with the 6-31+G+αp_2 basis set, respectively. (The symmetry in the labeling of the orbitals is based on a molecular orientation with the central carbon−carbon double bond lying along the *y* axis and all the carbon atoms lying in the *x*−*y* plane.) With this basis set there are three a_u and four b_{3g} DC solutions lying below 6.0 eV for 1 < α < 4.0.

The stabilization graph of the solutions a_u virtual orbitals and the free electron that were obtained with the 6-31+G+αp_2 basis set is shown in Figure 3a. The eigenvalues of the ODC solutions correlated well with the corresponding DC solutions when the energies are well below the stabilized π* orbital level. The lowest unfilled a_u orbital obtained from the ESKT calculations corresponds to the first DC solution for α < 4.0. The energy of the a_u π* SKT orbital is estimated from the avoided crossing with the ODC solution. The energy is 4.73 eV at α_{ac} = 2.60.

The stabilization graph of the b_{3g} π* virtual orbitals and free electron problem calculated with the 6-31+G+αp_2 basis set is shown in Figure 3b. The lowest unfilled b_{3g} orbital obtained from the ESKT calculations matches that of the first DC for α < 4.0. The second unfilled b_{3g} orbital matches the second DC for α < 1.7 and lies below that of the second DC for larger α value. According to Figure 3b, there are two avoided crossing regions below 6.0 eV. These avoided crossing regions are due to two b_{3g} π* orbital solutions together with one ODC solution because there is only one DC solution (third DC solution) around the avoided crossing regions. The energy of the first b_{3g} π* orbital (denoted as 2b_{3g}) obtained from the first avoided crossing is 4.45 eV at α_{ac} = 2.30. The energy of the second b_{3g} π* orbital (denoted as 3b_{3g}) obtained from the second avoided crossing is 5.04 eV at α_{ac} = 2.86.

The results of the various ESKT and KT calculations of the AEs for isotetralin are summarized in Table 1. To compare with experimental results, "corrected" AEs are also included in this table. The corrected values are obtained by subtracting a constant *b* from the original AE values to bring the calculated AE for the lowest π* anion state into agreement with experiment [i.e., $AE_{cor} = AE_{ESKT} - b$ (eV)]. In ESKT/6-31+G+αp_2 calculations, the constant *b* equals 2.85.

TABLE 1: Calculated and Corrected[a] AEs (eV) of Isotetralin Obtained from KT and ESKT Calculations

basis set	2 $^2B_{3g}$	2 ^2A_u	3 $^2B_{3g}$
ESKT method			
6-31G+αp_1	4.14 (1.60)	4.67 (2.13)	5.28 (2.74)
6-31+G+αp_2	4.45 (1.60)	4.73 (1.88)	5.04 (2.19)
6-31+G*+αp_2	4.42 (1.60)	4.73 (1.91)	5.04 (2.22)
KT method			
6-31G	4.96 (1.60)	5.41 (2.05)	5.06 (1.70)
6-31+G	3.05 (1.60)	4.00 (2.55)	3.80 (2.35)
6-31+G*	3.06 (1.60)	3.98 (2.52)	3.82 (2.36)
experiment[b]	1.60	1.80	2.25

[a] The corrected values (shown in parentheses) were obtained by subtracting the amount needed to bring the calculated AEs into agreement with experimental values for the lowest π^* anion states. [b] Reference 14.

First, we compare the calculation results of ESKT/6-31+G+αp_2 with KT/6-31+G. The corrected energies of the three π^* anion states obtained from the ESKT/6-31+G+αp_2 calculations are 1.60 ($2b_{3g}$), 2.19 ($3b_{3g}$), and 1.88 eV ($2a_u$), respectively. According to the electron transmission spectroscopy (ETS)[13] spectrum results, isotetralin has its pronounced features at 1.60 and 2.25 eV and a very weak feature near 1.80 eV.[14] Thus, the ESKT/6-31+G+αp_2 calculation can account quantitatively for the relative AEs when compared with the experimental results. The inclusion of a diffuse *d* function on the carbon basis set proves to be relatively unimportant, leading to changes in the energies of the π^* orbitals of <0.03 eV.

As may be seen from Table 1, the ESKT method gives the ordering of $2b_{3g} < 2a_u < 3b_{3g}$ whereas the KT method gives the ordering of $2b_{3g} < 3b_{3g} < 2a_u$. The results of the KT method without stabilization, however, cannot be trusted.

It is important to establish that the ESKT method is able to correctly predict the ordering of two close-lying unfilled orbitals. Studies of a wide range of molecules have shown that the ESKT method usually predicts splittings correct to 0.1 eV. For CHD, which is closely related to isotetralin, the error in the ESKT splitting is only 0.04 eV.

If our assignment $2b_{3g} < 2a_u$ is correct, then our calculated value for the $2b_{3g}/2a_u$ splitting is only 0.08 eV, which is consistent with the magnitude of the error in the splittings between the π^* orbitals of other related systems. If the orbitals were actually ordered $2a_u < 2b_{3g}$, the calculated splitting would be in error by 0.48 eV. This value is far from the aforementioned range. Therefore, we can be confident in the $2b_{3g} < 2a_u$ π^* assignment.

One possible source of error for relative energies of unfilled orbitals as determined from ESKT calculations is due to extraction of energies from the stabilization graph by the midpoint method. In determining the performance of the midpoint method, we have compared the results obtained from the midpoint method with the exact results of refs 6e and 16. This comparison indicates that the errors due to the extraction procedure should be <0.06 eV.[17] Another possible source of error is from the unequal neglect of relaxation and correlation corrections of the unfilled orbitals.

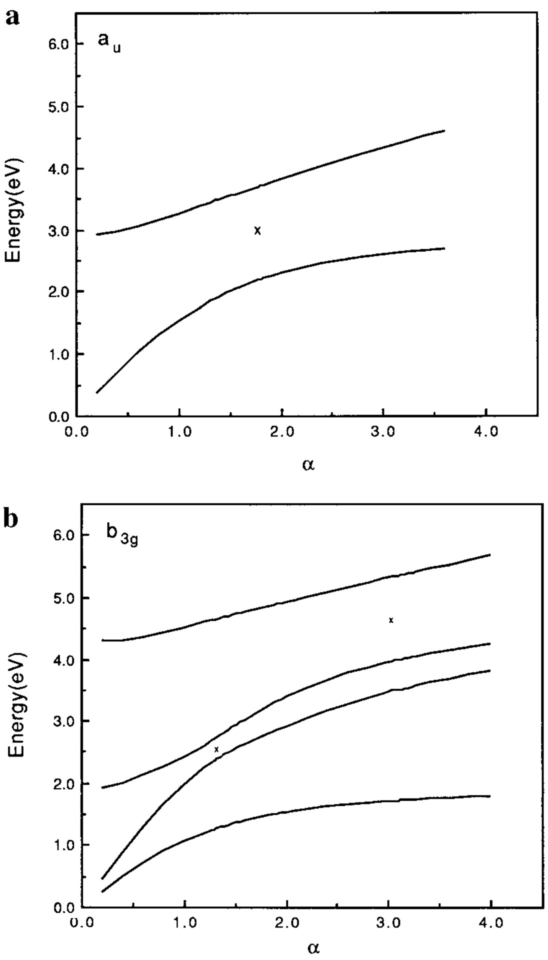

Figure 4. Stabilization graphs of eigenvalues of (a) a_u virtual orbitals, (b) b_{3g} virtual orbitals as a function of the scaling factor α for the trimer obtained with the 6-31+G+αp_2 basis set. The locations of α_{ac} are marked with x.

TABLE 2: Vertical Electron Attachment Energies (eV) of Ethylene and the Ethylene "Trimer" Obtained from the ESKT/6-31+G+αp_2 Calculations

<CCH	120°	140°
ethylene		
$^2B_{3g}$	2.93	2.72
ethylene trimer		
1 $^2B_{3g}$	2.46	2.53
1 ^2A_u	3.05	2.96
2 $^2B_{3g}$	4.70	4.67

b. Studies of TB and TS Interactions. To study the TB and TS interactions in the π^* orbitals, we performed the ESKT/6-31+G+αp_2 calculations on ethylene "trimer" and the middle ethylene of the trimer under two different CCH angles.[8] First, let us consider the results obtained from the calculations using the CCH angle of 140°. The stabilization graph of the energies as a function of scaling factor α for the lowest a_u virtual orbital of the trimer (denoted as $1a_u$) is shown in Figure 4a. The energies of the a_u π^* orbital obtained from the avoided crossing is 2.96 eV. The stabilization graph of the b_{3g} π^* virtual orbitals of the trimer is shown in Figure 4b. The energies of the first and second b_{3g} π^* orbitals (denoted as $1b_{3g}$ and $2b_{3g}$, respectively) obtained from the first and second avoided crossing are 2.53 and 4.67 eV, respectively. Table 2 gives the results of AEs for the ^2A_u and $^2B_{2g}$ states of the middle ethylene, and the "trimer" at two different CCH angles.

Then, by applying the fragment orbital method,[15] the π^* orbitals of the trimer can be constructed from those of the outer two ethylenes (i.e., the ethylene dimer), and that of the middle ethylene. The extent of interaction of b_{3g} π^* orbitals of the dimer and that of the middle ethylene can be taken as $\Delta E_1 - \Delta E_2$. Here, ΔE_1 is the splitting between two b_{3g} π^* orbitals of the trimer and ΔE_2 is the splitting between b_{3g} π^* orbitals of the dimer and that of the middle ethylene as shown in Figure 5. Likewise, the extent of interaction of π^* orbitals of two outer ethylene monomers can be taken to be ΔE_3, that is, the splitting

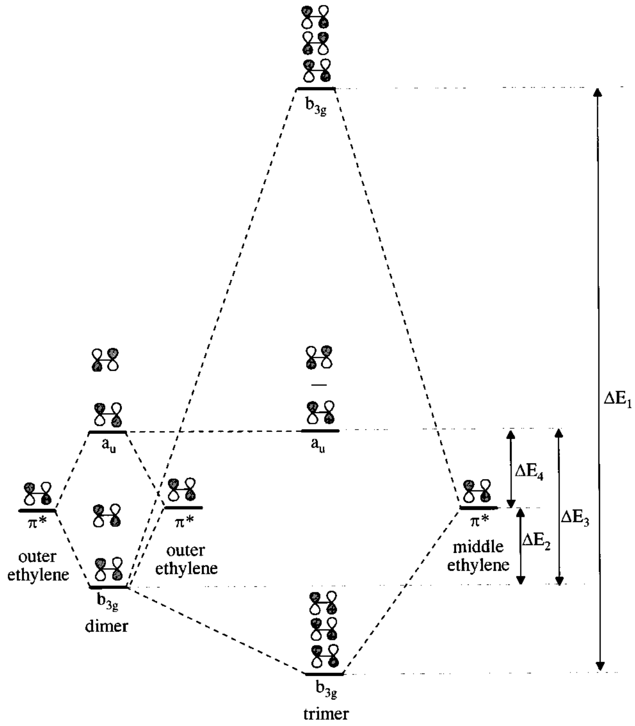

Figure 5. The π^* orbitals of the ethylene trimer constructed from those of the ethylenes dimer and that of the middle ethylene.

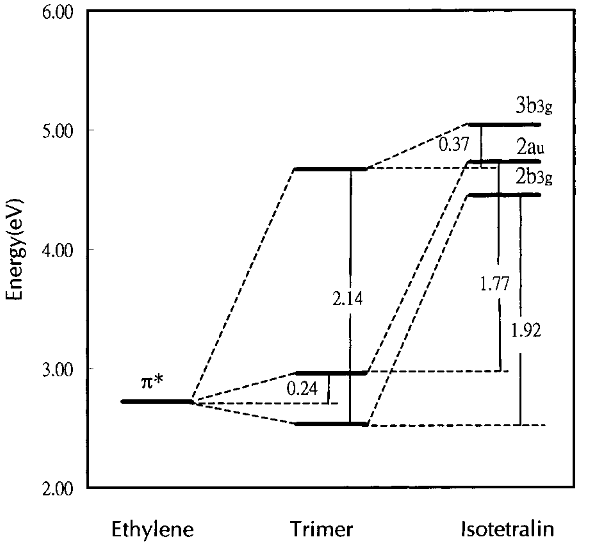

Figure 6. Correlation diagrams of the π^* orbital energies for ethylene, the ethylene timer, and isotetralin obtained from the ESKT calculations with the 6-31+G+αp_2 basis sets.

between two π^* orbitals of the dimer. Therefore, the overall magnitude of the TS interactions can be estimated by the amount $(\Delta E_1 - \Delta E_2) + \Delta E_3$. This amount is also equal to $\Delta E_1 + \Delta E_4$, where ΔE_4 is the splitting between a_u π^* orbital of the trimer and π^* orbital of the middle ethylene.

The magnitude of the TS interaction is calculated to be 2.38 eV for the CCH angles of 140°. The TS interaction is changed by only 0.02 eV when the CCH angle is changed from 120° to 140°. Therefore, problems caused by the internal hydrogens should be minor. Because isotetralin has one more π^* orbital than CHD, our ESKT/6-31+G+αp_2 calculations indicate that the magnitude of TS interactions for the π^* orbitals of isotetralin is ~0.50 eV larger than that of CHD.[6a]

The magnitudes of the TB interactions[8] are estimated by the differences in energies of π^* orbitals of the trimer and the corresponding π^* orbitals of isotetralin. The correlation diagram of the π^* orbital energies for ethylene, ethylene trimer, and isotetralin is given in Figure 6. Due to reasons of symmetry, all three π^* orbitals can mix with CH_2 pseudo-π orbitals. The ESKT/6-31+G+αp_2 calculations indicate that TB destabilization of $2b_{3g}$, $2a_u$, and $3b_{3g}$ π^* orbitals are 1.92, 1.77, and 0.37 eV, respectively.

Our predicted ordering of the π^* orbitals, $2b_{3g} < 2a_u < 3b_{3g}$, in isotetralin is the same as that in the ethylene trimer. This "normal" ordering of π^* orbitals is not the same as the inverted ordering in CHD, which has $a_u < b_{3g}$ (i.e., $\pi_-^* < \pi_+^*$ ordering). The main factor causing the difference in the ordering of a_u and b_{3g} π^* orbitals for these two systems is that the TB interactions destabilize both the $2b_{3g}$ and $2a_u$ π^* orbitals by about the same amounts in isotetralin. However, CH_2 pseudo-π orbitals do not mix with a_u π^* orbitals and the TB interactions only destabilize b_{3g} π^* orbital in CHD. Our calculated results also indicate that the total magnitude of TB interactions is about twice of TS interactions for isotetralin.

4. Conclusions

The energies of π^* anion states of isotetralin have been calculated by the ESKT method. Our predicted ordering of π^* orbitals is $2b_{3g} < 2a_u < 3b_{3g}$. This result is the same as that of ethylene trimer with only TS interactions present. This normal ordering is due to the fact that the TB interactions destabilize all the π^* orbitals.

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References and Notes

(1) (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Paddon-Row: M. N.; Wong, S. S. *Chem. Phys. Lett.* **1990**, *167*, 432. (c) Jordan, K. D.; Paddon-Row: M. N. *J. Phys. Chem.* **1992**, *96*, 1188. (d) Jordan, K. D.; Paddon-Row: M. N. *Chem. Rev.* **1992**, *92*, 395. (e) Paddon-Row: M. N.; Jordan, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 2952. (f) Paddon-Row: M. N.; Shephard, M. J.; Jordan, K. D. *J. Phys. Chem.* **1993**, *97*, 1743. (g) Nash, J. J.; Carlson, D. V.; Kasper, A. M.; Love, D. E.; Jordan, K. D.; Morrison, H. *J. Am. Chem. Soc.* **1993**, *115*, 8969. (h) Pearl, D. M.; Burrow, P. D.; Nash, J. J.; Morrison, H.; Nachtigallova, D.; Jordan, K. D. *J. Phys. Chem.* **1995**, *99*, 12381. (i) Mikkelsen, K. V.; Ratner, M. D. *Chem. Rev.* **1987**, *87*, 113. (j) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767.

(2) Koopmans, T. *Physica* **1934**, *1*, 104.

(3) Falcetta, M. F.; Jordan, K. D. *J. Phys. Chem.* **1990**, *94*, 5666.

(4) Falcetta, M. F.; Jordan, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 2903.

(5) Burrow, P. D.; Howard, A. E.; Johnston, A. R.; Jordan, K. D. *J. Phys. Chem.* **1992**, *96*, 7570.

(6) (a) Juang, C.-Y.; Chao, J. S.-Y. *J. Phys. Chem.* **1994**, *51*, 13506. (b) Chen, C.-S.; Feng, T.-H.; Chao, J. S.-Y. *J. Phys. Chem.* **1995**, *99*, 8629. (c) Chao, J. S.-Y. *Chem. Phys. Lett.* **1991**, *179*, 169. (d) Chao, J. S.-Y. *J. Phys. Chem.* **1993**, *97*, 4016. (e) Yu, L.; Chao, J. S.-Y. *J. Chin. Chem. Soc.* **1993**, *40*, 11. [Note: Chao, J. S.-Y. in (a) to (e) is Cheng, Hsiu-Yao who has adopted her maiden name as the second author in this paper.]

(7) (a) Hazi, A. H.; Taylor, H. S. *Phys. Rev.* **1970**, *A1*, 1109. (b) Taylor, H. S. *Adv. Chem. Phys.* **1970**, *18*, 91. (c) Fels, M. F.; Hazi, A. U. *Phys. Rev.* **1972**, *A5*, 1236. (d) Taylor, H. S.; Hazi, A. U. *Phys. Rev.* **1976**, *A14*, 2071.

(8) (a) Using the same procedure employed in refs 4 and 6a, estimates of the TB and TS interactions in the π^* states of isotetralin may be obtained from the HF calculations on an ethylene trimer with the ethylenic groups separated as in isotetralin. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (c) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Chem. Soc., Perkin Trans.* **1990**, *2*, 425.

(9) Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(10) Both ESKT/6-31+G+αp_2 and ESKT/6-31+G*+αp_2 calculations generate good $\Delta AE(\pi^*)$ values of 1,4-cyclohexadiene and benzene series (see ref 6).

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 (Revision E.2)*; Gaussian Inc.: Pittsburgh, PA, 1995.

(12) The CCH angles of the trimer are chosen to be the same as that of the ethylene dimer in refs 4 and 6a.

(13) (a) Sanche, L.; Schulz, G. J. *Phys. Rev.* **1972**, *5*, 1672. (b) Jordan, K. D.; Burrow, P, D. *Acc. Chem. Res.* **1978**, *11*, 341.

(14) The experimental AEs are taken from Professor K. D. Jordan's unpublished results.

(15) Jean, Y.; Volatron, F. In *An Introduction To Molecular Orbitals*; Burdett, J., Ed; Oxford University: New York, 1993.

(16) Jordan, K. D. *Chem. Phys.*, **1975**, *9*, 199.

(17) (a) The true energies of two branch points in a three-state avoided crossing model of ref 6e are $E_1 = 0.662$, and $E_2 = 1.266$. Their energies obtained from the midpoint method are: $E_1 = 0.663$, and $E_2 = 1.311$. Their magnitudes of error are 0.001 and 0.045, respectively. The separations of energies (denoted as ΔE_{ac}) of two eigenvalues of the avoided crossings at the point of their closet approach, α_{ac}, are 0.434 and 0.799, respectively. (b) Similarly, the magnitudes of error are 0.000, 0.000, and 0.020, for branch points in three two-state avoided crossing models of ref 6e (see Table 5 in ref 6e). Their values of ΔE_{ac} are 0.189, 0.340, and 0.477, respectively. (c) The magnitudes of error for two branch points in a two-state avoided crossing in model 1 of ref 16 are 0.058, and 0.011. Their values of ΔE_{ac} are 0.889 and 0.384, respectively. (d) The magnitude of error and the ΔE_{ac} for branch point in a two-state avoided crossing in model 2 of ref 16 are 0.001 and 0.097. The values of ΔE_{ac} for a_u and b_{3g} π^* orbitals of isotetralin are <0.2 and 0.7 eV, respectively. Therefore, their magnitudes of error and relative error due to the extraction of energies from the stabilization graph should be within 0.01, 0.05, and 0.06 eV, respectively.