

# Observation of a Very Large Orbital Interaction through Four Bonds. An Alternative Model of Orbital Interactions through Bonds

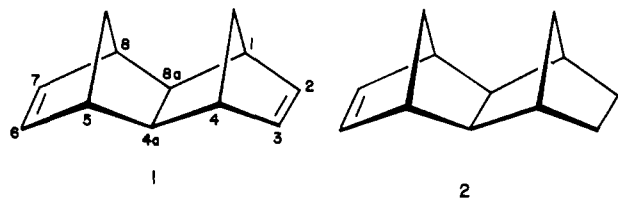
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In 1968, Hoffmann, Imamura, and Hehre reported calculations on diradical model systems which led to the now classic conceptual dissection of orbital interactions into through-space and through-bond varieties. These calculations indicated that the magnitude of orbital interactions through  $n$  bonds (OIT- $n$ -B) should diminish regularly with increasing  $n$ .<sup>1</sup> Experimental measures of this damping effect are not conclusive, despite the wealth of data that has been collected on OIT-3-B,<sup>2,3</sup> because only a few examples of OIT-4-B and OIT-5-B have appeared,<sup>4-6</sup> and these are often in systems where the magnitude of interaction can only be inferred indirectly. We now present direct experimental evidence that OIT-4-B can be as large as OIT-3-B. We also describe a simple general model of OITB that readily explains and predicts magnitudes and stereochemical aspects of OITB.

In the course of our studies of the chemical consequences of orbital interactions,<sup>7</sup> we have measured the He I photoelectron spectra (PES) of diene **1**, monoene **2**, and the saturated analogue.<sup>8</sup>



The PES of these molecules are given in Figure 1, and the ionization potentials (IPs) of these and related compounds are listed in Table I. The two  $\pi$  IPs of **1** differ by 0.87 eV, in spite of the

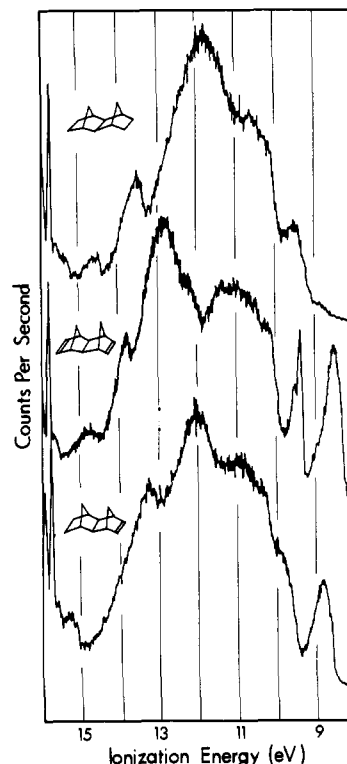


Figure 1. Photoelectron spectra of saturated, diene, and monoene dimethanonaphthalenes.  $\pi$  ionizations are the relatively sharp features to the right in the second and third spectra.

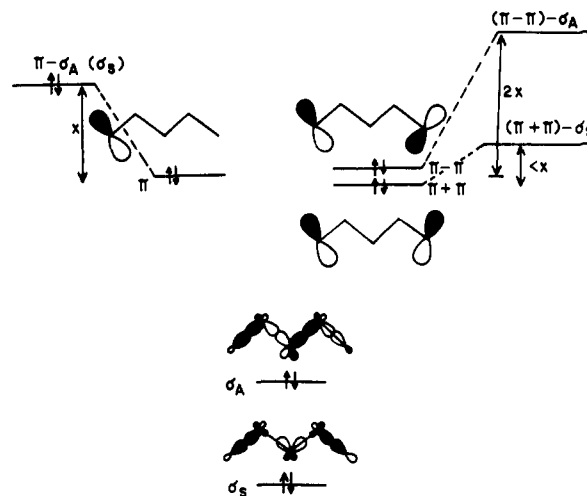


Figure 2. Schematic representation of  $\sigma$ - $\pi$  mixing in **1** and **2**. The  $\pi$  and top two  $\sigma$  orbitals before interaction are given in the middle. On the left:  $\pi$  (basis)-HO- $\sigma$ -MO mixing. On the right: mixing of  $\pi \pm \pi$  with HO- $\sigma$ -MO and SHO- $\sigma$ -MO.

Table I. Vertical  $\pi$  Ionization Potentials ( $\pm 0.03$  eV) and Orbital Energies ( $\epsilon_{\pi}$  STO-3G) of Dimethanonaphthalenes

compd	IP ( $\pi$ ), eV	$\epsilon_{\pi}$ STO-3G, eV	assignment
1	8.48	-7.46	$\pi - \pi$
	9.35	-8.35	$\pi + \pi$
2	8.85	-7.85	$\pi$
5	8.46 <sup>sa</sup>	-7.54	$\pi - \pi$
	8.90 <sup>sa</sup>	-8.06	$\pi + \pi$
6	8.78	-7.79	$\pi$
7	8.65	-7.69	$\pi$

impossibility of direct overlap, and the separation of  $\pi$  orbitals by four  $\sigma$  bonds. This 0.87-eV splitting energy is barely less than that typically found in those molecules exhibiting purely  $\pi$  OIT-3-B such as **3** (0.97 eV)<sup>3a</sup> and **4** (0.85 eV).<sup>3c,9</sup> Indeed, the  $\pi$

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(1) (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(2) Review: Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696.

(3) (a) Gleiter, R.; Heilbronner, E.; Hekman, M.; Martin, H. D. *Chem. Ber.* **1973**, *106*, 28. (b) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Tetrahedron Lett.* **1969**, 4025. (c) Brogli, F.; Eberbach, W.; Haselbach, E.; Heilbronner, E.; Hornung, V.; Lemal, D. M. *Helv. Chim. Acta* **1973**, *56*, 1933. (d) Paddon-Row, M. N.; Hartcher, R. *J. Am. Chem. Soc.* **1980**, *102*, 662.

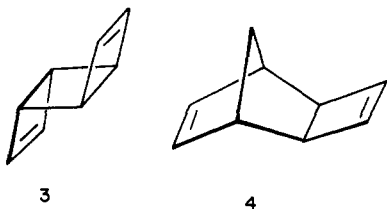
(4) Paddon-Row, M. N.; Hartcher, R. *J. Am. Chem. Soc.* **1980**, *102*, 671.

(5) (a) Martin, H. D.; Schwesinger, R. *Chem. Ber.* **1974**, *107*, 3143. (b) Bartetzko, R.; Gleiter, R.; Muthard, J. L.; Paquette, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5589. (c) Pasman, P.; Verhoeven, J. W.; de Boer, Th. J. *Tetrahedron Lett.* **1977**, 207.

(6) A particularly clear cut example of the dependence of OITB- $n$ -B on  $n$  concerns the series I-(C $\equiv$ C)-I. It was found that OITB between the  $\sigma$  lone pairs and the  $\sigma$  framework were attenuated with increasing  $m$ , being negligible for  $m = 3$  (corresponding to OIT-7-B): Haik, H. J.; Heilbronner, E.; Hornung, V.; Kloster-Jensen, E. *Helv. Chim. Acta* **1970**, *53*, 1073. Heilbronner, E.; Hornung, V.; Maier, J. P.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1974**, *96*, 4252. Bieri, G.; Heilbronner, E.; Jones, T. B.; Kloster-Jensen, E.; Maier, J. P. *Phys. Scr.* **1977**, *16*, 202.

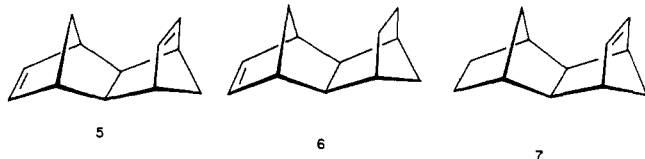
(7) Paddon-Row, M. N.; Lap, B. V.; Patney, H. K.; Warrrener, R. N. *Aust. J. Chem.* **1980**, *33*, 1493.

(8) The synthesis of these molecules will be reported in the full paper.

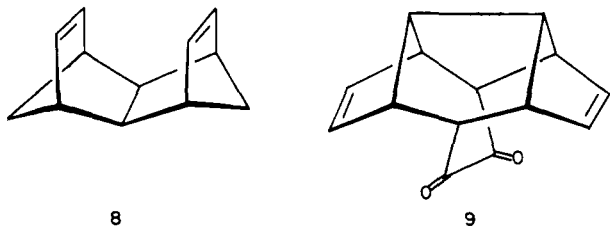


MO's in **1** are split as much as they are (mainly by a through-space mechanism) in norbornadiene (0.85 eV).<sup>10</sup> The IP split observed in **1** is much greater than that determined for **5** (0.31 eV),<sup>11</sup> and supports the prediction that an all trans (W) arrangement of  $\sigma$  bonds (as in **1**) is a more effective promoter of OITB than a cis-trans arrangement (as in **5**).<sup>1,15</sup>

Calculations on **1**, **2**, and **5-7** using the STO-3G basis set<sup>12,13</sup> give orbital energies which not only correspond remarkably well with experimental IPs ( $IP_{\text{expt}} = -0.98\epsilon_{\text{STO-3G}} + 1.16$ ) but also confirm the expectation<sup>1</sup> that the negative combination of  $\pi$  orbitals ( $\pi - \pi$ ) lies higher in energy than the positive combination ( $\pi + \pi$ ) in both **1** and **5**.



The splitting of the  $\pi$  levels in **1** represents the largest value so far reported that is exclusively due to OIT-4-B. Large  $\pi$  splitting energies have also been reported for **8** (1.26 eV)<sup>5a</sup> and **9** (0.85 eV),<sup>5b</sup> but these are due, in part, to the presence of reinforcing through-space interactions.<sup>22</sup>



Comparing **2** to **1**, or **6** and **7** to **5**, the  $\pi + \pi$  orbital of the diene is significantly more stable than that of the monoene(s). According to the currently accepted model of OITB,<sup>1-3</sup> this orbital lowering is a result of the mixing of  $\pi + \pi$  with the  $LU-\sigma^*-\text{MO}$ .<sup>14</sup> However, we believe that mixing of high energy vacant  $\sigma^*$  orbitals with the  $\pi + \pi$  combination in **1** cannot be sufficient to account for the large observed depression of  $\pi + \pi$  (the "depression effect"). The influence of the occupied  $\sigma$  orbitals, which are much closer in energy to  $\pi$  orbitals, must be far larger. Similar suggestions have been made for OIT-3-B.<sup>15</sup> We propose that the

(9) For systems such as **4** having nonequivalent  $\pi$  orbitals, the IP (or orbital) splitting energy is defined as the difference between the IP separation in the diene and that of a hypothetical model where the  $\pi$  orbitals do not interact. The latter is generally estimated from model systems.

(10) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745.

(11) The splitting energy reported for **5**<sup>5a</sup> (0.44 eV) is too large, since we have found that the model monoenes **6** and **7** have IP's differing by 0.13 eV (Table I).

(12) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. *QCPE* **1973**, *10*, 236. Geometries were "synthesized" from the fully optimized (STO-3G) geometry of norbornene.<sup>13</sup> The angle between the planes C1C4C4aC8a and C4aC5C8C8a (see **1**) was optimized and was found to be ca. 132° for each molecule studied.

(13) (a) Paddon-Row, M. N.; Houk, K. N.; unpublished results. (b) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N., submitted for publication.

(14) A small inductive effect can also lower  $\pi + \pi$ ,<sup>5b</sup> but this effect must be small in **1**, where the double bonds are separated by four  $\sigma$  bonds and in any case operates on both  $\pi + \pi$  and  $\pi - \pi$ .

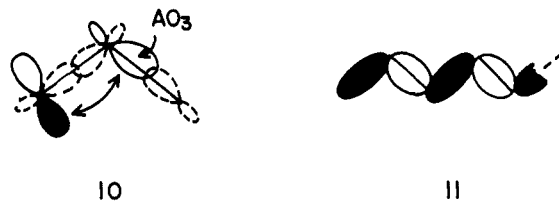
(15) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1976**, *98*, 4392. We acknowledge our indebtedness to these authors for major inspiration for the development of our model.

IP split in **1** and analogous molecules results from differential mixing of the  $\pi - \pi$  and  $\pi + \pi$  orbitals with framework occupied  $\sigma$  orbitals of appropriate symmetry. This provides not only a more satisfactory explanation of experiment but also a simpler predictive method, as described below.

The essential features of our revised OITB model are as follows: (1)  $\pi$  (or lone pair) orbitals of closed-shell systems interact through bonds principally by mixing only with occupied  $\sigma$  orbitals; (2) the orbital energies of the  $\pi \pm \pi$  combinations of dienes, and of the corresponding monoene  $\pi$  basic orbital, are all raised through mixing with the  $\sigma$  orbitals but by different amounts.<sup>24</sup>

This model is best understood, for example, as diagrammed in Figure 2. An important feature of our model is the raising of the  $\pi$  basis level, by an amount  $x$ , through its mixing with  $HO-\sigma-\text{MO}$  (there are no symmetry restrictions to this mixing). It is easily shown that the level of the symmetry adapted pair,  $1/[\sqrt{2}(\pi - \pi)]$ , is raised by twice the amount,  $2x$ , through its mixing with the antisymmetric  $HO-\sigma-\text{MO}$ .<sup>16</sup> However, the level of the symmetry adapted pair,  $(1/\sqrt{2})(\pi + \pi)$ , is only marginally raised ( $<x$ ) through mixing with the symmetric  $SHO-\sigma-\text{MO}$ . The large difference in the extent of the  $HO-\sigma-\text{MO}$  and  $SHO-\sigma-\text{MO}$  mixing with  $\pi - \pi$  and  $\pi + \pi$  orbitals, respectively, is due to two factors: the  $HO-\sigma-\text{MO}$  is higher in energy than the  $SHO-\sigma-\text{MO}$ , and the  $HO-\sigma-\text{MO}$  overlap with  $\pi - \pi$  is much larger than of  $SHO-\sigma-\text{MO}$  with  $\pi + \pi$ .

The latter occurs because the overlap of  $\sigma$  orbitals with  $\pi$  orbitals occurs principally via the allylic CC bond and then largely through overlap with that part of the  $\sigma$  MO which is contributed by the atomic orbital on the carbon adjacent to the  $\pi$  bond ( $AO_3$ ), as shown by the arrow in **10**. This particular atomic orbital has



a particularly large coefficient in the  $HO-\sigma-\text{MO}$  and a relatively small coefficient in the  $SHO-\sigma-\text{MO}$ . This conclusion can be derived in various ways, the simplest of which is to use the "C" approximation,<sup>17,18</sup> in which CC  $\sigma$  MO's are formed as linear combinations of  $sp^3$  hybrids. Using the simplest Hückel-type approximation ( $\beta_{i,i+1} = \beta$ ; all other  $\beta = 0$ ), the coefficients given in Table II are obtained. In general, the  $HO-\sigma-\text{MO}$  of an  $n$  bond  $\sigma$  system resembles the  $HO-\pi-\text{MO}$  of a polyene with  $n$  double bonds, as shown in Figure 2 for a four bond system, and as represented generally, if more crudely, in **11**.<sup>17b</sup> In our model, through-space mixing arises from raising of the  $\pi$  (or lone pair) orbital combination having the same relative phase as the two terminal bonds of the  $HO-\sigma-\text{MO}$ . The other combination of  $\pi$  (or lone pair) orbitals is raised very little by mixing with  $\sigma$  orbitals. This is supported experimentally by the very different band shapes in the PES of **1**. While the first band is broad, indicating substantial mixing with the  $\sigma$  framework, the second is sharp, implying that ionization arises from a more nearly localized  $\pi$  orbital.

The origin of the depression effect is therefore seen to be due to the raising of the  $\pi$  basis level brought about by its mixing with

(16) The raising of  $\pi$  by mixing with  $\sigma_A$  is  $H_{\pi\sigma_A}^2/\epsilon_{\pi-\sigma_A} = x$ , whereas that for mixing of  $\pi - \pi$  with  $\sigma_A$  is  $(2(1/\sqrt{2})H_{\pi-\sigma_A})^2/(\epsilon_{\pi-\sigma_A} - \epsilon_{\sigma_A}) = 2x$ , since each  $\pi$  orbital has a coefficient of  $1/\sqrt{2}$ .

(17) (a) Sandorfy, C.; Daudel, R. *C. R. Hebd. Seances Acad. Sci.* **1954**, *238*, 93. In this approximation the  $\sigma$  MO's are represented by linear combinations of C  $sp^3$  hybrid orbitals on C, and numerical values are obtained by using the Hückel procedure. (b) In general, the shapes of the  $\sigma$  MO's of an  $n$  bond  $\sigma$  system resemble those of the  $\pi$  MO's of a polyene having  $n$  double bonds.

(18) For recent applications of the  $\sigma$  MO theory, see: (a) Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 143. (b) Verhoeven, J. W. *Ibid.*, in press. (c) Dewar, M. J. S.; McKee, M. L. *Pure Appl. Chem.* **1980**, *52*, 1431. (d) Dewar, M. J. S. *Bull. Soc. Chim. Belg.* **1979**, *88*, 957. (e) Herndon, W. C. *Prog. Phys. Org. Chem.* **1972**, *9*, 99. (f) Herndon, W. C. *J. Chem. Educ.* **1979**, *56*, 448.

Table II. Coefficients of  $AO_3$  (see 10) in the HOMO and SHOMO of a Linear System of  $n$   $\sigma$  Bonds

$n$	coeff of $AO_3$	
	HOMO	SHOMO
2	0.37	0.60
3	0.42	0.23
4	0.41	0
5	0.39	0.12
6	0.37	0.18

the HO- $\sigma$ -MO rather than to the lowering of the symmetry adapted  $\pi + \pi$  combination through its mixing with LU- $\sigma^*$ -MO.<sup>19</sup> This result is general for OIT- $n$ -B ( $n > 2$ ) because the data in Table II show that the coefficient of  $AO_3$  in the HO- $\sigma$ -MO is greater than that in the SHO- $\sigma$ -MO. Our model also suggests that the splitting energy resulting from  $\pi$  (lone pair) OIT- $n$ -B is largely due to the mixing of a symmetry adapted pair of orbitals with the HO- $\sigma$ -MO.<sup>25</sup>

The model also makes clear other salient features of OITB: (1) The energy level ordering of the interacted  $\pi$  orbitals depends on the number,  $n$ , of intervening bonds: S is below A for even  $n$ , and S is above A for odd  $n$ .<sup>1</sup> This result immediately follows from the model, because the HO- $\sigma$ -MO is S for odd  $n$  and A for even  $n$ .<sup>30</sup> (2) The all-trans (W) arrangement of bonds is the most

(19) The simple model predicts that  $(E_{\pi-\pi} - E_{\pi}) / (E_{\pi} - E_{\pi+\pi}) > 1$ . That this ratio is only 0.74 for **1** is probably due to the neglect of small effects such as the additional raising of the basis level by mixing with lower lying  $\sigma$  MO's and the slight depression of the  $\pi + \pi$  level through its small mixing with  $\sigma^*$  LUMO.

(20) For the case  $n = 2$  we predict that  $(\pi - \pi)$ -HO- $\sigma$ -MO mixing and  $(\pi + \pi)$ -SHO- $\sigma$ -MO mixing to be comparable. It is therefore interesting to note that Heilbronner and Schmelzer have estimated that in norbornadiene both  $\pi + \pi$  and  $\pi - \pi$  levels are raised as a result of OIT-2-B and that the former level is raised more than the latter level. Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* 1975, 58, 936.

(21) Even OIT-9-B may be observable [ $AO_3(\sigma\text{HOMO}) = 0.37$ ,  $AO_3(\sigma\text{SHOMO}) = 0.24$ ] and may account for Zimmerman's observations of energy-transfer processes in [2]-rods: Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* 1980, 45, 3933.

(22) The  $\pi$  splitting energy in [4.4.2]propella-3,8-diene is only 0.3 eV.<sup>23</sup> Although the paper<sup>23</sup> equivocates about the origin of this split we are sure that it must be due (almost) exclusively to OIT-4-B. The small value of the splitting energy in the propellane compared with that observed for **1** (0.87 eV) could possibly reflect the conformation of the propellane. For example, if the  $\sigma$  framework connecting the  $\pi$  bonds had the cis-trans conformation (as opposed to the trans-trans conformation indicated in the paper<sup>23</sup>), then the splitting energy is consistent with that observed for **5** which also has the cis-trans arrangement of  $\sigma$  bonds.

(23) Dougherty, D.; Bloomfield, J. J.; Newkome, G. R.; Arnett, J. F.; McGlynn, S. P. *J. Phys. Chem.* 1976, 80, 2212.

(24) We draw attention to the nomenclature of interactions between orbitals and the intervening  $\sigma$  framework. The mixing of symmetry adapted combinations of orbitals with the orbitals is called OITB whereas the mixing of a single orbital with the  $\sigma$  orbitals is called hyperconjugation.

(25) The assumption that, in OITB,  $\pi$  (or lone pair) interactions occur principally through their mixing with  $\sigma$  orbitals has also been used by Heilbronner and his group in their analysis of photoelectron spectra of molecules exhibiting OITB but in a less explicit manner than described here. We have also learned that, in a letter to Professors D.C. Frost and L. Weiler (Sept 18, 1972), Professor E. Heilbronner described a more general formulation of our ref 16 which is also valid for the case where the molecule lacks symmetry.

(26) The available literature data suggest, however, that OIT- $n$ -B are attenuated fairly strongly with increasing  $n$ .<sup>6,28</sup> In fact, using a more realistic value for the resonance integral between two  $sp^3$  hybrid AO's attached to the same carbon atom ( $m\beta$ ,  $m = 0.35^{18c,d}$ ) leads to a greater attenuation of OITB- $n$ -B with  $n$ . Although the essential features of our model do not suffer from the use of the "C" approximation, the localized orbital technique, as developed by Heilbronner and co-workers,<sup>27</sup> would be more appropriate for placing the model on a firmer quantitative basis.

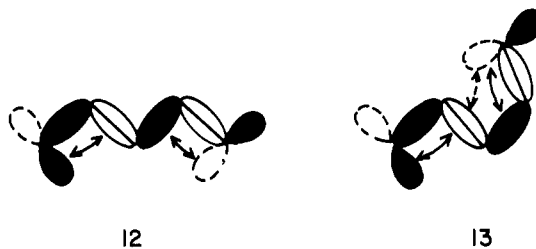
(27) (a) Bieri, G.; Dill, J. D.; Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* 1977, 60, 224. (b) Bischof, P.; Eaton, P. E.; Gleiter, R.; Heilbronner, E.; Jones, T. B.; Musso, H.; Schmelzer, A.; Stober, R. *Ibid.* 1978, 61, 547.

(28) It has been reported that  $\pi-\pi$  interactions in the series of nonconjugated acyclic dienes  $H_2C=CH(CH_2)_mCH=CH_2$  with  $m = 5-9$  diminish with increasing  $m$ .<sup>29</sup> Although these authors attribute these interactions to through-space effects, their supporting evidence is unconvincing and, until the conformations of these dienes have been determined more rigorously, we are inclined to believe that OITB could be largely responsible for the observations.

(29) Bunzli, J. C.; Burack, A. J.; Frost, D. C. *Tetrahedron* 1973, 29, 3735.

(30) Note Added in Proof: Since submission of this manuscript a similar treatment of the level ordering of orbitals interacting through bonds has recently appeared: Verhoeven, J. W.; Pasman, P. *Tetrahedron* 1981, 37, 943.

effective relay of OITB.<sup>1,15</sup> As mentioned, OITB give a splitting energy of 0.87 eV in **1** but only 0.31 eV in **5**. The  $\pi - \pi$  (dashed) and HO- $\sigma$ -MO's of **1** and **5** are represented in **12** and **13**, respectively. The antibonding interactions between  $\pi$  and allylic



bond AO's are represented by heavy arrows. In **13**, the bonding interactions represented by the dotted arrow cancels out some of the  $\pi - \sigma$  mixing. (3) Because the splitting energy depends to a large extent on the magnitude of the  $\pi$ -AO<sub>3</sub> interaction, it is evident from the coefficients in Table II that OIT- $n$ -B should decay only weakly with increasing  $n$  and should be easily observable for the case  $n = 6$ .<sup>21,26-29</sup> We intend to test this prediction by measuring the PES of further "norbornylogs" of **1**, which are currently being synthesized in our laboratories.

Finally, we note that OITB involving high-lying  $\pi^*$  MO's should involve mixing with  $\sigma^*$ , rather than  $\sigma$  orbitals, since the  $\pi^*$  levels presumably lie closer to the  $\sigma^*$  MO's than to the  $\sigma$  MO's. Here it is easily shown that the appropriate symmetry adapted pair of  $\pi^*$  MO's is lowered much more, through its mixing with the LU- $\sigma^*$ -MO, than the other pair of  $\pi^*$  MO's, through its mixing with the SLU- $\sigma^*$ -MO. We note that the Hoffmann model of OITB<sup>1</sup> represents a special case of our model, since the interacting orbital levels lie about midway between the HO- $\sigma$ -MO and LU- $\sigma^*$ -MO (i.e., such as p orbitals in carbon diradicals). In such a case, both  $\sigma$  and  $\sigma^*$  mix strongly with the radical orbitals.

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## Oxidation of Coordinated Ammonia to Nitrate

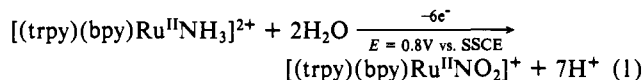
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We have discovered a well-defined reaction in which coordination of ammonia to ruthenium followed by oxidation leads to a rapid, quantitative conversion first to nitrite and then to nitrate. The reaction is remarkable in that it is rapid and involves only a single metal site.

A cyclic voltammogram of an aqueous solution of [(trpy)-(bpy)Ru<sup>II</sup>NH<sub>3</sub>]<sup>2+</sup> (trpy  $\equiv$  2,2',2''-terpyridine; bpy  $\equiv$  2,2'-bipyridine) at pH 6.8 shows a single irreversible oxidation wave at 0.84 V vs. the saturated sodium chloride calomel electrode (SSCE). Fixed potential electrolysis at 0.8 V results in the loss of six electrons per complex as shown by coulometry. The spectral,



voltammetric, and acid-base properties of the product are identical with those of an authentic sample of [(trpy)(bpy)Ru<sup>II</sup>NO<sub>2</sub>]<sup>+</sup>, thus establishing the stoichiometry shown in eq 1. Since it has been previously shown that further oxidation of [(bpy)<sub>2</sub>(py)RuNO<sub>2</sub>]<sup>+</sup>,