

bis(arene) complexes of ruthenium(0) are active catalysts in the absence of an alane<sup>2</sup> and bis(arene) complexes of molybdenum(0) are inactive at 140 °C in the presence and absence of trimethylaluminum (M. Millar and E. L. Muetterties, unpublished results).

(17) Address correspondence to the Department of Chemistry, Tulane University, New Orleans, La. 70118.

(18) Address correspondence to the Department of Chemistry, University of California, Berkeley, Calif. 94720.

Marcetta Y. Darensbourg,\*<sup>17</sup> E. L. Muetterties\*<sup>18</sup>

Department of Chemistry, Cornell University  
Ithaca, New York 14853

Received June 12, 1978

## Naphthalene-Butadiene Exciplex. An Extended Hückel Calculation

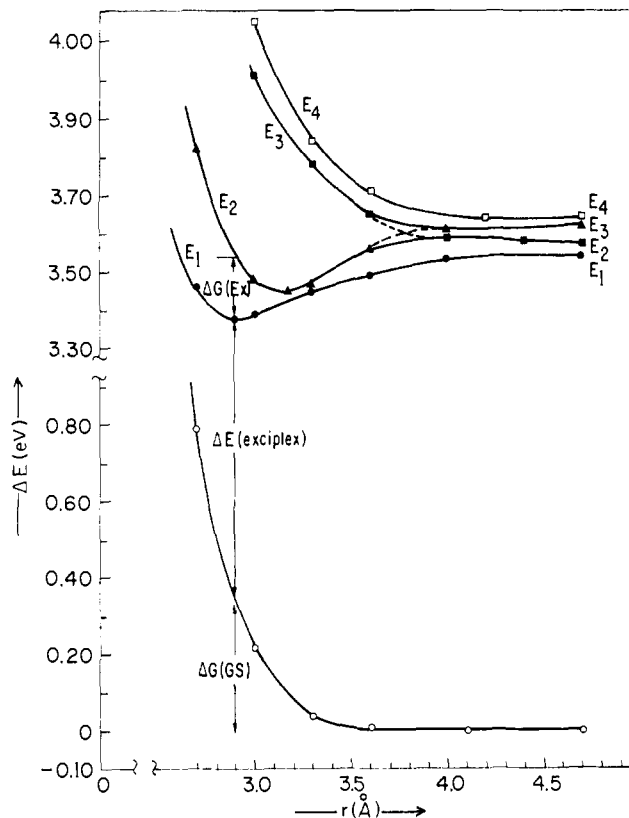
Sir:

In 1966 Hammond<sup>1</sup> reported the quenching of the excited singlet state of naphthalene by conjugated dienes. Since that time a large body of evidence has been gathered to support the contention that weakly bound excited-state complexes, exciplexes, mediate the acceleration of naphthalene radiationless decay during the quenching act. However, the electronic nature of the forces which stabilize the exciplex intermediate remains controversial. Weller<sup>2</sup> and Evans<sup>3</sup> have argued that charge-transfer interactions are the most important contributors to exciplex stabilization, while Hammond and co-workers<sup>4</sup> have suggested that, although charge transfer can be important, it need not be, and that excitation resonance and/or vibronic mixing can dominate in some systems. In support of this latter view, Weiss has presented evidence in the system triphenylphosphine-substituted anthracene<sup>5</sup> to show that the electronic nature of the exciplex intermediate can be systematically altered by substitution in the aromatic portion.

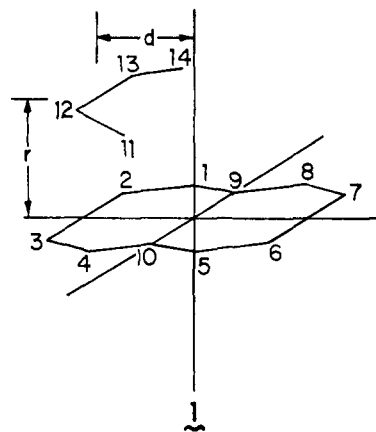
We present results of extended Hückel (EHT) calculations on the electronic states of the system naphthalene-butadiene which clearly indicate the importance of excitation resonance in stabilization of this exciplex pair. We also wish to suggest that relatively simple calculational approaches such as EHT can provide valuable insights into the nature of electronic interactions in exciplex models which quite closely parallel true experimental systems.<sup>6</sup>

We have used the EHT program of Hoffmann<sup>7</sup> as modified by Anderson<sup>8</sup> to include two-centered repulsions. Within the supermolecule approach we have searched for energy minima on the ground state and the four formal excited singlet surfaces of the system naphthalene (N)-*s-cis*-butadiene (B) with partial geometry optimization<sup>9</sup> programs developed at Du Pont.<sup>10</sup> State parameters have been calculated at various points on the surfaces in order to ascertain contributions from both charge and electronic mixing.

Figure 1 shows a projection of the  $E_{\text{tot}}(r,d)$  surfaces for B approaching N from above in a restricted coplanar fashion, i.e., **1**. The ground configuration ( $N^0 \cdots B^0$ ) is repulsive for  $r < 3.6$  Å for all values of  $d$ . The lowest excited singlet state  $E_1$  is weakly bound, minimizing at  $r = 2.90$  Å,  $d = 2.51$  Å, at an energy 0.17 eV (3.9 kcal/mol) below that of the separated species (and 0.19 eV (4.4 kcal/mol) below the separated configuration  $N^* \cdots B^0$ ). For large values of  $r$ , this state exhibits substantial charge transfer (0.996  $e^-$  at 5-Å separation), consistent with the configuration  $N^+ \cdots B^-$ .<sup>11</sup> However, at the minimum charge transfer is nearly absent (0.071  $e^-$  excess on B). Analysis of the calculated wave function coefficients in the vicinity of the minimum reveals substantial orbital interaction between the N and B subunits when compared with the localized MO's calculated for the separated (5 Å) species (Table I). The N $\cdots$ B local symmetry ( $C_s$ ) permits mixing of the N and B HOMO's and of their LUMO's. At distances  $r$  less than  $\sim 4$  Å, the system can only be viewed as a supermolecule whose



**Figure 1.** Calculated energies for the N $\cdots$ B electronic states as a function of interplanar separation,  $r$  (see **1**) at  $d = 2.51$  Å. Symbols refer to calculated points: ○ (GS, ground state); ● ( $E_1$ : excitation MO 36  $\rightarrow$  35); ■ ( $E_{2,3}$ : MO 37  $\rightarrow$  35); ▲ ( $E_{3,2}$ : MO 36  $\rightarrow$  34); □ ( $E_4$ : MO 37  $\rightarrow$  34). See note 12.



HOMO (MO 36<sup>12</sup>) is an antibonding composite of N- and B-localized HOMO's and whose LUMO (MO 35) is a bonding combination of the localized LUMO's. As a direct consequence of this mixing, the lowest excited state  $E_1$  is stabilized by removal of an electron from a HOMO having antibonding interactions between N and B and placement into an N-B bonding LUMO. This stabilization is reflected in positive overlap populations ( $C_1-C_{14}$ , 0.027;  $C_2-C_{13}$ , 0.005) between the N and B units in the excited state  $E_1$  at the minimum. Moreover, the analysis shows that the  $E_1$  state is best described as an excitation resonance state which exhibits considerable  $B^* \cdots N^0$  (38%) and  $B^0 \cdots N^*$  (55%) character and only a 7% charge-transfer component ( $B^- \cdots N^+$ ).

The approach of  $B^0$  to  $N^*$ , the experimentally observed quenching act, is considered by reference to calculated surface  $E_2$  of Figure 1. We find that  $E_2$  is very slightly repulsive ( $\sim 0.02$  eV) at  $r \approx 4$  Å, at which point an attempted surface crossing

**Table I.** Calculated  $C(p_z)$  Wave Function Coefficients for  $N \cdots B$  at  $r = 5 \text{ \AA}$  and  $r = 2.90 \text{ \AA}$ <sup>a</sup>

atom <sup>b</sup>	coefficient for MO <sup>c,d</sup>			
	34	35	36	37
$r = 5 \text{ \AA}$				
C <sub>1</sub>	+0.465	0	+0.397	0
C <sub>2</sub>	-0.308	0	+0.269	0
C <sub>9</sub>	+0.005	0	-0.010	0
C <sub>13</sub>	0	-0.434	0	-0.339
C <sub>14</sub>	0	+0.654	0	-0.573
$r = 2.9 \text{ \AA}$				
C <sub>1</sub>	+0.256	-0.359	+0.368	+0.152
C <sub>2</sub>	-0.203	+0.227	+0.230	+0.148
C <sub>9</sub>	+0.095	-0.047	-0.047	-0.111
C <sub>13</sub>	-0.305	-0.277	+0.225	-0.254
C <sub>14</sub>	+0.469	+0.429	+0.370	-0.417

<sup>a</sup>  $d = 2.51 \text{ \AA}$ . <sup>b</sup> See 1 for numbering. <sup>c</sup> See note 12; MO 34 is N-localized LUMO, 35 is B LUMO, 36 is N HOMO, 37 is B HOMO at  $r = \infty$ . <sup>d</sup> Symmetry designations within local  $C_s$  point group are 34 ( $a'$ ), 35 ( $a'$ ), 36 ( $a''$ ), 37 ( $a''$ ).

occurs with the next highest (bound) state  $E_3$ . Since the two state symmetries are the same ( $A''$ ), an avoided crossing will result, allowing access to the second minimum at  $r = 3.16 \text{ \AA}$  ( $d = 2.51 \text{ \AA}$ ). At the second minimum, and in the region  $4 \text{ \AA} > r > 3.16 \text{ \AA}$ , the states  $E_1$  and  $E_2$  are calculated to lie within 0.02–0.04 eV of one another. We therefore anticipate rapid interconversion among the upper states  $E_2$  and  $E_1$  in the interaction region. This path provides a plausible mechanism for the quenching of  $N^*$  by  $B^0$ , since, once access has been gained to the  $E_1$  minimum, rapid radiationless decay of the exciplex is to be expected by virtue of electronic mixing of the short-lived butadiene localized excited state into the longer-lived naphthalene localized state.

We note that the calculations reported here strictly apply only to the exciplex state uninfluenced by solvent. In fluid media, overall exciplex decay processes are dependent on factors which involve solvent, e.g., ion-pair separation. Mixing of ionic (CT) and excitation resonance configurations results in a positive binding energy for the exciplex state. In a polar solvent, exciplex binding energy is lower than in nonpolar solvents since ion-pair separation is increased. We suggest that the present calculations present an accurate picture of the configurationally mixed exciplex state in nonpolar solvents, and that the minimal contribution of CT stabilized configurations (7%) to the total exciplex state at the minimum is an important result which demands experimental study.

We believe that the EHT procedure provides an attractive framework for examination of the electronic nature of exciplex interactions in model systems which closely resemble actual experimental ensembles. We are extending this study to other systems<sup>13</sup> and to the use of other relatively simple and accessible molecular orbital techniques.

**Acknowledgments.** The authors thank Drs. T. Fukunaga and F. A. Van-Catledge for valuable criticism and advice.

## References and Notes

- Stephenson, L. M.; Whitten, D. G.; Vesley, G. F.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 3665–3666.
- Rehm, D.; Weller, A. *Isr. J. Chem.*, **1970**, *8*, 259–271.
- Evans, T. R. *J. Am. Chem. Soc.* **1971**, *93*, 2081–2082.
- Labianca, D. A.; Taylor, G. N.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 3679–3683; Taylor, G. N.; Hammond, G. S. *ibid.*, **1972**, *94*, 3684–3686, 3687–3692.
- Marcondes, M. E. R.; Toscano, V. G.; Weiss, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 4485–4490.
- Salem (Ramunni, G.; Salem, L. *Z. Phys. Chem. (Frankfurt Am. Main)*. **1976**, *101*, 123–135), Winnik (Maharaj, U.; Czizmadia, I. G.; Winnik, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 946–948), and Morokuma (Morokuma, K.; Neems, G. H.; Yamabe, S. *Tetrahedron Lett.* **1976**, 767–770) have reported ab initio results for several exciplex models. A CNDO treatment of triplet carbonyl-olefin exciplexes has been presented by Jaffé (Wilson, R. M.; Outcalt,

R.; Jaffé, H. H. *J. Am. Chem. Soc.* **1978**, *100*, 301–302). The only EHT application is to the benzene excimer (Chesnut, D. B.; Fritchie, C. J.; Simmons, H. E. *J. Chem. Phys.* **1965**, *42*, 1127–1128).

- FORTICON-8, Quantum Chemistry Program Exchange (QCPE), Program No. 344, 1977.
- Anderson, A. B. *J. Chem. Phys.* **1975**, *62*, 1187–1188.
- Geometries of N and B were generated using an Allinger force-field minimization (MMI) process (Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1–82). Coordinates for N were within 2% of crystal structure data. Those for B include C (terminal)–C (internal), 1.341 Å; C (internal)–C (internal), 1.344 Å; C–H, 1.09 Å. Though the internal C–C distance is short, the geometry does not significantly alter calculated parameters. In the present report we restrict our discussion to *s-cis* diene held in the face-to-face geometry, an orientation predicted by Salem (L. Salem, quoted in Cooke, R. S. Ph.D. Thesis, California Institute of Technology, 1969; p 96) to be important. Other geometries will be reported later.
- These programs are part of the TRIBBLE system, an interactive "computational workbench," specifically designed to make the computer easily accessible to laboratory chemists: D. Pensak, in preparation.
- EHT places the localized HOMO's and LUMO's of N and B in the following energy order: LUMO (N) > LUMO (B) >> HOMO (N) > HOMO (B), with  $E(\text{LUMO-HOMO})_N < E(\text{LUMO-HOMO})_B$ . Thus, the lowest energy excited state is formally  $N^+ \cdots B^-$ , followed by  $N^* \cdots B^0$ ,  $N^0 \cdots B^+$ , and  $N^- \cdots B^+$ , respectively, at infinite separation. More sophisticated calculations place LUMO (B) above LUMO (N) and eliminate this anomaly, which does not affect the present results in substance.
- The  $N \cdots B$  supermolecule is a system of 140 electrons, 70 MO's. Virtual orbitals are numbered 1–35, inclusive, while MO's 36–70 are doubly occupied in the ground configuration. MO 34 is associated, at large  $r$ , with the N-localized LUMO; likewise, MO 35 is LUMO (B), MO 36 HOMO (N), MO 37 HOMO (B). All the above are  $\pi$ -like  $C(p_z)$  ao combinations.
- Calculations in progress include  $N \cdots B$  exciplexes with *s-trans* diene; the effect of geometry relaxations (e.g., H bending) near the minimum; and the naphthalene-quadracycane exciplex.

David F. Eaton,\* David A. Pensak\*

Contribution No. 2584

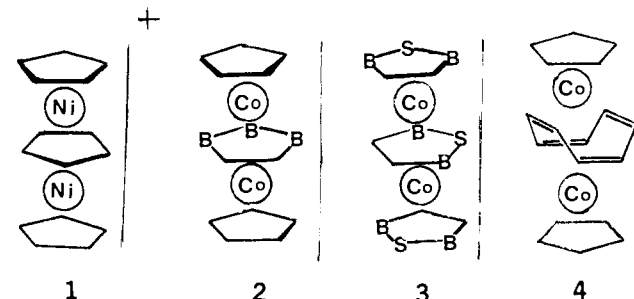
Central Research and Development Department  
E. I. du Pont de Nemours and Company  
Wilmington, Delaware 19898

Received June 12, 1978

## Electrochemical Properties of Bis(cyclopentadienylcobalt)cyclooctatetraene. Formation of a 34-Electron Triple-Decker Compound

Sir:

We report the electrochemical generation of the dication of bis( $\eta_5$ -cyclopentadienylcobalt)cyclooctatetraene,  $(\text{CpCo})_2\text{COT}^{2+}$ , a formal member of the so-called "triple-decker sandwich" class of molecules. This complex contains 34 valence electrons and is isoelectronic with the tris(cyclopentadienyl)nickel cation (1), the only charged triple-decker to be previously reported.<sup>1–3</sup>



Triple-decker complexes of the type 1–3 represent an intriguing class of organometallic compounds which has only recently been discovered.<sup>1–9</sup> All of the reported compounds contain either 30 or 34 valence electrons, a characteristic accounted for by the theoretical treatment of Hoffmann and co-workers.<sup>10</sup>

$(\text{CpCo})_2\text{COT}$  (4) has 18 valence electrons around each metal for a total of 36 electrons, and has been categorized as a "near miss" to the triple-decker class.<sup>10</sup> As part of our investigation of the redox properties of triple-decker sandwiches