of 4 kcal mole^{-1} for this E_a, based on a rate of less than 1 sec^{-1} and an A factor $\geq 10^{12}$. It does not seem reasonable that there should be such a barrier in view of the absence of a barrier to formation of a singlet excimer, which rules out any steric factors, either intramolecular or involving the matrix. We cannot rule out the possibility that the preferred geometry of a triplet excimer is not the same as the symmetrical sandwich preferred by the singlet isomer, and that this unknown configuration is not attainable in the rigid matrix. If such a barrier were to exist it would not interfere with excimer formation at the temperatures employed by Langelaar, *et al.*[3] We think it unlikely that such a barrier does really exist. Our results do not rule out the interpretation of Langelaar, *et al.* However, the equilibrium constant for formation of a triplet excimer would be small, probably less than 1, even at low temperatures, because of the low enthalpy of binding ($<10^3$ cm^{-1} = 3 kcal) and the appreciable entropy of association (−20 eu).[8] Thus, most of the triplets would be present as monomer in their experiments and, since the phosphorescence lifetimes are about the same, it would be very difficult to observe and identify dimer phosphorescence definitively. We suspect that the conclusions of Lim and Chakrabarti are not valid. Our findings are consistent with those of Kearns,[4] but it should be noted that dyes show excited dimer rather than excimer fluorescence. The failure of naphthalene to form a triplet excimer under our conditions suggests that the binding energy of this state is too small to compensate for the energy required to decrease intramolecular spacing to that of an excimer (3–3.2 Å). The instability of aromatic hydrocarbon triplet excimers relative to triplet monomers has been predicted recently by Lim.[11]

(11) A. K. Chandra and E. C. Lim, *J. Chem. Phys.*, **49**, 5066 (1968).

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Interaction of Nonconjugated Double Bonds

Sir:

The interaction of nonconjugated π-electron systems has attracted great theoretical and experimental interest.[1] It is clear that in neutral molecules experimental evidence for such interaction should be sought not in the total energy, but in spectral and ionization properties.[2] The most direct measure of this interaction is the difference in the ionization potentials of the interacting double bonds, relative to the ionization potentials of isolated, noninteracting systems. Through the technique of photoelectron spectroscopy[5] such measurements have become feasible and are now available for 1,4-cyclohexadiene, norbornadiene, and related molecules.[6] We wish to show here that two distinct symmetry-controlled mechanisms for interaction of π-electron systems, (1) direct through-space overlap and (2) through-bond or hyperconjugative interaction, may result in qualitatively divergent interaction patterns.

The model for dominant through-space interaction is norbornadiene (Figure 1). Such an interaction always places the positive overlap combination at lower energy, and accordingly the symmetric (with respect to plane 2) combinations of π and π^* levels should emerge below the antisymmetric. The SS–SA splitting is 0.43 eV in an extended Hückel calculation, much larger in a Hückel calculation,[1a] and 0.85 eV experimentally.[6]

Contrast the norbornadiene case with a model for optimal hyperconjugation, a planar 1,4-cyclohexadiene[7] (see Figure 2). We show in this figure only the σ orbitals which have π-type symmetry.[8] The SS double bond combination is destabilized by mixing with a CH_2 σ level. *The remarkable result is that the SS and SA levels are split by the hyperconjugative interaction in the opposite sense to the direct interaction.* The extended Hückel calculations for a planar model confirm the level ordering, and yield a splitting of 0.65 eV. The experimental result is 1.0 eV.[6] Of course the photoelectron spectrum does not tell us which level is lower, and in that sense confirmation of these predictions must await further physical studies.

We have also carried out "molecules in molecules" studies of the interaction of double bonds in these systems,[9] and these fully confirm the simple symmetry-based argument offered above.

An interesting level ordering reversal should be observed for bicyclo[2.2.2]octatriene *vs.* bullvalene (Figure 3). In the former the through-space interaction is dominant, leading to a splitting of the three π levels so that the more bonding degenerate e′ combination falls below the totally antibonding (between double bond units) a_2' level.[1a,10] In the case of bullvalene we construct the interaction between the three π levels and the Walsh orbitals of the cyclopropane ring.[10] The ordering of bonding π levels is clearly reversed, and extended Hückel calculations confirm this point.

(1) (a) C. F. Wilcox, Jr., S. Winstein, and G. McMillan, *J. Amer. Chem. Soc.*, **82**, 5450 (1960); (b) P. Radlick and S. Winstein, *ibid.*, **85**, 344 (1963); K. G. Untch, *ibid.*, **85**, 345 (1965); W. R. Roth, *Ann.*, **671**, 10 (1964); W. R. Roth, W. B. Bang, P. Goebbel, R. L. Sass, R. B. Turner, and A. P. Yü, *J. Amer. Chem. Soc.*, **86**, 3178 (1964); S. Winstein and F. P. Lossing, *ibid.*, **86**, 4485 (1964); S. Winstein in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 5; (c) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959); (d) R. C. Cookson, J. Henstock, and J. Hudec, *J. Amer. Chem. Soc.*, **88**, 1060 (1966).

(2) The situation differs markedly for charged species (ref 1b and 3) and diradicals (ref 4).

(3) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967).

(4) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

(5) D. W. Turner, *Proc. Roy. Soc., A*, **307**, 15 (1968).

(6) P. Bishof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).

(7) The actual molecular geometry is slightly bent, with a dihedral angle of 159°: H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969). See also G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 117 (1967); E. W. Garbisch, Jr., and M. C. Griffith, *J. Amer. Chem. Soc.*, **90**, 3590 (1968); R. C. Lord, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., 1968, No. PHYS 74; A. D. Buckingham, E. E. Burnell, and C. A. de Lange, *Mol. Phys.*, **16**, 521 (1969).

(8) Figure 2 shows the interaction with the bonding σ CH_2 levels of π-type symmetry. In principle one should include the antibonding σ^* levels of the same symmetry type in this kind of interaction diagram. Our experience (R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); R. Hoffmann, A. Imamura, and W. J. Hehre, *ibid.*, **90**, 1509 (1968)) has been that in hyperconjugative interactions mixing with the σ level is more important than that with σ^*. Two reasons for this emerge: (1) in calculations with overlap included the σ^* level is at very high energy; (2) overlap of adjacent p orbitals with σ is more efficient than with σ^*, since the latter has more nodes.

(9) E. Heilbronner and P. A. Straub, to be published.

(10) The argument here parallels that applied to the ordering of the cyclopropane orbitals in the Walsh model: A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

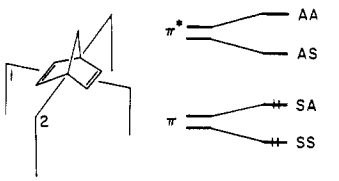


Figure 1. Norbornadiene levels before and after interaction through space. Levels are classified as symmetric (S) or antisymmetric (A) with respect to the mirror planes defined at left.

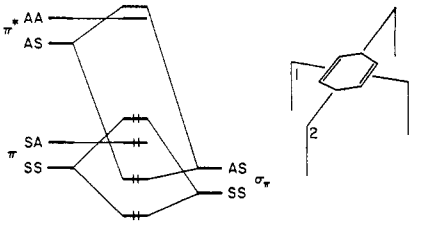


Figure 2. Interaction diagram for cyclohexadiene. The symmetry elements are the mirror planes defined at right. In the interaction diagram the π and π^* levels are placed at left and the CH_2 σ orbitals of the correct symmetry to mix with the π levels are at right.

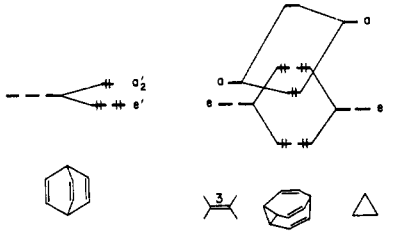
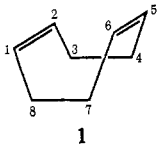


Figure 3. Interaction diagrams for barrelene (left) and bullvalene (right). For the latter we consider the mixing of the three ethylene π levels with the Walsh orbitals of the cyclopropane ring.

In 1,5-cyclooctadiene (**1**) the experimental splitting between the two π bands is less than 0.2 eV.[11] The



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through-space interaction must be significant in the boat conformation,[12] as evidenced by a calculation on a model of two ethylenes positioned identically with the double bonds in **1**. The calculated splitting is 1.67 eV, with SS lower, as expected. In cyclooctadiene itself there is superimposed an interaction with the SS combination of the 3–4, 7–8 σ bonds, ideally oriented for coupling the two π-electron systems.[1d,13] This through-bond coupling destabilizes the π-SS combination, lowering the level splitting to a computed 0.48 eV. The latter value is sensitive to the geometry assumed for **1**. In a chair conformation the through-space interaction is absent and the through-bond coupling dominates.

Acknowledgment. This work was supported by the National Science Foundation (GP 8013), the National Institutes of Health (GM 13468), and the Schweizerische Nationalfonds Project No. 4651.[14]

(11) E. Heilbronner, to be published.

(12) Cyclooctadiene conformations are discussed by J. D. Dunitz in "Perspectives in Structural Chemistry," Vol. II, J. D. Dunitz and J. A. Ibers, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, p 1.

(13) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1509 (1968).

(14) This is contribution No. 5 to Applications of Photoelectron Spectroscopy; for contribution No. 4 see E. Haselbach, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem.*, **18**, 897 (1969).

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Received October 31, 1969

Metal Complexes As Ligands. A New Class of Polynuclear Dithiolate Complexes

Sir:

As an approach to the systematic synthesis of coordination oligomers we have been investigating[1] the possibility of using anionic coordination complexes as ligands for coordinatively unsaturated, metal-containing Lewis acids. We have noted that, in weakly coordinating solvents, solutions of the transition metal dithiooxalate complexes,[2-4] $M^{II}(Dto)_2^{2-}$ (I), where M =

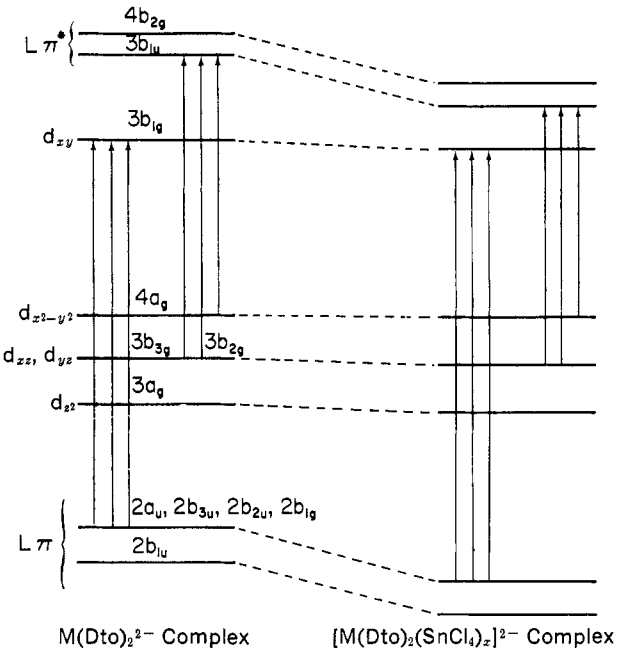

Figure 1. Energy level diagram for $M(Dto)_2^{2-}$ (ref 10) and $[M(Dto)_2(SnCl_4)_x]^{2-}$ complexes.

Ni, Pd, Pt, Cu, or Fe, react with the R_xSnCl_{4-x} species (x = 0, 1, 2; R = n-butyl). These reactions are always accompanied by pronounced color changes which occur as a result of a bathochromic shift of the first (low en-

(1) D. Coucouvanis, paper presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) C. S. Robinson and H. O. Jones, *J. Chem. Soc.*, 62 (1912).

(3) F. A. Dwyer and A. M. Sargeson, *J. Amer. Chem. Soc.*, **81**, 2335 (1959).

(4) (a) E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 1475 (1935); (b) the benzyl triphenylphosphonium ($BzPh_3P^+$) salts of the Ni(II), Pd(II), Pt(II), and Cu(II) dithiooxalato complexes are X-ray isomorphous. The structure of the $K_2Ni(Dto)_2$ complex has been determined (ref 4a). The nickel(II) ion is four-coordinate and sulfur bonded in the rigorously planar complex anion.