than those in III; ring opening in III therefore leads in effect to untwisted II. Rotation to form the normal twisted allene takes place only after the transition state is passed, *i.e.*, when the ring opening is effectively complete.

The calculated activation energies for the isomerizations of I to II are surprisingly large, 50 kcal/mol for Ia and 38 kcal/mol for Ib. These values seem unreasonable at first sight, given that allene is formed[6] by reaction of carbon atoms with ethylene in a neon matrix at −190°. However, on further reflection one realizes that the reaction paths of Figure 1 correspond to the particular normal mode of vibration which interrelates I and III; almost the whole of the energy liberated in the exothermic combination of the olefin with ^{1}S carbon to form I should therefore be converted into translational energy directly along the reaction path and the system should consequently pass straight over the transition state and on to I. Since the energy available (~80 kcal/mol) is much greater than the activation energy for conversion of I to II, it is unlikely that the system will be quenched before crossing the transition state, since the time available is half that of a single molecular vibration. The only danger is that the system may not be quenched fast enough to trap II; this explains why addition of a moderator (neon) to the reaction mixture increases the yield of allene.[5,6] It is also easy to see on this basis why neither ^{1}D nor ^{3}P carbon atoms give allenes; in the case of ^{1}D carbon, the initial reaction is less exothermic, while in the case of ^{3}P the conversion of I to II would involve an intersystem crossing. Consequently in both cases products are formed[6] that are derived from I (spiropentane and cyclopropylidene derivatives). Indeed, the failure of ^{1}D carbon to form allene would be very difficult to explain if the activation energy for conversion of I to II were not large. It should be added that our estimates of the activation energies may well be too high by *ca.* 12 kcal/mol since the MINDO/2 method underestimates[8a] the strain energies of cyclopropanes by this amount.[9]

Allenes are also formed by reactions in solution where the carbenes, I, could have been intermediates, and this has been attributed to facile rearrangement of I to II.[11-15] Such processes, however, involve reactions of metals or metal alkyls with 1,1-dihalocyclopropanes and there is now abundant evidence that the intermediates in them are not free carbenes, but "carbenoids," in which the carbene is coordinated to the metal. Such a complex, $C_3H_4M^+$, is in effect a metallated cyclopropyl cation and could well rearrange more readily that I itself; we are at present calculating the potential surfaces for such reactions. It is interesting that the one reaction in solution that has been reported in which a free carbene would be expected to be an intermediate, *i.e.*, the reaction of N-nitroso-2,3-diphenylcyclopropylurethan with alkoxide in isobutene, led to a spiropentane formed by trapping of the intermediate diphenylcyclopropylcarbene[15] rather than to diphenylallene.

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(9) A referee has suggested that the transition state (III) might correspond to an orbital crossing and that configuration interaction might then reduce the calculated activation energy. This is not the case; the eigenvectors indicated no orbital crossing. It should be pointed out in this connection that our procedure has given[8a] good estimates of activation energies for rotation about CC bonds in ethylene and the cumulenes, processes in which orbital crossing does occur. Presumably this is because implicit allowance is made in the procedure for electron correlation by our use of parameters chosen to fit experimentally determined energies of atoms and molecules; inclusion of configuration interaction would then lead to an overestimate of the correlation energy. A similar situation arose in the treatment of radicals by a π approximation[10] in which the use of an open-shell SCF method gave heats of atomization that were too large.

(10) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, **90**, 1953 (1968).

(11) W. v. E. Doering and P. M. La Flamme, *Tetrahedron*, 2, 75 (1958).

(12) L. Skattebøl, *Tetrahedron Lett.*, 167 (1961).

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(14) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962).

(15) W. M. Jones, M. H. Grasley, and W. S. Brey, *J. Amer. Chem. Soc.*, **85**, 2754 (1963).

(16) Robert A. Welch Postdoctoral Fellow.

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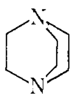
Long-Range Couplings between Lone Pair Electrons and Double Bonds[1]

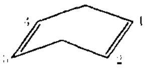
Sir:

Heilbronner and his collaborators[2] have recently shown by high-resolution photoelectron spectroscopy that there are strong interactions between the nitrogen lone pair AO's in dabco (I), and between the π MO's of 1,4-cyclohexadiene (II), norbornadiene (III), and bicyclo[2.2.2]octadiene (IV). The ionization potentials of nitrogen lone pair electrons, or olefinic π electrons, are less than those of electrons in σ bonds; I–IV each showed two distinct low-lying ionization potentials that must arise from mutual interaction of the lone pairs in I, or π MO's in II–IV.

Hoffmann and his collaborators[3] had studied this problem in the case of I and concluded that there should be a large interaction between the nitrogen AO's and that this should arise not from a direct interaction across space but rather by a kind of hyperconjugative interaction *via* the intervening carbon atoms. Since the theoretical methods available to Hoffmann, *et al.*, were rather crude, and since we had become interested in this problem in the case of II–IV,[4] we have now examined it in detail, using a semiempirical SCF MO procedure (MINDO/2)[5] which has been shown to give good predictions of ground-state properties, including ionization potentials.[4,5] The contribu-



I



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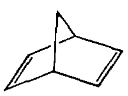
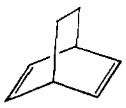


III



IV

V

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(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(2) P. Bischoff, J. A. Hashmall, E. Heilbronner, and V. Horning, (a) *Tetrahedron Lett.*, 4025 (1969); (b) *Helv. Chim. Acta*, **52**, 1745 (1969).

(3) R. Hoffmann, A. Imamura, and W. J. Mehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

(4) N. Bodor, M. J. S. Dewar, and S. D. Worley, *ibid.*, **92**, 19 (1970).

(5) (a) M. J. S. Dewar and E. Haselbach, *ibid.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, in press.

Table I

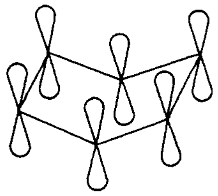
θ, deg	110	115	120	130	140	150	160	180
ΔE(II), eV	−1.706	−1.290	0.917	−0.181	0.325	0.724	0.994	1.241
ΔE(III), eV	−0.244	0.029	0.230	—	—	—	—	—

tions of various types of coupling can be studied by seeing how the splitting changes when the integrals corresponding to individual coupling processes are set equal to zero. The parameters used here (part X[5b]) lead to results for hydrocarbons very similar to those of ref 5a.

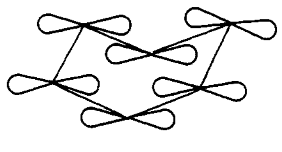
The MINDO/2 method predicted the first two ionization potentials of I to be 8.46 and 9.82 V (difference, 1.36 V), in reasonable agreement with experiment,[2a] *i.e.*, 7.52, 9.65 (2.11). When the integrals representing direct interactions between the nitrogen AO's (*i.e.*, $\beta_{NN'}{}^{c}$ (NN,N′N′)) were set equal to zero, the calculated splitting remained almost unchanged (1.31 V). The splitting therefore does *not* arise from direct interactions across space. Further studies showed that it in fact arises almost entirely from an indirect interaction *via* the pσ components of the CC bonds, as indicated in V. Two-thirds of the interaction is due to one-electron couplings, comprised in the resonance integrals $\beta_{ij}{}^{c}$, and one-third to long-range correlation effects, comprised in the two-electron terms $P_{ij}(ii,jj)$. In agreement with Hoffmann, *et al.*,[3] we find the highest occupied MO, corresponding to the first ionization potential, to be symmetric with respect to reflection in the plane of symmetry bisecting the CC bonds; if the splitting were due to a direct NN interaction, the highest occupied MO would have been antisymmetric.

In cyclohexadiene (II) the calculated splitting (1.01 V) is in excellent agreement with experiment (1.00 V[2b]). The highest occupied MO is symmetric for reflection in the plane of symmetry passing through the methylene groups; if the splitting were due to direct π–π interactions, the highest occupied MO would have been antisymmetric. In this case, however, omitting the direct interaction *increases* the splitting. Thus, omitting the 1–5 and 2–4 interactions gave a splitting of 1.33 V; omitting the 1–4 and 2–5 interactions gave 1.17 V. Here there is evidently a significant direct coupling (~0.5 V) between the orbitals in question, and this acts in opposition to the dominant indirect coupling through the methylene groups. The latter arises almost entirely by the π-type coupling indicated in VI rather than the σ-type coupling of VII; as in I, two-thirds of the coupling arises from one-electron terms and the rest from two-electron terms. The direct coupling is also almost entirely of the corresponding π type (*cf.* VIII).

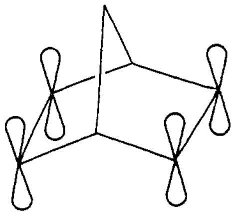
In III, the calculated splitting (0.03 V) is much less than that observed[2b] (0.86 V), and this time the highest occupied MO is antisymmetric with respect to the plane of symmetry passing through the bridgehead atoms. Omitting the direct interactions increased the splitting but inverted the order of the top two MO's. Omitting the π-type interaction (VIII) led to a change of 0.23 V, and omitting the σ-type interaction (IX) a change of 0.41 V. Omitting the indirect π-type interaction (V) left the order of MO's unchanged but increased the splitting by 0.21 V, while omitting the indirect σ-type interaction (VII) led to a corresponding change of 0.83 V. Here again the direct and indirect interactions have opposite effects on the relative energies of the symmetric and antisymmetric MO's. Since the direct interaction should decrease with a decrease in the angle (θ) between the nodal planes of the double bonds, since this angle is less in III than in II, and since the splitting in II is due mainly to the indirect interaction, it is not surprising that the splitting in III is less than in II. Our failure to predict it quantitatively in the case of III may be partly due to an error in the value of the dihedral angle θ. As Table I shows, the splitting is very sensitive to the dihedral angle; here ΔE is the difference (eV) in energy between the two highest MO's, a negative sign implying that the antisymmetric combination is the higher. The experimental values for θ are: II,[6a] 159.3, III,[6b] 115°. A more likely factor is our use of simple Slater–Zener AO's in calculating orbital overlap; this must lead to an underestimate of the long-range interactions, since Slater–Zener AO's are more "condensed" than the "correct" Hartree-Fock AO's. The fact that we calculate the splitting correctly for II, where the direct interaction is almost entirely of π type (*cf.* VIII), suggests that the error occurs mainly in the estimation of the σ-type direct interaction (*cf.* VIII) which predominates in the case of III.



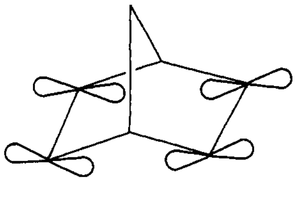
VI



VII



VIII



IX

Calculations for IV implied that the highest occupied MO is predominantly composed of the olefinic π MO's and is antisymmetric with respect to reflection in the C–CH_2–CH_2–C plane, the splitting being 0.3 V (obsd,[26] 0.58 V). Since the dihedral angle in IV is greater than that in III, the contribution of direct σ-type coupling (VII) should be less; on this basis, we would predict the direct coupling in IV to predominate, as in III, and that we should underestimate the splitting through a smaller amount than in III.

It would appear therefore that the direct and indirect couplings between double bonds in compounds

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(6) (a) H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969); (b) Y. Morino, K. Kuchitsu, and A. Yakozeki, *Bull. Chem. Soc. Jap.*, **40**, 1552 (1967).

such as II–IV are comparable, their relative magnitudes depending on the geometry.

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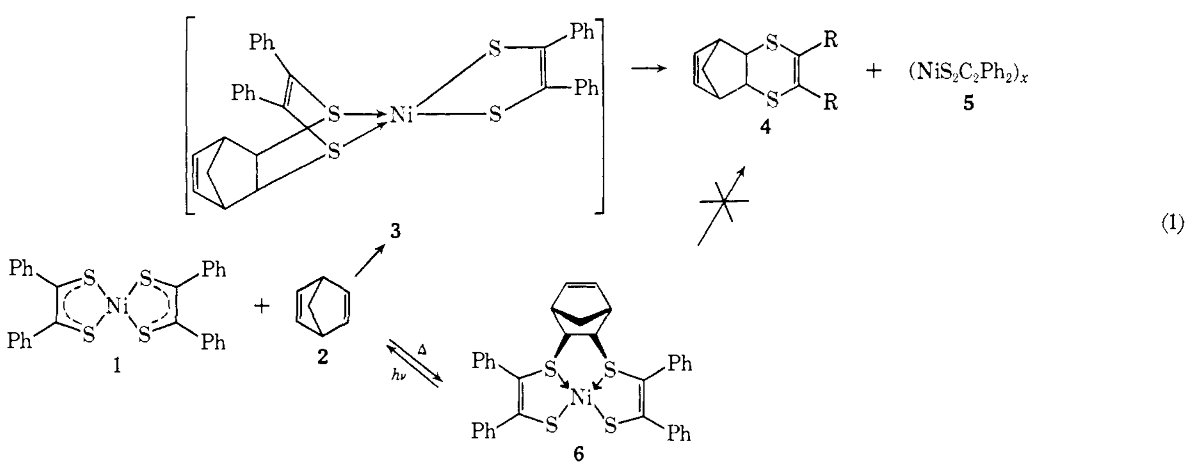
Structure, Alkylation, and Macrocyclic Derivatives of Bicyclo[2.2.1]hepta-2,5-diene Adducts of Metal Dithienes

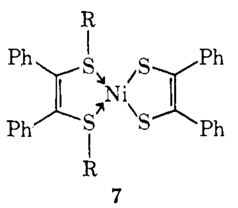
Sir:

Light-sensitive 1:1 adducts of group VIII metal bisdithienes such as $NiS_4C_4Ph_4$ (**1**, Ph = phenyl) with norbornadiene (bicyclo[2.2.1]hepta-2,5-diene, **2**) were first reported in 1965,[1] but their intricate nature is only now beginning to be understood. In view of the facile formation of the adduct **4** on reaction of **1** with **2** (eq 1) the complex $NiS_4C_4Ph_4 \cdot C_7H_8$ (mp 165° dec) was considered to be an intermediate in this reaction and was suggested to have structure **3**.[2]

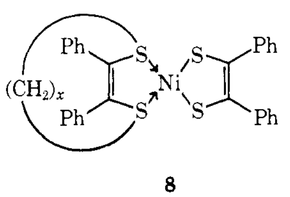


(1)

Wing, *et al.*,[3] recently reported the structure of a norbornadiene adduct of $NiS_4C_4(CF_3)_4$, in which the olefin is linked to two sulfur atoms of the complex, as shown in **6**. Whereas the reaction of **1** with **2** is slow at room temperature, requiring days for the completion, the addition of **2** to the CF_3-substituted complex occurs within seconds.[3] The possibility is thus not excluded that both adducts have different structures. A study was therefore undertaken to establish the structure of $NiS_4C_4Ph_4 \cdot C_7H_8$ by chemical means. If the adduct were the intermediate **3** in the formation of **4** (eq 1) the latter should form directly on thermal decomposition. The adduct would in principle behave as the known[2] complexes of type **7** or the new chelates of type **8**, which are obtained for x = 5–12 on reaction of $NiS_4C_4Ph_4^{2-}$ with the corresponding α,ω-dibromoalkanes at high dilution. For example, the complex with x = 10 forms green crystals, mp 150° dec.



7



8

Anal. Calcd for $C_{38}H_{40}S_4Ni$: C, 66.74; H, 5.91; S, 18.76. Found: C, 66.74; H, 5.94; S, 18.94.

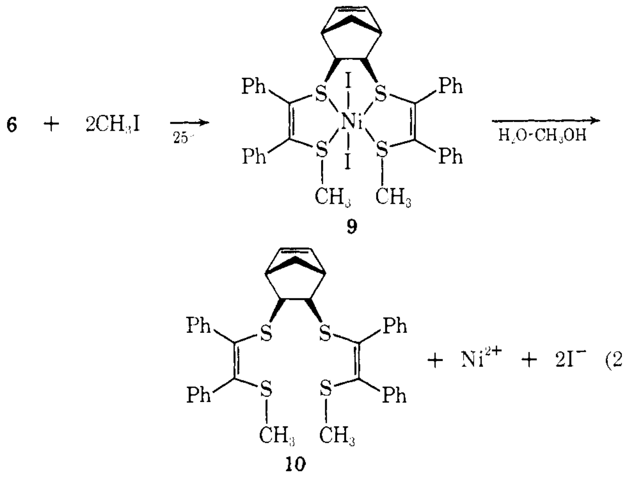
Bisdihaloalkyl derivatives were obtained on reaction of $NiS_4C_4Ph_4^{2-}$ with excess of alkylating agent, or for $x < 5$. Both **7** and **8** yield the unsaturated thioether on thermolysis. However, this is not the case for the norbornadiene adduct. On thermal decomposition, norbornadiene, $NiS_4C_4Ph_4$, NiS, and 2-phenylthianaphthene are formed, but no trace of **4**. Furthermore, no reaction is observed with phosphine ligands under conditions where complexes of type **7** undergo rapid ligand displacement. Chemical proof of structure **6** was obtained by alkylating $NiS_4C_4Ph_4 \cdot C_7H_8$ with excess methyl iodide in CH_2Cl_2 at room temperature. A yellow adduct **9**, mp 250° dec, was obtained (eq 2).

Anal. Calcd for $C_{37}H_{34}S_4I_2Ni$: C, 48.99; H, 3.68; S, 13.77; I, 27.24, Ni, 6.28. Found: C, 48.65; H, 3.45; S, 13.48; I, 29.8; Ni, 6.67.

Complex **9** hydrolyzes in H_2O–CH_3OH or dilute aqueous alkali to produce the free ligand **10** (mp 139°).

Anal. Calcd for $C_{37}H_{34}S_4$: C, 74.45; H, 5.38; S, 20.09; mol wt, 637.0. Found: C, 74.49; H, 5.39; S, 20.10; mol wt, 645 (osmometric in $ClCH_2CH_2Cl$).

The structure of **10** was confirmed through nmr measurements. An alkylation reaction similar to eq 2



was used to synthesize the first nickel chelate **11** of an unsaturated macrocyclic sulfur chelate by refluxing **6**

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[1] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 1483 (1965).

[2] G. N. Schrauzer and H. N. Rabinowitz, *ibid.*, **90**, 4297 (1968).

[3] R. M. Wing, G. C. Tustin, and W. H. Okamura, *ibid.*, **92**, 1935 (1970).