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THE STABILIZATION OF CENTERS WITH SIX VALENCE ELECTRONS THROUGH ELECTRON-RICH THREE-CENTER BONDING

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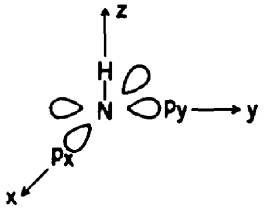
Abstract—A possible method to stabilize a singlet state of a nitrene (or any other 6-valence electron center) is to approach it in a symmetrical manner with two lone pairs. The resultant electron-rich 3-center bond is generally unstable with respect to a 2-center bond. The 3-center geometry may however be stabilized when the atoms involved carry low lying *d* orbitals. The electronic structure of thiothiophthenes is investigated in context and a general analysis of the feasibility of electron-rich 3-center bonding in the first and second rows of the periodic table is presented.

THE electronic structure of a simple nitrene is clear.[1] There are three relatively high energy orbitals: an approximate lone pair along the z direction and a degenerate p_x, p_y pair on N. In an isolated NH two electrons must be placed in p_x and p_y and it



is clear that the ground state of the system will be a triplet, with essentially one electron in p_x, one in p_y. One way to possibly stabilize a singlet state of NH, normally an excited state of the isolated molecule, is to introduce a distinction between p_x and p_y. If the energy splitting between these one-electron orbitals becomes sufficiently great[2] (perhaps of the order of 1·5 eV) then there is a good chance that the ground state will be the singlet, identifiable as arising primarily from a configuration with two electrons in the lower energy level. The differentiation of the p_x and p_y levels could be accomplished intramolecularly by proper choice of the substituent R in RN; our interest here is in a novel *intermolecular* method. This involves the approach of two lone pairs (ammonia molecules, say) along the y (or x) axis in a geometry illustrated in Fig. 1. We can anticipate the result of a detailed calculation by considering the symmetry of the interacting levels.

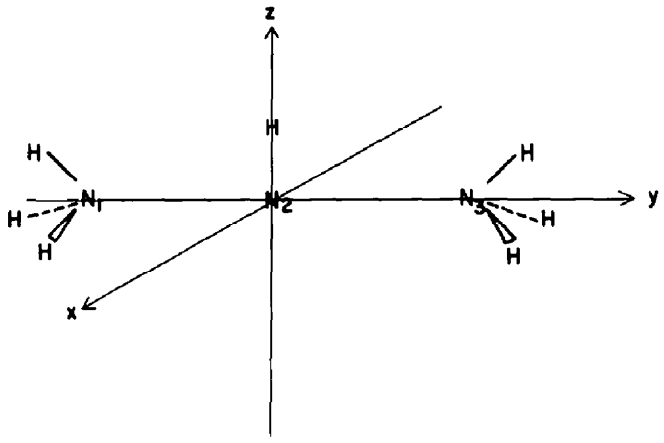
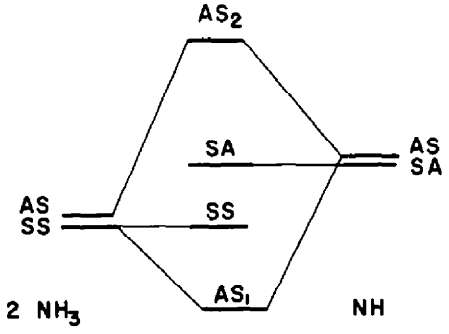


FIG. 1 Coordinate system for the interaction of a nitrene with two NH_3 molecules. The origin of the Cartesian coordinate system is at the nitrene nitrogen, N_2 and the NH_3 molecules are located along the y axis. The nitrene H is along the $+z$ axis.

Let us specify the symmetry or antisymmetry of the levels with respect to 1. the xz plane, 2. the yz plane. (see Fig. 1). The nitrene p_x orbital is thus SA, the p_y AS. Assuming a symmetric approach of the ammonias, the lone pairs give rise to an SS and AS combination. The interaction diagram is drawn below.



Six electrons (4 from the 2 NH_3 lone pairs, 2 from the nitrene) are placed in the lowest three molecular orbitals. Four go into the p type electron-rich 3-center bond along the y axis (the AS_1, SS, orbitals) and two into the remaining nitrene orbital (p_x, SA). The differentiation among the nitrene p orbitals has been accomplished essentially by destabilizing the p_y orbital by incorporating it into a 3-center system.

We proceeded further with some extended Hückel calculations. The orbital exponents and Coulomb integrals are the same as used previously[3] except for an H 1s exponent of 1·3. The N—H distances were taken as 1·00 in NH, 1·01 in NH_3; the HNH angles were 107°. The symmetrical approach of two NH_3 molecules yields the energy levels of Fig. 2.

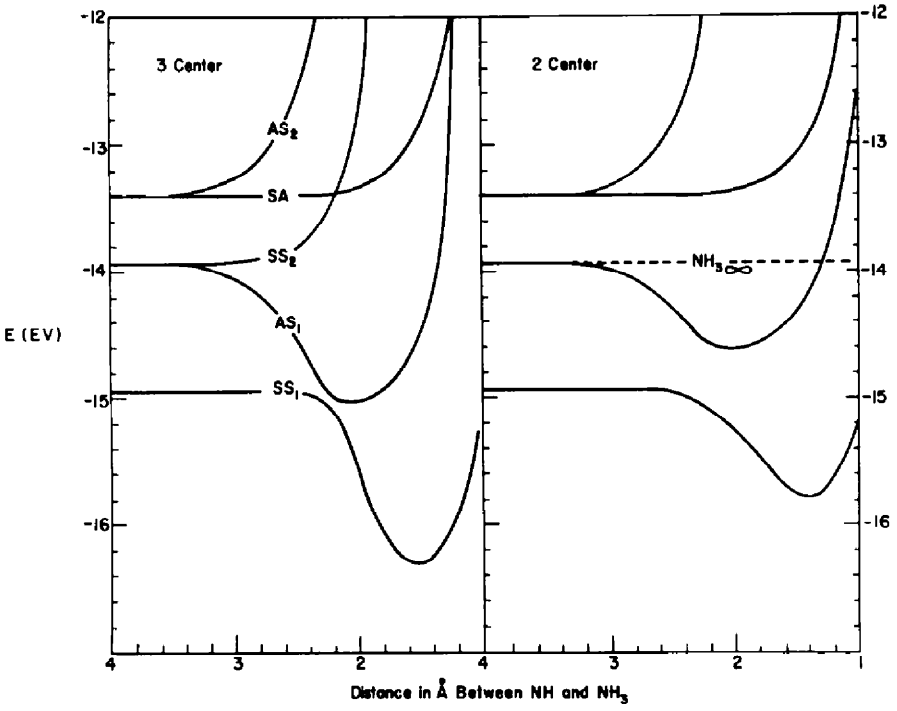
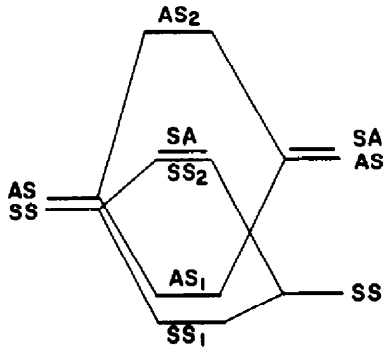


FIG. 2 The behavior of the individual energy levels near −14 eV for a three-center symmetrical approach of two NH_3 molecules to an NH (left) and a two-center approach of an NH_3 to an NH (right).

The general features of the interaction diagram we drew above are confirmed. The AS levels from the NH and the 2 NH_3 interact strongly at large distances, whereas the SA level is quite insensitive to the approach. The unexpected feature is the destabilization of the SS level from the NH_3 lone pair combination.

This is a result of interaction with a lower SS level, the approximate lone pair of the nitrene. We underestimated this interaction, due to the rather long range s-p σ overlap. The revised interaction diagram appears as follows:



It is clear from this level diagram that one of the expectations of this numerical experiment is satisfied—at approach distances below about 2·2 Å there is a region where a large splitting of SA and AS_2 is present, and thus the possibility of a singlet ground state.

It thus seems to us reasonable that the singlet state of a nitrene should be stabilized in a basic medium relative to the vapor phase. There appears to be some evidence for such a conclusion.[4] It should also be noted that interaction with lone pairs may be accomplished intramolecularly as well. We believe that this factor is significant in the stabilization of singlet dihalomethylenes and dialkoxymethylenes, whose electronic structure we discussed in some previous work.[2] It should also be possible to achieve

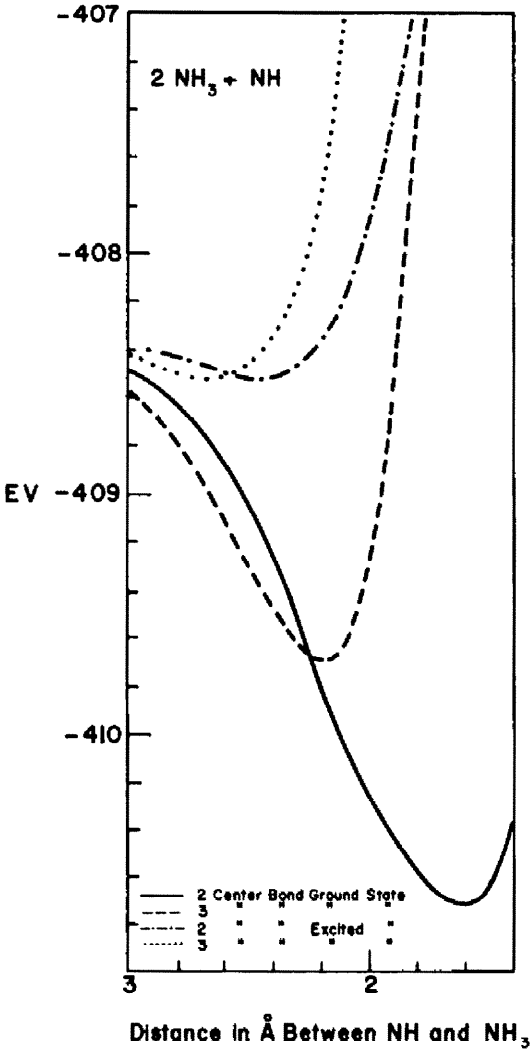
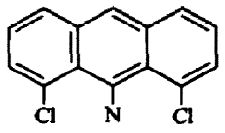


FIG. 3 Ground and excited configuration energies for two- and three-center approaches of NH_3 to NH.

through molecular architecture other geometries favorable for singlet nitrene stabilization. An example is shown below (I). In a model for this geometry (II), an extended Hückel calculation gave a p_x–p_y splitting of 0·52 eV.



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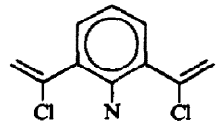
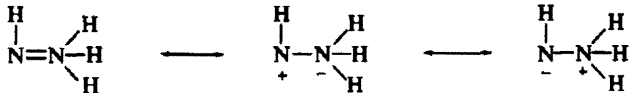


II

We now want to examine the total energy of the system. Despite the destabilization of the SS_2 orbital the total complex is stabilized with respect to $2NH_3$ and NH at infinite separation. The total energy has a minimum at a N_1–N_2 = N_2–N_3 distance of around 2·2 Å, with a net stabilization of nearly 1·4 eV. The potential energy curve for the three-center system and its first excited configuration are shown in Fig. 3. There they are compared with corresponding curves for a 2-center bond. In the 2-center approach we bring together an NH and a single NH_3. To provide a common zero of energy with the 2-center approach, we add the energy of another NH_3 at infinity. There is only a single plane of symmetry in this approach. The individual energy levels are displayed in Fig. 2 whereas the total energy for ground and excited configurations is shown in Fig. 3. There is a deeper minimum for the 2-center approach, at a separation of about 1·6 Å. The result is the molecule $HN—NH_3$,



which no doubt would prefer to rearrange to its more stable isomer-hydrazine.

As implied by the curves of Fig. 3, the 3-center minimum is thus not a true minimum but a saddle point, unstable with respect to an unsymmetrical distortion leading to bonding with one NH_3 and removal of the other NH_3 to infinity. This is apparent in Fig. 4 where we have constructed a contour diagram of the energy surface for independent variation of N_1–N_2 and N_2–N_3. Nevertheless, the fact that at all large distances a 3-center system appears to have an advantage over a 2-center arrangement was encouraging and we proceeded to explore different ways in which the 3-center bond could be made still more stable.

We first tested the scope of the effect by approaching instead of NH_3 the isoelectronic CH_3^- and OH_3^+ as well as the lone pairs of two H_2O molecules. We also brought two NH_3 near an oxygen atom. The resulting potential curves are shown in Fig. 5.

The general features of these curves are the same, only the magnitude of the 2- and 3-center bonding varies. None of the minima are as deep as in the NH_3—NH—NH_3 case. The latter has the most favorable ratio of 3- to 2-center bonding.

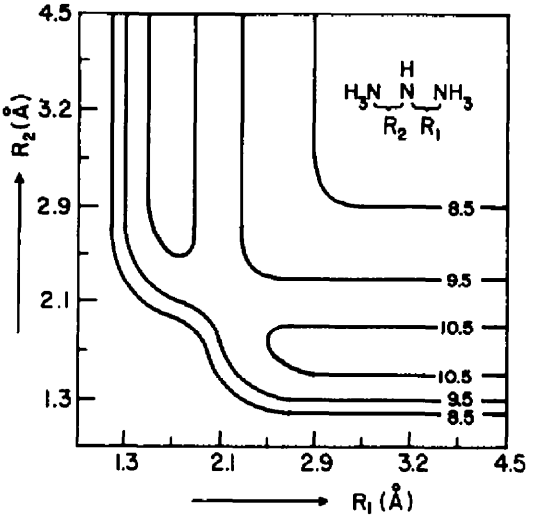


FIG. 4 Contour diagram for a general linear approach of two NH_3 to an NH. The contours represent binding energies in eV with respect to an arbitrary zero of energy.

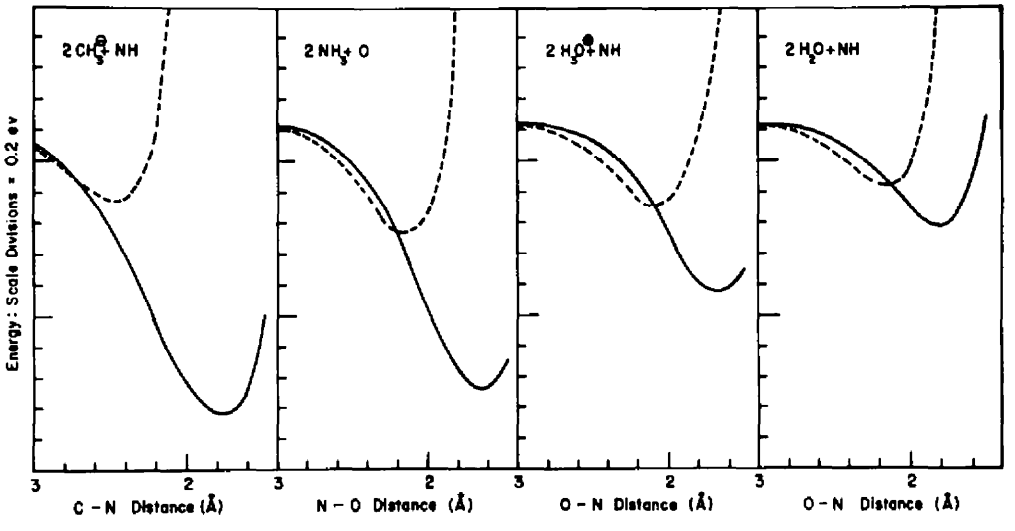
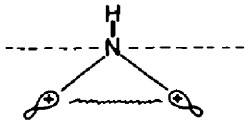


FIG. 5 Potential energy curves for 2 center (solid line) and 3 center (dashed line) approaches for various isoelectronic systems. The energy scale is the same for all cases and we have also chosen the same energy at infinite separation for all systems.

Still another attempt to stabilize the SS orbital did not work out. We reasoned that if the 3-center system were bent (in the xy plane) then the nonbonding orbital might be stabilized as a consequence of the increased 1-3 overlap. The extent of



stabilization of the 3-center bonding, however, turns out to be decreased for any reasonable angle of bending. We are not sure why this is so but some possibilities may be: 1. The 1–3 overlap is increased but the more important 1–2 and 2–3 overlaps are decreased by bending. 2. The nonbonding SS_2 level is anyway destablized by interaction with the lower SS_1 level. The latter is essentially a nitrene lone pair and bending should increase its mixing with SS_2.

In another variation on the above idea we kept the $2NH_3$ molecules linearly aligned along the y axis (Fig. 1), but moved the NH molecule along the z axis out of colinearity of N_2 with N_1–N_3 line. The variation of energy with N—H displacement is shown in Fig. 6. Over a range of N_1–N_3 distances the lowest energy is clearly obtained for a linear N_1–N_2–N_3 arrangement.

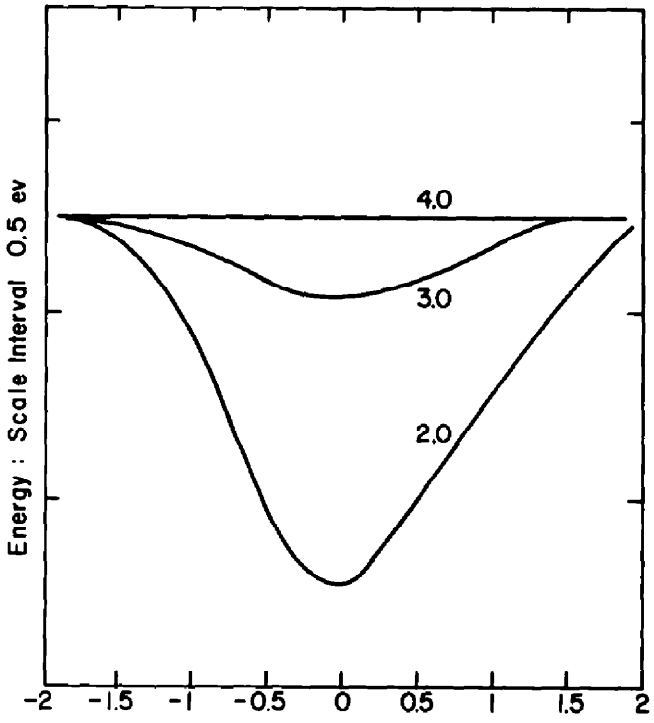


FIG. 6 Variation of energy with displacement of NH along the z axis (see text and Fig. 3). The horizontal axis represents the position of the NH nitrogen atom along the z axis as defined in Fig. 3. The labels on the curves give the N_1–N_2 distance for N_2 at z = 0.

We next decided to try to form a metastable or stable 3 center bond by constructing a system in which the fast rising SS_2 orbital would in some way be prevented from its ascent. This could be accomplished by introducing above it an empty orbital of the same symmetry. This in turn could be done in two ways: The central atom is bonded to another atom with low lying empty *d* or *s* orbitals or the central atom itself has such orbitals available.

Examples of the first point would be N—Cl, R—SO_2—N and the nitrenes generated by decomposing transition metal azides. For our calculations we chose NCl. Fig. 7 illustrates the calculated energies of two- and three-center bonding with and without 3d orbitals on Cl.* The inclusion of 3d orbitals does indeed stabilize the 3-center bond, but a metastable system is not achieved. We have not investigated a sulfonyl nitrene.

For the second point we have investigated the interaction of a S atom with the lone pairs of two H_2S molecules.† Fig. 8 shows the curves with and without d orbitals

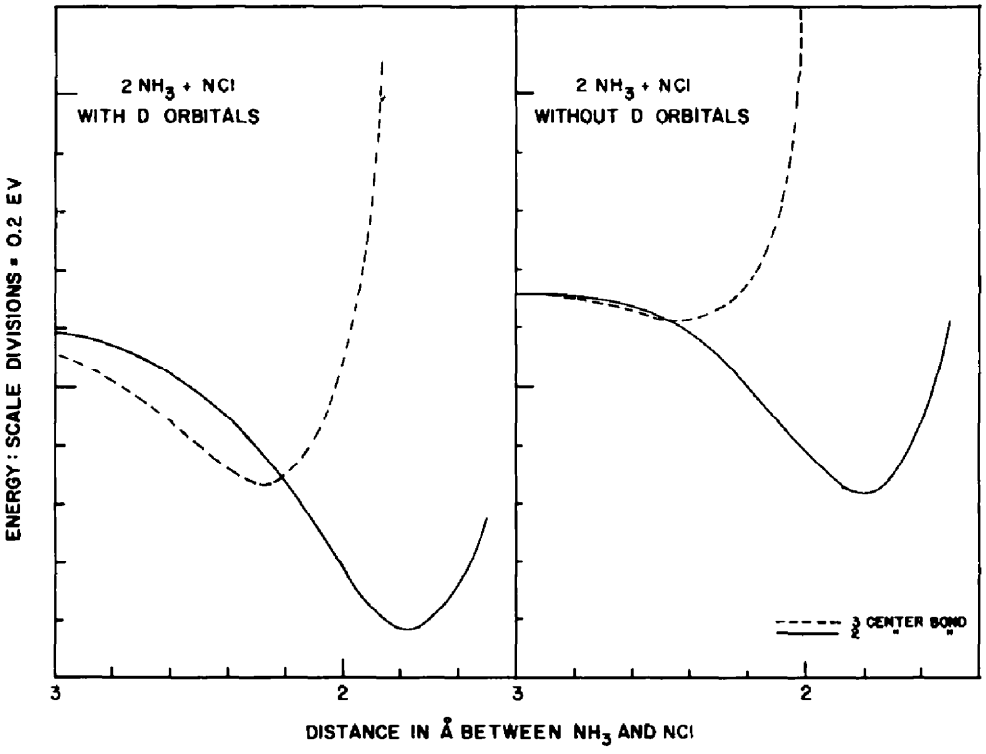


FIG. 7 Ground and excited configuration energies for two- and three-center approaches of NH_3 to N—Cl, with and without 3d orbitals.

* The N—Cl distance was 1·75 Å. For chlorine we chose the Coulomb integrals $H_{ii}(3s) = -30{\cdot}0$ eV, $H_{ii}(3p) = -15{\cdot}0$ eV, $H_{ii}(3d) = -4{\cdot}0$ eV. The Slater exponents are from Clementi and Raimondi.[5] The 3d exponent was taken as 1·00. The Cl Coulomb integrals and exponents are a guess, making for a somewhat tighter and lower energy 3d orbital than in atomic Cl.

† For the S—H distance we took 1·33 Å, and for the H—S—H angle 92°. The Slater exponents were from Clementi and Raimondi[5] except for the sulfur 3d orbitals, estimated at 0·8. The valence state ionization potentials were estimated as $H_{ii}(3s) = -20{\cdot}0$ eV, $H_{ii}(3p) = -13{\cdot}3$ eV, $H_{ii}(3d) = -4{\cdot}0$ eV.

on sulfur. Again the inclusion of 3d orbitals stabilizes the 3-center bond system, and while we cannot trust the details of the calculation there appears to be a true subsidiary minimum here for a 3-center bond.

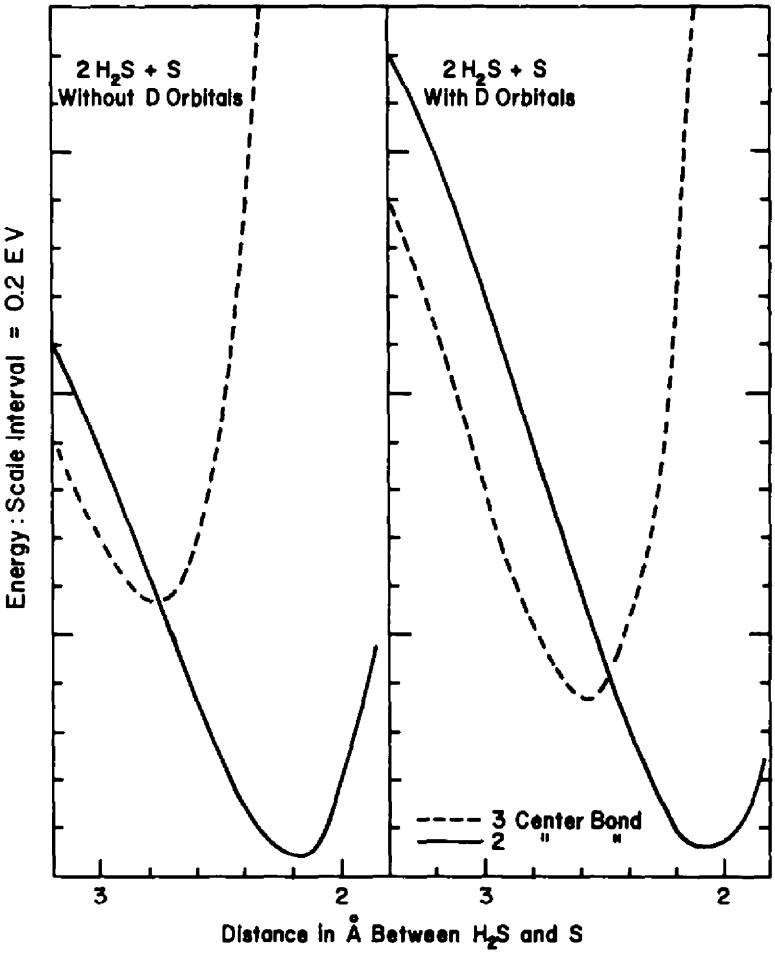


FIG. 8 Ground and excited configuration energies for two- and three-center approaches of H_2S to S, with and without 3d orbitals.

The essential feature of the intramolecular interaction of two lone pairs with a nitrene p orbital is the formation of a four electron 3-center bond. We would like to elaborate on the general features of this type of bonding below.

Electron-deficient 3-center bonding is an established and useful theoretical concept most beautifully elaborated in the boron hydride field.[6] From three atomic

orbitals one forms three molecular orbitals. Two cases (*s* or *p*) may be distinguished, depending on the nature of the central orbital participating (Fig. 9).

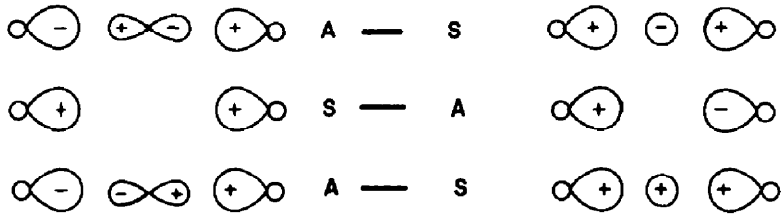
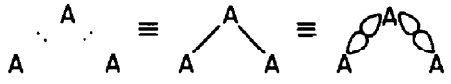


FIG. 9 Two types of three center bonding. At right an s orbital of the central atom participates, at left a p orbital. The symmetry designations signify symmetry (S) or antisymmetry (A) with respect to the plane bisecting the three center system.

In electron-deficient bonding, two electrons are used to bind the three atoms. We define an electron-rich three-center bond as arising in the above system when four electrons are used to bind the three centers.

It is important at this point to distinguish 4-electron 3-center bonding from two 2-electron bonds connecting a central atom with two terminal atoms. The latter case also involves four electrons but four orbitals instead of three. Consider the case



As usual, one must be able to translate the localized σ picture implied by the sketch at right above to the equivalent properly symmetry-adapted, delocalized, molecular orbitals. This is done in Fig. 10.

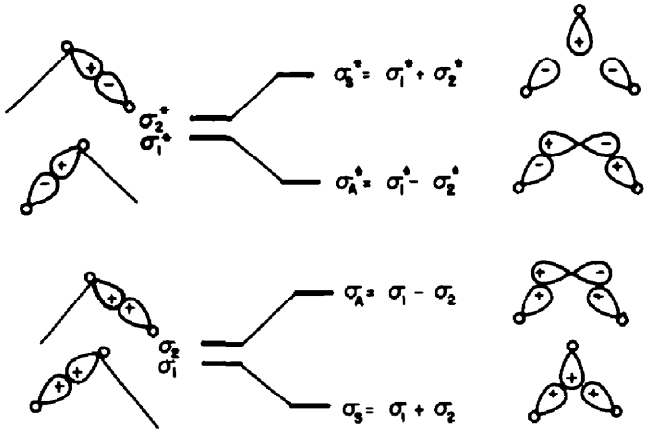


FIG. 10 A rough description of the transformations of two localized σ bonds (with their corresponding σ* orbitals) into delocalized symmetry-adapted molecular orbitals. The ordering of the molecular orbitals is a guess. The only essential feature of the diagram is which orbitals are bonding and which are antibonding. The ordering within each set is really of secondary importance.

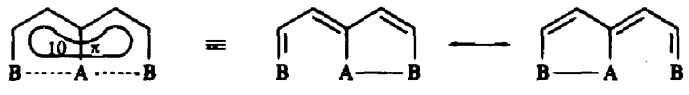
It is to be noted that the 2-center bonding scheme contains two bonding orbitals, whereas the 3-center orbitals have one bonding, one non-bonding. The non-bonding orbital appears to contribute nothing to vicinal bonding (1–2 or 2–3) but may in fact be slightly 1–3 bonding or antibonding, depending on whether a p or an s type system is involved. Since normal 2-center bonds are particularly strong among elements of the first row of the periodic table, it is not expected that electron-rich 3-center bonding should compete favorably with normal 2-center bonding. Thus, whereas electron-rich 3-center bonding has been explored in the interhalogen compounds,[7] and the isolectronic xenon and other rare gas compounds,[8–10] it has not been much discussed for the lighter elements. The one case which has been studied is the transition state for an S_N2 displacement at a saturated carbon.[11] The transition state involves a four electron 3-center bond and it could in fact be said that

it appears to be a transition state and not an intermediate as a result of the relative instability of the electron-rich 3-center bonding.

If the transition state for an S_N2 substitution is considered as an electron-rich 3-center bond (with X^- and Y^- providing lone pairs and CH_3^+ acting as a 6-valence center) then it can be extrapolated from our calculations on the interaction of two H_2S molecules with an S atom that in the first row it will be a true transition state but in the second row has the possibility of being a local minimum, i.e. an intermediate. The isolation of organic pentacovalent silicon compounds[12] and some experimental evidence on substitution reactions[13] on Si may be in agreement with this, and we plan to investigate the potential surface for the S_N2 reaction further.

It occurred to us further that an electron-rich 3-center bond involving three second row elements could be further stabilized when all three atoms are incorporated in a π-electron system. The further stabilization should not be expected to be overwhelming since the equilibrium distance for a 3-center bond is reached at a stage where p–p π overlap is still small. Probably the largest effect could be expected if the 3-center system B—A—B completes an aromatic six or ten π-electron system. We also should consider that the apparent optimum BAB angle is near 180°.

A 10 π-electron molecule which can attain a near linear electron-rich 3-center bond is I



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The molecule with B=A=sulfur is thiothiophthene. The unusual properties of the σ system of this and related molecules have been pointed out previously.[14–17] X-ray crystallographic studies indicate an unsymmetrical A—B—A′ system, with

A—B 2·52, B—A′ 2·18 in one,[18] A—B 2·51, B—A′ 2·22 Å in another[19] unsymmetrical derivative.*†

We carried out some calculations on a model thiothiophthene, with and without 3d orbitals on sulfur.‡ We displaced the central sulfuratom from a symmetrical location toward the terminal sulfuratoms and obtained the potential energy curves of Fig. 11. These show a clear preference for an unsymmetrical structure when 3d

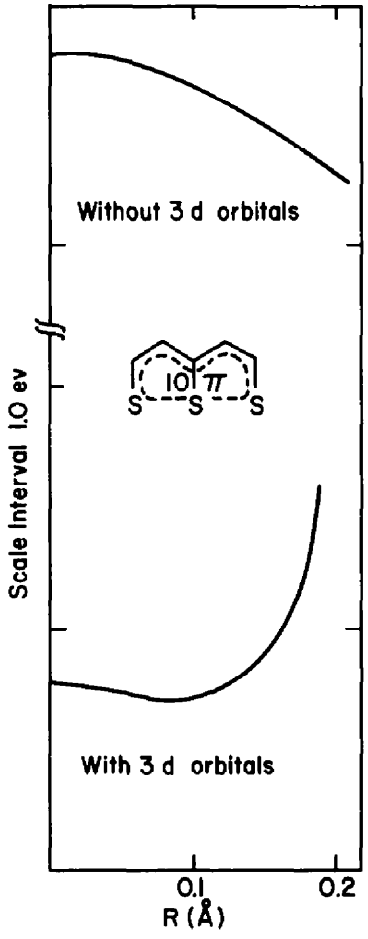

FIG. 11 Potential energy curves for horizontal displacement of the central sulfuration of thiothiophthene, with and without 3d orbitals on S. The horizontal axis measures displacement of the central sulfuration from the symmetrical position.

orbitals are not utilized and a nearly symmetrical and very flat minimum when 3d orbitals are included. While we do not have much experience with the use of 3d orbitals on 2nd row atoms, the few calculations we have done on sulfur and phos-

* A previous structure determination on a methyl substituted compound indicated a symmetrical A—B—A system.

† Analogous compounds with A=B=S, A′=Se have also been studied.

‡ The CC, CS and SS distances were initially those of Ref. 20, with CH assumed 1·1 Å, and CCH angles 120°. The sulfur parameters were those of footnote † on page 000.

phorus molecules with unusual geometries (like SF_4, PF_5) have shown little effect of presence or absence of 3d orbitals on details of geometry. In this context the results on thiothiophthene are unusual but we believe they are reliable. They are also in qualitative agreement with the structural determinations.

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REFERENCES

[1] R. S. Mulliken, *Rev. Mod. Phys.* **4**, 1 (1932); G. Herzberg, *Spectra of Diatomic Molecules*, (2nd Edition) pp. 341, 369. Van Nostrand (1950).
[2] R. Hoffmann, G. D. Zeiss and G. W. Van Dine, *J. Am. Chem. Soc.* **90**, 1485 (1968).
[3] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963); *Ibid.* **40**, 2745 (1964).
[4] W. Lwowski and R. L. Johnson, *Tetrahedron Letters* 891 (1967).
[5] E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963).
[6] W. N. Lipscomb, *The Boron Hydrides*. Benjamin, New York (1963).
[7] R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.* **73**, 4321 (1951).
[8] R. E. Rundle, *Ibid.* **85**, 112 (1963).
[9] C. A. Coulson, *J. Chem. Soc.* 1442 (1964).
[10] H. H. Hyman, *Noble Gas Compounds*. The University of Chicago Press, Chicago (1963).
[11] R. Daudel and O. Chalvet, *J. Chim. Phys.* **53**, 943 (1956).
[12] R. Rudman, W. C. Hamilton, S. Novick and T. Goldfarb, *J. Am. Chem. Soc.* **89**, 5157 (1967).
[13] L. H. Sommer, *Stereochemistry, Mechanism and Silicon*. McGraw-Hill, New York (1965).
[14] G. Giacometti and G. Rigatti, *J. Chem. Phys.* **30**, 1633 (1959). See also K. Maeda, *Bull. Chem. Soc. Japan* **33**, 1466 (1960); **34**, 785, 1166 (1961).
[15] S. Bezzi, C. Garbuglio, M. Mammi and G. Traverso, *Gazz. Chim. Ital.* **88**, 1226 (1958).
[16] E. Klingsberg, *J. Am. Chem. Soc.* **85**, 3244 (1963); *J. Heterocyclic Chem.* **3**, 243 (1966); G. Pfister-Guillouzo and N. Lozac'h, *Bull. Soc. Chim.* 153 (1963).
[17] H. Behringer, M. Ruff and R. Wiedenmann, *Chem. Ber.* **97**, 1732 (1964).
[18] S. M. Johnson, M. G. Newton, I. C. Paul, R. J. S. Beer, D. Cartwright, *Chem. Comm.* 1170 (1967).
[19] A. Hordvik, E. Sletten and J. Sletten, *Acta Chem. Scand.* **20**, 2001 (1966).
[20] M. Mammi, R. Bardi, C. Garbuglio and S. Bezzi, *Acta Cryst.* **13**, 1048 (1960).
[21] J. H. van den Hende, *J. Am. Chem. Soc.* **88**, 5045 (1966).