

corresponding one-electron energies of their highest filled orbitals intersect (inset, Figure 1).

Since ψ_{S_2} and ψ_{A_2} are both overall totally symmetric, the noncrossing rule dictates that they mix in a manner represented by the configuration interaction function $\bar{\psi} = c_{S_2}\psi_{S_2} + c_{A_2}\psi_{A_2}$. Denoting the bonding hybrids on carbons C₁ and C₄ by h_1 and h_4 , respectively, we have $\phi_S = h_1^S + h_4^S + \dots$ and $\phi_A = h_1^A - h_4^A + \dots$, which are analogous to the g and u combinations of $1s_A$ and $1s_B$ in H₂. The dotted terms indicate the smaller contributions to ϕ_S and ϕ_A from other centers in the molecule. We recall that variations in the CI coefficients as a function of R serve to alter the relative amounts of covalent and ionic character. In the limiting case where hybrids in ϕ_S and ϕ_A are identical and their overlap is neglected, the ratio of covalent and ionic contributions is given explicitly by $(C_{S_2} - C_{A_2})/(C_{S_2} + C_{A_2})$, and we shall employ this quantity as a rough measure of bonding character in the discussion of actual cases which follows.

Ideally, one could simultaneously obtain the orbitals for ψ_{S_2} and ψ_{A_2} , as well as the coefficients C_{S_2} and C_{A_2} , in a unified self-consistent procedure (multiconfiguration SCF). We have, however, taken the following, simpler approach. For small values of R (≤ 1.648 Å) where the SCF energies are well separated, ψ_{S_2} is taken as the SCF solution, and ψ_{A_2} is constructed from the 58-electron core of ψ_{S_2} and its virtual ϕ_A . At larger R values (≥ 1.948 Å), where the ψ_{S_2} and ψ_{A_2} SCF energies become closer, we have carried out two alternative CI calculations: first with ψ_{S_2} (SCF) and ψ_{A_2} (virtual) and then with ψ_{A_2} (SCF) and ψ_{S_2} (virtual). The validity of this essentially two-electron approach is indicated by the fact that similar CI energies (constant to within $\pm \sim 3$ kcal; see Figure 1) and coefficients are obtained from either choice for ψ_{S_2} and ψ_{A_2} .¹²

Figure 1 plots the CI energy as a function of R and clearly shows the persistence of an inner (1.54 Å) and outer minimum (2.51 Å) of similar depth, with a separating barrier at ~ 1.95 Å, whose height is ~ 29 kcal/mol above the inner minimum. The inner well corresponds to the valence-bond structure III, in which there is 57:43 covalent to ionic bonding. The outer minimum at 2.54 Å corresponds to 97% covalent character and is best represented in valence bond terms as the diradical



i.e., analogous to the case of H₂ at large separation, we find that CI gives proper dissociation into two weakly interacting electrons, insofar as a two particle description is valid.

The sizable barrier between roughly symmetric wells of ~ 29 kcal/mol suggests that III could be expected to have a lifetime of several hours at room temperature within the inner well.¹³ Since our calcu-

(12) CI calculations using orbitals from triplet SCF calculations yield a singlet CI energy curve roughly parallel to that in Figure 1 for $R \geq 1.9$ Å and a few kilocalories lower in energy. We feel, however, that at the level of approximation adopted, the singlet SCF orbitals provide the best overall basis for studying the bridgehead-bridgehead interaction in III.

(13) The least-energy path must cross the singlet barrier, since the triplet energy is >1 eV above the singlet at $R \sim 1.95$ Å. At the crossing point, which occurs for a substantially greater value of R (~ 2.3 Å),

lated barrier must be considered uncertain by at least a few kilocalories per mole, a precise estimate of the lifetime is not possible. At any rate, the barrier seems rather low for a process which is symmetry forbidden in the orbital sense,⁶ thus demonstrating how useful quantitative calculations can be in complementing predictions based on orbital symmetry. The stability of the inner minimum species is important, since the interconversion of the outer minimum diradical to dimethylenecyclohexane symmetry is symmetry-allowed, and, though the barrier for this process is of unknown magnitude, most synthetic attempts at [2.2]-propellane do, in fact, give this latter Grob fragmentation product.²

Acknowledgment. This work was performed under the auspices of the U. S. Atomic Energy Commission. It was supported in part by a Grant-In-Aid to J. M. S. from the Research Corporation and by the National Science Foundation (Grant GP-29554).

the triplet must lie below the singlet, in the level of approximation used here.¹⁴

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Received January 18, 1972

A Flexible and Directed Synthesis of Azoxyalkanes¹

Sir:

Azoxyalkanes are currently of great interest. Four naturally occurring examples, macrozamin,² cycasin,³ elaiomycin,⁴ and LL-BH872 α ,⁵ exhibit potent biological properties; the initial three are carcinogenic,⁶ the latter possesses antifungal qualities.^{6,7} Recently, studies of the photolytic closure of azoxyalkanes to oxadiaziridines have appeared,^{8,9} and photoisomerization now makes acyclic *cis*-azoxyalkanes available.^{9,10}

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(10) Oxidation of *cis*-azoalkanes can also be used.^{9c} Previous reports of *cis*-azoxyalkanes are discussed by Woodward and Wintner.¹¹ Cyclic

fins.²⁴ The yield of azoxyalkane is thus limited, but variation of reaction conditions may permit augmented N-alkylation and better yields. Note that alkylation of the diazotates' other nitrogen (yielding *N*-alkyl-*N*-nitrosoamines) is a minor process. Synthesis of the authentic *N*-nitrosoamines, followed by gc analysis of the crude reaction mixtures accompanying 1 and 6, limit *N*-nitrosoalkane formation to less than 5%.

By uv^{9a,b} and nmr,^{9,12} our azoxyalkanes are *trans* (see eq 1 and 2).²⁵ Because the diazotates from which they come are probably of *syn* configuration,²⁶ reactions 1 and 2 could lead directly to *trans*-azoxyalkanes by nucleophilic attack of the diazotate on RX, with retention of the N=N configuration.

The new azoxyalkane synthesis meets generality requirements 1-3. Our synthesis of (*S*)-4 from (*S*)-butane-2-diazotate (method 1) shows that it can partly meet the chirality requirement, 4. The CD spectrum of (*S*)-4 closely resembled those of (*S*)-ONN-1-cyclohexylazoxyethane²¹ and elaiomycin.^{5b} We are studying stereospecific synthetic routes to azoxyalkanes in which the chiral center is bonded at the =N(O) position.

Our synthesis generates primary and secondary *trans*-azoxyalkanes of varied structure. Superior syntheses of *tert*-azoxyalkanes¹⁵ complement our work. Coupled with photoisomerization,^{8,9} we can gain access to new O-position isomers, *cis*-azoxyalkanes, and oxadiaziridines as well. The potential for the synthesis of naturally occurring azoxyalkanes is patent, and we are exploring such possibilities.

Acknowledgments. We thank the National Science Foundation and the National Institutes of Health for financial support. R. A. M. thanks the Massachusetts Institute of Technology for its hospitality.

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(28) American Cyanamid Co. Educational Awardee.

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Received April 7, 1972

Geometry of Nickel(II) Complexes

Sir:

Nickel(II) forms many complexes with octahedral, square-planar, and tetrahedral geometries and a smaller number of five-coordinate compounds¹ with other stereochemical arrangements. It is generally considered that a combination of steric and electronic factors determines which of the three common geometries is assumed by a given compound. Steric factors clearly operate in the sense that bulky ligands are most favorable to tetrahedral geometry and least favorable to octahedral geometry. The mode of operation of the electronic effects is much less clear in spite of ex-

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tensive discussion of the subject.²⁻⁴ We wish to present some new data on the structure of thiourea (tu) complexes of nickel(II) in solution and to suggest a simple rationale for their geometries.

Measurements of visible spectra, magnetic moments, conductivity, and molecular weights of nickel(II) complexes of thiourea and substituted thiourea at room temperature have been reported^{2,5} and have provided evidence for all three geometries. We have undertaken nmr and other studies of a number of these complexes over a wide range of temperature primarily to elucidate ligand exchange mechanisms. We report here data on four complexes chosen to illustrate the geometric possibilities. Ni(tu)₆(ClO₄)₂ gives conducting solutions in acetone and has a magnetic moment ranging from 2.3 (+27°) to 3.2 BM (-90°), and the nmr spectrum indicates fast ligand exchange involving a paramagnetic complex at room temperature. In the presence of excess ligand the exchange is barely frozen out at -90°. (The dimethylthiourea complex is similar but the ligand exchange is slow at -90° giving complexed resonances at -101.4, -19.9, and -12.1 ppm from TMS.) All data are consistent with octahedral Ni(tu)₆²⁺ being the only species present at -90° with some dissociation to square-planar Ni(tu)₄²⁺ at higher temperatures. Solutions of Ni(tu)₂Cl₂ in acetone are nonconducting at all temperatures and the magnetic moment varies from 3.5 (+27°) to 3.8 BM (-90°). The nmr of this complex shows fast exchange with dissociated ligand at +27°, but at -90° one of the two complexed tu protons (chemical shift -104.8 ppm) which result from restricted rotation about the C-N bond is no longer exchanging with free ligand. Free ligand and the second complexed ligand proton give an averaged resonance at -11.3 ppm. The species present is tetrahedral Ni(tu)₂Cl₂ at all temperatures. Ni(tu)₆Br₂ in acetone has a moment varying from 3.6 BM at +27° to 1.2 BM at -94°. It has a small conductivity at room temperature which increases at low temperature. The nmr spectrum at -90° has four resonances. Two show contact shifts (-110.3 and -20.2 ppm) and are attributed to tetrahedral Ni(tu)₂Br₂. One arises from free ligand (-8.9 ppm) and the fourth at -9.3 ppm is assigned to a diamagnetic complex. This latter compound must be ionic since its formation is accompanied by an increase in conductivity. The concentration of the analogous iodide complex is decreased by addition of (CH₃)₄NI (experiment carried out at -50° in the fast exchange region). On the other hand it cannot be Ni(tu)₄²⁺ since at -90° in the presence of excess ligand this species is completely converted to Ni(tu)₆²⁺. It must therefore be square-planar Ni(tu)₂Br⁺.⁶ Ni(tu)₆I₂ has a

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(6) A referee has suggested that the species formulated as Ni(tu)₅²⁺ or Ni(tu)₅X⁺ may be diamagnetic, five-coordinated Ni(tu)₅²⁺ or Ni(tu)₅X⁺. We consider these assignments less likely for several reasons. At room temperature optical spectra consistent with square-planar Ni(tu)₄²⁺ have been reported. The susceptibility and nmr data show that diamagnetic Ni(tu)₅²⁺ is not formed at low temperatures in the perchlorate solutions. At -90° the relative intensities of the "free ligand" and "diamagnetic complex" nmr peaks agree better with the ratios expected for Ni(tu)₅X⁺ than they do for Ni(tu)₅X⁺. We also find that this complex exchanges ligands by an associative process. A dissociative mechanism might have been expected for a five-coordinate compound. Although not conclusive these arguments incline us against postulating five-coordinate complexes.