methyls; loss of the bridging methano group, though not intense, is relatively more important in **5** (26%) than in **1** (19%) or **2** (18%).

Mixtures of **5** and **1** from initial column chromatography of the dehydrogenation reaction were assayed quantitatively by nmr and subjected to catalytic hydrogenation in absolute ethanol using 10% palladium on charcoal. After absorption of the calculated amount of hydrogen for the mixture, the only product which could be isolated was the saturated metacyclophane **2** (90%). Conversely, dehydrogenation of **2** with DDQ gave mixtures of **1**, **5**, and **2**, although in much lower yields.

In solutions and in the solid state **5** demonstrates under ultraviolet light a bright reddish and yellow fluorescense, respectively, while crystals or solutions of **1** show a moderate blue fluorescence. This observation, the noted shift to lower field of the comparable protons, and increased ultraviolet absorption in the series **2** → **1** → **5** suggest that the ethylene bridges of **5** and **1** experience a definite conjugation with the aromatic rings. Idealized models constructed from the Dreiding set show the planar aromatic rings forming an angle at the methylene bridge of 75° in **2** and 85° in **5**, and indicate that the ethylenic orbitals are set at an angle of 45° with the benzenoid orbitals, thereby providing sufficient overlap for conjugation.[13] Although the bond angles, bond distances, and deformation of the aromatic rings, if any, can only be known from a detailed X-ray analysis, such models are believed to show the over-all geometry of these molecules reasonably well.[14]

The data presented here show clearly that **5** is the structure of the dehydrogenation product of **1** and that spontaneous reorganization to **6** does not occur. Indeed, none of our data suggests the presence of any of **6** due to equilibration with **5**. However, isomerization of **5** to **6** is currently being explored both photochemically and thermally. Initial pyrolysis experiments carried out on micro samples of **5** in sealed ampoules under nitrogen indicate the formation of a new material (mp 277–279°) at 250 ± 5° which has an ultraviolet absorption spectrum essentially identical with that of **4**, mp 278–280° [$\lambda_{\max}^{\text{cyclohexane}}$ 243 mμ (ϵ 41,750), 253 (56,200), 265 (12,150), 276 (26,250), 288 (47,100), 318 (4530), 332 (12,200), 348 (30,350), 367 (43,400), and 388 (1500); τ_{TMS} ($CDCl_3$): singlets at 1.90 (4, –CH=CH–), 6.14 (6, OCH_3), and 7.19 (12, CH_3)], the DDQ dehydrogenation product of **3**. These spectra are very similar to published absorption spectra of pyrenes.[15] This observation might indicate that **5** is converted to **4** possibly (though not necessarily) by isomerization to **6**, which loses the methano bridge irreversibly to give the pyrene **4**. A more detailed investigation is in progress.

$$\begin{tikzcd} \mathbf{5} \arrow[r, "250^\circ"] & {[\mathbf{6}]} \arrow[dr, "-CH_2"] & \\ & & \mathbf{4} \\ & \mathbf{3} \arrow[ur, "DDQ"'] & \end{tikzcd}$$

Since **5** is recovered on pyrolysis at temperatures below 250°, the $M^+ - CH_2$ fragmentation in its mass spectrum (225°) must be due to electron-impact rather than thermal fragmentation.

H. B. Renfroe
Geigy Research Laboratories
Division of Geigy Chemical Corporation
Ardsley, New York 10502

Received February 17, 1968

---

[13] See L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., pp 482–483.

[14] Professor V. Boekelheide has informed the writer of an X-ray crystallographic analysis by Dr. A. Hanson of 8,16-oxido-*cis*-[2.2]-metacyclophane, which shows only slight deformation of the aromatic rings. We are appreciative of stimulating discussions with Professor Boekelheide pertaining to this research.

[15] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957.

Factoring of the Isotropic Shift in Paramagnetic Cobalt(II) Complexes[1]

Sir:

One of the major problems in interpreting the isotropic shift of paramagnetic complexes involves factoring out the pseudocontact contribution to the observed shifts so that the contact contribution can be obtained. The latter is related to the spin density at a proton. An approximation that has been used[2–5] in interpreting the shifts of the diadducts of nickel(II) and cobalt(II) acetylacetonates (acac) is that the mechanisms of spin delocalization are identical for the two metal ions, varying only in magnitude. The observed shifts in the $Ni(acac)_2$ adducts are assumed to be caused by the contact interaction. When there is more than one proton in the ligand, the ratio of the shifts of the various protons in the nickel(II) complex would equal those in the cobalt(II) complex in the absence of a pseudocontact contribution in the latter. The discrepancy in the ratios is attributed to the pseudocontact contribution. Knowing the geometric factor and assuming that the ratios for the contact contribution are the same in cobalt(II) and nickel(II), the total isotropic shift in the cobalt complex can then be factored into the contact and pseudocontact contributions.

We were very much concerned about the assumption that the ratios and hence the spin delocalization mechanisms are identical in six-coordinate cobalt(II) and nickel(II) complexes[2–4] such as those having O_h, D_{4h}, and D_3 symmetry. Cobalt(II) has unpaired spins in the "d" orbitals pointing in between the ligands which are capable of π bonding and nickel(II) does not; hence one would expect different mechanisms. We report here isotropic shifts for $Co(bipy)_3^{2+}$ and $Ni(bipy)_3^{2+}$ (bipy = bipyridine) which conclusively prove that the mechanisms for spin delocalization are different for the two metal ions and invalidate the factoring procedure,[2–4] based on the assumption that they are equivalent at least for this system. It also makes suspect the assumption[6] that the mechanisms are alike in the D_3 complexes $Co(acac)_3^-$ and $Ni(acac)_3^-$ and weakens the general application of this assumption to six-coordinate cobalt(II) and nickel(II) complexes. The measured shifts are reported in Table I.

---

[1] Abstracted in part from the Ph.D. Thesis of M. L. Wicholas, University of Illinois, 1967.

[2] W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

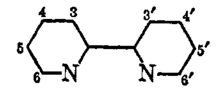
[3] R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **87**, 5350 (1965).

[4] R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **88**, 1399 (1966).

[5] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

[6] W. D. Horrocks, Jr., R. A. Fischer, J. R. Hutchinson, and G. N LaMar, *J. Am. Chem. Soc.*, **88**, 2436 (1966).

Table I. Isotropic Shifts[a] for $Co(bipy)_3^{2+}$ and $Ni(bipy)_3^{2+}$



Compound	$\Delta\nu_{6,6'}$	$\Delta\nu_{5,5'}$	$\Delta\nu_{4,4'}$	$\Delta\nu_{3,3'}$
$Ni(bipy)_3Cl_2 \cdot 2H_2O$	. . .	−2227	−363	−3151
$Co(bipy)_3Cl_2 \cdot H_2O$	−4855	−2313	−365	−4471

[a] Relative to the diamagnetic complex $Fe(bipy)_3Cl_2 \cdot 2H_2O$.

For ease in presentation we shall start by making an assumption we intend to prove wrong; namely, that the mechanisms are identical in the cobalt(II) and nickel(II) complexes. By showing that this leads to an untenable result in our otherwise rigorous calculation, we will have disproved this assumption. If the mechanisms are identical, it follows that for any 2 nonequivalent protons, say i and j, $(\Delta\nu_i)_{Ni}/(\Delta\nu_j)_{Ni} = (\Delta\nu_i)_{Co}/(\Delta\nu_j)_{Co}$, where $\Delta\nu_i$ is the *contact* shift for proton i. For $Co(bipy)_3^{2+}$, $\Delta\nu_i = \overline{\Delta\nu}_i - X_i$, where $\overline{\Delta\nu}_i$ is the *observed isotropic* shift and X_i is the pseudocontact shift. Equation 1 results.

$$(\Delta\nu_i)_{Ni}/(\Delta\nu_j)_{Ni} = (\overline{\Delta\nu}_i - X_i)_{Co}/(\overline{\Delta\nu}_j - X_j)_{Co} \quad (1)$$

For octahedrally coordinated complexes having axial symmetry, the pseudocontact shift is given by[7]

$$\left(\frac{\Delta\nu}{\nu}\right)_i = \frac{-\beta^2 S(S+1)(g_{\parallel} - g_{\perp})\mathrm{F}(g_{\parallel},g_{\perp})}{3kT}\left[\frac{3\cos^2\theta_i - 1}{r_i^3}\right]$$

The term $(3\cos^2\theta_i - 1)/r_i^3$ is often called the geometric factor which is denoted by G_i. F is a simple linear function of $g_{\parallel}$ and $g_{\perp}$, the value of which depends upon the symmetry of the complex and the magnitudes of T_{1e} and τ_c. The geometric factors, G_i and G_j, are then calculated from a knowledge of the geometries of the cobalt(II) complexes. Since $G_i/G_j = X_i/X_j$, one can solve for X_i in terms of X_j, substitute this into eq 1, and then solve for X_j. The same calculation is repeated using the data for protons j and k and again solving for X_j. The two values of X_j, which are calculated independently, are then compared for consistency. If they are close in magnitude, one may say that the mechanisms are identical in $Co(bipy)_3^{2+}$ and $Ni(bipy)_3^{2+}$, but if, however, the two calculated pseudocontact shifts for X_j are radically different, this implies that the spin delocalization mechanisms are different and that $(\Delta\nu_i)_{Ni}/(\Delta\nu_j)_{Ni} \neq (\Delta\nu_i)_{Co}/(\Delta\nu_j)_{Co}$.

For the calculation of the geometric factors for $Co(bipy)_3^{2+}$, a cobalt–nitrogen bond length of 2.04 Å was used along with an NCoN angle of 86.8°. Bond lengths and bond angles for the ligand were selected from the X-ray structural determination of the structure[8] of $[Cu(bipy)_2I]I$, and any differences in bond lengths in this and our complexes are insignificant in this calculation. The geometric factors, G, at the various protons, for $Co(bipy)_3^{2+}$ are as follows: $G_{6,6'} = 2.56 \times 10^{-2}$, $G_{5,5'} = 3.37 \times 10^{-3}$, $G_{4,4'} = 1.68 \times 10^{-3}$, and $G_{3,3'} = 7.85 \times 10^{-3}$.

By using the isotropic shifts for the 4,4′ and 5,5′ protons, the equation $G_i/G_j = X_i/X_j$, and the proper geometric factors, $X_{4,4'}$ is calculated to be 19 cps. By using the contact shifts for the 4,4′ and 3,3′ protons and the proper geometric factors, $X_{4,4'}$ is calculated to be −320 cps. If the g tensor is isotropic for the nickel(II) complex, the above inconsistency proves that the spin delocalization mechanisms in $Co(bipy)_3^{2+}$ and $Ni(bipy)_3^{2+}$ are different and *a priori* assumption of an equivalent mechanism for spin delocalization in cobalt(II) and nickel(II) cannot be made. If there is anisotropy in the g tensor in the nickel(II) complex, the factoring procedure we are attacking is obviously invalid.

Acknowledgment. We wish to acknowledge the support by the National Science Foundation through Grant No. GP 5498.

Mark L. Wicholas, Russell S. Drago
W. A. Noyes Laboratory, University of Illinois
Urbana, Illinois
Received January 8, 1968

The Stereochemistry of Hydride Attack in the Reduction of 1-*t*-Butyl-3-phenylallyl Alcohol

Sir:

The well-known reaction of propargylic alcohols with lithium aluminum hydride (LAH) to produce *trans*-allylic alcohols has recently received attention because of the synthetic utility of the organoaluminum intermediate formed.[1] Moreover, with certain substrates it has been found possible, by varying the nature of the hydride reagent used, to direct initial hydride attack to either the 2 or the 3 position.[1]

A key point in the elucidation of the mechanisms of these interesting reactions is the establishment of the role of the oxygen in activating proximate multiple bonds to attack.[2] Undoubtedly the first step in these reactions is the formation of an O–Al bond, as evidenced by the immediate liberation of hydrogen on mixing an alcohol with LAH. The question, then, is whether the function of the aluminum bound to the oxygen is to donate a hydride to the multiple bond or to facilitate intermolecular hydride attack from another aluminum.

This question is not easily answered in a propargylic system; either mechanism could explain the observed *trans* stereochemistry. Therefore, we turned our attention to an allylic system designed to provide an unequivocal stereochemical answer to the problem of whether hydride attack is intra- or intermolecular.[3]

Previous results with the rearrangement of the xanthate of *trans*-1,3-di-*t*-butylallyl alcohol exclusively to the *trans* dithiocarbonate suggested that this system existed in only one conformation.[4] However, attempts to reduce the allylic alcohol in refluxing tetrahydrofuran (THF) with a variety of hydride reagents led almost entirely to recovered starting material. This

---

(7) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(8) G. A. Barclay, B. W. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 5691 (1963).

(1) E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *J. Am. Chem. Soc.*, **89**, 4245 (1967).

(2) Alkynes and conjugated alkenes also are reduced by LAH, but much severer conditions are required: E. F. Magoon and L. H. Slaugh, *Tetrahedron*, **23**, 4509 (1967).

(3) A study of the relative stereochemistry of the two hydrogens added to the double bond in the LAH reduction of the cinnamyl system has recently been carried out by E. I. Snyder, *J. Org. Chem.*, **32**, 3531 (1967).

(4) W. T. Borden and E. J. Corey, unpublished results.