tic acid,[12] thiostreptine shows a singlet (3 protons, 2′-methyl) at $\tau = 8.7$, a doublet (3 protons, ω-methyl) centered at $\tau = 8.4$, $J = 6$ and single protons at $\tau = 6.4$ (3′-H), 4.4 (1′-H) and 1.2 (5-H).

Thiostreptine can be regarded as derived from β,γ-dihydroxyisoleucine and cysteine. It is interesting to note its relationship to the antibiotic hydroxyaspergillic acid,[13] which is a derivative of β-hydroxyisoleucine.

(12) The n.m.r. spectrum was taken soon after preparing the solution. After a few days at room temperature it had changed considerably, and on paper chromatograms a second as yet unidentified spot, yellow with ninhydrin and turning purple, was observed. The same component was detected when solutions, or even solid samples of II, were stored at room temperature.

(13) J. D. Dutcher, *J. Biol. Chem.*, **232**, 785 (1958).

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NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. LONG-RANGE SPIN COUPLINGS IN VINYLACETYLENE[1]

Sir:

The failure of long-range spin coupling to be observed in the high-resolution proton magnetic resonance spectra of vinylacetylene and propargylaldehyde has been cited[2] as evidence against hyperconjugation as a mechanism for long-range coupling in unsaturated compounds. The reasoning involved has been challenged recently by Hoffman and Gronowitz[3] on theoretical grounds.

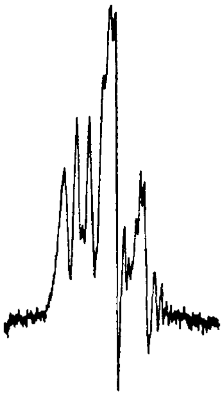

Fig. 1.—Splitting of acetylenic proton resonance of vinylacetylene in benzene solution at room temperature at 60 Mc. taken with Varian A-60 spectrometer. The splitting between the extreme peaks is 2.05 ± 0.05 cps. The appearance of the spectrum is very sensitive to the chemical shifts of the vinyl protons.

It is our belief that further theoretical discussions of this subject must take into account the fact that the couplings in question are by no means negligibly small (*i.e.*, <0.5 cps.) as reported.[2] This is clearly illustrated by Fig. 1 which shows the n.m.r. spectrum of the acetylenic proton of vinylacetylene in benzene solution under very high resolution (<0.20 cps.). The couplings which correspond to the observed splittings are $J_{13} = -2.17$ cps., $J_{14}(cis) = 0.70$ cps., and $J_{14}(trans) = 0.92$ cps. (all ± 0.05 cps.) for vinylacetylene[4] and 0.58 ± 0.05 cps. for propargylaldehyde. The reality of the long-range couplings in vinylacetylene has been further confirmed beyond any question by the proton spectrum of $CH_2{=}CHC{\equiv}CD$, which substance shows the calculated simplification of the vinyl resonances expected for reduction of the magnitude of the relevant couplings by a factor of seven (the H to D gyromagnetic ratio).

A complete analysis of the n.m.r. spectrum of vinylacetylene and its monodeuterated analog will be published later.

(1) Supported in part by the Office of Naval Research and the Undergraduate Research Participation Program of the National Science Foundation.

(2) M. M. Kreevoy, H. B. Charman and D. R. Vinard, *J. Am. Chem. Soc.*, **83**, 1978 (1961).

(3) R. A. Hoffman and S. Gronowitz, *J. Am. Chem. Soc.*, **83**, 3910 (1961).

(4) The signs of the J values are relative to positive signs being taken for couplings within the vinyl group.

(5) National Institutes of Health Postdoctoral Fellow, 1959–61.

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SQUARE PLANAR-TETRAHEDRAL ISOMERISM AMONG SOME COMPLEXES OF NICKEL(II). A NEW TYPE OF GEOMETRIC ISOMERISM

Sir:

Considerable attention has been given in recent years to the structure of nickel(II) complexes and, as a result, a number of tetrahedral[1] or distorted tetrahedral[2,3] complexes have been characterized, while most of the earlier supposed examples of such complexes have been shown to contain nickel(II) in various octahedral environments. For example, $[NiX_2(P\text{-}n\text{-}Bu\text{-}Ph_2)_2]$ ($X = Cl, Br, I$) recently were found to be paramagnetic ($\mu_{eff} = 3.2\text{–}3.4$ B.M.) and tetrahedral (probably distorted) in the crystalline state. It was thought that the structure of the complexes in solution was either distorted tetrahedral or *cis*-planar and that the magnetic and spectral properties of the solutions could be accounted for in terms of the thermal population of two neighboring energy states, one corresponding to a diamagnetic and the other to a paramagnetic molecule. An alternative interpretation in terms of an equilibrium between a *trans*-planar diamagnetic form and a tetrahedral (or *cis*-planar) paramagnetic form was thought to be less likely.[2]

We have investigated recently the reactions of Ph_2EtP with nickel halides and, from ethanolic solution, have obtained the complexes (I)–(III), (Table I).

An interesting feature of the series (I)–(III) is that the chloride alone is diamagnetic and thus square planar in the solid state. On the other hand, the bromide and iodide are paramagnetic and hence have tetrahedral structures both by analogy with the corresponding complexes of Ph_3P[2] and

(1) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(2) (a) M. C. Browning, R. F. B. Davies, D. J. Morgan, L. E. Sutton and L. M. Venanzi, *ibid.*, 4816 (1961), and previous work by Venanzi, *et al.*, *ibid.*, 2705 (1961); 719 (1958).

(3) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961), and references therein.