Table I. Exchange of Aromatic Protons of Hydroxyindoles with Deuterium Oxide

	Nuclear magnetic resonance spectral data^a					
Compound	4-H	5-H	6-H	7-H	2-H	3-H
4-Hydroxyindole^b	....	6.40 d	6.85 m	6.85 m	6.95 d	6.50 d
4-Hydroxyindole-3-^{2}H	....	6.38 d	6.82 m	6.80 m	7.02 s	....
5-Hydroxyindole^b	6.95 d	....	6.68 dd	7.20 d	7.11 d	6.26
5-Hydroxyindole-3,4-^{2}H	....	....	6.68 d	7.18 d	7.14 s	....
6-Hydroxyindole^b	7.35 d	6.62 dd	....	6.75 d	6.81 d	6.30
6-Hydroxyindole-3,7-^{2}H	7.35 d	6.60 d	....	(80%)	6.92 s	....
7-Hydroxyindole^b	6.68 dd	6.98 dd	6.46 dd	....	7.08 d	6.33 d
7-Hydroxyindole-3-^{2}H	6.59 dd	6.93 dd	6.48 dd	....	7.13 s	....
Serotonin^c	6.86 d	....	6.66 dd	7.16 d	7.02 s	....
Serotonin-4^{2}H	....	....	6.68 d	7.17 d	7.03 s	....
Bufotenine^c	6.90 d	....	6.65 dd	7.13 d	7.00 s	....
Bufotenine-4-^{2}H	....	....	6.67 d	7.15 d	7.00 d	....
5-Hydroxytryptophan^c	6.95 d	....	6.70 dd	7.18 d	7.08 s	....
5-Hydroxytryptophan-4-^{2}H	....	....	6.70 d	7.20 d	7.08 s	....
Melatonin^b	7.02 d	....	6.70 dd	7.24 d	6.98 s	....

[a] Values are expressed in δ units (parts per million). Symbols s, d, dd, and m stand for singlet, doublet, a doublet of doublets, and an unresolved multiplet, respectively. [b] Solvent deuteriochloroform. [c] Solvent deuterium oxide.

indole, did not exchange under these conditions, nor did phenol itself.

The 4-^{3}H derivative of bufotenine, required for biosynthetic studies,[7] was prepared in this manner (New England Nuclear Corp.) and was purified by preparative paper chromatography (Whatman No. 1, 1-butanol–1.0 *N* ammonium hydroxide, 22:5). The 4-^{3}H proton was quite labile under acidic and basic conditions and formed tritiated water which was then isolated in a cold trap of a lyophilization apparatus.[8] Passage of a solution of bufotenine-4-^{3}H through a short Dowex 50 column at pH 4, an IRC-50 column at pH 6.5, or a deactivated charcoal column[9] resulted, respectively, in the loss of activity, as THO, of 50, 15, and 8%. Treatment for 5 min at 0° with 0.4 *N* perchloric acid or 1% trichloroacetic acid gave losses of 16 and 5%. Treatment with trimethylamine, water, and dimethylformamide at 60° (see above) resulted in complete loss of tritium as THO during 2–3 hr. Exchange reactions of bufotenine and 5-hydroxytryptophan with D_2O were followed by nmr spectroscopy. In 1.0 *N* DCl $t_{1/2}$ was <5 min, whereas in 1.0 *N* NaOD $t_{1/2}$ was approximately 7 hr. Under such mild conditions phenol, catechol, and hydroquinone do not exchange.[10,11] Acid catalysis causes complete exchange of both the 4- and 6-protons: 5-hydroxytryptophan on heating with 1.0 *N* DCl at 50° for 1 hr is converted quantitatively to 5-hydroxytryptophan-4,6-$^2H_2$.

Analogously 5-hydroxytryptophan-4-^{3}H was prepared and compared with the radioactive 5-hydroxytryptophan resulting from tryptophan-5-^{3}H by the action of hydroxylase from neoplastic mast cells from mice.[1] Both the synthetic and the enzymatic product lost their tritium at the same rate either on incubation at 50° for 60 min in 10% trichloroacetic acid or on digestion with 0.8 *N* NH_4OH.[1]

This intramolecular shift of tritium or deuterium during enzymatic hydroxylation of indoles from the 5 position to the 4 position is analogous to the 4→3 shifts of ^{2}H and ^{3}H in *para*-substituted phenyl derivatives, such as phenylalanine-4$^{3(2)}$H,[12,13] acetanilide-4$^{3(2)}$H,[14] and even of chlorine in 4-chlorophenylalanine.[15]

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Orientation and Motion of Vinyl Radicals in Neon Matrices

Sir:

We have observed the epr spectrum of vinyl radicals produced by vapor-phase pyrolysis of the iodide and trapped near 4°K in a neon matrix under conditions which have been shown to produce preferentially oriented samples.[1,2] The spectrum obtained can be accommodated with the isotropic parameters from liquid-phase measurements[3] and with dipolar couplings in model systems,[4] provided the following assumptions are made: (1) highly oriented samples are produced in which the carbon–carbon axis is aligned perpendicular to the surface of the flat sapphire rod on which the matrix is deposited; (2) motional averaging of the epr spectrum occurs about the axis of preferential alignment; and (3) the β-hydrogens are magnetically equivalent on the time scale of these measurements (10^{-8} sec).

Spectra obtained for two mutually perpendicular orientations of the sample in the magnetic field are shown in Figure 1. The line shapes and their dependence on sample orientation are more characteristic of single crystals than of powders, indicative of the high degree of alignment. In each of the extreme orientations shown, the spectrum consists essentially of a triplet of doublets, with second-order splitting of the innermost doublet members resolved. The relative simplicity of the spectrum requires an axially symmetric

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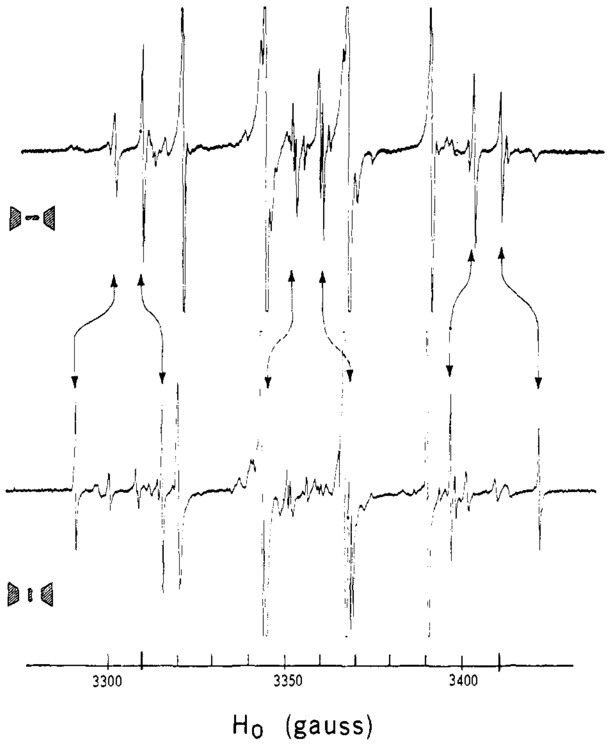


Figure 1. Electron spin resonance spectrum of vinyl (and methyl) radicals trapped in neon for two indicated orientations of the matrix in the magnetic field. Arrows indicate the strong lines identified with vinyl radicals, the remaining stronger lines being due to methyl.

three-spin system with two equivalent members.[4] The observed splittings are given in Table I. By assuming the unique principal axis of the hyperfine tensor to be perpendicular to the surface of the matrix, one derives the isotropic and dipolar couplings also listed in Table I. The isotropic couplings agree closely with the splittings observed in the liquid,[3] substantiating the identity of the radicals. Our failure to observe the expected[5,6] orthorhombic hyperfine tensor makes it necessary to assume motional averaging of two of its components, which most reasonably occurs about the axis of least inertia approximately coincident with the carbon–carbon bond. In-plane rotation of methyl radicals in "soft" matrices has been inferred from relative intensity data,[7,8] and rotation of the molecular plane is evidenced by our failure[9] to observe anisotropy in the ^{13}C splitting of $^{13}CH_3$ radicals trapped in the same way as the vinyl radicals in this experiment.

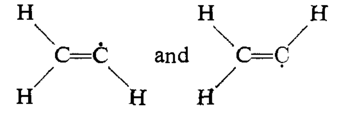
Table I. Hyperfine Splittings[a] in Trapped Vinyl Radicals

	Doublet	Triplet
I. Observed splittings (Figure 1)		
Perpendicular orientation (top)	7.6	50.5
Parallel orientation (bottom)	24.6	52.5
II. Hyperfine interactions		
Isotropic	13.3	51.5
Dipolar		
Parallel	11.3	1.3
Perpendicular	−5.7	−0.7

[a] In gauss at operating frequency of 9436 MHz.

Anomalies in the g values of SiH_3, GeH_3, and SnH_3 have also been interpreted on the basis of rotation.[8]

The spectrum also implies equivalent β-hydrogens. Such equivalence can be easily understood if the α-carbon is linearly hybridized; the odd electron would be in the 2p orbital of the α-carbon directed in the molecular plane perpendicular to the carbon–carbon σ bond. If the α-carbon is trigonally hybridized, however, one must assume that the radical is inverting rapidly ($>10^{10}$ sec^{-1}) between the two equivalent bent configurations



The dipolar parts of the coupling constant to the α-hydrogen shown in Table I are in good agreement with the linear model.[4] However, our results imply that the isotropic coupling to this hydrogen is positive, which is easier to reconcile with a bent structure.[10] It is not possible to distinguish between the two structures on the basis of our experiments. One should note, however, that the observed isotropic coupling to the α-hydrogen has very nearly the same magnitude as that observed in a liquid system for which much slower inversion between the bent configurations (10^7–10^9 sec^{-1}) was proposed in order to account for the absence of the central portion of the expected spectrum.[3]

The implied orientation of vinyl radicals in a neon matrix is opposite from that previously observed for linear molecules such as CuF_2 and bent molecules such as NO_2 and NF_2, where the molecular plane was found to be oriented parallel to the surface.[1,2,11] However, both vanadium oxide and propargyl radicals have since been found to orient, like vinyl, with their axis of least inertia normal to the surface.[9] In the case of vinyl radicals, both the rotation and the apparent lowering of the inversion barrier appear to be associated with the oriented sites, since spectra obtained previously[10] from radicals produced by photolysis of HI in acetylene and argon show none of these characteristics. This suggests that the vinyl radicals in our experiment may be incorporated substitutionally into oriented crystals[12] of neon. We obtain spectra like the original one[10] when argon or krypton is used as a matrix, and in neon vinyl radicals can occupy both types of site to varying extents depending on experimental conditions.

We are making use of the progressive complication of the spectrum in an attempt to analyze it in detail when all motions are frozen out.

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The Molecular Structure of 2-Nitronitrosoethane Dimer

Sir:

The preferred representation of the bonding in C-nitroso dimers has been a subject with a long history of speculation and controversy.[1-7] Two valence struc-

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