that a radical mechanism is operative in these reactions.

No isomerization at C-14 occurred when the solvent, cyclohexane, was replaced by *t*-butyl alcohol or methyl alcohol. Other hydrocarbon solvents, capable of dissolving mercuric bromide (*e.g.*, hexane) could however replace cyclohexane.

Since we assumed that the bromine radicals were responsible for the epimerization reaction, we have tried to use other sources of these radicals. A cyclohexane solution of 14α steroid **1b** was thus irradiated in the presence of bromine and of bromotrichloromethane. No more than 10% of the epimerized 14β derivative **2b** was formed. However, irradiation with the same light source in the presence of 0.15 equiv of N-bromosuccinimide resulted in a 50% conversion of 17β-acetoxy derivative **1b** to its 14β epimer **2b**, and in the presence of 1 equiv in a 90% conversion. The 17-ketone **1f** was also epimerized to the 14β-17-ketone **2f** in 50% yield when irradiated in cyclohexane solution in the presence of 1.5 equiv of N-bromosuccinimide.

Work on further applications and on the mechanism of this isomerization reaction is now in progress.

Acknowledgment. This work was supported by a grant of the Ministry of Commerce and Industry of Israel.

(9) The solution irradiated contained equivalent concentrations of the phenol and of the 14α-steroid **1b** (3 m*M* each). The phenol did not act as a uv filter as indicated by irradiation of the same compound, **1b** (3 m*M*), in the presence of much higher concentrations of benzene (30 m*M*) which resulted in 80% epimerization to **2b**.

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The Molecular and Electronic Structure of Vitamin B_{12r}, Cobaloximes(II), and Related Compounds

Sir:

Vitamin B_{12r} is of interest as a low-spin Co(II) d^7 complex in which the cobalt ion could be five coordinated owing to the attachment of 5,6-dimethylbenzimidazole to the corrin ligand by the peculiar sugar phosphate "loop." However, it is possible that the interaction of this ligand with the metal is sufficiently strong only in Co(III) derivatives of the vitamin, and that in vitamin B_{12r} solutions four-coordinated species may also be present. To establish the molecular structure of vitamin B_{12r} in solution, esr spectroscopy was applied. Several authors[1-3] have previously reported esr measurements on vitamin B_{12r}. However, thus far no definite conclusions concerning the molecular or electronic structure were possible, primarily because of the low resolution of the spectra obtained.

Solutions of vitamin B_{12r} were prepared, *e.g.*, by reducing pure vitamin B_{12a} with $NaBH_4$ in water or water–methanol at pH 2.2.[4] Most measurements were performed in neutralized solutions under argon at 90°K. A spectrum of vitamin B_{12r} is shown in Figure 1. The *g* tensor is axially symmetrical with $g_\perp = 2.24$ and $g_{||} = 2.014$. The high-field signal is split due to the interaction of the electron with ^{59}Co ($I = 7/2$), with $\langle A_{Co} \rangle = 108$ G. Six of the eight expected lines are observed. The remaining two are hidden under the intense low-field signal. The latter is not well resolved and consists of a superposition of absorptions due to nuclear transitions belonging to $g_\perp$.

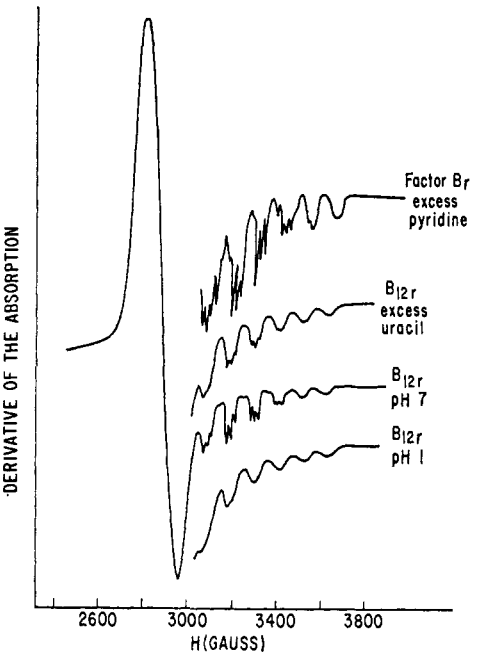

Figure 1. Esr spectra of vitamin B_{12r} under various conditions in frozen aqueous solutions at 90°K. Note the different ^{14}N shf splitting multiplicity of Factor B_r in the presence of excess of pyridine, consistent with the formation of 1:1 and 1:2 adducts of Factor B_r with pyridine.

The observed axial symmetry and the *g* values are very similar to those found[5] for cobalt phthalocyanine (Table I). Accordingly, vitamin B_{12r} must possess a similar electronic ground state. From the observed axial symmetry of the *g* tensor the placement of the unpaired electron can be limited to either the d_{z^2} or the $d_{x^2-y^2}$ orbital. Of these two the latter is eliminated in view of the absence of shf splitting due to the in-plane nitrogen atoms of the corrin system. The unpaired electron consequently must be in the $3d_{z^2}$ orbital just as in the case of cobalt phthalocyanine.[5] This conclusion becomes unambiguous in view of the observed sensitivity of the esr signal to changes in the axial environment and, more specifically, the observation of the shf splitting due to the axial ligand. Thus, the cobalt components of $g_{||}$, particularly those with $M_I = +3/2, +1/2$, and $-1/2$, are split into three lines through the interaction with ^{14}N ($I = 1$), with $\langle A_N \rangle = 17.5$ G (Figures 1 and 2). This shf structure diminishes in solutions of pH 1 due to the protonation of the axial ligand and is absent in the esr spectrum of reduced "Factor B," which does not contain benzimidazole. The Co(II) ion in vitamin B_{12r} thus is essentially five coordinated under our conditions of measurement (Figure 2). The addition of excess of pyridine, benzim-

(1) H. P. C. Hogenkamp, H. A. Barker, and H. S. Mason, *Arch. Biochem. Biophys.*, **100**, 353 (1963).
(2) H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Proc. Roy. Soc.* (London), **A288**, 352 (1965).
(3) R. H. Yamada, S. Shimizu, and S. Fukui, *Arch. Biochem. Biophys.*, 117, 675 (1966).
(4) Well-resolved esr spectra were also obtained by reducing vitamin B_{12a} with mercaptans at neutral pH. Concerning the esr spectrum of vitamin B_{12a} in solution due to self-reduction, see L. P. Lee and G. N. Schrauzer, *J. Am. Chem. Soc.*, **90**, 5274 (1968).
(5) J. M. Assour, *ibid.*, **87**, 4701 (1965).

Table I. Experimental Data at 90°K

Compound (base, added in excess)	g	g	$\langle A_{Co} \rangle$, gauss	$\langle A_N \rangle$, gauss	^{14}N shf-splitting multiplicity
Vitamin B_{12r} (none, H_2O)	2.22	2.107	108	17.5	3
Vitamin B_{12r} (pyridine)	2.22	2.011	105	17.5	3
Vitamin B_{12r} (imidazole)	2.27	2.022	100	18	3
Vitamin B_{12r} (uracil)	2.27	2.017	108	18	3
Vitamin B_{12r} (adenine)	2.27	2.017	108	18	3
Factor B_r (none, H_2O)	2.27	2.017	108		
Factor B_r (adenine)	2.24	2.005	108	17.5	3
Factor B_r (uracil)	2.23	2.007	114	16	3
Factor B_r (pyridine)	2.24	2.011	108	18	3,5
Vitamin B_{12r} (cyclohexyl isocyanide)	2.216	1.999	87		
Factor B_r (cyclohexyl isocyanide)	2.217	1.999	87		
$Co(Dmg)_2$ (none, H_2O)	2.20	1.980	87		
$Co(Dmg)_2$ (pyridine)	2.29	2.023	80	11.5	5
Co(phthalocyanine) (pyridine)[b]	2.268	2.016	78	11.4	5
$Co(Dmg)_2 \cdot SbPh_3)_2$ solid[a]					
$Co(Dmg)_2 \cdot PPh_3)_2$ solid[a]					
$Co(Dmg)_2 \cdot 2Py$ solid[b]	2.117				
$Co(Dmg)_2 \cdot 2PBu_3$ solid[b]	2.134				
$Co(Dmg)_2$ ($NC-CH_3$)	2.241	2.009	113	20	3
$Co(Dmg)_2$ (imidazole)	2.272	2.025	87	18	3

[a] Solid sample diamagnetic. [b] Unresolved signal.

idazole, or uracil to solutions of vitamin B_{12r} does not change the esr spectrum; in particular, the ^{14}N shf splitting multiplicity remains the same, indicating that six-coordinated adducts are not formed. All the above-mentioned bases except pyridine form 1:1 adducts with Factor B_r. Factor B_r with excess pyridine produces an esr spectrum with the ^{14}N shf splitting multiplicity of 3 and 5, consistent with the formation of 1:1 and 2:1 adducts (Figure 1). The ^{14}N shf structure of vitamin B_{12r} disappears on addition of cyclohexyl isocyanide due to the displacement of the coordinated 5,6-dimethylbenzimidazole (Table I). Complete substantiation of the conclusions concerning vitamin B_{12r} was obtained through esr measurements on cobaloximes(II). The esr signals of polycrystalline samples of $Co(Dmg)_2 \cdot 2B$ (B, *e.g.*, is pyridine or triphenylphosphine) are not resolved (Figure 3). The presumably dimeric, diamagnetic 1:1 base adducts $[Co(Dmg)_2 \cdot B]_2$, if pure and not contaminated by the 1:2 adducts, do not show esr signals in the polycrystalline state but dissociate into

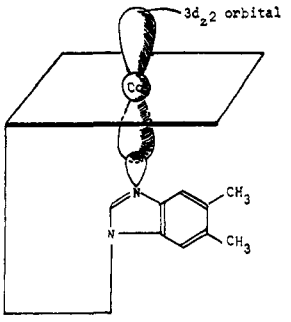

Figure 2. Structure of vitamin B_{12r} in neutral solution.

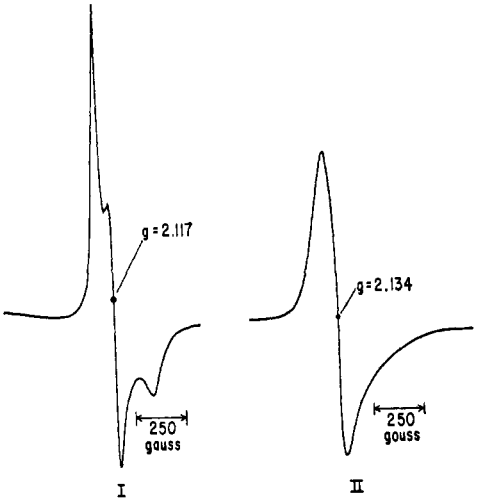

Figure 3. Esr signals of polycrystalline $Co(Dmg)_2 \cdot 2Py$ (I) and of $Co(Dmg)_2 \cdot 2P(n\text{-}C_4H_9)_3$ (II) at 90°K.

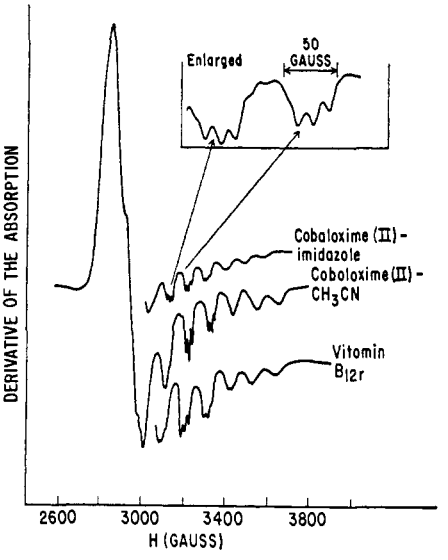

Figure 4. Esr spectra of vitamin B_{12r}, cobaloxime(II) in the presence of excess acetonitrile, and cobaloxime(II) with excess imidazole at 90°K (frozen solutions). The enlarged portion shows the ^{14}N shf multiplicity.

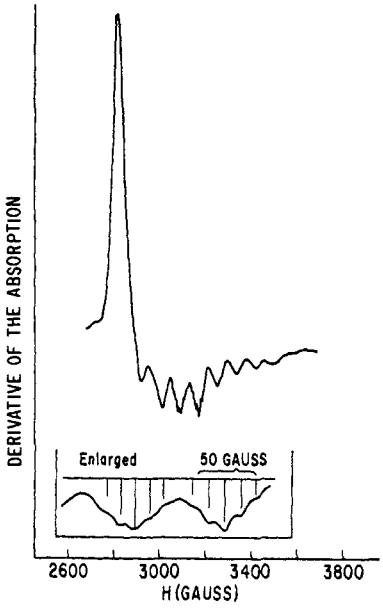

Figure 5. Esr spectrum of cobaloxime(II) in the presence of excess pyridine, at 90°K (frozen solutions in water), with the enlarged portion showing ^{14}N shf splitting due to the interaction of the cobalt with two molecules of the base.

paramagnetic species in solution.[6] In solid solutions at 90°K the esr spectra of the 1:1 adducts of cobaloximes(II)[7] with acetonitrile or imidazole are almost indistinguishable from those of vitamin B_{12r} (Figure 4, Table I). It is furthermore of interest that a 1:2 adduct is formed with pyridine (Figure 5), in conspicuous analogy to the behavior of Factor B_r.

Acknowledgment. This work was supported by National Science Foundation Grant GB 6174 and PRF Grant No. 3486-A3 from the Petroleum Research Fund, administered by the American Chemical Society.

(6) G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).

(7) "Cobaloximes" are bis(dimethylglyoximato)cobalt complexes. Dmg in Table I denotes the dimethylglyoximato monoanion.

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Proton Couplings in Cyclohexane

Sir:

An uncounted number of vicinal and geminal proton couplings are known for substituted cyclohexanes.[1] As these parameters are unknown for cyclohexane, we wish to present our determination of them here.

Specifically deuterated cyclohexene, **1**, of greater than 97% isotopic purity was synthesized through the Diels–Alder dimerization of perdeuteriobutadiene[2] and ethylene. The synthesis of **2** was accomplished by homogeneous catalytic deuteriumation of **1** using tris(triphenylphosphine)rhodium(I) chloride catalyst,[3] nitrogen purged benzene solvent, and 2 atm of deuterium at room temperature.

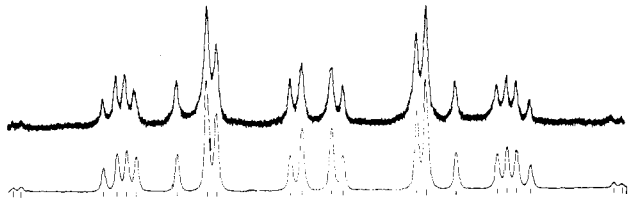
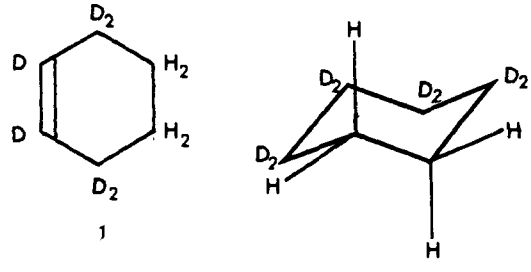
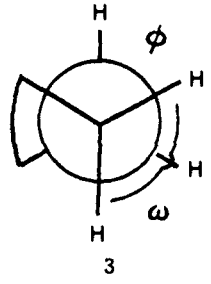


Figure 1. Deuterium-decoupled pmr spectrum of a 5% solution of **2** in CS_2 (mole/mole) at −103°. The total width of the spectrum is 63.58 cps. The bottom spectrum is the computed one.[7]

At 38°, the deuterium decoupled pmr spectrum[4] of a 5% (mole/mole) solution of **2** in CS_2 consists of a single resonance at τ 8.6014 ± 0.0003 ppm. Comparison with τ 8.5805 ± 0.0003 ppm for cyclohexane, determined under the same conditions, gives a deuterium isotope shift (upfield) of −1.25 cps. Lowering the sample temperature to −103° reduced the frequency of chair–chair conformational interconversion[5] to the extent necessary to give the AA'BB' spectrum shown in Figure 1. Each absorption of the spectrum has a full width at half-height comparable to that for TMS (*i.e.*, between 0.4 and 0.5 cps). Six TMS side-band calibrated spectra were determined at this temperature and the averaged[6] transition frequencies used for a hand analysis based upon repeated spacings.[7] Statistical refinement of the parameters was effected through an iterative least-squares fit of the observed and computed spectra.[8] The resulting solution parameters are collected in Table I.





(1) See A. A. Bothner-By, *Advan. Magnetic Resonance*, 1, 149 (1965), for a survey of some of the more reliable proton couplings.

(2) D. Craig and R. B. Fowler, *J. Org. Chem.*, **26**, 713 (1961).

(3) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

(4) The nmr spectra were determined on a Varian A-60 spectrometer with an NMR Specialties HD60A heteronuclear decoupler.

(5) For earlier variable temperature measurements on cyclohexane see F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Amer. Chem. Soc.*, **84**, 386 (1962); F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 145 (1964); F. A. Bovey, F. P. Hood III, E. W. Anderson, and R. L. Kornegary, *J. Chem. Phys.*, **41**, 2041 (1964).

(6) Standard deviations of all transition frequencies were less than 0.08 cps, with the majority being less than 0.06 cps.

(7) E. W. Garbisch, Jr., *J. Chem. Educ.*, **45**, 480 (1968).

(8) Computations were performed on a CDC 6600 using the LAOCOON III program provided by A. A. Bothner-By. The plotting program was provided by S. Castellano and modified for our use by B. Hawkins.