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Nuclear Magnetic Resonance Study of Metal Complexes. I. A Conformational Analysis of D-(*l*)-Propylenediamine Chelate Rings of Diamagnetic Cobalt(III), Palladium(II) and Platinum(II) Complexes

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Proton magnetic resonance (PMR) spectra of tetracyano-*l*-propylenediamine cobalt(III) ion and bis(*l*-propylenediamine) platinum(II) and palladium(II) ion have been measured in deuterated water and analyzed according to Castellano and Waugh's exact analysis. The values of coupling constants clearly indicate that the *l*-propylenediamine chelate rings in these diamagnetic complexes have fixed λ-*gauche* form in aqueous solutions at room temperature.

Recent researches have shown that high resolution proton magnetic resonance spectroscopy provides useful information on the structure of a variety of organic compounds in solution, but only a few papers have reported on its application to metal

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complexes.[1] It is known that ethylenediamine (en) and propylenediamine (pn) coordinate to various metal ions to form nonplanar *gauche* chelates. Spees *et al.*[2] measured proton magnetic resonance (PMR) spectra of various metal complexes containing ethylenediamine and propylenediamine, and showed that the ethylenediamine chelate changes its conformation rapidly from λ- to δ-*gauche* form (IUPAC, 1966) and *vice versa* in an aqueous solution at room temperature. No clear experimental evidence has been given, however, concerning the chelate conformation of propylenediamine ring in solution.

Propylenediamine chelate ring was considered to be less labile to such conformational change, because the preference for the methyl group to be equatorial to the chelate ring would make one of the conformers more stable. The energy difference between the conformers with the methyl group in the axial and the equatorial direction was estimated to be about 2 kcal/mol, and it was supposed that about ninetyfive per cent of the ligand has the methyl group equatorial even in a solution at room temperature.[3]

We have measured PMR spectra of the diamagnetic complexes, $K[Co(CN)_4(l\text{-pn})]$, $[Pt(l\text{-pn})_2]Cl_2$ and $[Pd(l\text{-pn})_2]Cl_2$ and obtained significant information on the conformation of the *l*-propylenediamine chelate ring.

Experimental

Preparation of the Complexes. *Potassium Tetracyano-l-propylenediamine Cobalt(III) Dihydrate* $K[Co(CN)_4(l\text{-pn})]\cdot 2H_2O$. A mixture containing 5.0 g of $K_3[CoI(CN)_5]$[4] and 1.5 g of *l*-propylenediamine in 50 m*l* of water was warmed on a water bath at 80°C until the color changed to yellow. The solution was cooled, filtered, and evaporated to almost dryness under reduced pressure at 60°C. The residue was treated with 100 m*l* of absolute methanol and filtered. The crude complex was precipitated by adding 95% ethanol to the filtrate, filtered off, washed with absolute ethanol and ether. The product was recrystallized from methanol solution by adding 95% ethanol.

Found: C, 27.62; H, 4.60; N, 26.44%. Calcd for $C_6H_{12}N_6O_2KCo$. C, 26.91; H, 4.52; N, 26.90%.

Other complexes used in this work were the lots prepared in our previous work.[5]

Measurements. Proton magnetic resonance spectra of $K[Co(CN)_4(l\text{-pn})]$, $[Pt(l\text{-pn})_2]Cl_2$ and $[Pd(l\text{-pn})_2]Cl_2$ were recorded with Varian A-60, T-60 and HA-100 spectrometers. The spectra of $K[Co(CN)_4(l\text{-pn})]$ and $[Pt(l\text{-pn})_2]Cl_2$ were obtained in deuterated water and in a mixture of pyridine and deuterated water. The spectra of $[Pd(l\text{-pn})_2]Cl_2$ were measured in deuterated water. Sodium trimethylsilylpropanesulfonate (Na-TMS) was used as an internal reference. In all the solvents, hydrogen atoms of the amino groups were deuterated rapidly and only the C–H resonance was observed. Diamagnetic contributions of the complex and the solvent on the chemical shifts have not been corrected. To facilitate the analysis of spectra, nuclear magnetic double resonance technique was used; *i.e.* the methyl signal was decoupled to give a simpler ABC pattern with HA-100 spectrometer. All the measurements were made at about 39°C.

The coupling constants, the chemical shifts and the intensities were calculated with a HITAC 5020 electronic computer at the University of Tokyo. The Fortran program for Castellano and Waugh's[6] exact analysis was kindly supplied by Dr. J. Cavanaugh at Research Department, Socony Mobil Oil Company, Inc., Paulsboro, New Jersey, U.S.A. to whom our sincere thanks are due.

Results and Discussion

The spectra of $K[Co(CN)_4(l\text{-pn})]$ in deuterated water are shown in Fig. 1. Whenever amino group hydrogens are deuterated, propylenediamine $ND_2CH(CH_3)CH_2ND_2$ should give an $ABCX_3$ pattern. One sharp doublet and one triplet were observed at about 1.25 and 2.38 ppm, respectively. That the splitting (J=6.0 cps for the doublet and 12.3 cps for the triplet) is not affected by the outer magnetic field strength indicates that these splittings are brought about by the spin-spin coupling. The doublet is safely assigned to the methyl signal, and its integrated intensity is three times as large as that of the triplet. In the lower field, complicated signals appear in the region from 2.80 to

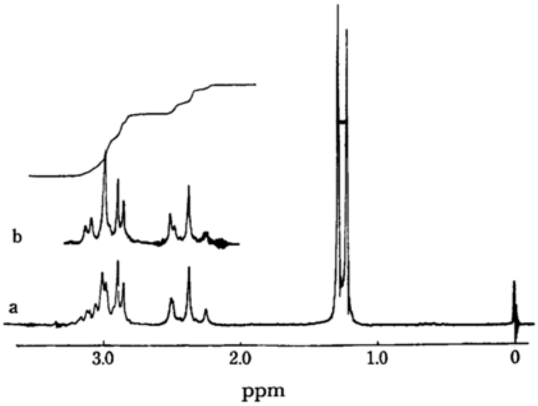

Fig. 1. 100 MHz PMR spectrum of $K[Co(CN)_4(l\text{-pn})]$ in D_2O (a) and the double resonance spectrum irradiated on the methyl signal (b).

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[2] S. T. Spees, Jr., L. J. Durham and A. M. Sargeson, *Inorg. Chem.*, **5**, 2103 (1966).

[3] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

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[5] H. Ito, J. Fujita and K. Saito, This Bulletin, **40**, 2584 (1967).

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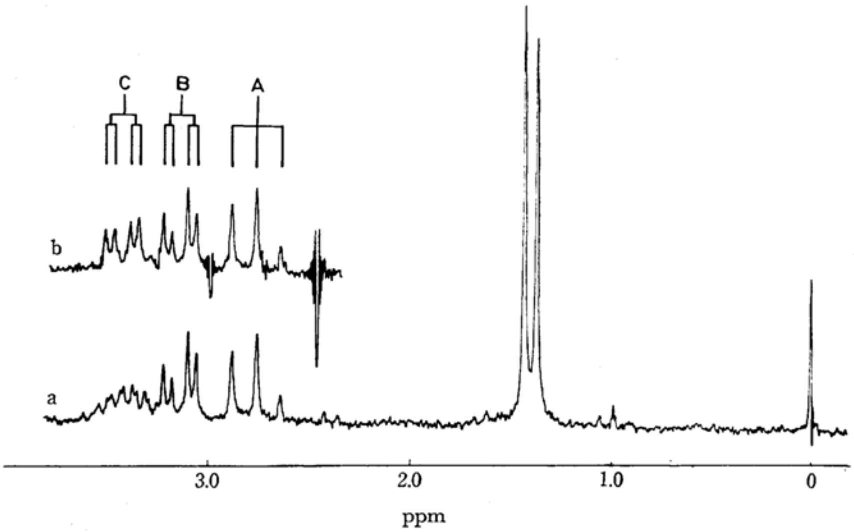

Fig. 2. 100 MHz PMR spectrum of K[Co(CN)$_4$(l-pn)] in pyridine-D$_2$O mixed solvent (a) and the double resonance spectrum irradiated on the methyl signal (b).

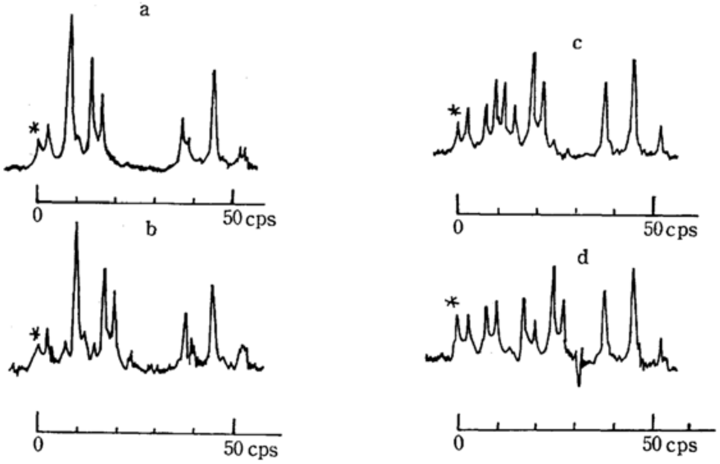

Fig. 3. The methine and methylene part of 100 MHz PMR double resonance spectra irradiated on the methyl signal of K[Co(CN)$_4$(l-pn)] in pyridine-D$_2$O mixed solvents (Chemical shifts from * peak). Approximate ratios (by volume) of pyridine to water are as follows; (a) 0, (b) 0.231, (c) 0.455 and (d) 0.600

3.20 ppm. The integrated intensity ratio of these signals to that of the doublet is two thirds. Although the signal of methine proton appears usually at a lower field than those of methylene protons, the spectra are too complicated to be analyzed further. Thus we used the nuclear magnetic double resonance technique. Irradiation at 1.25 ppm (the region of the methyl signal) made the signals from 2.80 to 3.20 ppm region less complicated, as shown in Fig. 1-b. Conversely, irradiation at the lower region of the complicated signals (3.10 ppm) converted the methyl doublet into a single sharp peak. This indicates that the signals at the lower region of the complicated part correspond to the methine proton. The double resonance spectrum obtained on irradiation at the methyl region should consist of ABC or ABB′ pattern, which gives rise to fifteen lines including three combination bands. However, the signals arising from methylene and methine group overlap with each other to make the analysis of spectrum still difficult.

The PMR spectra of K[Co(CN)$_4$(l-pn)] in pyridine-D$_2$O mixed solvents irradiated in the methyl signal region are shown in Fig. 2. With increase in the amount of pyridine, the whole signal shift to a lower field and the complicated part splits into two quartets as shown in Fig. 3. The higher field quartet is shifted to a lower field to a less extent as compared with the other quartet. The extent of splitting of these groups of signals remains unchanged with the change in molar ratio of pyridine to water. Since coupling constants are not affected by changing solvents, these quartets were considered to be brought about by the spin-spin coupling. We denote tentatively the triplet, the higher quartet and the lower quartet A, B and C, respectively. Their integrated intensities are equal.

All the experiments described above lead to the assignment that A and B are due to protons of CH_2 group and C to that of CH group (Fig. 2). On the basis of these eleven lines of the spectra in aqueous pyridine solutions, we have calculated the coupling constants, the chemical shifts and the intensities, according to Castellano and Waugh's exact analysis⁶⁾ (Tables 1 and 2).

Two possible conformers can exist when *l*-propylenediamine coordinates to a metal, *λ-gauche* and *δ-gauche* form with the methyl group equatorial and axial to the chelate ring, respectively (Fig. 4). The *λ-gauche* form can provide three kinds of coupling: a *geminal*, a *trans* and a *gauche*. On the other hand, the *δ-gauche* form gives two different kinds of coupling: one *geminal* and two *gauche*. Karplus,⁷⁾ Lemieux and Lown,⁸⁾ and Abraham and Mclauchlan⁹⁾ calculated theoretical values of vicinal coupling

TABLE 1. CHEMICAL SHIFTS AND SPIN-SPIN COUPLING CONSTANTS (in cycle/sec) OF $K[Co(CN)_4(l\text{-pn})]$ IN PYRIDINE-DEUTERATED WATER MIXED SOLVENTS

Pyridine / D_2O	Chemical shifts			Coupling constants		
	C	B	A	AB	BC	AC
0.600	−30.9	−2.1	33.0	−12.4	4.4	12.4
0.455	−28.2	−8.1	36.2	−12.5	4.4	12.4
0.23	−26.2	−10.5	36.6	−12.8	4.4	12.7

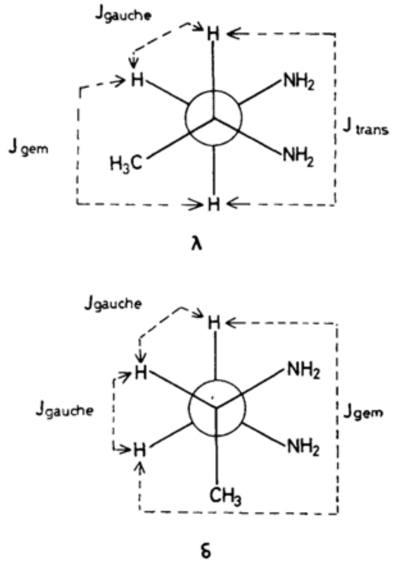

Fig. 4. The schematic diagram of spin-spin couplings for λ-and *δ-gauche* conformer.

TABLE 2. CALCULATED AND OBSERVED INTENSITIES

$K[Co(CN)_4(l\text{-pn})]$			$[Pd(l\text{-pn})_2]Cl_2$			$[Pt(l\text{-pn})_2]Cl_2$*		
Position (cps)	obsd	calcd	Position (cps)	obsd	calcd	Position (cps)	obsd	calcd
−69.28		0.0	−61.76		0.0	−64.20		0.0
−39.97	0.9	0.7	−40.84	0.8	0.8	−37.90	0.9	0.7
−35.67	0.9	0.9	−36.54	1.0	0.9	−33.60	0.7	0.9
−27.67	1.1	1.0	−31.04	1.0	1.0	−27.90	1.1	1.0
−23.37	1.1	1.4	−26.74	1.2	1.3	−23.60	1.2	1.3
−11.27	1.0	0.8	−5.82		0.0	−9.60	0.9	0.7
−6.97	0.7	0.6	−5.44	0.6	0.6	−5.30	0.6	0.5
1.03	1.4	1.5	−1.14	0.5	0.5	2.60	1.4	1.6
5.33	1.0	1.1	6.96	1.7	1.6	2.70		0.0
5.94		0.0	11.26	1.5	1.3	6.90	1.2	1.2
22.34	1.5	1.6	19.78	1.6	1.7	21.00	1.2	1.6
34.64	1.9	1.1	29.58	1.1	1.2	31.00	1.1	1.1
34.64		1.0	32.18	0.8	0.6	33.20	1.1	0.7
46.94	0.6	0.6	41.98	0.5	0.5	43.20	0.6	0.5
63.34		0.0	67.38		0.0	61.50		0.0

* The influence of the satellites due to ^{195}Pt ($l=1/2$) was ignored.

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TABLE 3. THEORETICAL AND CALCULATED VALUES OF SPIN-SPIN COUPLING CONSTANTS (in cycle/sec) OF K[Co(CN)$_4$(*l*-pn)]

	Experimental	Theoretical	
J_{trans} (CA)	12.4	11.0	16.1
J_{gauche} (BC)	4.4	2.0	4.0
J_{gem} (AB)	−12.4	13.2	13.4

constants, which are dependent on the dihedral angle between two vicinal CH bonds. Barfield and Grant[10] calculated the *geminal* coupling constants for methane derivatives on the basis of the valence bond approach. These values are shown in Table 3.

The coupling constant J_{AB}(−12.4 cps) is undoubtedly for *geminal*, because A and B are the signals of methylene protons. The constants J_{BC} and J_{AC} are, therefore, of vicinal coupling. Of these, J_{BC} (4.4 cps) is in good agreement with the theoretical value of the *gauche* coupling constant.

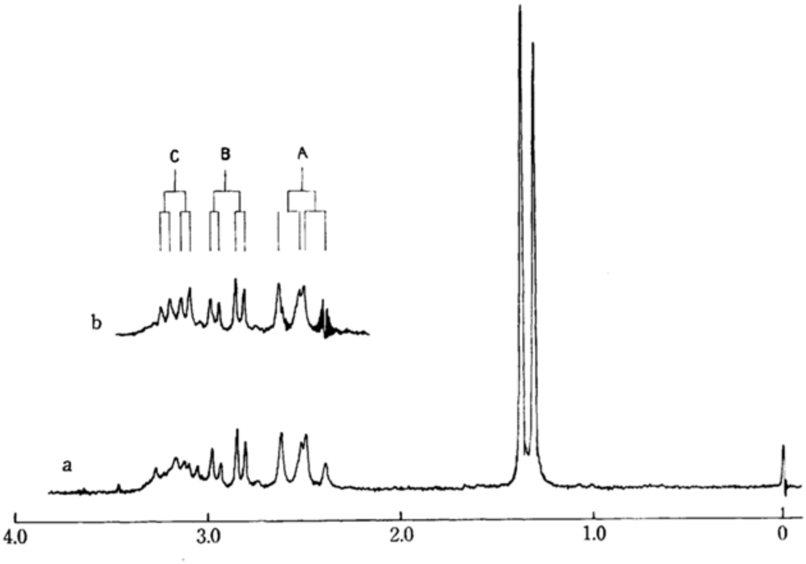

Fig. 5. 100 MHz PMR spectrum of [Pt(*l*-pn)$_2$]Cl$_2$ in D$_2$O (a) and the double resonance spectrum irradiated on the methyl signal (b).

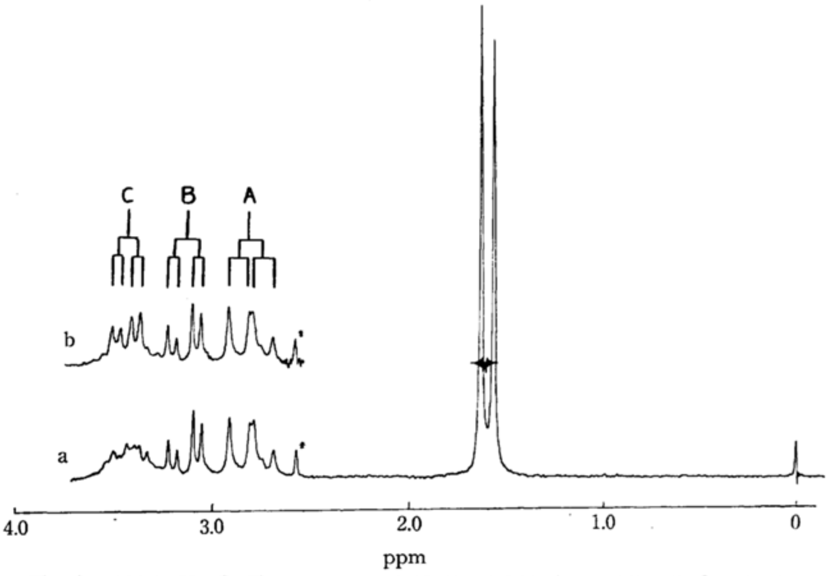

Fig. 6. 100 MHz PMR spectrum of [Pt(*l*-pn)$_2$]Cl$_2$ in pyridine-D$_2$O mixed solvent (a) and the double resonance spectrum irradiated on the methyl signal (b).

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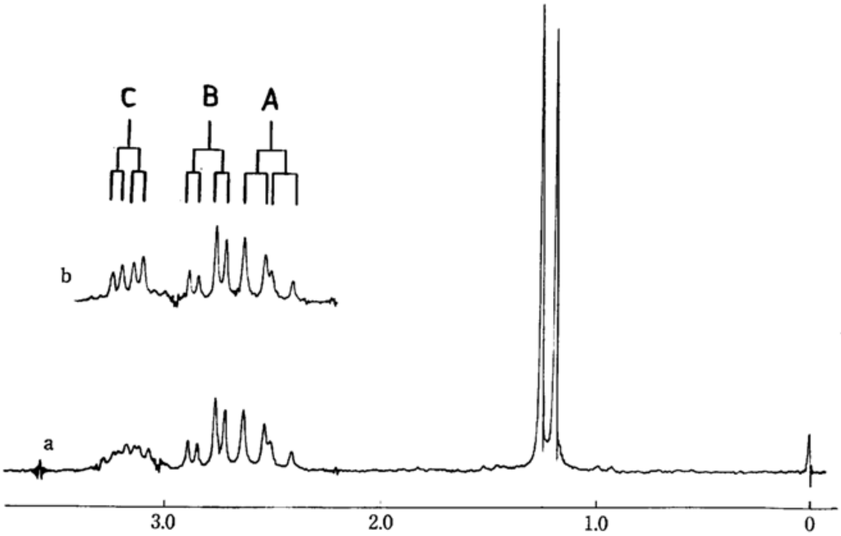


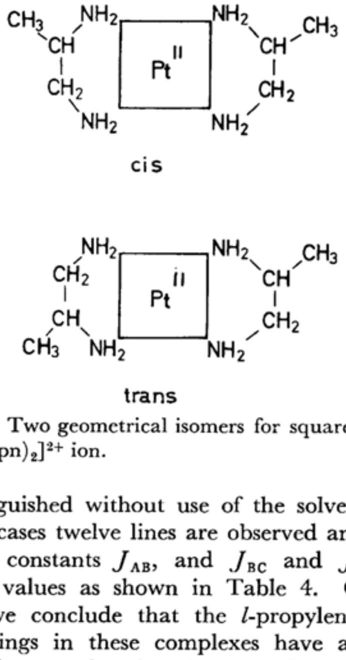
Fig. 7. 100 MHz PMR spectrum of $[Pd(l\text{-}pn)_2]Cl_2$ in D_2O (a) and the double resonance spectrum irradiated on the methyl signal (b).

TABLE 4. CALCULATED CHEMICAL SHIFTS AND SPIN-SPIN COUPLING CONSTANTS (in cycle/sec) OF $[Pd(l\text{-}pn)_2]Cl_2$ IN DEUTERATED WATER AND $[Pt(l\text{-}pn)_2]Cl_2$ IN PYRIDINE-DEUTERATED WATER

	Chemical shifts			Coupling constants		
	C	B	A	AB	BC	CA
$[Pd(l\text{-}pn)_2]Cl_2$	−33.3	4.3	29.0	−12.5	4.2	9.9
$[Pt(l\text{-}pn)_2]Cl_2$	−30.2	−0.3	30.5	−12.3	4.3	10.0

The constant J_{AC} is 12.4 cps and agrees well also with the theoretical *trans* coupling constant. These results indicate that the *l*-propylenediamine chelate ring has a *λ-gauche* form, and that A and B are due to the axial and the equatorial proton, respectively. The coupling constants J_{AC} and J_{AB} must have accidentally coincided with each other.

The large difference of the chemical shifts between the methylene protons may also support fixed *λ-gauche* form of the *l*-propylenediamine chelate ring. On the basis of the above assignment the axial proton gives a signal at a higher field than the equatorial proton does. This is consistent with the observation for substituted cyclohexanes.[11]



cis

trans

Fig. 8. Two geometrical isomers for square planar $[Pt(l\text{-}pn)_2]^{2+}$ ion.

The PMR spectra of $[Pt(l\text{-}pn)_2]Cl_2$ in deuterated water and in a mixture of pyridine and deuterated water, and $[Pd(l\text{-}pn)_2]Cl_2$ in deuterated water are shown in Figs. 5, 6 and 7. These spectra are not significantly different from that of $K[Co(CN)_4(l\text{-}pn)]$, except that the difference of the chemical shift between B and C protons is large enough to be distinguished without use of the solvent effect. In these cases twelve lines are observed and all the coupling constants J_{AB}, and J_{BC} and J_{AC} have different values as shown in Table 4. On these results, we conclude that the *l*-propylenediamine chelate rings in these complexes have also fixed *λ-gauche* form under the given conditions.

Two geometrical isomers are possible for bis-*l*-propylenediamine complex of a planar type shown in Fig. 8. The chemical environment for protons should be different between these two isomers. Such a difference, however, would be too small[1] to be detected by the present spectrometer.

In Table 2 are listed the values of observed and calculated intensities. They seem to agree with each other satisfactorily, to support our assignments.

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[11] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York (1959), p. 392.