9. ^{1}H- and ^{13}C-NMR. Studies of Some Metal Complexes of *o, o'*-Dihydroxyazobenzenes

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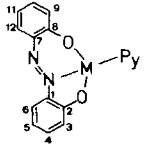
(8.XI.78)

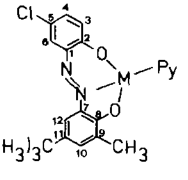
Summary

The aromatic ^{1}H- and ^{13}C-NMR. spectra of some metal complexes of *o,o'*-dihydroxyazobenzenes are shown to be useful in distinguishing the two possible isomers (acolar and discolar) stemming from the non equivalence of the two ligating azo nitrogen atoms. The ortho aromatic carbon atoms, C(6) and C(12) experience relatively large upfield shifts between 12.8 and 15.7 ppm when the adjacent nitrogen atom is coordinated. The protons attached to these carbon atoms are shifted downfield. The values $^nJ(^{15}N, ^{13}C)$ for the ligand 2,2'-dihydroxy-3-methyl-4'-chloro-5-(*t*-butyl)-^{15}N-azobenzene are reported.

Introduction. - Our interest in metal complexes of *o,o'*-dihydroxyazobenzenes, *e.g.* of type I, led us to investigate some of the ^{1}H- [1] and ^{15}N-NMR. [2] characteristics of these molecules. For compounds containing a suitably positioned CH_3 group, ^{1}H-NMR. methods are useful in distinguishing which of the two nitrogen atoms in isomeric complexes such as II and III is coordinated to the metal. When a pair isomers can be synthesized containing a single ^{15}N enriched isotope, the nitrogen-15 chemical shift and, when the metal has a nuclear spin I = 1/2, the $^1J(M, ^{15}N)$ coupling constant provides a useful probe for the site of coordination. Although both the ^{1}H- and ^{15}N-studies are useful, the former



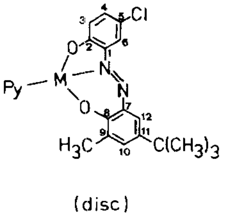
I M = Pd



(ac)

IIa M = Pd

IIIa M = Pt



(disc)

IIb

IIIb

requires that a CH_3 group be present and the latter necessitates a time consuming special synthesis. Since there are many cases where either or both of these conditions are not readily fulfilled we thought it of further interest to study the aromatic protons and carbon atoms of the molecules since these are almost always present.

Experimental part. - ^1H- and ^{13}C-NMR. spectra were recorded using a *Bruker* HX-90 spectrometer operating in *Fourier* transform mode. ^1H-NMR. spectra for the Pd-complexes I, IIa and IIb were also measured at a field strength corresponding to 360 MHz. Chemical shifts are reported relative to TMS for both ^1H and ^{13}C. The ^{13}C-NMR. spectra were assigned using selective and off-resonance decoupling methods in conjunction with the two and three bond coupling constant data stemming from the completely coupled spectra. The selective decoupling experiments were facilitated by the proton data stemming from the 360 MHz data. The proton assignments were supported *via* homonuclear double resonance work. Specifically, it was possible to unambigously identify H–C(10) *via* its long-range coupling to the CH_3 protons, and therefore H–C(12) *via* its coupling to the proton at C(10).

The synthetic procedures have been described previously [1]. All of the complexes gave satisfactory microanalyses and the measurements were carried out on analytically pure materials.

Results and Discussion. - In *Tables 1* and *2* are shown ^1H- and ^{13}C-NMR. data, respectively for the azo complexes. As may be seen from *Table 1* the proton resonances derived from the carbon-atoms *ortho* to the nitrogen atoms in complexes I, IIa and IIb shift to lower field when the tridentate ligand is bound to palladium. Thus, for I, H–C(6) shifts downfield by 0.47 ppm and H–C(12) by 0.31 ppm. In the poly substituted isomeric complexes IIa and IIb a similar effect is observed. Of potential diagnostic value is the observation that coordination to a nitrogen atom shifts proton H–C(6) in IIb (and H–C(12) in IIa) further downfield than H–C(12) (or H–C(6)). Thus the coordination chemical shift $\Delta\delta$ ($=\delta$ complex$-\delta$ ligand) for the proton *ortho* to coordinated nitrogen is larger by 0.16, 0.13 and 0.11 ppm in I, IIa and IIb respectively. This change may be attributed to the development of a partial positive charge on the nitrogen atom which is coordinated to the metal. This can change the local electronic environment of the proton *via* both resonance and inductive effects, with a low field shift as consequence. Therefore, where the proton spectrum of this type of derivative is assignable one can use these data to distinguish between the two isomeric forms IIa and IIb.

The changes in the ^{13}C-resonance positions of C(6) and C(12) are considerably larger than those found for the corresponding protons. In I, $\Delta\delta$ for C(6)

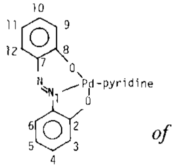
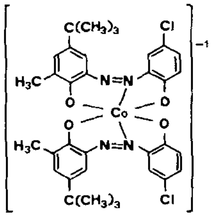


Table 1. ^1H-*NMR. Characteristics*[a,b]
of Some o,o'-*Dihydroxyazobenzene Complexes of Palladium*

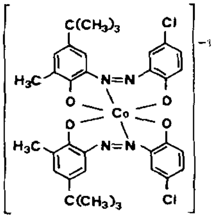
	H–C(3)	H–C(4)	H–C(5)	H–C(6)	H–C(9)	H–C(10)	H–C(11)	H–C(12)
(I)	7.32	7.42	6.91	8.18 (7.71)	7.11	7.26	6.72	8.02
(IIa)	7.15 (6.98)	7.26 (7.27)	–	7.93 (7.68)	–	7.20 (7.30)	–	7.88 (7.50)
(IIb)	6.90 (6.98)	7.13 (7.27)	– –	8.00 (7.68)	– –	7.39 (7.30)	–	7.71 (7.50)

[a] In ppm relative to TMS in $CDCl_3$.
[b] Values for the free ligand appear in parenthesis under the appropriate value for the complex.

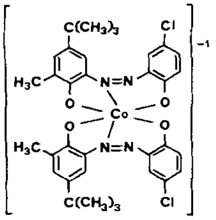
is − 13.6 ppm, whereas Δδ for C(12) is +2.5. Thus coordination of the nitrogen atom results in a relatively large upfield shift in the protonated carbon atom adjacent to the site of complexation. For complexes II-IV this upfield shift varies from 12.8 to 14.7 ppm in the discolar isomers and from 14.3 to 15.7 ppm in the acolar isomers (see *Table 2*). Since these derivatives encompass Co-, Pd- and Pt-complexes it would seem that this upfield coordination chemical shift is not sensitive to the nature of the metal. Thus if the C(6) and C(12) resonances can be readily assigned we have a second alternative whereby we may distinguish the



IV b



IV c



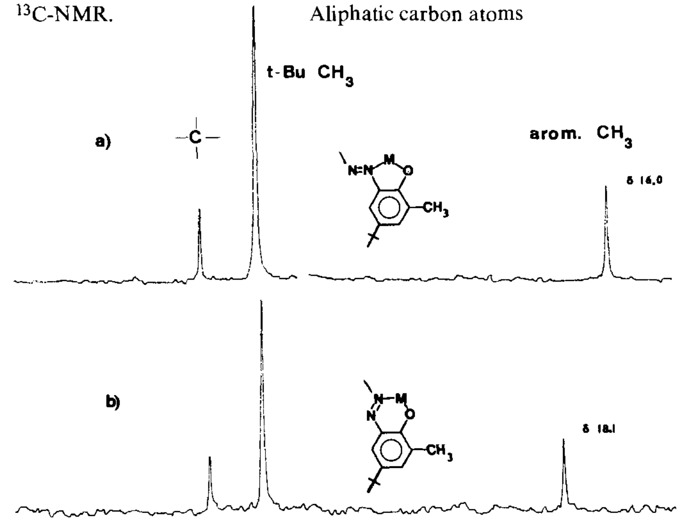
IV a

Table 2. ${}^{13}C$ *Chemical Shifts*[a]) *of C(6) in the Discolar and C(12) in the Acolar Isomers*

	δ C(6)	Δδ	δ C(12)	Δδ	CH_3
I	117.6 (131.2)	− 13.6			
IIa			111.1 (125.4)	− 14.3	16.0 (15.5)
IIb	116.7 (129.6)	− 12.9			18.3
IIIa			110.9 (125.4)	− 14.5	16.0
IIIb	116.8 (129.6)	− 12.8			18.1
IVa[b])			109.8 (125.4)	− 15.6	16.3
IVb[b])	114.9 (129.6)	− 14.7			17.4
IVc[b])	115.1 (129.6)	− 14.5	109.7 (125.4)	− 15.7	16.3, 17.4
Va					26.3 (18.6)
Vb					22.4
VIa					26.1
VIb					22.7

[a]) Values in ppm from TMS as $CDCl_3$ solutions.

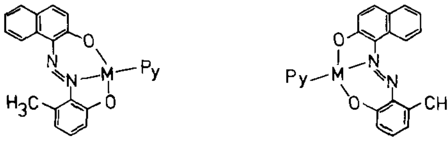
[b]) The octahedral Co-complexes were measured in DMSO-d_6 and are 2:1 complexes.



Figure

acolar and discolar isomers. We are not, as yet, certain as to the source of this upfield shift; however, it does not seem to be related to any significant change in the resonance interaction of the azo nitrogen atom with the benzene ring since the position of C(4) in I is changed only a few tenths of a ppm relative to the free ligand.

Of additional interest are the changes in δ $^{13}CH_3$ as a function of the nitrogen coordination for the complexes II-VI. A typical example is shown in the *Figure.* For CH_3 groups *ortho* to the oxygen-function, the discolar isomers IIb, IIIb and IVb, show somewhat larger downfield shifts than do the acolar isomers IIa, IIIa and IVa (see *Table 2*) whereas the reverse is true for when the methyl lies *ortho* to the nitrogen azo nitrogen-atom as in complexes V and VI. This observation is in keeping with our previous ^{1}H-NMR. spectra [1].

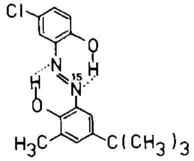


(ac) (disc)

Va M=Pd **Vb**

VIa M=Pt **VIb**

As part of a previous study we had occasion to synthesize substituted *o,o'*-dihydroxyazobenzene VII containing one isotopically enriched ^{15}N atom (>95% ^{15}N) attached to C(7). The $^{13}C\{^1H\}$-NMR. spectrum of this tridentate ligand shows a number of relatively small splittings due to the ^{15}N ($I = 1/2$) isotope. Of interest is the observation that the couplings to C(12) (8.4 Hz) and C(11) (3.7 Hz) are significantly larger than those to C(8) (1.2 Hz) and C(9) (not observed). The dependence of $^{n}J(^{15}N, H)$ [3] and $^{n}J(^{15}N, ^{13}C)$ on the orientation of the nitrogen lone-pair in a variety of organic molecules has been observed. Thus in *N*-nitrosoamines [4] and oximes [5] similar differences in $^{2}J(^{15}N, ^{13}C)$ have been observed and it is reasonable that our data represent yet another manifestation of this effect. This dependence in our type of molecule is worth noting since, should the unambiguous assignment of C(12) prove difficult, the recognition of this relatively large coupling could prove of value. We did not observe a coupling of the ^{15}N to C (6).



VII

Taken together it would seem that ^{1}H- and ^{13}C-NMR. spectroscopy offer additional probes for molecular structure in molecules such as ours.

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