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Benzene Induced Shift for Some Organometallic 8-Quinolinolato Complexes: A New Criterion for the Interaction of Nitrogen with Metal

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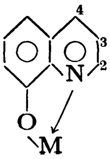
Synopsis. The benzene induced shift was measured for some organometallic 8-quinolinolato complexes. A large upfield shift (0.5—0.7 ppm) of the 2-proton of the 8-quinolinolato ligand was found in benzene when the nitrogen in the 8-quinolinolato ligand coordinated to the metal. But the shift was small (0—0.3 ppm) in the absence of nitrogen coordination.

The striking chemical shift difference of the proton resonance of molecules having polar sites caused by changing the solvent from an inert solvent such as carbon tetrachloride to benzene has been applied in many configurational studies[1–3] since the phenomenon was discovered by Bothner-By and Click[4] and Reeves and Schneider.[5] Various explanations have been put forward to interpret the phenomenon.[4,6–13] The phenomenon has been expressed by a large anisotropy of the benzene ring. Ronayne and Williams[8] have pointed out that the benzene induced shift, $\Delta=\delta'-\delta_{\mathrm{benzene}}$($\delta'$ is the chemical shift of protons in inert solvents such as carbon tetrachloride, chloroform, cyclohexane, or in the pure liquid, and $\delta_{\mathrm{benzene}}$ is the value in benzene), is positive for the protons in the neighborhood of the positively polarized sites of the molecule and negative for the protons near the negatively polarized sites. In fact, they have shown that in 4-methylpyridine, the 3-proton and the 4-methyl protons give positive Δ values and the 2-proton gives a negative Δ value. Ford and Hart[14] have shown that in tetraalkylammonium tetraalkylborates the alkyl groups of tetraalkylammonium cation give positive Δ values and the tetraalkylborate anion shows a negative Δ value.

In the present paper the benzene induced shift has been measured for some organometallic 8-quinolinolato complexes to study the coordination of the nitrogen in the 8-quinolinolato ligand to the metal.

Results and Discussion

As can be seen from Table 1, the 3- and 4-protons of the 8-quinolinolato ligand of 8-methoxyquinoline, 8-quinolinol, and all organometallic 8-quinolinolato complexes were found to show large positive Δ values. The Δ value of the 2-proton of 8-methoxyquinoline, in which the nitrogen is free from coordination or hydrogen bonding, was very small. Trimethyl(8-quinolinolato)silane and -germane also gave rather small Δ values for the 2-proton. The value is almost the same as that of 8-quinolinol. These compounds have shown the absorption maximum at around 320 nm and, therefore, have been considered to have a non-chelated 8-quinolinolato ligand.[15] On the other hand, in the complexes with a chelated 8-quinolinolato ligand, such as trimethyl(8-quinolinolato)tin, and in the protonated 8-methoxyquinoline, the Δ value of the 2-proton was positive and large. The amount of upfield shift is almost the same as those of the 3- and 4-portons. Other organometallic complexes with a chelated 8-quinolinolato ligand, which show the absorption maximum at about 350 nm, gave similar results. The Δ value of the 2-proton of the 8-quinolinolato ligand, therefore, may be used as a new criterion of coordination of nitrogen. The interaction of the lone pair of nitrogen in the 8-quinolinolato ligand with the metal may remove the negatively polarized charges from the nitrogen. The result leads to large positive Δ values of the 2-proton, in accordance with an empirical rule that Δ value is positive when the protons are in the neighborhood of a positively polarized site of a molecule.[7,8]



Meinema and Noltes[16] have reported that in trimethyl(8-quinolinolato)antimony chloride, the nitrogen in the 8-quinolinolato ligand does not coordinate to antimony, on the basis of the UV spectra of this complex. We[17] have, on the other hand, expected a weak interaction of nitrogen with antimony for the corresponding bromide. One of complications in these trimethyl(8-quinolinolato)antimony halides is that the UV spectra of these complexes depend on the concentration.[18] If the Δ value criterion can be applicable to these 8-quinolinolato complexes, the data in Table 1 indicate that these complexes belong to the complexes with the chelated 8-quinolinolato ligand.

In trimethyl(8-quinolinolato)antimony carboxylates, the chemical shift of the 2-proton appears at a rather low magnetic field, as compared with that of trimethyl(8-quinolinolato)antimony halides and 8-quinolinol, although the values of the 3- and 4-protons are almost the same as other 8-quinolinolato complexes. The Δ values of the 2-proton of these trimethyl(8-quinolinolato)antimony carboxylates is small and in some cases negative. One of possible reasons for these results is that the magnetic anisotropy of the carbonyl group in the carboxylato ligand affects the intramolecular 2-proton.* In these complexes, the absorption maximum appears in the region between that of typically chelated complexes and that of non-chelated compounds.[18] Therefore, the coordination of nitrogen to antimony is probably weak, if present at all.

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* The chemical shift of the 2-proton was not affected even if the concentration of these complexes was changed.

Table 1. Chemical shift in dichloromethane and benzene induced shift of some organometallic 8-quinolinolato complexes (δ value)[a]

Compound	2-H	3-H	4-H	CH_3-M	Ligand[b]	λ_{max}
8-MeQ[c]	8.77(+0.04)	7.31(+0.45)	8.02(+0.40)			297[d]
$[8\text{-MeQH}]^+$[e]	9.16(+0.71)	8.13(—)[f]	9.10(+1.02)			—[g]
8-Quinolinol[h]	8.69(+0.25)	7.37(+0.69)	8.11(+0.66)			320
$(CH_3)_3SiOx$	8.65(+0.25)	7.34(+0.69)	8.15(+0.66)	0.36(−0.11)		315[i]
$(CH_3)_3GeOx$[i]	8.68(+0.32)	7.27(+0.54)	8.00(+0.45)	0.58(−0.02)		320
$(CH_3)_3SnOx$[h]	8.53(+0.53)	7.34(+0.62)	8.17(+0.56)	0.45(−0.02)		332[j]
$(CH_3)_2Sn(Ox)NCS$[h]	8.67(+0.68)	7.58(+0.88)	8.50(+0.88)	0.97(−0.39)		361
$(C_2H_5)_2InOx$[k]	8.51(+0.58)	7.44(+0.79)	8.23(+0.71)			370
$(C_2H_5)_2TlOx$	8.42(+0.50)	7.35(+0.58)	8.14(+0.48)			380
$(CH_3)_4SbOx$	8.49(+0.48)	7.27(+0.59)	8.09(+0.43)	1.06(+0.07)		380[l]
$(CH_3)_3Sb(Ox)Cl$	8.60(+0.60)	7.34(+0.62)	8.08(+0.54)	1.91(+0.17)		353[m]
$(CH_3)_3Sb(Ox)Br$	8.69(+0.70)	7.37(+0.78)	8.17(+0.69)	2.07(+0.27)		352[m]
$(CH_3)_3Sb(Ox)O_2CCH_3$	9.06(−0.20)	7.41(+0.60)	8.20(+0.59)	1.64(+0.06)	1.96(−0.10)	340[m]
$(CH_3)_3Sb(Ox)O_2CCH(CH_3)_2$	9.10(−0.24)	7.43(+0.66)	8.19(+0.62)	1.62(+0.06)	1.14(−0.14) 2.43(−0.17)	341[m]
$(CH_3)_3Sb(Ox)O_2CH$	8.95(−0.26)	7.40(+0.65)	8.13(+0.57)	1.69(+0.16)	8.21(−0.30)	332[m]
$(CH_3)_3Sb(Ox)O_2CCH_2Cl$	9.10(−0.07)	7.46(+0.71)	8.23(+0.67)	1.62(+0.06)	4.04(+0.16)	338[m]
$(CH_3)_3Sb(Ox)O_2CCHCl_2$	9.07(+0.02)	7.46(+0.70)	8.22(+0.70)	1.72(+0.25)	5.89(−0.04)	334[m]
$(CH_3)_3Sb(Ox)O_2CCCl_3$	9.03(+0.07)	7.47(+0.76)	8.24(+0.74)	1.80(+0.33)		334[m]

a) Value in parentheses is the Δ value. b) Chemical shift of the carboxylato group. c) 8-Methoxyquinoline. d) Ref. 17. e) 8-Methoxyquinoline in 0.1 ml CF_3COOH and 0.5 ml CH_2Cl_2 or C_6H_6. f) Obscured by other signals. g) Not measured. h) Ref. 19. i) Ref. 15. j) Ref. 20. k) Ref. 21. l) Ref. 16. m) Ref. 18.

Experimental

The UV spectra were recorded on a Hitachi model 124 spectrometer with 1 mm quartz cells. The PMR measurements were made with a JEOL JNM-PS-100 spectrometer operating at 100 MHz. The chemical shift (δ) was measured relative to tetramethylsilane as the internal standard. Solvents were purified by distillation.

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