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^{13}C-Nuclear magnetic resonance of some triaryl- and tri-alkylantimony and -bismuth derivatives

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THE ^{13}C-NMR technique was already applied to various kinds of organometallic compounds[1a, 2]. Recently the additivity parameters of the chemical shifts of ^{13}C-NMR for organotin compounds were studied by Holloway[3], however, the effect of antimony or bismuth on the NMR of carbons was not clarified yet. The authors have studied the ^{13}C-NMR of some organoantimony and -bismuth compounds to find that the substituents containing antimony or bismuth also obey the additivity rule of the ^{13}C-NMR. These metals give downfield shift to the NMR of bonding and vicinal carbons.

EXPERIMENTAL

Tervalent compounds, R_3M, where $R = CH_3$, C_2H_5, C_6H_5, *p*-tolyl and *p*-chlorophenyl; M = Sb and Bi, were obtained from the metal chloride and the Grignard reagent by the method mentioned in the references[4–6]. The pentavalent compounds, R_3MX_2, where X = Cl and Br, were obtained by the direct halogenation of the tervalent compounds with free halogen[7, 8]. The pentavalent derivatives of carboxylic acids or phenols were obtained from the free ligand and the organometal bromide by the metathesis in benzene medium using triethylamine as a deprotonation reagent. The purity of the products was checked by the chemical analyses as well as by their ^{1}H-NMR. All the chemical shift data were obtained in chloroform solution at approximate 20% w/v concentration, using 60 MHz C60-HL NMR spectrometer of JEOL Co. Ltd. Benzene, cyclohexane, and acetic acid were used as the external standard. The results were obtained from 32 to 128 times accumulation of the measurements.

RESULTS AND DISCUSSION

Typical ^{13}C-NMR chemical shifts of the derivatives of triphenylantimony and others are shown in Tables 1 and 2. The chemical shifts of phenyl carbons are shown by ppm unit downward from benzene carbon signal. (the $\delta_C^{C_6H_6}$ is 128·79 ppm vs TMS) The chemical shifts of alkyl carbons are shown by (ppm) value vs TMS = 0, downward +). The ^{1}H-NMR is also shown by (ppm) values (TMS = 0, downward +). The carbon positions of the phenyl group are counted from the one bonded directly to the metal, and the number of the carbons of the alkyl chain is also numerated from the metal-bonding one.

The assignment of the peak of each phenyl carbon of them was

Table 1. ^{13}C-NMR of some triphenylantimony and -bismuth derivatives (ppm) ($\delta_C^{C_6H_6}$ = 128·79 ppm vs TMS)

A. Phenyl group bonding to the central metal directly

Compounds	^{13}C-NMR (C_6H_6 = 0, downward: +)				^{1}H-NMR of para proton (TMS = 0, downward: +)
	C-1	*ortho*	*meta*	*para*	
Ph_3Sb	10·8	8·6	0·9	1·2	7·39
Ph_3Bi	*	10·1	0·3	3·0	7·39
Ph_3SbCl_2	12·5	6·6	2·2	4·3	7·59
Ph_3SbBr_2	13·6	6·2	2·2	4·3	7·58
$Ph_3Sb(Bz)_2$	10·7	6·3	1·8	3·6	7·53
$Ph_3Sb(Ph)_2$	*	8·0	1·8	3·9	7·47
$Ph_3Sb(Pr)_2$	11·4	6·2	1·6	3·2	7·50
Ph_3BiBr_2	28·6	7·1	4·3	4·3	7·60
$Ph_3Bi(Bz)_2$	32·9	6·4	2·0	3·7	7·64

*not found.

B. Phenyl group of benzoic acid and phenol bonding to the central metal

Compounds	^{13}C-NMR (C_6H_6 = 0, downward: +)					^{1}H-NMR of para proton (TMS = 0, downward: +)
	C-1	*ortho*	*meta*	*para*	COO–	
$Ph_3Sb(Bz)_2$	4·5	2·3	0·5	5·1	42·5	7·36
$Me_3Sb(Bz)_2$	4·1	1·8	0·1	4·1	42·3	7·40
$Ph_3Bi(Bz)_2$	5·5	2·0	0·3	3·3	44·8	7·46
free HBz	0·7	1·5	−0·3	5·0	43·9	7·52
$Ph_3Sb(Ph)_2$	*	−7·5	1·2	−9·6		6·59
$Me_3Sb(Ph)_2$	*	−7·0	2·1	−8·0		6·66
free HPh	26·2	−13·3	1·0	−7·7		6·88

*not identified.

Abbreviations: Ph, phenyl; Me, methyl; HBz, benzoic acid; HPr, propionic acid; H(Ph), phenol.

Table 2. ^{13}C-NMR of some alkyl carbons of organo-anitomy and -bismuth compounds (ppm)

	Compounds	^{13}C-NMR (TMS = 0, downward: +) C-1	C-2	C-3	C-4	COO-
Alkyl group	$Me_3Sb(Bz)_2$	13·1				
	$Me_3Sb(p\text{-}CB)_2$	13·3				
	$Et_3Sb(p\text{-}CB)_2$	25·0	11·2			
	$Et_3Sb(p\text{-}CB)_2$	42·8	12·9			
	$(n\text{-}Bu)_3SbBr_2$	46·2	29·7	26·8	17·2	
Ligand	$Ph_3Sb(Pr)_2$	51·2	29·7	16·8		179·9
	$Ph_3Bi(Pr)_2$	47·9	27·8	11·4		176·6
	free HPr	53·2	28·5	10·2		181·9

Abbreviations: Ph, phenyl; Me, methyl; Et, ethyl; *n*-Bu, *n*-butyl, HBz, benzoic acid; H(*p*-CB), *p*-chlorobenzoic acid; HPr, propionic acid.

obtained referring the data to those of substituted derivatives, as the additivity of the benzene carbon shielding by two substituents is applicable in these cases, too. In the case of triphenylantimony(III), for example, the data were compared with those of tris(*p*-tolyl)-, tris(*o*-tolyl)- and tris(*p*-chlorophenyl)-antimony(III). In these cases, each benzene ring has the Ar_2Sb-group as a substituent. The carbon shielding effect of the Ar_2Sb- group should be different, when the Ar-group is not the same. In the practical measurement, however, the difference is small, and their shielding effect is practically the same as that of the $(C_6H_5)_3Sb$-group. Consequently, the ^{13}C-NMR peaks of a series of compounds were assigned to give the best coincidence between the observed values and the calculated ones assuming the shielding of each benzene ring carbon is given by the group and $(C_6H_5)_2Sb$- group bonded to the ring. The shielding effect of the former two was obtained from Levy's data[9–11a] shown in Table 3, and the latter was obtained from the observed chemical shifts of carbons of $(C_6H_5)_3Sb$ as shown in Tables 1 or 4.

In the case of tris(*p*-tolyl)antimony(III), the C-1 carbon of the tolyl group (the carbon directly bonded to antimony), receives the shielding effect both from Ph_2Sb– and a methyl group. The carbon atom is at the C-1 position of the Ph_2Sb– group, and the group gives + 10·8 ppm shift as in the case of the Ph_3Sb as is shown in Tables 1A or 4A. At the same time, the carbon is at the para position of a methyl group and the latter gives the carbon − 2·9 ppm shift as is shown in the $-CH_3$ column of Table 3. Consequently, if the additivity rule is applicable in this case, the total shielding effect of these substitution groups should be $+10{\cdot}8-2{\cdot}9 = +7{\cdot}9$. In the same way, the shielding effect to the *ortho* carbon was calculated as $+8{\cdot}6+(-0{\cdot}1) = +8{\cdot}5$. The calculated values in Tables 4A and 4B were obtained by the same process, and they were compared with the observed values; the coincidence between them is quite reasonable. The same calculation method is also applicable to the benzene carbons of the R_3SbL_2 type pentavalent compounds; both of the benzene ring bonded directly to the metal, and to the aryl group of the carboxylato or phenolato ligand.

The chemical shift of the carbon in *para* position to the metal, is shown to be proportional to the electron density of the benzene ring[11b]. In the cases of Ar_3SbL_2 as well as Ar_3BiL_2 type compounds, the value was about 4 ppm lower than that of the free benzene. The ^{1}H-NMR of the proton bonding to the *para* carbon of the benzene ring also shifts to the lower field as are shown in Tables 1A and 1B. Consequently, the antimony or bismuth bonded to the benzene ring withdraws electrons from the hydrocarbon group. The Hammett σ parameter of Ar_2Sb- and that of Ar_2SbL_2- obtained from the *para*-carbon shielding[1b] are about + 0·1 and + 0·4 respectively, and they are corresponding with such substituents as halogen atom and a carbonyl group, respectively.

Table 3. Aryl carbon shielding in some monosubstituted benzenes. (ppm) (shift from C_6H_6 carbon signal; downward: +)

Substituted group	C-1	*ortho*	*meta*	*para*
-Cl	+ 6·2	+ 0·4	+ 1·3	− 1·9
$-CH_3$	+ 8·9	+0·7	− 0·1	− 2·9

Table 4. Calculated and found chemical shifts (ppm) ($C_6H_6 = 0$, downward: +, where $\delta_{C}^{C_6H_6} = +128{\cdot}79$ vs TMS)

A. Aryl group bonded directly to the metal

Compounds		C-1	*ortho*	*meta*	*para*
Ph_3Sb	Found	10·8	8·6	0·9	1·2
$(p\text{-tolyl})_3Sb$	Calcd.	7·9	8·5	1·6	10·1
	Found	7·0	8·3	1·8	10·4
$(o\text{-tolyl})_3Sb$	Calcd.	11·5	17·5(8·5*)	1·6 (− 2·0*)	1·1
	Found	10·0	17·5(8·5*)	2·1 (− 1·0*)	1·5
Ph_3SbBr_2	Found	13·6	6·2	2·2	4·3
$(p\text{-C})_3SbBr_2$	Calcd.	11·7	7·5	2·6	10·5
	Found	10·8	7·1	2·0	10·8
$Ph_3Sb(Bz)_2$	Found	10·7	6·3	1·8	3·6
$(p\text{-tolyl})_3Sb(Bz)_2$	Calcd.	7·8	6·2	2·5	12·5
	Found	6·8	6·3	2·2	13·5

B. Aryl group of the ligand

Compounds		C-1	*ortho*	*meta*	*para*
$Ph_3Sb(Ph)_2$	Found	32·7	− 7·5	1·2	− 9·6
$Ph_3Sb(p\text{-}CP)_2$	Calcd.	30·8	− 6·2	1·6	− 3·4
	Found	31·3	− 6·4	1·2	− 5·0
$Ph_3Sb(p\text{-}MP)_2$	Calcd.	29·8	− 7·6	1·9	− 0·7
	Found	30·2	− 7·8	1·9	− 0·8
$Me_3Sb(Bz)_2$	Found	4·1	1·8	0·1	4·1
$Me_3Sb(p\text{-}CB)_2$	Calcd.	2·2	3·1	0·5	10·3
	Found	3·6	3·7	0·7	10·9

Abbreviations: Ph, phenyl; Me, methyl; (*p*-C), *p*-chlorophenyl; H(Bz), benzoic acid; H(*p*-CB), *p*-chlorobenzoic acid; H(Ph), phenol; H(*p*-CP), *p*-chlorophenol; H(*p*-MP), *p*-cresol.

*The phenyl carbon, on the opposite side of the methyl group.

The chemical shifts of C-1 carbon (the carbon where the metal is bonded) and the *ortho* one are more complicated. The *ortho* carbon should receive the same polar effect as the *para* one. However, the observed peak of *ortho* carbon appears in much lower field than that of the *para* one; *ortho*-*para* = 2 ~ 4 ppm. The peak of C-1 carbon was sometimes not found probably because of the broadening due to the quadrapole effect of the central metal, especially in the case of bismuth tervalent compounds. Consequently, C-1 and *ortho* carbon atoms receive some short range effect from the metal, and the effect is stronger than that of the change of electron density of the ring.

The effect of the central metal to the ^{13}C-NMR of the benzene ring of aryl carboxylato- or phenolato- groups is much smaller than the effect on the directly bonded aryl group. The longer distance between the metal and the ring, as well as the existance of the intermediate oxygen atom may decrease the effect. As shown in Tables 1B and 2, the NMR peaks of the *para* carbon of the ligand as well as ^{1}H-NMR of the proton bonded to the *para* carbon are not affected seriously by the change of hydrocarbon groups bonded directly to the central metal.

In cases of alkyl derivatives, the ^{13}C-NMR of the carbon atom directly bonded to antimony shifts to downfield, while those of the farther carbons make less shifts as in the case of aryl derivatives (see Table 2). The change of the shielding of alkane carbons due to the substitution of the methyl group of the alkane with R_2SbBr_2-group is approximately as follows; C-1: +25 ppm, C-2: −4 ppm, C-3: +4 ppm, C-4 +3 ppm. In the cases of R_3SbL_2, where R = alkyl group, HL = phenol or carboxylic acid, the chemical shift of the alkyl C-1 is much smaller (~ 10 ppm) than the dihalo derivatives. On the other hand, the difference of the shielding effect by Ph_2SbBr_3- and Ph_2SbL_2- group, to the C-1 carbon of a phenyl group, is not so drastic as in the case of alkyl derivatives.

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On the spectral properties of β-dioximato ligands and complexes. A proton resonance and i.r. study

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THE spectral properties of β-dioximes and β-dioximato complexes described by us in previous works included i.r. spectra of AADO and Fe(III)–$AADO_2$[1], including the Mössbauer spectra of the latter; EPR spectra of the β-dioximato–AADO and BADO, Cu(II) complexes[2], UV spectra of AADO, BADO and Cu(II)–$(BADO)_2$ complexes[3] and the i.r. spectra of BADO and Cu(II)–(BADO) [4]. UV and visible spectra of Cu–β-dioximates[5] and Ni–β-dioximato complexes[6] were previously reported by us.

In this work, we report and discuss:

(1) The NMR spectra of acetylacetone dioxime (AADO) and benzoylacetone dioxime (BADO) and

(2) The i.r. spectra properties of BADO and $Cu(BADO)_2$.

No previous proton resonance studies of AADO and BADO appear to have been made. Castells and Colombo reported results on benzoylacetaldehyde and the mono-oxime of benzoylacetone[7].

EXPERIMENTAL

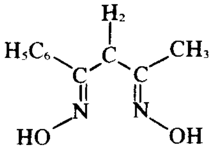
The ligands and complexes were prepared according to published methods[1–4]. Proton resonance (NMR) spectra were recorded using a Varian HA 100 D, 100 MC machine in D_2O solution. NMR spectra of BADO were recorded in $CDCl_3$ or CCl_4, owing to its very low solubility in D_2O. IR spectra were recorded from KBr discs, using the Perkin–Elmer Model 21 Spectrometer.

RESULTS AND DISCUSSION

(a) *Proton resonance spectra of AADO and BADO.* The NMR spectrum of AADO in D_2O solution consists of two single bands: at $\delta = 2\cdot28$ ppm (protons of the methyl group adjacent to the oxime group) and at $\delta = 3\cdot52$ ppm (γ methylene proton adjacent to the oxime groups). The resonance line of the protons of the γ carbon appears at a considerably lower field.

NMR spectra of BADO, recorded in a $CDCl_3$ solution show a band at 1·6 ppm for the protons of the methyl group adjacent to the oxime group (in D_2O solution this band is at 2·04 ppm).

The non-equivalence of the γ methylene protons, which are enantiotopic due to the asymmetry of the BADO molecule, results in a typical AB pattern at $\tau = 3\cdot15$ and 3·63, with J = 17·6 Hz. This AB pattern indicates the possibility of restricted rotation of the aliphatic chain. This pattern may be due to the existence of an equilibrium between open chain (anti, syn) and cyclic (oxime) isomers, in the solution:



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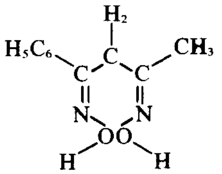

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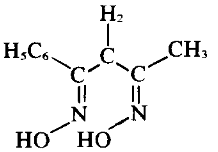
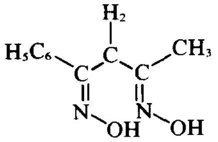


III



(IV)

amphi

The AB pattern bands obtained in the BADO case appear to be slightly split, probably because of the small difference between forms III and IV. As stated in the IR study of these molecules[4], the *cis*(amphi) tautomeric form is responsible for the intramolecular hydrogen bonding (N–H–O). The broad signal which appears at $\delta = 5\cdot6$ ppm is probably due to the NH proton of the nitrone form of the oxime group or the H of the NHO hydrogen bond of the cyclic (amphi) form.

The methylene hydrogens of the anti- and syn- forms clearly give rise to the bands at $\delta = 3\cdot75$ and 3·98 ppm, as in the case of benzoylacetone monoxime[7].