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A DIPOLE MOMENT AND NMR STUDY OF $(CH_3)_3M_{IVB}NCX$ (M_{IVB} = C, Si, Sn; X = O, S) COMPOUNDS IN SOLUTION

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Summary

The dipole moments of $(CH_3)_3M_{IVB}NCX$ (M_{IVB} = C, Si, Sn; X = O, S) have been studied. In the partial NCX moment the X atom should be the negative end of the dipole and the vector direction $\overrightarrow{NCX}$. The influence of the partial $2s^2$ lone-pair moment has been taken into account and the trend of the dipole moments should be primarily determined by the ∠MNCX bond angle. This is in accordance with structural data. The moments of $(CH_3)_3M_{IV}$ NCS compounds are greater than those of the corresponding isocyanates. This is also valid for organic derivatives. A stronger contribution proposed. In the $(CH_3)_3SiNCX$ compounds some back-donation effect of the nitrogen lone-pair to the empty silicon *d* orbitals should occur. NMR measurements on monomeric RNCX compounds also reveal a greater electron delocalisation to the NCS group than to the NCO group consistent with the results on dipole moments.

Introduction

Organometallic pseudohalides have been well studied by means of IR, Raman [1-4] and UV [5] spectroscopy. Some electron diffraction [6,7] and X-ray diffraction [8] studies have also been reported. From these it was deduced that the triatomic pseudohalide groups NCO/CNO and NCS/CNS are linked to the metal via the nitrogen atom giving rise to the "iso" structure of these compounds. Orville-Thomas [9] came to a similar conclusion for HNCO and HNCS on the basis of bond-stretching force constants [9]. Other parameters used in the discussion of these results were VB resonance structures and ∠MNCO bond angle variations.

However, the dipole moments and a NMR study of the Group IVB organometallic isocyanates and isothiocyanates $(CH_3)_3M_{IVB}NCX$ (M_{IVB} = C, Si, Sn; X = O, S) have not been reported.

Experimental

The technique for determining the dipole moments on 0.2—0.3 *M* solutions in benzene has been published [26].

The NMR results were obtained on a Bruker Physik HFX spectrometer. The INDOR technique was used to measure the ^{119}Sn, ^{29}Si and ^{13}C chemical shifts. The small ^{13}C—C—H satellite separation of $(CH_3)_3CNCO$ and $(CH_3)_3CNCS$ did not permit measurement of the ^{13}C chemical shift of the central carbon atom. The compounds were investigated as 25% solutions in benzene using 5 mm NMR tubes, the benzene signal being used to lock the field H_0.

The ^{1}H and ^{29}Si chemical shifts are expressed in δ ppm values vs. the ^{1}H and ^{29}Si resonance of $Si(CH_3)_4$ and the ^{119}Sn chemical shifts in δ ppm values vs. the ^{119}Sn resonance of $Sn(CH_3)_4$. Positive values are shift deviations to higher frequencies, i.e. lower field.

Results and discussion

Dipole moments

The dipole moments of the compounds studied in this investigation, together with those of some organic isocyanates and isothiocyanates taken from the literature [10-12], are recorded in Table 1. The dipole moments of the isothiocyanates are seen to be always higher than those of the corresponding isocyanates. Moreover, the values increase in going from HNCX (X = O, S) to $(CH_3)_3SnNCX$ (X = O, S), except for the silicon compounds which show lower values than their carbon analogues.

Before the interpretation of these results is undertaken a discussion about the direction of the NCX moment i.e. $-\overleftarrow{NCX}$ or $-\overrightarrow{NCX}$ is needed, since some controversy about it exists in the literature [13, 14]. The —NCO and —NCS group is always considered to be a linear triatomic group. Entelis and Nesterov [12] proposed that the direction of the NCO vector moment in organic compounds RNCO (R = H, CH_3) should be opposite to that of the $\overrightarrow{RN}$ moment, i.e. $\overleftarrow{NCO}$. Their conclusion was based firstly on the assumed values 1.42 D for $\mu(N-H)$ (derived from $\mu_{(N(CH_3)_3)}$ 0.6 D), and secondly on the decrease in going from CH_3NCO (2.81 D) to HNCO (1.59 D). The observation that the isothiocyanates have higher moments than the isocyanates is taken as evidence supporting their thesis, because normally the opposing moment $\mu(\overleftarrow{NCO})$ is expected to be smaller than $\mu(\overleftarrow{NCS})$ due to the relative electronegativities $\chi_O > \chi_S$.

On the other hand Hunter and Partington [13] assume the vector moment $\mu(NCS)$ to be in the opposite direction (i.e. $\overrightarrow{NCS}$) in phenylisothiocyanates, with a value of 2.2 D.

From our observations on the $(CH_3)_3M_{IVB}NCX$ compounds the thesis of Entelis and Nesterov is difficult to maintain. Considering electronegativities and bond-distances, the following sequence of partial moments is expected: $\mu(\overrightarrow{Sn-N}) > \mu(\overrightarrow{Si-N}) > \mu(\overrightarrow{C-N})$. From Entelis' theory one would then expect a

TABLE 1

DIPOLE MOMENTS OF ISOCYANATES AND ISOTHIOCYANATES

Compound	μ (D)	Compound	μ (D)
HNCO	1.59[a]	HNCS	1 72[a]
CH_3NCO	2.81[a]	CH_3NCS	3.18[a]
$(CH_3)_3CNCO$	2.87	$(CH_3)_3CNCS$	3.58
$(CH_3)_3SiNCO$	2.76	$(CH_3)_3SiNCS$	3.39
$(CH_3)_3SnNCO$	4 55	$(CH_3)_3SnNCS$	5.64

[a] Values taken from Entelis and Nesterov [13]

decrease in the dipole moments for $(CH_3)_3MNCX$ in going from the carbon to the tin compounds because the $\overrightarrow{\mathrm{M{-}N}}$ moment which is opposite to $\mu(\overleftarrow{\mathrm{NCS}})$ and $\mu(\overleftarrow{\mathrm{NCO}})$ increases. Entelis' interpretation was based upon the high value of $\mu_{(\mathrm{N-H})}$ derived from the value of $\mu_{(\mathrm{NH_3})}$. Coulson [15] and Syrkin [16] however have argued that that free electron-pair of nitrogen contributes to a great extent to this moment. They explain the low value of $\mu(NF_3)$ (0.18 D) by a strong compensating moment of the $2s^2$ electron-pair, $\overleftarrow{\mathrm{C}}\!:\ \overrightarrow{\mathrm{N{-}F}}$. In NH_3 this partial lone-pair moment has the same direction as the N—H moment, $\overleftarrow{\mathrm{C}}\!:\ \overrightarrow{\mathrm{N{-}H}}$, and so gives rise to the high observed value of $\mu(NH_3)$, which then is clearly not a measure of the polarity of the N—H bond alone. This "intrinsic" polarity of the N—H bond is considered as rather small and to use 1.42 D for the partial moment μ(NH) in calculations of molecular moments seems unjustified. The direction of the $2s^2$ electron lone-pair moment with respect to the other partial moments should be taken into account. According to Coulson [15], values of 1.5 D or more should not be excluded for this moment. Absolute values however are difficult to determine since they depend on the hybridisation state of the $2s^2$ electron lone-pair and this is determined by the nature of the substituent on the nitrogen atom [9, 15, 17]. From these considerations it follows that in discussions of the dipole moments of the $(CH_3)_3M_{IVB}NCX$ (X = O, S) compounds the hybridisational state of the nitrogen lone-pair will play an important role.

On the other hand it is known [2, 3, 5-8] that the MNCX bond generally is a bent bond. Simultaneous consideration of the ∠MNCX bond angle and the directions of the partial moments ($\overrightarrow{\mathrm{NCX}}$, $\overrightarrow{\mathrm{M{-}N}}$, $\overleftarrow{\mathrm{C\!:\,N}}$) yields a qualitative explanation for the increasing trend in the dipole moments going from HNCX to $(CH_3)_3SnNCX$. In Fig. 1 it is assumed that the nitrogen atom is in a pseudo sp^2 hybridisational state; two lobes are for σ-bonds to R and C and the third lobe is occupied by the lone-pair. The remaining $2p^1$ electron on nitrogen is used in forming the π-double bond to C. Let us take the —N=C=X axis as the main molecular axis. An increase of the angle α increases the projection of the partial $\overrightarrow{\mathrm{R{-}N}}$ moment on the molecular axis. If we assume a simultaneous decrease of the β angle the projection of the lone-pair electron moment opposite to $\mu(\overrightarrow{\mathrm{NCX}})$ will decrease and both factors will tend to increase the value of the molecular moment. This is consistent with the structural data [6-8] given in Table 2 and explains the increasing trends along the columns of Table 1 as well as between the —NCO and the —NCS series.

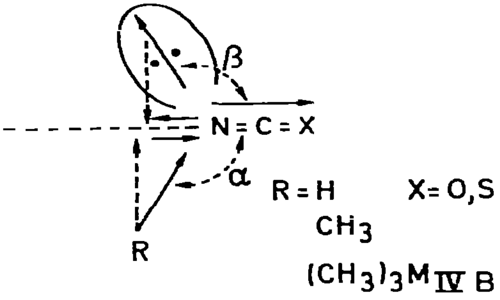

Fig. 1.

The steadily increasing trend of the dipole moments is however broken for the $(CH_3)_3SiNCX$ compounds (Table 1). We believe that this deviation must be explained by back-donation of the nitrogen lone-pair into the empty silicon *d* orbitals, $(CH_3)_3Si\overset{\leftarrow}{=}NCX$ resulting in a lowering of the $\overrightarrow{Si{-}N}$ moment versus the $\overrightarrow{C{-}N}$ moment. This view is supported by the Si—N bond distances [6] found in $(CH_3)_3SiNCS$ and $(CH_3)_3SiNCO$, 1.76 Å and 1.78 Å respectively (Table 2), which are obviously smaller than the sum of the covalent radii of Si and N i.e. 1.87 Å. This contraction can also be explained by some double-bond character of the Si—N bond.

Another characteristic feature of the dipole moment data in Table 1 is that the isothiocyanates always show higher values than the isocyanates. This does not correlate with the relative electronegativities of O and S which would tend to make the partial —N=C=S moment lower than the =N=C=O moment, so that, other factors remaining equal, the isothiocyanates should show lower molecular moments than the isocyanates.

An explanation of this controversy might be that there is an important contribution of a VB resonance structure $R\overset{+}{N}{\equiv}C{-}\overset{-}{X}$ for X = S, increasing the partial $\overrightarrow{NCS}$ moment relative to $\mu(\overrightarrow{NCO})$. Theoretical arguments in this respect were formulated by Syrkin [16]. He assumes that sulphur may exhibit stronger electron-acceptor properties than oxygen by the use of its empty *d* orbitals; furthermore the electron-affinity of sulphur (47 kcal) is higher than that of oxygen (35 Kcal). Therefore when sulphur and oxygen are conjugated with a powerful electron-donor like nitrogen, the electron delocalisation to sulphur may become greater than to oxygen. As a result the $\overrightarrow{NCS}$ partial moment should increase relative to $\mu(\overrightarrow{NCO})$. Also this mechanism implies a decrease of the N lone-pair moment in the isothiocyanates. The lone-pair moment being opposite to the NCX moment, this delocalisation would result in a second contribution tending to make the RNCS moments larger than the RNCO moments.

The foregoing considerations should also result in an increase of the ∠RNCS bond angles vs. those of ∠RNCO. The structural data in Table 2 indeed shows that ∠RNCS bond angles are always greater than these of RNCO, for example in $(CH_3)_3SiNCS$ ∠ SiNCS = 154°, and ∠ SiNCO = 150° in $(CH_3)_3SiNCO$.

In MO language the VB resonance contribution, $R{-}\underset{+}{N}{\equiv}C{-}\overset{-}{S}$, should lead to an increased ∠ RNCS bond angle because the hybridisation around the nitrogen atom comes closer to *sp* hybridisation giving rise to a RNCS configuration approaching a linear RNCS system.

(continued on p 351)

TABLE 2

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN ISOCYANATES AND ISOTHIOCYANATES[a]

Compound	r(Si—N) or r(Sn—N)	r(C—N)	r(N=C)	r(C=O)	r(C=S)	∠ (H)MNC
HNCO			1.207 ± 0.01	1.71 ± 0.01		128.1° ± 0.5
HNCS			1.216 ± 0.002		1.561 ± 0.002	130.25° ± 0.25
CH_3NCO		1.47	1.19 ± 0.03	1.18 ± 0.03		125°, 140°
CH_3NCS		1.47	1.22		1.56	142°
H_3SiNCS	1.71 ± 0.01		1.211 ± 0.01		1.56	180°
$(CH_3)_3SiNCO$	1.76		1.20 ± 0.01			150° ± 2°
$(CH_3)_3SiNCS$	1.78		1.18 ± 0.01	1.18 ± 0.01	1.56 ± 0.01	154° ± 3°
$(CH_3)_3SnNCS$ (polymer)	2.15		1.15		1.64	173°

[a] Values from ref. 27.

TABLE 3

NMR PARAMETERS OF $(CH_3)_3MNCX$ AND CH_3NCX (M = C, Si, Sn; X = O, S)

Compound	Chemical shifts (ppm)				Coupling constants (Hz)		
	$\delta(^1H)$	$\delta(^{119}Sn)$	$\delta(^{29}Si)$	$\nu(^{13}C)$ (MHz)	$J(^{119}Sn—C—H)$	$J(^{29}Si—C—H)$	$J(^{13}C—H)$
$(CH_3)_3SnNCO$	+0.494	+82.737 (20%)			60.4		129.8
		+86.551 (1.25%)			57.3		
$(CH_3)_3SnNCS$	+0.6	+58.706 (20%)			63		132.4
		+67.949 (1.25%)			61.6		
$(CH_3)_3SiNCO$	−0.043		+3 637			6.8	120.2
$(CH_3)_3SiNCS$	−0.083		+5.372			6.8	120.4
$(CH_3)_3CNCO$	+1.058						126.9
$(CH_3)_3CNCS$	+0.957						128
CH_3NCO	+2.379			22.630644			143.1
CH_3NCS	+2.687			22.630709			144.4

NMR spectra

The NMR parameters are reported in Table 3. The ^{1}H shifts will not be discussed because it has been clearly established [18] that, in general, dispersion forces and anisotropy effects determine the observed trend.

However, in monosubstituted trialkyl Group IVB compounds the electronegativity effect is valid for the chemical shifts of ^{13}C [19], ^{29}Si [18-21] and ^{119}Sn [18, 19, 22, 23] (with substituents directly bonded to the Group IVB metal). The resonances for these nuclei were studied on a series of solutions with concentrations ranging from 20 down to 1.25 weight %. Table 3 gives only the data for the two extreme concentrations because the shifts of the parameters were continuous over this concentration gradient.

The ^{119}Sn chemical shift for $(CH_3)_3SnNCO$ is at lower field than for $(CH_3)_3SnNCS$, irrespective of the concentration of the solution. This observation is not in agreement with a greater inductive electron-withdrawing effect of the NCS group relative to NCO. On the other hand the coupling constants, $J(^{119}Sn{-}C{-}H)$ and $J(^{13}C{-}H)$ show the highest values in $(CH_3)_3SnNCS$. For the analogous $(CH_3)_3Si$ and CH_3 compounds the ^{29}Si resonance and the ^{13}C resonance respectively occur at lowest field for NCS substitution, and the ^{13}C—H coupling constants show the highest values. This is in agreement with a greater electron--withdrawing capacity of the NCS group.

If we now turn back to the $(CH_3)_3SnNCS$ compound we believe that the NMR data on the $(CH_3)_3SnNCX$ compounds should be understood in the light of the special structural behaviour of these compounds. Indeed, the strongly polymeric nature of $(CH_3)_3SnNCS$ in the solid state was clearly established by X-ray investigation [24] and obviously the remarkable high field ^{119}Sn resonance originates from strong association even in dilute solution i.e. $(CH_3)_3SnNCS$ ... Sn--, yielding a five-coordinate trigonal bipyramidal structure around the tin nucleus. This increases the shielding of the ^{119}Sn nucleus [22, 25] and results also in an increase of the ^{119}Sn—C—H and ^{13}C—H coupling constants due to the sp^2 character of the Sn—C orbitals in the equatorial plane of the trigonal bipyramid.

$(CH_3)_3SnNCO$ also associates but to a lesser extent. This is clearly borne out by the lower values of the ^{119}Sn—C—H coupling constants compared with those of $(CH_3)_3SnNCS$, and the markedly lower concentration effect observed on the ^{119}Sn chemical shifts for the $(CH_3)_3SnNCO$ compound.

Finally it must be noted that the polymeric nature of these compounds must also contribute to the high dipole moments observed, due to the increase of the Sn—N moment as a consequence of the greater "*d*" character of the bonding orbital.

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