Tetrahedron Letters No. 52, pp 5341 - 5344, 1972. Pergamon Press. Printed in Great Britain.

CHARGE DENSITY DISTRIBUTION IN ORGANO-METAL SULFIDES BY MEANS OF ^{13}C NMR AND $S_{2p_{3/2}}$ ESCA CHEMICAL SHIFTS.

S.PIGNATARO
Istituto Chimico Ciamician-Università di Bologna

L.LUNAZZI
Istituto Chimica Organica e Industriale-Università di Bologna

and

C.A.BOICELLI, R.DI MARINO, A.RICCI, A.MANGINI and R.DANIELI
Laboratorio dei Composti del Carbonio contenenti Eteroatomi e loro Applicazioni
del C.N.R., OZZANO EMILIA (Bologna)

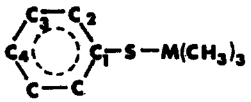
(Received in UK 13 November 1972; accepted for publication 30 November 1972)

The nature of the metal-sulfur bond in metal sulfides is still a debated problem in organometallic chemistry. The most recent papers rationalize the data obtained in terms of a $p\pi \rightarrow d\pi$ bond between the filled p orbitals of the sulfur and the empty d orbitals of the metal(1). We present in this paper a parallel NMR and ESCA study of some metal-sulfides of the general formula C_6H_5-S-M-$(CH_3)_3$ (M= =C,Si,Ge,Sn,Pb), which shows the importance of such a bond. This is obtained by measuring the ^{13}C NMR and $S_{2p_{3/2}}$ ESCA chemical shifts which, in the series examined, can be rationalized in terms of charge density variations on the carbon(2) and sulfur(3) atoms respectively.

On the basis of measurements made on a number of sulfur derivatives, it has been shown(3) that the chemical shift of the S_{2p} Ionization Energy of an homogeneus series of compounds is correlated to the charge density on this atom. The $S_{2p_{3/2}}$ Ionization Energy sequence reported in the Table suggests therefore that the charge density (C.D.) on the sulfur atom does essentially decrease with the increase of the atomic number of M. This finding can be easily understood taking into account that increasing the atomic number of M the d orbitals should be more effective for a $p\pi \rightarrow d\pi$ bond$^{(4)}$: this should in turn decrease the charge density on the sulfur atom and increase it on the metal. If this model is correct, the charge density variations observed on the sulfur atom should be reflected not only on the metal but on all the other centers of the molecule too.

TABLE

$S_{2p_{3/2}}$ Ionization Energy (IE) and ^{13}C NMR chemical shifts in:

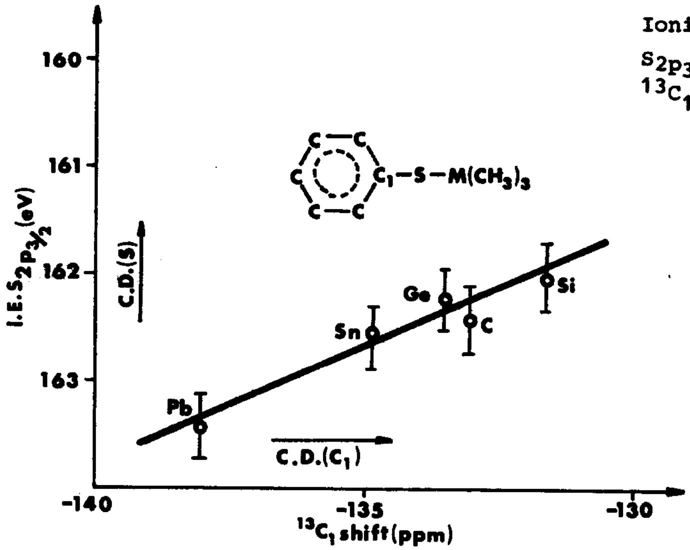


M	$IE_{S_{2p_{3/2}}}$ ^{a}	^{13}C-NMR shifts (ppm)^b					Electronegativity of M$^{(c)}$
		C_I	C_2	C_3	C_4	CH_3	
C	162.4	133.0	137.5	128.2	128.5	32.0	2.60
Si	162.0	131.6	134.9	128.3	126.5	2.0	1.90
Ge	162.2	133.4	134.7	128.2	126.1	1.5	2.00
Sn	162.6	134.8	134.6	128.2	125.6	-3.0	1.93
Pb	163.4	138.0	134.5	128.1	125.1	10.3	2.45

a) The ESCA measurements were carried out with an AEI ES100 Electron-Spectrometer, using Mg K_α radiation (1253.6 eV). The spectrometer was tuned so as to give small C_{1s} and O_{1s} satellites at 233.0 eV. above the main peaks. These small peaks were produced by the AlK_α radiation (1486.6 eV) coming from the spectrometer window.The evaporated samples were condensed in thin film on a cooled gold surface. The Au $4f_{7/2}$ line (84 eV) from this surface was obtained together with the sulfur doublets and was used for calibration purpose. The reported I.E.'s refer to measurements in which the spin-orbit doublet of the sulfur 2p electrons was well resolved. The high resolution of the spectra was indeed taken as the only criterion to ensure that negligible charging up phenomena were taking place during the measurements. b) The ^{13}C-NMR spectra were recorded on a JEOL PS 100 NMR Spectrometer operating at 25.15 MHz in CW mode with complete proton decoupling. The shifts were measured with respect to CCl_4 as solvent and converted to the TMS scale. (G.C.Levy, J.D.Cargioli. J.Magn.Res. 6, 143 (1972). c) Ref.5.

The ESCA method can be, at least in principle, very easily used to obtain C.D. information about all the atoms of the periodic Table except hydrogen. The fact that the metal changes along the series examined, however, prevents one obtaining direct information on this point in the molecule by mean of an ESCA study of the various inner electrons of the metal themselves. Furthermore the ESCA study of the carbon atoms of complex organic molecules is always very difficult since the present resolution of the technique is rather poor and the various non-equivalent atoms give an unresolved C_{1s} band whose deconvolution is very often doubtful. The information on the charge density distribution on the other parts of the molecule were therefore sought by ^{13}C NMR: the corresponding chemical shift variations of an homogeneous series of aromatic compounds have been shown$^{(2a)}$ to depend upon the C.D. on the carbon atoms themselves.

In the third column of the Table the ^{13}C NMR chemical shifts of the benzene carbon atom directly bonded to sulfur are reported. These shifts should correspond to a charge density on the C_1 carbon atom which increases in the series Si<C<Ge<Sn <Pb. By plotting the I.E.'s of the $S_{2p_{3/2}}$ electron versus the ^{13}C NMR chemical shift of the C_1 carbon atoms a linear correlation is found (see figure). This shows that, as expected, the variation of the C.D. on the sulfur atoms parallels that on the attached C_1 carbon atoms.



Ionization Energy of the $S_{2p_{3/2}}$ electrons versus $^{13}C_1$ NMR shifts.

The NMR/ESCA correlation was theoretically predicted$^{(6)}$ for a given atom of an homogeneous series of molecules, whenever the NMR chemical shift variation along the series was due to the diamagnetic contribution. This was experimentally found for the carbon atom of a series of halogenated methanes$^{(7)}$. Very recently however, some doubt on the validity of the previous theoretical arguments has been raised$^{(8)}$.

Our results do not pretend to support either of these theories, but they seem particularly interesting since they allow one to strengthen the conclusions obtained by investigation of one center of the molecule with those obtained from another point using an independent physical method.

Information on the C.D. of the metals can be indirectly obtained by examining the ^{13}C NMR of the methyl carbons. The Table reports the ^{13}C NMR chemical shifts of such carbon atoms together with the electronegativity of the metals (columns 7 and 8 respectively). As appears from the Table, the chemical shift data cannot be interpreted only in terms of the different electronegativity of the metals, since they bear a different charge which is likely to influence the shielding of the methyl carbons. According to the $p\pi \rightarrow d\pi$ model, this shielding should be strongest for the lead derivative. A survey of the Table shows that the methyl carbon NMR chemical shift of this compound is clearly at higher field than that expected on the grounds of an electronegativity effect alone. This result is also in agreement with the fact that the lead derivative also shows the highest coordination number of solvent molecule(9).

The ^{13}C NMR shifts for the other atoms of the benzene ring (columns 4-6 of the Table) are smaller and therefore difficult to rationalize on the basis of the present approach. Further work is in progress to rationalize these shifts with a more detailed model, possibly involving a through space interaction(10) between the metal and the benzene ring.

One of us (S.P.) would like to thank C.N.R. for financial support.

REFERENCES

1) E.W.Abel and D.A.Armitage in Adv. in Organometal.Chem., Vol.2, pp1(1965), and references therein.

2) a) G.E.Maciel and J.J.Natterstadt, J.Chem.Phys.42,2427(1965); b) E.F.Mooney and P.H.Winson in Ann.Rev.NMR Spectr.,Vol.2,pp153(1969), Academ.Press, New York.

3) K.Hamrin, G.Johansson, U.Gelius, A.Fahlman, C.Nordling and K.Siegbahn, Phys. Scripta,1,286(1970).

4) A.J.Smith, W.Adcock and W.Kitching, J.Am.Chem.Soc.,92,(1970),6140.

5) A.L.Allred and E.G.Rochow, J.Inorg.Nuclear Chem.,1958,5,269.

6) H.Basch, Chem.Phys.Letters,5,337(1970).

7) R.E.Block, J.Magn.Res.,5,155(1971).

8) U.Gelius and K.Siegbahn, Paper n.18 presented to the Trans.Faraday Conference on Photoelectron Spectroscopy, Brighton, Sept.(1972).

9) A.Ricci, R.Danieli, G.Pirazzini and C.Boicelli, to be published.

10) M.J.S.Dewar, R.Golden and J.M.Morris, J.Am.Chem.Soc.,93,(1971),4187.