Journal of Organometallic Chemistry, 135 (1977) 327—331

CARBON-13 NMR STUDIES OF DIPHENYL DICHALCOGENIDES, $(C_6H_5)_2X_2$ (X = S, Se, Te)

ALAIN FORCHIONI,
Service de Chimie-Physique, C.E.N. de Saclay, B.P. No. 2, 91190 Gif-sur-Yvette (France)

VINICIO GALASSO,
Istituto di Chimica, Universita di Trieste, Trieste (Italy)

KURT J. IRGOLIC
Department of Chemistry, Texas A & M University, College Station, Texas 77843 (U.S.A.)

and GIUSEPPE C. PAPPALARDO *
Istituto di Chimica Generale, Universita di Catania, Catania (Italy)

(Received February 16th, 1977)

Summary

The ^{13}C NMR chemical shifts and spin-lattice relaxation times for diphenyl disulfide, diselenide and ditelluride have been measured and assigned. The shielding effects experienced by the carbon atoms are qualitatively discussed in terms of the inductive and mesomeric properties of the dichalcogen group. The attempt to calculate the magnetic shielding tensors for the ^{13}C nuclei in terms of the Pople theory gave unsatisfactory results.

Introduction

As part of continuing studies of the physical properties, especially the conformational properties, of diaryl dichalcogenides, $(RC_6H_4)_2X_2$ (X = S, Se, Te) [1—4], the natural abundance ^{13}C NMR spectra of diphenyl disulfide, diselenide and ditelluride have been measured. This study was undertaken to evaluate the usefulness of ^{13}C NMR data for the elucidation of conformational problems in the diaryl dichalcogenide systems.

Experimental

Diphenyl disulfide was obtained from Aldrich Chemical Co. and purified by crystallization from alcohol. Diphenyl diselenide was purchased from Eastman

Kodak and recrystallized from absolute ethanol. Diphenyl ditelluride was synthesized as described previously [5].

The ^{13}C NMR spectra were obtained with a Varian XL-100-15 system operating in the PFT mode at 25.16 MHz. The dichalcogenide samples were examined as 1 M solutions in $CDCl_3$ using 12 mm NMR tubes. The instrument was locked on the deuterium signal of $CDCl_3$. TMS was used as internal reference. The chemical shifts are precise to ±0.1 ppm. Spin-lattice relaxation times, T_1, were measured by the inversion-recovery method using the standard $(180° - \tau - 90° - T)$ pulse sequence. The delay time T was at least five times longer than the longest relaxation time determined in these experiments. Eight τ values each were used for the determination of T_1 by a least-squares analysis of the time-dependent peak heights. The estimated accuracy of the observed T_1 values is better than ±5%. The ^1H NMR spectrum of a saturated solution of diphenyl ditelluride in $CDCl_3$ was recorded on a Varian HA-100 spectrometer. Two well separated multiplets (8.2—8.4 ppm, 2H; 7.5—7.8 ppm, 3H) were observed.

Results and discussion

The spin-lattice relaxation times, T_1, and the ^{13}C-chemical shift for the diphenyl dihalcogenides are listed in Table 1.

Spin-lattice relaxation times are very helpful in assigning carbon resonances. Quaternary carbon resonances can be easily determined because carbon atoms not bonded to any hydrogen atoms generally relax one order of magnitude slower than hydrogen-bearing carbon atoms [6]. Carbon atoms in *para*-position to substituents in monosubstituted benzenes relax much faster than quaternary carbon atoms and faster than the carbon atoms in the *ortho*- and *meta*-positions [7].

When these rules are applied to the diphenyl dichalcogenides, which can be considered to be dimers of the monosubstituted benzenes C_6H_5X, the resonances at 137.0 (S), 130.9 (Se) and 108.0 ppm (Te) must be assigned to the carbon atoms to which the chalcogen atom is bonded. The resonances at 127.1 (S), 127.6 (Se) and 128.0 (Te) must then be attributed to the carbon atoms in *para*-positions (Table 1). The assignments of the remaining signals (Table 1) to the carbon atoms in the *ortho*- and *meta*-positions are based on results reported

TABLE 1

^{13}C CHEMICAL SHIFTS AND SPIN-LATTICE RELAXATION TIMES OF 1 M DIPHENYL DICHALCOGENIDES SOLUTIONS IN $CDCl_3$

$(C_6H_5)_2X_2$ X =	C-1	*Ortho*	*Meta*	*Para*
S	137.0 [a]	129.0	127.5	127.1
	(50) [b]	(6.4)	(6.4)	(5.0)
Se	130.9	131.5	129.1	127.6
	(50)	(6.8)	(6.8)	(3.7)
Te	108.0	137.6	129.2	128.0
	(50)	(5.7)	(5.7)	(2.8)

[a] The ^{13}C chemical shifts are reported in δ (ppm) relative to internal TMS. [b] The spin-lattice relaxation times, T_1, are given in seconds.

for closely related monosubstituted benzenes [7] and on qualitative considerations of the potential influence of the chalcogen atoms on these carbon atoms.

The most striking aspect of the carbon resonances in the series of the diphenyl dichalcogenides is the large difference between the chemical shifts of the carbon atoms (C-1) bonded to the chalcogen atoms. The chemical shift moves upfield from 137.0 ppm for $(C_6H_5)_2S_2$ to 130.9 ppm for $(C_6H_5)_2Se_2$ and finally to 108.0 ppm for the ditelluride. Relative to benzene (128.8 ppm) the disulfide and diselenide C-1 resonances are shifted downfield, whereas the ditelluride C-1 resonance is moved upfield. The deshielding of the *ortho*-carbon atoms monotonically increases in the series S—Se—Te with an 8.6 ppm difference between the resonances in the disulfide and the ditelluride. The chemical shifts of the *meta*- and *para*-carbon atoms follow the trend observed for the *ortho*-carbon atoms, which is opposite to that found for the C-1 carbon atoms. The chemical shifts for the *meta*- and *para*-carbon atoms are very close to the ^{13}C-benzene shift and do not differ by more than 1.7 ppm (Table 1).

The *ortho*-^1H resonances show the same downfield trend within the series of the diphenyl dichalcogenides (7.50 ppm, S [2]; 7.62 ppm, Se [8]; 8.30 ppm, Te) as observed for the *ortho*-^{13}C signals. A similar correlation seems to hold for the *meta*- and *para*-resonances (7.27 ppm, *meta*-H, S; 7.20 ppm, *para*-H, S, in $CDCl_3$ [2]; 7.22 ppm, 3H, Se, CH_2Cl_2 [8]; 7.70 ppm, 3H, Te, in $CDCl_3$). However, only the diphenyl disulfide ^1H NMR spectrum has been analyzed in detail [2].

The observed ^{13}C-chemical shifts can be qualitatively rationalized in terms of the influence of the dichalcogenide group on the electron distribution within the phenyl rings. The Pauling electronegativities of the chalcogen atoms are 2.5 (S), 2.4 (Se) and 2.1 (Te). The S—S and Se—Se groups are, therefore, expected to remove electron density primarily from the carbon atoms to which they are bonded more efficiently then does the Te—Te group. According to these considerations the ^{13}C-shifts of the C-1 carbon atoms could move upfield with increasing atomic number of the chalcogen atom in the series $(C_6H_5)_2X_2$. This has been confirmed experimentally (Table 1). Magnetic anisotropy effects originating in the X_2-group might also influence the electron density on and the chemical shift of the C-1 carbon atom. These anisotropy effects, which are difficult to evaluate, should, however, be negligible for all other carbon atoms. The ^{13}C-chemical shifts of the *ortho*-, *meta*- and *para*-carbon atoms move downfield with decreasing electronegativity of the X-atom in the diphenyl dichalcogenides. These trends, which cannot be explained on the basis of electronegativities, are, however, in accord with the decreasing ability of the chalcogen atoms (their decreasing +M effect) to transfer charge from their lone electron pairs into the aromatic rings as their atomic number increases. The appropriate sulfur orbitals, for example, would overlap more efficiently with the ring orbitals than the tellurium orbitals. The *ortho*-, and to a lesser degree the *para*-carbon atoms, will, therefore, be more negative in the disulfides than in the ditellurides resulting in ^{13}C-disulfide resonances for these carbon atoms upfield from the respective ditelluride signals.

The two *ortho*- and the two *meta*-carbon atoms in the dichalcogenides $(C_6H_5)_2X_2$ (X = S, Se, Te) are equivalent, because only one signal is observed for each of the two pairs of carbon atoms. The measured chemical shifts are, therefore, values averaged over a number of conformations arising through rotation about the C_6H_5—X bond. These results support the assumption of freely rotating or widely oscillating aryl groups in diaryl dichalcogenides, which was employed in attempts to elucidate the conformations of these compounds on the basis of their dipole moments [2,3,4].

In order to assist in the assignment of the ^{13}C-resonances and to interpret the trends in the ^{13}C chemical shifts observed in the three diphenyl dichalcogenides investigated, quantum-mechanical calculations of the magnetic shielding tensors for the ^{13}C nuclei based on the Pople theory [9] were carried out. In the perturbation problem CNDO wavefunctions calculated with sp basis sets within the framework of the approximations and parametrization proposed by Clark [10] and theoretical singlet transition energies were used. The relevant parameters were $I_s = 20.400$ eV, $I_p = 12.322$ eV, γ(SeSe) = 9.121 eV, $\xi_s = 2.7250$, $\xi_p = 1.8875$ for Se, and $I_s = 19.539$ eV, $I_p = 12.219$ eV, γ(TeTe) = 8.985 eV, $\xi_s = 2.180$, $\xi_p = 1.510$ for Te. Experimentally determined geometric parameters [11] with the phenyl rings lying in C_1—X—X planes were used in the calculations.

The theoretical shielding effects, calculated as the sum of local diamagnetic and paramagnetic contributions, do not at all correlate well with the experimental chemical shifts. The following values, for instance, were obtained for diphenyl disulfide (position of carbon atom, total electron density, theoretical and experimental ^{13}C shift relative to benzene given): C-1, 3.8954, 13.35, —8.2; *ortho*, 4.0677, 19.14, —0.2; *meta*, 3.9961, 18.17, 1.3; *para*, 4.0450, 29.76, 1.7. No proportionality has been found between the MO-predicted total electron densities and the measured chemical shifts.

These failures may be caused not only by deficiencies of the zero-order wavefunctions, e.g., due to the neglect of inner and outer (*d*) orbitals and inappropriate parametrization of the heavy atoms, but also by the inherent limits of the Pople model of neighbour atom effects as sum of "local" atomic contributions. The diffuse valence orbitals of the chalcogen atoms may indeed effectively combine with the carbon atom orbitals and make significant contributions as expressed by $\langle X\ np/r^{-3}/C\ 2p\rangle$ to the shielding constants of the carbon atoms. Unfortunately, calculations for the large $(C_6H_5)_2X_2$ systems at a level of sophistication higher than the one employed in the treatment described above, are presently not possible.

Acknowledgement

This work was supported by C.N.R. of Italy.

The financial support by the Robert A. Welch Foundation of Houston, Texas of those parts of these investigations which were carried out at Texas A & M University, is gratefully acknowledged.

References

1 G.C. Pappalardo, Spectrochim. Acta A, 29 (1973) 2055.
2 G.C. Pappalardo and S. Gruttadauria, Z. Phys. Chem. N.F., 94 (1975) 179.
3 G.C. Pappalardo, S. Gruttadauria and K.J. Irgolic, J. Organometal. Chem., 97 (1975) 173.
4 G.C. Pappalardo, K.J. Irgolic and R.A. Grigsby, J. Organometal. Chem., in press, Jom 8673.
5 W.S. Haller and K.J. Irgolic, J. Organometal. Chem., 38 (1972) 97.
6 F.W. Wehrli, in G.C. Levy (Ed.), Topics in Carbon-13 NMR Spectroscopy, Vol. II, Wiley, New York, 1976, p. 343.

7 J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972.
8 K.J. Wynne and P.S. Pearson, Inorg. Chem., 11 (1972) 1196.
9 J.A. Pople, J. Chem. Phys., 37 (1962) 53.
10 D.T. Clark, Tetrahedron, 24 (1968) 2663.
11 R.E. Marsh, Acta Crystallogr., 5 (1952) 458; J.D. Lee and M.W.R. Bryant, ibid. B, 25 (1969) 2094; G. Llabres, O. Dideberg and L. Dupont, ibid. B, 28 (1972) 2438.