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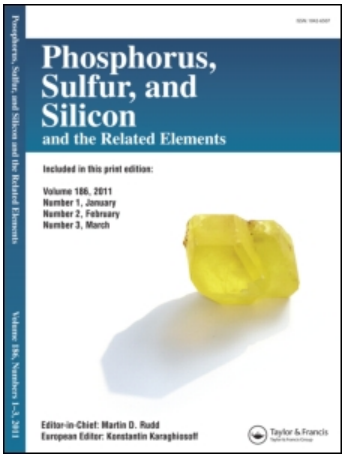

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Bernatowicz, P. , Stefaniak, L. , Kloc, K. , Mhizha, S. and Mlochowski, J.(1998) 'A ^{13}C, ^{15}N and ^{77}Se NMR Study of Some Diseleno Sulfonamides', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 625 — 628
To link to this Article: DOI: 10.1080/10426509808546011
URL: http://dx.doi.org/10.1080/10426509808546011

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Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 625-628
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Printed in Malaysia

A ^{13}C, ^{15}N AND ^{77}Se NMR STUDY OF SOME DISELENO SULFONAMIDES

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^{13}C, ^{15}N and ^{77}Se NMR data are reported for ten title compounds. Some linear correlations of selenium, nitrogen and carbon chemical shifts values are described. A number of one- and two- bond ^{77}Se-^{13}C coupling constants values are also given.

Keywords: ^{13}C NMR; ^{15}N NMR; ^{77}Se NMR; diseleno sulfonamides

INTRODUCTION

It is well known that selenium compounds are extensively studied as biological response modifiers, drugs and dietary microcomponents[1], so we are surprised that there are only two articles in literature concerning research on nitrogen containing diselenides by means of ^{15}N NMR.[2,3] The present work which includes results of such a investigations together with ^{13}C and ^{77}Se data appears thus very timely. Results of measurements are reported for ten diselenides substituted with various groups which however always contain sulfonamidic part.

RESULTS AND DISCUSSION

The results obtained from ^{13}C, ^{15}N and ^{77}Se NMR measurements are given in Table 1.

The ^{13}C signal assignments were obtained from a consideration of $^{1}J(^{77}Se\text{-}^{13}C)$ for C-1 and $^{2}J(^{77}Se\text{-}^{13}C)$ for C-2. Remaining carbon atoms were recognized by means of selective ^{1}H INEPT measurements. The ^{15}N signals of all compounds occur between -258 and -298 ppm in agreement with previous studies.[4] Similar comment applies to positions of ^{77}Se signals which are found between 438 and 451 ppm (in typical range for diaryl diselenides).[5,6]

Chemical shifts of selenium, nitrogen and carbon-2 atoms for four compounds containing aliphatic substituents at sulfonamidic group are linearly correlated to one another. Sequence of compounds on these lines are always the same, and depends on kind of substituent: methyl, n-propyl, cycloheksyl, t-butyl. Chemical shift of sulfonamidic nitrogen atom is going downfield about 10 ppm per each carbon atom added in β position. It is so called β effect and is well described in literature.[7] This effect is followed by changes in selenium chemical shifts (about 4 ppm upfield per additional carbon atom in β position to nitrogen) and carbon-2 atom chemical shifts (about 1.5 ppm downfield per additional carbon atom in β position to nitrogen). It is very interesting that changes in electronic structure spread linearly in so big part of molecule (selenium atom is 6 bonds far away from centre of changes in molecule).

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Table 1 ^{13}C, ^{15}N, and ^{77}Se MR data for some diseleno sulfonamides

		^{13}C-1 δ [ppm] [a] $^{1}J(^{77}Se-^{13}C)$ [Hz] [b]	^{13}C-2 δ [ppm] [a] $^{2}J(^{77}Se-C)$ [Hz] [b]	^{13}C-3 δ [ppm] [a]	^{13}C-4 δ [ppm] [a]	^{13}C-5 δ [ppm] [a]	^{13}C-6 δ [ppm] [a] $^{2}J(^{77}Se-C)$ [Hz] [b]	^{77}Se δ[ppm] [a]	^{15}N δ [ppm] [a]
1	R = H	127.0 (145.9)	142.2 (11.5)	128.2	127.4	132.8	130.9	444.2	-286.4
2	R = methyl	127.9 (146.6)	137.8 (11.1)	129.4	127.6	133.4	131.6 (6)	450.1	-297.9
3	R = n-propyl	127.7 (148.8)	139.2 (11.6)	129.3	127.5	133.1	130.9	446.4	-285.6
4	R = cycloheksyl	127.4 (147.1)	140.3 (11.0)	129.3	127.6	133.0	130.8	441.3	-272.3
5	R = t-butyl	127.4 (146.2)	142.1 (10.7)	129.3	127.3	132.8	130.8 (6)	438.5	-266.1
6	R = phenyl	127.8 (146.2)	137.7 (11.4)	130.2	127.6	133.7	130.7	443.5	-261.1
7	R = p-chlorophenyl	127.8 (148.3)	137.4 (11.6)	130.2	127.7	133.8	130.8	446.0	-261.7
8	R = p-methylphenyl	127.8 (148.0)	137.8 (11.0)	130.1	127.5	133.6	130.7	443.8	-263.1
9	R = p-carboxyphenyl	127.9 (147.9)	137.5 (10.0)	130.3	127.8	133.9	131.0	445.1	-258.3
10	R = p-methoxyphenyl	127.8 (149.0)	137.7 (11.1)	130.1	127.5	133.5	130.5	445.3	-264.6

(a) The chemical shifts are expressed with respect to the following standards: ^{15}N-CH_3NO_2 (δ=0 ppm), ^{77}Se-Me_2Se (δ=0 ppm), ^{13}C-TMS (δ=0 ppm)

(b) Absolute values of spin-spin couplings in brackets

EXPERIMENTAL

All investigated compounds are new and their synthesis will be published in future.[8]

The NMR measurements were taken on a Bruker AM 500 instrument operating at room temperature in DMSO-d_6. Proton decoupling was employed for the ^{13}C and ^{77}Se measurements while ^{1}H INEPT of 90 Hz was used for ^{15}N experiments.

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ACKNOWLEDGMENTS

This work was partially supported by the Polish State Committee for Scientific Research, grant number 3 T09A 044 08.

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