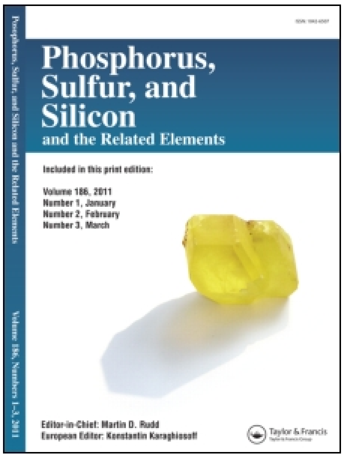

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Levy, Amalia , Biedermann, P. Ulrich , Cohen, Shmuel and Agranat, Israel(1998) 'Selenium and Tellurium Tricyclics. Conformational Effects on ^{77}Se and ^{125}Te NMR Spectra', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 139 — 142

To link to this Article: DOI: 10.1080/10426509808545939

URL: http://dx.doi.org/10.1080/10426509808545939

Organic Chemistry: Invited Lectures

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 139–142
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Gordon and Breach Science Publishers imprint
Printed in Malaysia

SELENIUM AND TELLURIUM TRICYCLICS. CONFORMATIONAL EFFECTS ON ^{77}Se AND ^{125}Te NMR SPECTRA

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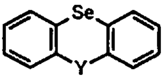
A series of selenium and tellurium tricyclics (**1**,**2**) have been synthesized and their ^{77}Se and ^{125}Te NMR chemical shifts determined. Semiempirical MNDO-PM3 calculations on representative **1** and **2** have been used to characterize their folded and planar conformations. The results indicate a pronounced effect of the conformations on these chemical shifts.

Keywords: heterocycles; conformation; ^{77}Se and ^{125}Te chemical shifts; folding; semiempirical calculations.

Selenium tricyclics (**1**), and tellurium tricyclics (**2**), serve as synthons for the synthesis of selenium- and tellurium-bridged overcrowded aromatic enes (**3**,**4**). We report the results of a ^{77}Se and ^{125}Te NMR spectroscopic study of these heterocyclics. We note a pronounced conformational effect of the folded tricyclics on the NMR chemical shifts.



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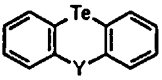

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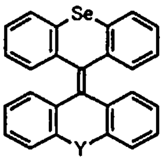

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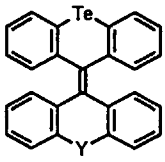

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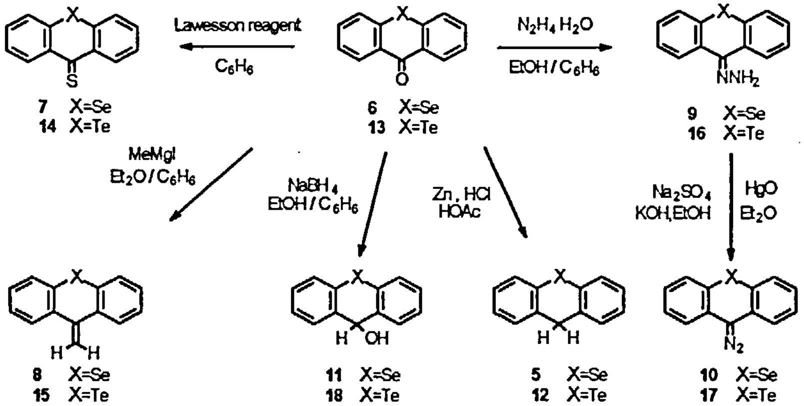
The following compounds have been studied: 9*H*-selenoxanthene (**5**)[1], 9*H*-selenoxanthen-9-one (**6**)[2,3], 9*H*-selenoxanthene-9-thione (**7**)[4], 9-methylene-9*H*-selenoxanthene (**8**), 9*H*-selenoxanthen-9-one hydrazone (**9**), 9-diazo-9*H*-selenoxanthene (**10**), 9*H*-selenoxanthen-9-ol (**11**)[5], 9*H*-telluroxanthene (**12**)[6,7], 9*H*-telluroxanthen-9-one (**13**)[6-8], 9*H*-telluroxanthene-9-thione (**14**), 9-methylene-9*H*-telluroxanthene (**15**), 9*H*-telluroxanthen-9-one hydrazone (**16**), 9-diazo-9*H*-telluroxanthene (**17**), and 9*H*-telluroxanthen-9-ol (**18**)[9]. 9*H*-selenoxanthen-9-one (**6**)[2,3], and 9*H*-telluroxanthen-9-one (**13**)[6,8] served as starting materials in the present investigation. The syntheses of **5**, **7-12** and **14-18** are outlined in Scheme 1. Compounds **8-10**, and **14-17** are new.



SCHEME 1 Outline of the syntheses of **5**, **7-12** and **14-18**.

Table 1 gives the ^{77}Se and ^{125}Te NMR chemical shifts of compounds **5-18**, dibenzoselenophene (**19**)[10], dibenzotellurophene (**20**)[10], diphenyl selenide (**21**)[11], and diphenyl telluride (**22**)[11]. Compounds **5-20** are formally bridged diphenyl selenides or diphenyl tellurides. The ^{77}Se and ^{125}Te NMR chemical shifts of the selenium and tellurium tricyclics are significantly shielded relative to **19** and **20**. Gronowitz, *et al.* have shown that in the series of 4,4'-disubstituted diphenyl selenides, the ^{77}Se NMR chemical shifts vary in a regular way with the character of the substituent, electron donating and withdrawing groups causing large upfield and downfield shifts, respectively[11,12]. An analogous trend has been revealed in the diaryl telluride series[11]. However, in the selenium and tellurium tricyclics series, electronic effects, which formed the basis for the above trends, are not sufficient to explain the variations in the ^{77}Se and ^{125}Te chemical shifts. Cases in point are the downfield shifts of **5** *versus* **6** and of **12** *versus* **13**, in spite of the electron withdrawing *ortho*-carbonyl substituent in **6** and **13**.

TABLE 1 ^{77}Se and ^{125}Te NMR chemical shifts of **5-21**

Se Compd (1)	Y	$\delta^{77}Se^{a}$ (ppm)	$\Delta\delta$ (ppm)	Te Compd (2)	Y	$\delta^{125}Te^{b}$ (ppm)	$\Delta\delta$ (ppm)	Te/ δSe
6	C=O	334.7	0.0	**13**	C=O	473.4^{c}	0.0	1.40
5	CH_2	353.2	-18.5	**12**	CH_2	515.8	-42.4	1.46
7	C=S	363.1	-28.4	**14**	C=S	529.9	-56.5	1.45
8	$C=CH_2$	336.8	-2.1	**15**	$C=CH_2$	514.6	-41.2	1.52
10	N_2	318.7	16.0	**17**	N_2	499.5	26.1	1.56
9	NNH_2	352.9	-18.2	**16**	NNH_2	544.9	-71.5	1.54
11	CHOH	330.8	3.9	**18**	CHOH	484.6	-11.2	1.46
19	—	451	-116.3	**20**	—	654	-180.6	1.45
21	Ph_2Se	412	77.3	**22**	Ph_2Te	688	214.6	1.66

[a] In $CDCl_3$ (reference: Me_2Se in $CDCl_3$)[13].

[b] In $CDCl_3$ (reference: Me_2Te in C_6D_6)[13]. [c] In DMSO-d_6, δ(13) = 471.5ppm[13].

The crystal structures of **12** and **13** indicate that **13** is essentially planar[14], while **12** adopts a folded conformation (Ar/Ar dihedral 129.6°)[8,15]. The similarity of the ^{77}Se chemical shifts of **6** and **8** ($\Delta\delta^{77}Se$ = -2.1 ppm) and the pronounced downfield shift of **15** relative to **13** ($\Delta\delta^{125}Te$ = -41.2ppm) should also be noted. A previous correlation between ^{77}Se and ^{125}Te NMR chemical shifts in related heterocycles gave a linear relationship with a slope of 1.3[10]. Most of the Se, Te pairs of tricyclics in Table 1 give $\delta Te/\delta Se$ ratios of 1.40-1.46. The pair of dibenzofulvenes **15** and **8** gives a $\delta Te/\delta Se$ ratio of 1.52, pointing perhaps to different conformations. Semiempirical MNDO-PM3 calculations on representative Se and Te tricyclics substantiate this interpretation. The calculations indicate that the folded Cs conformations are more stable than the corresponding planar C_{2v} conformations; $\Delta H^{o}_{f}(C_{2v})$- $\Delta H^{o}_{f}(Cs)$: 9.3 (**5**), 4.6 (**6**), 3.7 (**8**), 18.3 (**12**), 16.0 (**13**), and 25.4 (**15**) kJ/mol. The $\Delta\Delta H^{o}_{f}$ values are considerably higher in the tellurium tricyclics (**2**) than in the selenium tricyclics (**1**). The degree of folding is reflected in the Ar/Ar dihedrals (τ): 137.5^{c}(**5**), 149.1°(**6**), 157.7°(**8**), 129.6°(**12**), 134.3°(**13**), and 132.7°(**15**). The calculations predict remarkably well the folding of the x-ray structure of **12** but fail to predict the planar conformation of **13**. According to previous *ab initio* (HF/3-21G) calculations, **6** and **13** should be planar[16]. The low $\Delta\Delta H^{o}_{f}$ values and relatively low degree of folding (high τ) of **6** and **8** are noted. Contrary to **8**, **15** is highly folded and its $\Delta\Delta H^{o}_{f}$ is substantial. The NMR data cast doubt on the "cross-conjugation" argument offered to explain the different ^{125}Te chemical shifts of **12** and **13**[17]. In conclusion, the results call for a consideration of the *conformations* of the selenium and tellurium tricyclics as important contributors that determine the chemical shifts.

Acknowledgments

We deeply thank Professor V. I. Minkin and Professor I. D. Sadekov, (Rostov University, Rostov-on-Don, Russia) for valuable discussions, advice and encouragement.

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