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MULTINUCLEAR NMR STUDY OF A FIVE-MEMBERED RING DITELLURIUM DERIVATIVE

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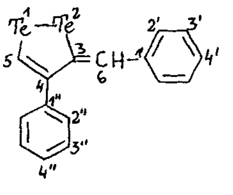
^{125}Te, ^{1}H and ^{13}C NMR data are presented for a five-membered ring ditellurium derivative. The signals are assigned by means of integration and correlation spectroscopy. The NMR data are most consistent with the presence of one of the two possible structures.

INTRODUCTION

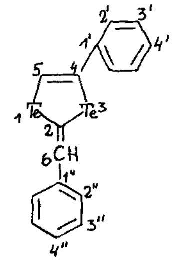
The main aim of this investigation was to attempt to distinguish between structures A and B of a five-membered ring ditellurium compound. From the standpoint of the present NMR studies, structures A and B are very similar and it is not easy to distinguish between them. As discussed below the accumulated NMR data from ^{1}H, ^{13}C and ^{125}Te studies show that the balance of the structural evidence favours structure A.

RESULTS AND DISCUSSION

The chemical shifts obtained from ^{1}H, ^{13}C and ^{125}Te NMR measurements are reported in Table 1. The ^{1}H data are assigned as follows. The signals for H-5 and H-6 are deshielded with respect to the aromatic signals and appear as two separate resonances. The aromatic ^{1}H signals are found between 7·1 and 7·4 ppm. From the signal patterns and integration we find that, with increasing shielding, the aromatic resonances correspond to signals from protons 3′, 2″, 3″, 4″, 4′ and 2′.



A



B

The ^{1}H signal of 8·8 ppm is a doublet with a splitting of 1 Hz. Following irradiation of the broad signal found at 7·9 ppm, the doublet splitting of the 8·8 ppm signal collapses, showing the presence of coupling between these two ^{1}H signals. Irradiation of the 7·1 ppm signal causes the broad signal at 7·9 ppm to split into a 1 Hz doublet, showing coupling between this pair of protons. Consequently, the broad signal at 7·9 ppm is assigned to H-6 and the signal at 8·8 ppm thus belongs to H-5.

From the ^{1}H–^{1}H COSY spectrum, coupling between H-5 and H-6 is noted, thus confirming the assignment made on the basis of the irradiated ^{1}H spectra. From the aromatic region of this COSY spectrum it is possible to distinguish between two sets of signals corresponding to the two phenyl rings in the molecule by means of the coupling from H-6 to the *ortho*-protons H-2′. The *meta* and *para* ^{1}H signals for this ring are assigned from the corresponding relative signal intensities and correlation data. The remaining aromatic ^{1}H signals are assigned to the other phenyl ring and the groups of proton are assigned by means of integration.

Turning to consideration of the ^{13}C NMR data given in Table 1, in the ^{1}H decoupled ^{13}C spectrum 12 signals are observed. From the relative signal intensities the

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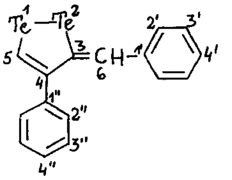
Table 1. ^{125}Te, ^{1}H and ^{13}C chemical shifts for a five-membered ring ditellurium derivative



Atom	Chemical shift (ppm)[a]	Atom	Chemical shift (ppm)[a]
Te-1	956·7 ($\nu_{1/2}$ = 19 Hz)[b]	C-3	92·9
Te-2	1035·5 ($\nu_{1/2}$ = 40 Hz)	C-4, C-1′, C-1″	139·4, 140·5, 141·4
H-5	8·8	C-5	120·4
H-6	7·9	C-6	137·0
H-2′	*ca* 7·1	C-2′	125·6
H-3′	*ca* 7·4	C-3′	128·7
H-4′	*ca* 7·2	C-4′	126·7
H-2″ H-3″	*ca* 7·35	C-2″	127·2
H-4″	*ca* 7·3	C-3″	129·1
		C-4″	127·7

[a] ^{125}Te chemical shifts are expressed with respect to Me$_2$Te$_2$ in DMSO as standard, for which a chemical shift of 63·0 ppm is assumed (Me$_2$Te = 0 ppm).

[b] J_{TeTe} = 469 Hz.

quaternary carbon signals are distinguished from those bearing protons. The proton coupled ^{13}C NMR spectrum permits us to determine the number of attached protons. The relative signal intensities found in this spectrum indicate the numbers of equivalent ^{13}C nuclei contributing to each signal. To obtain a complete ^{13}C signal assignment ^{13}C–^{1}H COSY spectra were obtained. Thus the C-5 and C-6 signals are assigned by means of their coupling to the previously assigned H-5 and H-6 protons, respectively. Since the phenyl protons have already, been assigned, the directly bonded carbons are apparent from their connectivity in the ^{13}C–^{1}H COSY spectrum for large 150 Hz couplings. In the corresponding COSY spectrum for small couplings (6 Hz), a correlation is found between H-2′ and C-3, thus permitting the C-3 signal assignment at 92·9 ppm. This is further confirmed by a correlation between the H-6 and C-3 signals. The three remaining, quaternary, carbons C-4, C-1′ and C-1″ appear within a 2 ppm range, centred on 140·5 ppm, and are not individually assigned.

However, even such a fully assigned set of proton and carbon data cannot distinguish between structures A and B. The best tool to do this seems to be ^{125}Te NMR. The proton decoupled ^{125}Te spectrum has two signals at $\delta = 956{\cdot}7$ and 1035·5 ppm. The upfield signal is about twice as sharp, $\nu_{1/2} = 19$ Hz, than the downfield signal and has ^{125}Te–^{125}Te satellite lines with a splitting of 469 Hz. This coupling constant is a key point for distinguishing between forms A and B. Unfortunately, in the literature there are very few data concerning tellurium couplings. For linear systems, one-bond ^{125}Te–^{125}Te couplings are in the range 170–270 Hz.[1] For cyclic compounds ^{1}J coupling data are available only for multicyclic cationic species: Te$_6^{4+}$, Te$_4^{2+}$ and Te$_3$Se^{+2}.[2,3] These values, depending on geometry, are in the range 600–1100 Hz. In the literature there are no data for long-range Te–Te couplings. We can only estimate these data from ^{125}Te–^{77}Se and ^{77}Se–^{77}Se systems.[2,4] For example, in the SeTe$_3^{2+}$ cation,[2] $^{1}J_{TeSe} = 157$ Hz, $^{2}J_{TeSe} = 96$ Hz and $^{1}J_{TeSe} = 48$ Hz. For couplings dominated by the Fermi contact interaction it is to be expected that the ratio J_{TeTe}/J_{TeSe} in analogous situations should be equal to -2.[5] Hence, for a Te–Te two-bond coupling we should expect a value of about 200 Hz and for $^{3}J_{TeTe}$ about 100 Hz. Both of these values are much smaller than the observed coupling. Comparing all these data, we can conclude that the observed coupling of 496 Hz can only be a one-bond coupling and that structure A is the correct one for the compound under investigation.

We can also assign two tellurium chemical shifts. Lohner and Praefcke[6] and Kalabin *et al.*[7] found that aromatic substitution in the close neighbourhood of a tellurium atom generates a strong deshielding of ^{125}Te signals, so we can assign the signal of 1035·5 ppm to the atom in position 2 and the signal at 956·7 ppm to the tellurium atom in position 1.

The analysis and interpretation of the multinuclear NMR data presented here demonstrate the ability of such investigations to distinguish between closely related structures for a given molecule. In this particular case, ^{125}Te NMR seems to be the most powerful method for structural analysis.

EXPERIMENTAL

The compound under investigation was prepared from tellurium and phenylacetylene in the KOH–HMPA–$SnCl_2$–H_2O system according to the procedure described by Potapov *et al.*[8]

The NMR spectra were measured on a Bruker AM 500 spectrometer operating at 500 MHz for ^{1}H, 125·76 MHz for ^{13}C and 157·98 MHz for ^{125}Te. The ^{1}H and ^{13}C NMR spectra were run in DMSO solution under standard conditions with internal TMS as a reference. For ^{125}Te measurements, 10 mm sample tubes with external reference (Me_2Te_2 in DMSO, $\delta = 63$ ppm from Me_2Te) were used. Spectral parameters for the ^{125}Te measurements were: spectral width 10^5 Hz, pulse width 25 μs, relaxation delay 2 s, number of scans 22 800 and acquisition time 0·3 s; Waltz decoupling was used.

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