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A MÖSSBAUER INVESTIGATION OF SOME HETEROCYCLIC  
TELLURIUM COMPOUNDS

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Summary

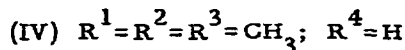
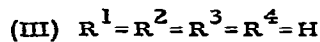
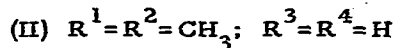
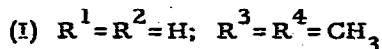
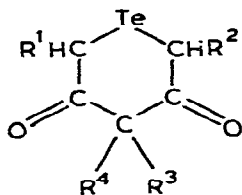
The  $^{125}\text{Te}$  Mössbauer parameters of some substituted tellurium(II) acetylacetonates are interpreted in terms of their molecular and crystal structures and the population of low energy conduction bands by non-bonding electrons.

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Introduction

Although the acetylacetonate derivatives of tellurium have been known for many years [1] the nature of the products as tellurium heterocycles [2]

(Figure 1) and their crystal structures [3-8] have only recently been reported. Despite the several  $^{125}\text{Te}$  Mossbauer investigations of



organotellurium compounds which have been collated [9] to give enhanced descriptions of structure and bonding in these materials, the data for heterocyclic tellurium compounds are sparse and only a few compounds, mainly of an aromatic nature, have received attention [10].

It was of interest therefore to extend the  $^{125}\text{Te}$  Mossbauer studies to aliphatic tellurium heterocycles and with this purpose we report here the results of an investigation of the tellurium(II) acetylacetonates described above.

### Experimental

The compounds were prepared according to methods which have been previously described [1].

The  $^{125}\text{Te}$  Mossbauer spectra were recorded using a  $^{125}\text{Sb/Rh}$  source with both source and absorber at 4.2 K.

### Results and discussion

The  $^{125}\text{Te}$  Mossbauer parameters are recorded in Table 1.

TABLE 1

 $^{125}\text{Te}$  MOSSBAUER PARAMETERS FOR TELLURIUM(II) ACETYLACETONATES

Compound	$\delta$ ( $\pm 0.08$ ) /mms $^{-1}$	$\Delta$ ( $\pm 0.01$ ) /mms $^{-1}$	$\Gamma$ /mms $^{-1}$	$\chi^2$
(I) $\text{C}_7\text{H}_{10}\text{O}_2\text{Te}$	0.70	12.77	6.51	1.06
(II) $\text{C}_7\text{H}_{10}\text{O}_2\text{Te}$	0.39	10.99	6.92	1.02
(III) $\text{C}_5\text{H}_6\text{O}_2\text{Te}$	0.42	9.81	6.90	0.97
(IV) $\text{C}_8\text{H}_{12}\text{O}_2\text{Te}$	0.47	10.59	6.50	0.87
(V) $\text{C}_7\text{H}_{10}\text{O}_2\text{Te}$	0.41	11.25	7.02	1.06

The small chemical isomer shifts,  $\delta$ , and large quadrupole splittings  $\Delta$ , are within the ranges generally expected for organic derivatives of tellurium(II) [9]. Since  $\Delta R/R$  is positive for the  $^{125}\text{Te}$  Mössbauer transition [11] the isomer shifts may be associated with removal of 5s electron density from the tellurium atom and the quadrupole splittings related to the imbalance in the 5p orbital population [9].

The Mössbauer parameters for all the tellurium(II) acetylacetonates except (I) fall within a narrow range and reflect the similar structures [3, 5-8] of compounds (II - V) where the C-Te-C bond angle of ca.  $90^\circ$  suggests that bonding occurs primarily through the p-orbitals. The Mössbauer parameters are in agreement with this interpretation being larger than those of diaryl tellurides [9] where the greater bond angles (e.g.  $101^\circ$  in di-p-tolyl telluride [12]) are indicative of a mode of bonding which is intermediate between  $p^3$  and  $sp^3$ .

The main structural difference between compound (I) and the other

tellurium(II) acetylacetonates is the smaller C-Te-C bond angle of  $86.4^\circ$  [4] which cannot be rationalised in terms of a simple combination of tellurium s and p orbitals. On first inspection the small bond angle may reasonably be associated with enhanced repulsion by the lone pair of electrons on the tellurium atom. Both Mossbauer parameters for this compound are larger than those recorded for compounds (II - V) and are indicative of a relatively higher s-electron density at the tellurium nucleus and a larger p-orbital imbalance around the tellurium atom. Clearly it is difficult to correlate the crystallographically determined small bond angle and the proposed high stereochemical activity of the tellurium lone pair with the Mossbauer parameters which imply that the lone pair is 5s in character and contributes significantly to a high electron density at the tellurium nucleus. Indeed it would be reasonable to expect that any significant stereochemical activity of the 5s lone pair would be reflected in a smaller isomer shift in compound (I) as compared with the other compounds (II - V).

An examination of the intermolecular packing of the tellurium(II) acetylacetonates shows that the yellow materials (II - V) have intermolecular Te ---- Te associations of ca.  $4\text{Å}$  [3, 5-7] which give rise to polymeric chains of tellurium atoms. The methyl groups in these compounds are equatorial to the heterocyclic ring. The colour of compound (I) is less intense and although the molecular structure is essentially the same there is no evidence [4] of short intermolecular Te ---- Te associations as in compounds (II - V). It would appear that one of the two methyl groups which occupy the positions designated by R<sup>3</sup> and R<sup>4</sup> in compound (I) is axial to the heterocyclic ring and sterically prevents the formation of short intermolecular Te ---- Te associations.

The significance of such close intermolecular distances in coloured tellurium compounds has been noted during structural investigations in the

past [13]. It has also been suggested [14-19] that colour in other p-block elements, particularly those of tin and antimony which also give lower than expected <sup>119</sup>Mössbauer chemical isomer shifts, may be explained by the direct population of low energy conduction bands by non-bonding valence electrons.

It is suggested here that the low <sup>125</sup>Te <sup>119</sup>Mössbauer chemical isomer shifts in the yellow associated tellurium(II) acetylacetonates (II - V) are indicative of the population by  $5s^2$  non-bonding tellurium electrons of conduction bands formed by overlap of orbitals on intermolecularly associated tellurium atoms. The donation and movement of these non-bonding valence electrons in the conduction bands gives rise to the colour and the consequent reduction of the 5s electron density at the tellurium nucleus is reflected in the chemical isomer shift which is smaller than expected. The smaller quadrupole splitting in the tellurium(II) acetylacetonate compounds (II - V) as compared with unassociated compound (I) reflects the higher degree of coordination and symmetry of the tellurium atom in the associated species.

The aromatic tellurium heterocycle called phenoxtellurine,  $C_{12}H_8OTe$ , which is unassociated with a C-Te-C bond angle of  $89.4^\circ$  [20] gives <sup>125</sup>Te <sup>119</sup>Mössbauer parameters ( $\delta$ ,  $0.24 \text{ mms}^{-1}$ ,  $\Delta 11.2 \text{ mms}^{-1}$ ) [10] which are similar to those observed in the associated tellurium(II) acetylacetonates (II - V). The data have been attributed [10] to greater p-character in the Te-C bonds and enhanced lone pair character of the tellurium 5s electrons. However, as in the associated tellurium(II) acetylacetonates (II - V), the chemical isomer shift is lower than would be expected for a p-bonded species with a bond angle of ca.  $90^\circ$ . It is interesting that whereas this low value for  $\delta$  in compounds (II - V) could be related to the delocalisation of electrons into a conduction band formed by overlap of orbitals on intermolecularly associated heavy atoms, the phenoxtellurine molecule has no abnormally short intermolecular Te ---- Te distances [20]. However in

phenoxtellurine the tellurium atom is bonded to two aromatic carbon atoms and it would seem that in this case the delocalisation of 5f electron density into the aromatic  $\pi$  system gives rise to a low s electron density at the tellurium nucleus and the concomitant smaller chemical isomer shift. Indeed in dibenzotellurophene,  $C_{12}H_8Te$ , the even smaller Mössbauer parameters ( $\delta$  0.14 mins<sup>-1</sup>;  $\Delta$  9.3 mms<sup>-1</sup>) [10] may reflect a similar process which in this compound with a C-Te-C bond angle of 81.7° and intermolecular Te ---- Te associations of 4.056 Å [21], is enhanced by the additional delocalisation of electrons into the conductance bands as previously described. In this respect it is quite reasonable that dibenzotellurophene gives the lowest of chemical isomer shifts which are observed in the tellurium heterocycles and also the smallest quadrupole splitting which reflects the higher coordination about tellurium.

Hence delocalisation of electrons into a  $\pi$  bonded aromatic ring or into a low energy conductance band formed by overlap of orbitals on intermolecularly associated heavy atoms may be more important in explaining the <sup>125</sup>Te Mössbauer parameters of heterocyclic tellurium compounds than a consideration of the bond angle alone. Indeed whereas the bond angle of 81.7° in dibenzotellurophene could be attributed to steric restrictions the tellurium(II) acetylacetonate compounds (I - V) with related ring skeletons and similar Te-C bond lengths suggest that the anomolous C-Te-C bond angle in compound (I) is a manifestation of the bonding. In this respect it seems that differences in quadrupole splitting may depend more on the bond orbital population and coordination than in small variations in intramolecular bond angles.

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