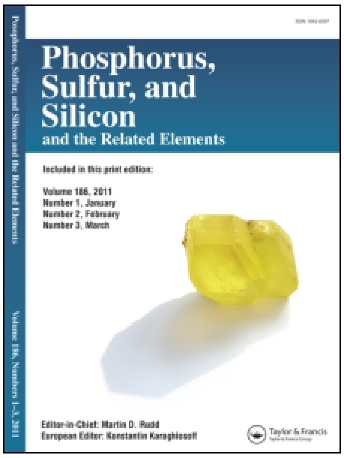

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Badyal, Jsaranbir , Herr, Magali , McWhinnie, William R. , Hamor, Thomas A. and Paxton, Keith(1998) 'INVESTIGATIONS OF HETEROCYLIC SYSTEMS CONTAINING NITROGEN-TELLURIUM BONDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 141: 1, 221 — 229

To link to this Article: DOI: 10.1080/10426509808033734
URL: http://dx.doi.org/10.1080/10426509808033734

Phosphorus, Sulfur and Silicon, 1998, Vol. 141, pp. 221-229
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INVESTIGATIONS OF HETEROCYLIC SYSTEMS CONTAINING NITROGEN-TELLURIUM BONDS

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(Received 19 May, 1998; Revised 23 June, 1998)

The syntheses of 2,1,3-benzotellaradiazole and 3,4-dimethylbenzo-2,1,3-telluradiazole were attempted by reacting tellurium dioxide with the relevant diamine. The structures of the synthesised tellurium compounds, however, were not as expected. The attempted synthesis of 2,1,3-benzotelluradiazole yielded, instead, its hydrated analogue; benzo-2-telluroxo-1,3-diazole (**1**). The high melting point and lack of solubility in all common solvents of (**1**) suggests that it may exist in a polymeric form in the solid state. The attempted synthesis of 3,4-dimethylbenzo-2,1,3-telluradiazole afforded, in small yield, an organic compound, 1-amino-3,4,7,8-tetramethylphenazine (**2**), the crystal structure of which was elucidated. This compound is believed to have arisen from the removal of tellurium from the expected diazole, thus yielding a highly reactive intermediate. An attempt to trap this intermediate using dimethyl fumarate proved unsuccessful. The use of tellurium tetrachloride as the tellurium source, in place of tellurium dioxide, yielded 3,4-dimethylbenzo-2,2dichloro-2,1,3-telluradiazole.

Keywords: Benzo-2-telluroxo-1,3-dihydrodiazole; 3,4-dimethylbenzo-2,2-dichloro-2,1,3-telluradiazole; 1-amino-3,4,7,8-tetramethylphenazine

1. INTRODUCTION

2,1,3-Telluradiazoles were first reported in 1982[1] and have since been the subject of relatively little investigation. They have been characterised as crystalline, ribbon polymeric materials, thus accounting for their chalcogenadiazole non-typical properties such as high melting points, non-volatility and poor solubility in common solvents.[1,2,3,4] The group of Chivers

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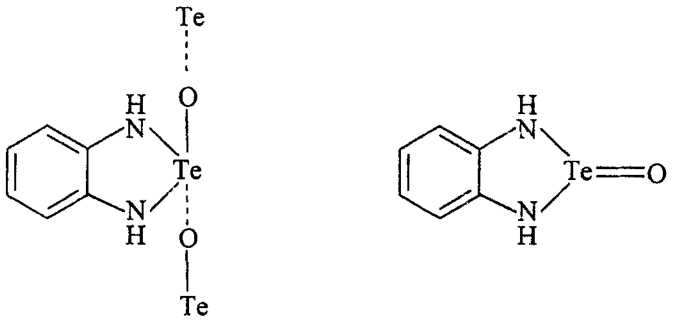
et al recently isolated a dibutyl derivative of 2,1,3-benzotelluradiazole.[5] The X-ray structural determination of this compound revealed that it exists in the solid state as a weakly associated dimer with intermolecular Te-N contacts of 2.628(4) Å. Most recently, the synthesis of 4,5,6,7-tetrafluoro-2,1,3-benzotelluradiazole has been described[6] and unlike the 2,1,3-telluradiazoles, this compound has high volatility and a strong affinity for double bonds. However, there have been no reports of the parent 2,1,3-benzotelluradiazole although the analogous seleniun compound is known,[7] having been successfully prepared from the reaction of selenium dioxide with 1,2-diaminobenzene.

The aim of the present study was to synthesise 2,1,3-benzotelluradiazole and its dimethyl derivative using tellurium dioxide and the relevant diamine. The synthesis of the dimethyl derivative was also attempted using $TeCl_4$ instead of the dioxide.

2. DISCUSSION

The reaction of 1,2-phenylenediamine with tellurium dioxide (approximately 1:1 ratio) was carried out in the absence of solvent due to the insolubility of the dioxide in common solvents. The desired 2,1,3-benzotelluradiazole was not obtained; instead the hydrated product, benzo-2-telluroxo-1,3-dihydrodiazole (**1**) was isolated, as indicated by the presence of ν(NH) at 3363–3384 cm^{-1} and ν(TeO) at 638–748 cm^{-1} in the infrared spectrum. This compound readily sublimed when heated and is very insoluble in all common solvents. These observations suggest that there is some association in the solid state and hence the structure of (**1**) may well be polymeric (see fig. 1). This behaviour in the solid state is analogous to that observed for 2,1,3-telluradiazole which has been shown to have a crystalline ribbon polymeric structure.[1] The mass spectrum of (**1**) does not display a peak for the parent ion but there is a peak at m/z = 234 which corresponds to the 2,1,3-benzotelluradiazole ion. Hence it should be possible to drive off the water from $C_6H_6N_2TeO$ to obtain the 2,1,3-benzotelluradiazole.

The reaction of 4,5-dimethyl-1,2-phenylenediamine with tellurium dioxide was carried out in the hope of isolating the dimethlyl derivative of 2,1,3-benzotelluradiazole which would be expected to be more soluble in



(polmeric structure) (molecular structure)

(1)

FIGURE 1 The two possible structures of benzo-2-telluroxo-1,3-dihdrodiazole

common solvents. However, only indirect evidence of the formation of the desired compound was obtained. Thus, an organic derivative (**2**) which could possibly have arisen from the detellurated product of the diazole was characterised crystallographically (fig. 2) (see below). Scheme 1 illustrates a plausible route for the formation of this material. It is postulated that the reaction proceeds *via* a telluroxodihydrodiazole intermediate (**a**) which loses water to give the telluradiazole (**b**) . Loss of tellurium from (**b**) then gives a highly reactive intermediate (**c**) which attacks a second molecule of the diamine, thereby yielding the product, 1-amino-3,4,7,8-tetramethylphenazine (**2**) . A recent report on quinoxolino-fused sultines and their applications in Diels-Alder reactions indicated that it might be possible to trap the proposed intermediate (**c**), and thus lend experimental support to the speculations made on the possible mechanism giving rise to (**2**). Unfortunately, attempts to trap intermediate (**c**) in the presence of dimethyl fumarate proved unsuccessful.

The preparation of 2,1,3-benzotelluradiazole derivatives using $TeCl_4$ as a tellurium source has been reported.[6] Since our attempts to synthesise 2,1,3-benzotelluradiazoles using tellurium dioxide afforded only the hydrated products, it was considered that the use of $TeCl_4$ would be more likely to yield the desired products. Hence a reaction of 3,4-dimethyl-1,2 phenylenediamine with $TeCl_4$ was carried out in the presence of 1,2-dichlorobenzene (subsequently, nitrobenzene was found to be equally effective); the product isolated was formulated as $C_8H_8N_2TeCl_2$ (**3**), mass

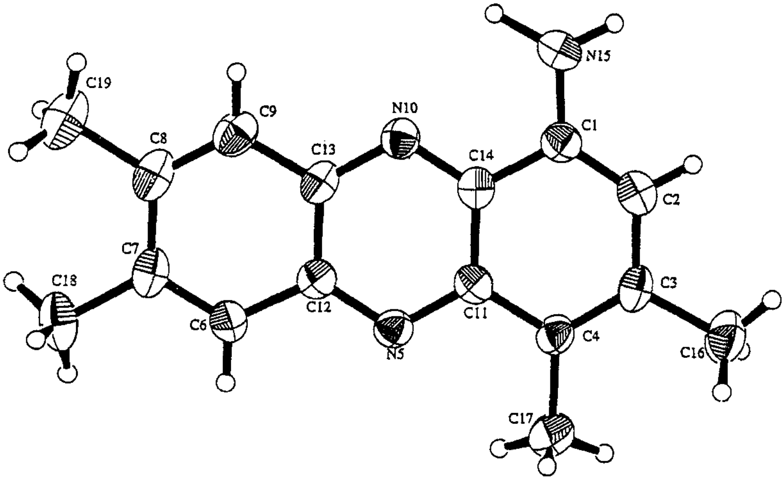
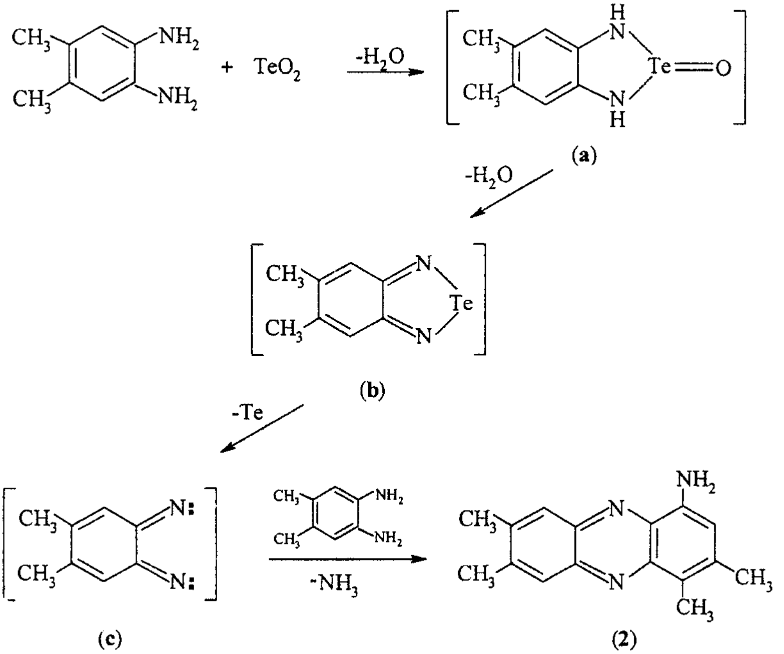


FIGURE 2 ORTEP[10] view of the molecule **2**. Thermal ellipsoids are drawn at the 30% probability level

spectrometry providing good supporting evidence. In addition to the molecular ion, peaks of higher mass number were also present in the mass spectrum. A peak at m/z = 464 provides a good fit for $C_{16}H_{16}Cl_2N_4Te$ and a more significant peak is observed at m/z = 360 corresponding to a cation of composition $C_8H_8Cl_2N_4Te$; both species probably arise from thermal decomposition during the vapourisation process. The infrared spectrum of the product shows the absence of N-H stretching vibrations indicating that deprotonation of the amino-groups has been achieved. Hence, together with evidence from a previous report,[6] it is clear that $TeCl_4$ is a useful reagent for synthesising 2,1,3-benzotelluradiazoles although, in this instance, the dichlorotellurium(IV) derivative was obtained.

Crystallography

Selected bond lengths for **2** are shown in Table I, figure 2 Sshows an ORTEP[10] representation of the molecule. The bond lengths are generally in good agreement with those measured[11] in the parent compound, phenazine; see Table I, which contains also the corresponding values for phenazine. Significant differences, however, occur in the C(3)-C(4) and



SCHEME 1 Possible route to the formation of (2) from the reaction of TeO_2 with 4,5-dimethyl-1,2- phenylenediamine

C(7)-C(8) bonds, which are respectively longer by 0.034 and 0.026 Å than in phenazine. These differences are paralleled, to some extent, by the results of semi-empirical molecular orbital calculations using the AM1[12] approximation, which indicate a lengthening of 0.013 Å for these bonds in the substituted phenazine when compared with analogous calculations for the parent (see Table I). Both experimental and theoretical results thus indicate a bond lengthening effect of *ortho*-dimethyl substitution. The fact that for both structures (with just two exceptions) all the experimental lengths are shorter than the corresponding AM1 values, may be explained by the effect of thermal libration[13] on the experimental lengths.

The aromatic core of the molecule is planar to within 0.026 Å, with substituents deviating by up to 0.078 Å from this plane. A more detailed analysis of the molecular geometry reveals a slight bending of the molecule about the N(5)...N(10) line [by 1.0(2)°], each half of the aromatic core being planar to within <0.01 Å.

TABLE I Selected bond lengths (Å) for molecule **2** compared with corresponding bond lengths in phenazine[11] and bond lengths calculated by the AM1 method. Phenazine values are based on molecular symmetry 2/m(C_{2h})

	Molecule 2		*Phenazine*	
	(expt)	*(AM1)*	*(expt)*	*(AM1)*
N(5)-C(11)	1.347(5)	1.358	1.342	1.355
N(5)-C(12)	1.348(6)	1.353	1.342	1.355
N(10)-C(13)	1.345(5)	1.354	1.342	1.355
N(10)-C(14)	1.337(6)	1.354	1.342	1.355
C(1)-C(2)	1.365(7)	1.384	1.352	1.361
C(1)-C(14)	1.433(6)	1.466	1.425	1.444
C(2)-C(3)	1.417(6)	1.420	1.416	1.426
C(3)-C(4)	1.386(6)	1.375	1.352	1.361
C(4)-C(11)	1.424(6)	1.447	1.425	1.444
C(6)-C(7)	1.353(7)	1.366	1.352	1.361
C(6)-C(12)	1.436(6)	1.442	1.425	1.444
C(7)-C(8)	1.442(7)	1.439	1.416	1.426
C(8)-C(9)	1.357(7)	1.366	1.352	1.361
C(9)-C(13)	1.426(6)	1.441	1.425	1.444
C(11)-C(14)	1.425(6)	1.455	1.438	1.455
C(12)-C(13)	1.432(6)	1.451	1.438	1.455

3. EXPERIMENTAL AND RESULTS

3.1 General

1,2-Phenylenediamine, 4,5-dimethyl-1,2-phenylenediamine, tellurium dioxide and tellurium tetrachloride were all obtained from Aldrich and used as received. Solvents were dried using appropriate methods, and all reactions were carried out under an atmosphere of dinitrogen.

3.2 Physical measurements

Proton (300.133) and ^{13}C (75.469) NMR spectra were obtained at the indicated frequencies (MHz) with a Bruker AC-300 instrument for $CDCl_3$ solutions using $SiMe_4$ (^{1}H, ^{13}C) as the standard. XPS data were recorded on a VG-Scientific ESCALAB 200-D instrument using MgK$_\alpha$ (1254 eV) radiation Infrared spectRa were recorded on a Bio-Rad FTS-40A spectrometer, and electron impact (EI) and FAB mass spectra were obtained from the EPSRC service at University College, Swansea. Elemental analyses were carried out by Medac Ltd, Department of Chemistry, Brunel University.

3.3 Reaction of 1,2-phenylenediamine with tellurium dioxide

Teliurium dioxide (1.75 g, 11 mmol) together with 1,2-phenylenediamine (1.08 g, 10 mmol) were placed into a round bottomed flask fitted with a reflux condenser. The two solids were mixed together at room temperature before heating under an atmosphere of dinitrogen in the absence of light. During heating, a red-orange vapour was released which solidified onto the walls of the condenser, yielding orange needle-like crystals. After 15 minutes, the heating was stopped and a brown solid remained at the bottom of the flask. The orange crystals were directly recovered from the reflux condenser, while the brown solid was purified by cold finger sublimation, thus yielding a further crop of orange crystalline material. The crystals did not melt but sublimed when heated and were found to have low solubility in both acetone and chloroform. The identity of the crystals was confirmed as benzo-2-telluroxo-1,3-dihydrodiazole, $C_6H_6N_2OTe$ (**1**); yield 0.50 g, 20% based on 1,2-phenylenediamine. Anal. Found: C, 27.9; H, 2.60; N, 11.0. $C_6H_6N_2TeO$ requires C, 28.8; H, 2.40; N, 11.2. NMR ($CDCl_3$): ^1H, δ 7.48(q, 2H, ArH), 7.24(q, 2H, ArH), 4.41(s, 2H, NH); ^{13}C, δ 165.1, 128.3 127.7 (Ar). EI mass spectrum: m/z = 234 ($M^+ - H_2O$), ^{130}Te.

3.4 Reaction of 4,5-dimethyl-1,2-phenylencdiamine with tellurium dioxide

Tellurium dioxide (1.75 g, 11 mmol) was placed into a round bottomed flask together with 4,5-dimethyl-1,2-phenylenediamine (1.36 g, 10 mmol). The mixture was heated under similar conditions to those above, and an orange vapour was gradually released which solidified onto the walls of the condenser as a bright orange powder. The heating was stopped after one hour to leave a black solid at the bottom of the flask which was shown to be a mixture of starting materials. The orange powder was recovered and chromatographed on a column of TLC-grade silica gel using petroleum ether : ethyl acetate (7:1) as the eluant, thus giving a yellow band preceded by a fast eluting red band. Collection of the two fractions followed by evaporation of solvent yielded a small quantity of a red solid from the first eluate and a yellow solid from the second eluate. The yellow solid was shown by infra-red spectroscopy to be unreacted 4,5-dimethyl-1,2-phenylenediamine The red solid was redissolved in 15 cm^3 of a 2:1 mixture of hexane : dichloromethane and the solution was slowly cooled over a period of several days to eventually yield red crystals. The identity of the crystals was confirmed by X-ray crystallography to be an organic compound named as 1-amino-3,4,7,8-tetramethylphenazine and having the molecular formula of $C_{16}H_{17}N_3$ (**2**); yield 0.05 g, 4% based on 4,5-dimethyl-1,2-phenylenediamine. No suitable NMR data were collected for this compound. FAB mass spectrum: m/z = 251 (M^+), 237 (M^+-N).

3.5 Reaction of 4, 5 -dimethyl-1,2-phenylenediamine with tellurium tetrachloride

Tellurium tetrachloride (0.67 g, 2.5 mmol) and 4,5-dimethyl-1,2-phenylenediamine (0.45 g, 3.3 mmol) were dissolved in 1,2-dichlorobenzene (40 cm^3) and heated, with stirring, under reflux for one hour, during which time a dark precipitate gradually formed. After cooling to room temperature, the mixture was filtered to give a fine black powder, the identity of which was confirmed as 3,4 -dimethylbenzo-2,2-dichloro-2,1,3-telluradiazole, $C_8H_8N_2TeCl_2$, m.p. > 230°C; yield 0.16 g, 20% based on $TeCl_4$. Anal. Found: C, 29.2; H, 3.08; N, 8.60. $C_8H_8N_2TeCl_2$ requires C, 29.0; H, 2.42; N, 8.46. NMR ($CDCl_3$): ^1H, δ 7.49(s, 2H, ArH), 2.32(s, 6H, CH_3); ^{13}C, δ 160.1, 140.1, 121.3 (Ar), 20.5 (CH_3). EI mass spectrum: m/z= 332 (M^+), 304 (M^+-N_2), ^{130}Te.

3.6 Crystallographic analysis of 2

Reflection intensities and cell dimensions were measured from a weakly diffracting crystal, size approximately 0.3 × 0. 1 × 0. mm, mounted on a Rigaku R-AXIS II area detector diffractometer. Using MoK_α radiation, 3861 reflections were measured [θ 2.625.2 °, $I>\sigma(I)$], of which 1538 were unique [R(int) 0.052].

Crystal data

$C_{16}H_{17}N_3$, M_r= 251.3, monoclinic, *C2/c*, $a = 23.161(9)$, $b = 8.275(4)$, $c=$ 14.850(7) Å,β=106.19(2)°, V=2733 $Å^3$, $Z = 8$, $D_c = 1.222$ g cm^{-3}, μ (MoK_α)= 0.074 mm^{-1}.

The structure was determined[8] by direct methods and refined[9] by least squares with anisotropic displacement parameters for non-hydrogen atoms. Hydrogen atoms were placed in calculated positions, except those of the amino- substituent, which were located from a difference map and freely refined witn isotropic displacement parameters. Function minimised: $\Sigma w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.085P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Final R, $wR2 = 0.1472$, 0.1941. For 949 observed reflections $[I>2\sigma(I)]$, R, $wR2 = 0.0658$, 0.1558. Maximum shift/e.s.d. ratio <0.001. Residual electron density +0.14 to -0.17 e A^{-3}. The rather high R values are probably due to the large number of weak reflections present in the data.

Supplementary Material

Atomic coordinates, thermal parameters, and full lists of bond lengths and angles

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