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Letter

4-Nitrobenzyl Tellurocyanate. Preparation and Crystal Structure

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Organic compounds containing the cyanate group, the thiocyanate group and the selenocyanate group, ROCN, RSCN and RSeCN, respectively, have been known for a very long time and a large number of these compounds has been synthesized and characterized.[1] Organic tellurocyanates, RTeCN, on the other hand, is a class of compounds which is far from fully explored. Apart from some claims in the patent literature,[2] there are presently known only six compounds containing the tellurocyanate group; R in RTeCN being 1-azulene,[3] 2-formylphenyl,[4] benzyl,[5] phenyl,[6] 4-methoxyphenyl[6] and 2-nitrophenyl.[6]

The difficulties in preparing organic tellurocyanates are primarily due to the weakness of the carbon–tellurium bonds.[7,8] However, the stability of the $[RTeCN(X)]^-$-anion prevents the synthesis alkyl tellurocyanates from alkyl halides and onium tellurocyanates,[9] the only stable salts of the latter anion.[7]

Recently, Cava and co-workers[5] have shown that these difficulties can be circumvented by applying a solution of alkali metal tellurocyanates in dimethyl sulfoxide, made *in situ*, as the source of the tellurocyanate ion. By this method they prepared benzyl tellurocyanates in fairly high yield, eqn. (1).

$$KTeCN + PhCH_2Cl \xrightarrow[-KCl]{DMSO} PhCH_2TeCN \qquad (1)$$

We now want to report on 4-nitrobenzyl tellurocyanate which is readily prepared according to eqn. (1) from 4-nitrobenzyl chloride. This compound, in contrast to the unsubstituted benzyl tellurocyanate,[5] is very stable in the solid state and can be stored for months in daylight and moist air. When dissolved in the usual organic solvents the compound slowly disintegrates with the formation of elemental tellurium, especially in warm solvents. The high stability of the nicely crystalline material allowed its crystal structure to be determined. This communication represents the first structural report on a compound containing the TeCN-group.

Experimental. Preparation of 4-nitrobenzyl tellurocyanate. To a solution of potassium tellurocyanate in 75 ml dimethyl sulfoxide, made *in situ* from 1.63 g potassium cyanide, was added dropwise 5.15 g 4-nitrobenzyl chloride, 20 % excess, dissolved in 25 ml dimethyl sulfoxide. The mixture was finally stirred for 2 h whereupon a slightly pink colourization could be observed. 250 ml water was then added to precipitate the organic product, a greenish sticky solid, fairly dark due to elemental tellurium. The solid was twice dissolved in benzene, filtered, and the solution evaporated to dryness to remove traces of water. The compound was finally twice dissolved in acetone, filtered, and rapidly precipitated with diethyl ether at 0 °C. Yield of green-yellow crystals, 3.5 g, 49 %, m.p. 123 °C (dec.). (Found: C 33.49; H 1.94; N 9.78. Calc. for $C_8H_6N_2O_2Te$: C 33.16; H 2.09; N 9.67). IR(KBr): 2157 and 430 cm^{-1}. UV(MeCN): Shoulder to NO_2-peak at ~342 nm, log $\varepsilon \leq \sim 3.33$. NMR(MeCN): 4.36 (s,2H), 7.91 (multiplet, 4H). Mass spectrum: $M^{\cdot+}$ 292 (13), 290(11), 288 (7); m/e 136 (100), 401 (3). All operations with $TeCN^-$ and the organic tellurocyanate were performed in argon-flushed and carefully dried solvents.

Crystal structure determination. Suitable prismatic crystals for the X-ray study were grown in dichloromethane and had approximate dimensions 0.1 × 0.2 × 0.2 mm. Intensity data were collected at ambient temperature on an Enraf-Nonius CAD4 automatic diffractometer using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). No decomposition could be observed during X-ray exposure. Calculations were performed with the CAD4 Structure Determination Package, revised in 1979.

Crystals of 4-nitrobenzyl tellurocyanate are monoclinic, space group $P2_1/c$, with cell dimension: $a = 4.749(1)$ Å; $b = 16.717$ (2) Å: $c = 11.753(2)$ Å and $\beta = 93.26(1)°$. With $Z = 4$ the calculated density is 2.066 g cm^{-3}. Out of 2724 unique reflections 2083 with $I > 2.0\ \sigma(I)$ were retained for the structure analysis. Full matrix least squares refinement gave

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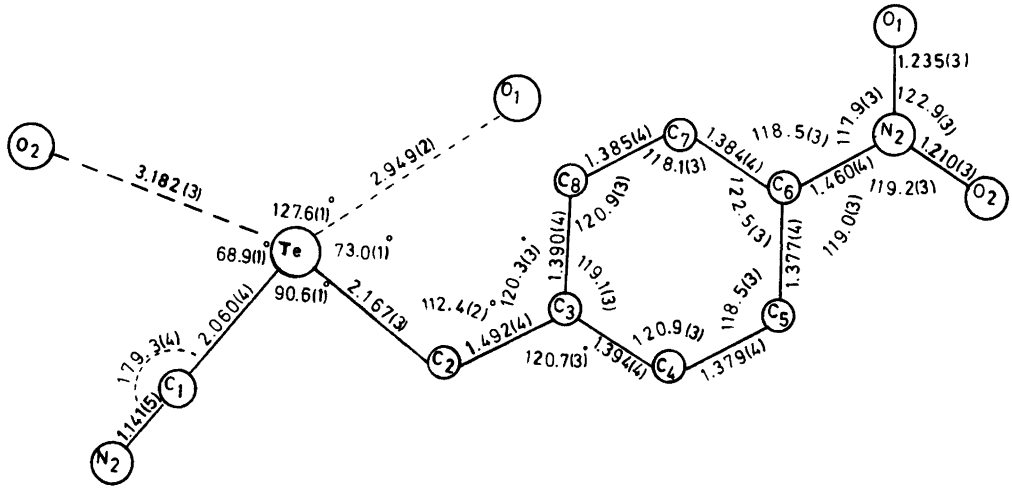

Fig. 1. Atom labelling scheme of 4-nitrobenzyl tellurocyanate with bond lengths and bond angles including standard deviations.

a final R-value of 0.027 ($R_w = 0.030$). The ESD of an observation of unit weight, S, was 1.181.

Fig. 1 shows the atom labelling scheme of the molecule, bond lengths and bond angles including standard deviations. There are two distinctly different Te–C bond lengths in the molecule; Te–C_1 and Te–C_2 being 2.060(4) and 2.167(3) Å, respectively. The Te–C_1 bond length is of the same order as what has recently been observed in a preliminary structure determination in this laboratory of bis(triphenylphosphine)iminium tellurocyanate.[10] Apparently, in the present compound and in the $TeCN^-$ ion, the Te–C_1 bond has some multiple bond character. The Te–C_2 bond length is of the expected order of magnitude for a Te–C single bond.[11,12] The C_1TeC_2 bond angle is 90.6(1)° and is in agreement with what has been observed in Me_3TeBPh_4.[11]

The tellurium atom forms two strong intermolecular "secondary bonds"[13] to oxygen atoms of 2.949(2) Å and 3.182(3) Å. These two bonds and the two Te–C bonds are strictly coplanar; the sum of the Te-bond angles being 360.0°. 4-Nitrobenzyl tellurocyanate in the crystalline state may thus be considered a distorted square planar tellurium (II) complex[14] containing two ligands with strong *trans*-effect, *i.e.* the 4-nitrobenzyl group and the cyano group. The present compound must owe its stability in the crystalline state to the intermolecular contacts between the tellurium atom and the two oxygen atoms. In addition, the tellurium atom forms very weak bonds to two oxygen atoms, mutually opposite to the plane, of 3.566(3) and 3.881(3) Å.

Fig. 2 shows the Newman projections along the Te–C_2 bond (I) and (II) the C_2–C_3 and the

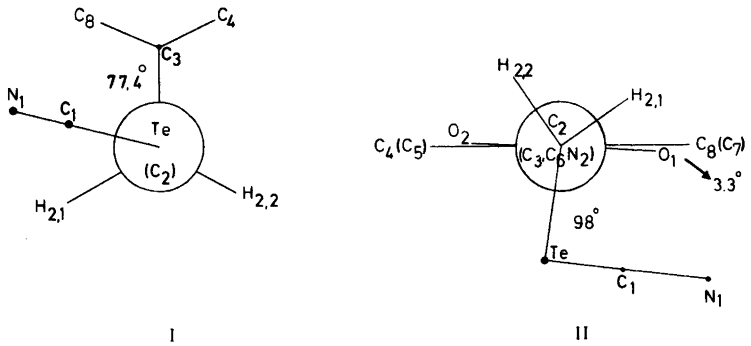

Fig. 2. Newman projections along the Te–C_2 bond (I) and along the C_2–C_3 and the C_6–N_2 bonds (II).

C_6-N_2 bonds. From (I) is apparent that the TeCN-group is *syn*-clinal (*gauche*) to the C_2-C_3 bond (torsion angle of 77.4°), a conformation which also has been observed in some organic thiocyanates.[15] The TeC_2C_3 plane makes an angle of 98.0° with the benzene ring while the nitro group is twisted 3.3° from the aromatic ring as shown in (II). The two N–O bond lengths and the two C_6NO bond angles are different; this may be due to the stronger $Te-O_1$ bond, *cf.* Fig. 1. The benzene ring is planar within experimental error, but distorted as observed in numerous compounds containing one or more nitro-groups.[16,17]

A detailed description of the crystal structure of 4-nitrobenzyl tellurocyanate together with the corresponding selenocyanate and thiocyanate will be published shortly. Positional and thermal parameters are obtained on request to the authors.

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