

Chemical consequences of intramolecular Te ← N coordination in tellurium-containing aromatic azomethine derivatives

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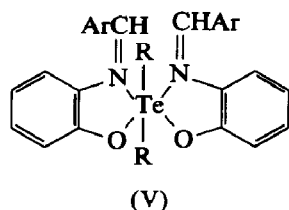
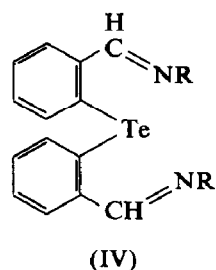
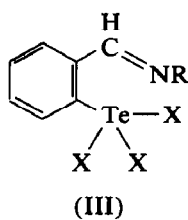
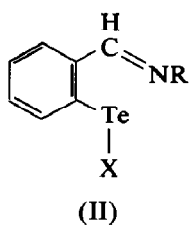
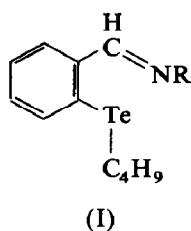
Abstract

Owing to stabilization by Te ← N coordination in the aromatic tellurenyl compounds containing the azomethine function in the *ortho* position of the aryl ring, the synthesis of the novel organic tellurium compounds, tellurenyl azides and tellurenic acid esters and anhydrides becomes possible. The influence of the Te ← N coordination on the reactions of 2-butyltelluro- and 2-halogenotellurenylbenzalanimines is described.

Introduction

We have previously shown [1–6] that a strong intramolecular Te ← N coordination by the azomethine nitrogen occurs in aromatic aldimines I–V possessing a Te-containing substituent in the position *ortho* to the CH=N group. Such coordination is crucial to the thermal stability and determines the reactivity of these compounds.

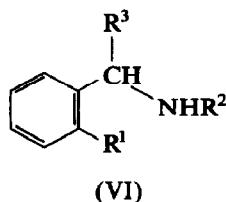
Like the *ortho*-positioned carbonyl [7–9], nitro [10] and diazo functions [11–13], the azomethine group *ortho* to the TeX groups strongly stabilizes tellurenyl halogenides, II. In contrast to the unstable noncoordinated tellurenyl halogenides, compounds II form crystals which upon heating melt before they decompose. Whereas arylalkyl tellurides ArTeR can be readily oxidized to tetracoordinate tellurium derivatives ArTeX₂R by reaction with sulfur chloride or halogens [14,15], 2-butyltellurobenzalanimines I under these conditions undergo cleavage of the Te–C_{sp³} bond to give the dicoordinate tellurium derivatives II [1,2]. Diorganyl(diaroxy)telluranes (V) containing azomethine groups in the aryl rings were found to be very stable to hydrolysis even under prolonged contact with water at ambient temperature, whereas diorganyl (dialkoxy) telluranes R₂Te(OR)₂, in which no Te ← N coordinate bonds are present, rapidly decompose even in atmospheric moisture [16].



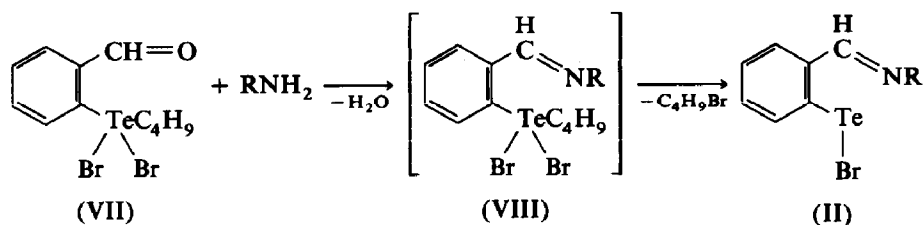
I, II	R
a	4-CH ₃ C ₆ H ₄
b	C ₆ H ₅
c	4-CH ₃ OC ₆ H ₄
d	2,4,6-(CH ₃) ₃ C ₆ H ₂
e	4-IC ₆ H ₄
f	(CH ₃) ₃ C
g	4-BrC ₆ H ₄

Results and discussion

No reaction occurs between 2-butyltellurobenzaldehydes, I, and NaBH₄ under prolonged refluxing in ethanolic solutions, though the oxygen analog of I, 2-methoxybenzal-*p*-toluidine, is readily reduced under the same conditions to the secondary amine, VI (R¹ = OCH₃, R² = C₆H₄CH₃-*p*, R³ = H), typical of an azomethine reaction.



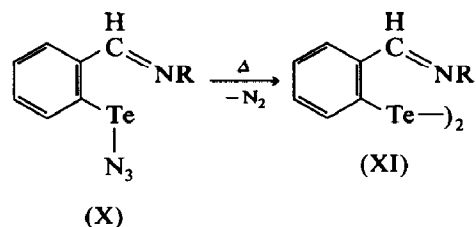
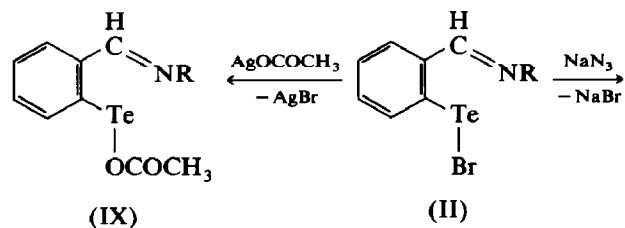
The strong stabilization of the type II 10-Te-3 structures by the Te ← N coordination permits the preparation of these not only by cleavage of the C₂,₃-Te bonds by halogenolysis of 2-butyltellurobenzaldehydes I but also by reaction of (2-formylphenyl)butyltellurodibromide VII with primary amines. The reaction most probably proceeds via the intermediate σ -telluranes VIII which readily abstract butyl bromide to give the bromotellurenyl azomethines, II.



Halogen exchange in noncoordinate tellurenyl halogenides is practically unknown. In the case of 2-halogenotellurenyl benzalanilines, II, which have intramolecular $\text{Te} \leftarrow \text{N}$ coordination, the halogens attached to the coordinated tellurium atom readily undergo various exchange reactions. Reaction of the azomethine IIa with silver acetate gives tellurenyl acetate, IXa, in high yield. IXa is a little described organic derivative of two-coordinate tellurium which was previously exemplified only by acetoxytellurenyl azobenzene [12].

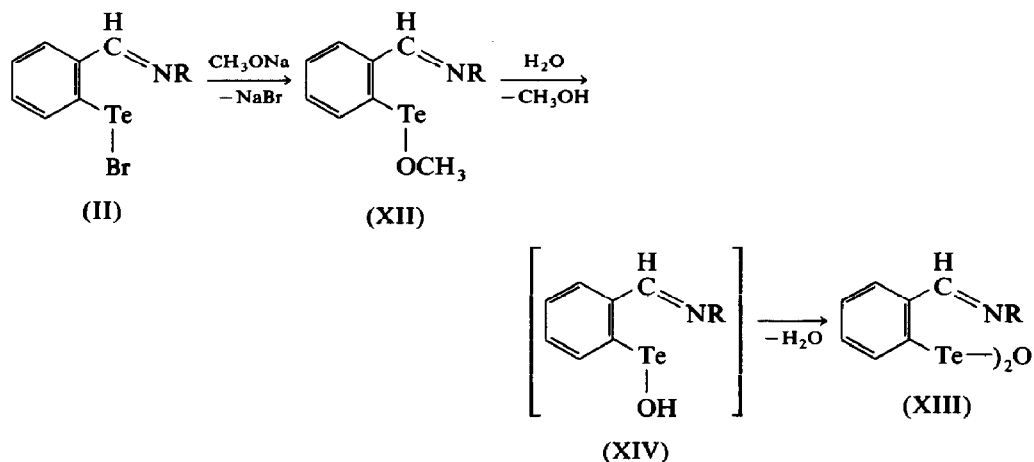
Reaction of tellurenyl bromides with sodium azide in acetone solution has given the first examples of the tellurenyl azides X in yields $\leq 70\%$. Compounds X are crystalline, stable compounds showing the azide IR absorption at $2033\text{--}2040\text{ cm}^{-1}$. Elimination of nitrogen occurs only at elevated temperature in solution to give the ditellurides XI.

Thus the intramolecular $\text{Te} \leftarrow \text{N}$ coordination causes the high stability of compounds X. Actually, all the attempts to prepare phenylselenyl azide by exchange of chlorine in phenylselenyl chloride with azide ion failed since the phenylselenyl azide initially formed immediately decomposes to give diphenyldiselenide. Thus the ArSeX compounds are more stable than their tellurium analogs, it would be difficult to preparatively isolate tellurenyl azides in which tellurium center does not participate in intramolecular coordination.

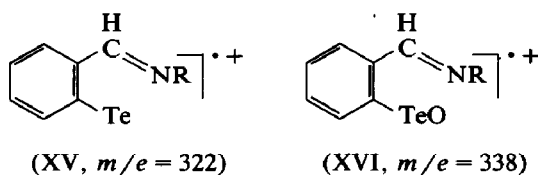


The first aryltellurenic acid ester (XII) has been prepared and isolated pure from the reaction of tellurenyl bromide IIb with sodium methoxide in CHCl_3 . XII is stable for long periods if stored without access of moisture. Compounds XII are convenient precursors to the unprecedented aryltellurenic acid anhydrides, XIII, which were synthesized by hydrolysis of the esters, XII from the spontaneous dehydration of the intermediate tellurenic acids, XIV. It was found that compounds described as arylselenenic acids [19–22] by Rheinboldt are actually the acid

anhydrides [23–25]. The structure of aryltellurenic acid anhydrides is stabilized by the coordination of the tellurium center to the imine nitrogen, whereas arylselenenic acids are stabilized by coordination of selenium to the nitro or carbonyl groups.

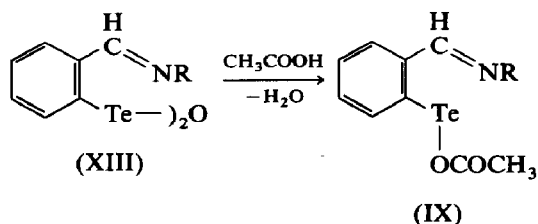


The anhydrides XIII are stable crystalline compounds whose structure was confirmed from their spectral data and by their reactions. No molecular ion has been observed in the mass spectrum of compound XIIIa, but the fragments, m/e 322 and 338, correspond to products of breaking of one of the Te–O bonds, namely, XV and XVI respectively. The ion with m/e 322 has been also observed in the mass spectrum of the congeneric ditelluride, XIa.



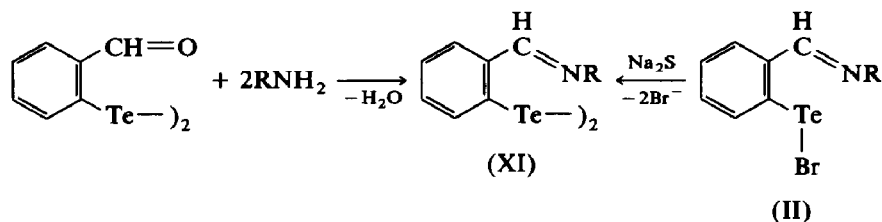
If the low field shifts of the azomethine proton resonances are ignored, the ^1H NMR spectra of anhydrides XIII closely resemble those of respective ditellurides XI. Thus the chemical shift of azomethine proton of anhydride XIIIb is 8.91 ppm whereas for ditelluride XIb this proton is observed in the ^1H NMR spectrum at 8.68 ppm (in CDCl_3).

Compounds XIII react with acetic acid to give tellurenyl acetates IX as expected from the assignment to aryl tellurenic acid anhydrides. Compounds IX thus obtained are identical with the tellurenyl acetates prepared by the usual anion exchange reactions*.



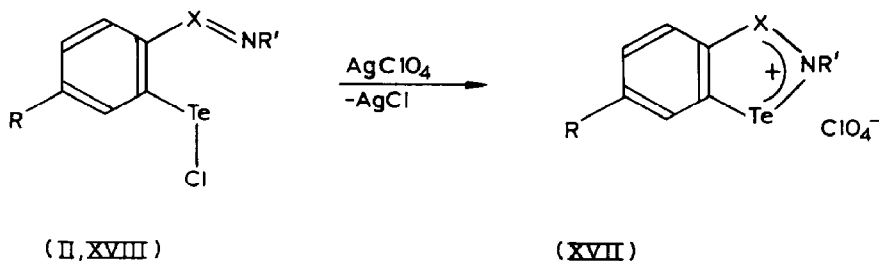
* The reactions of the aryltellurenic acid anhydrides suggest that the compound prepared by reaction of 2-bromotellurenylphenyl benzophenone with KOH which Renson [26] described as bis(2-benzoylphenyl) ditelluride is in fact 2-benzoylphenyltellurenic acid anhydride.

In order to obtain additional evidence of the identity of the products of the hydrolysis of aryltellurenic esters to the anhydrides (XIII), and the ditellurides, XI, containing substituents R identical with those in XIII, were prepared by reduction of the relevant tellurenyl halogenides, II, with sodium sulfide or by reaction of di(2-formylphenyl)ditelluride with primary amines.



The 2-halogenotellurenyl benzalanilines, II, were also used to prepare some benzoisotellurazole derivatives [27]. Reaction of 2-chlorotellurenyl benzal-*p*-toluidine IIa with silver perchlorate in acetone solution gives *N*-(4-methylphenyl)benzoisotellurazolium perchlorate XVII (X = CH, R = H, R' = 4-CH₃C₆H₄). *N*-Phenyl-XVII (X = CH, R = H, R' = C₆H₅) and *N*-(4-bromophenyl)-XVII (X = CH, R = H, R' = 4-BrC₆H₄) were similarly prepared. Up to now, the only example of benzoisotellurazolium cation salts that has been described is *N*-methylbenzoisotellurazolium iodide, prepared by an alkylation of benzoisotellurazole with methyl iodide [28].

When 4,4'-dimethyl-2-chlorotellurenyl azobenzene XVIII (X = N, R = CH₃, R' = 4-CH₃C₆H₄) was treated with silver perchlorate, the first ever benzotelluradiazolium salt, 6-methyl-2-*N*-(4'-methylphenyl)benzotelluradiazolium perchlorate, XVII (X = N, R = CH₃, R' = 4-CH₃C₆H₄), was obtained.



Experimental

The ¹H NMR spectra were recorded with a Tesla BS-487C (80 MHz) instrument. HMDS, was employed as the internal standard. IR spectra were recorded by use of a UR-20 spectrophotometer with Nujol. Mass spectra were recorded by use of a Finnigan 4021 instrument equipped with a direct injection system (ionizing energy 70 eV, emission current 0.25 mA).

The 2-butyltellurobenzalanilines and 2-halogenotellurenyl benzalanilines were prepared by procedures described previously [1,2].

Reaction of 2-butyltellurobenzal-4'-methylaniline Ia with NaBH₄. To a solution of 11.6 g (0.03 mol) Ia in 70 ml of ethanol under reflux, was added a solution of 2.88 g (0.06 mol) NaBH₄ in 60 ml of 1 *N* aqueous NaOH dropwise with stirring during 15 min. After 1 h refluxing, the solution was partly evaporated and the residue was

treated with 70 ml of CHCl_3 and an equal volume of water. The mixture was filtered, the organic layer was separated, washed carefully with water and dried over CaCl_2 . The CHCl_3 was completely evaporated off by exposure to air. The crystalline yellow residue (10.8 g, 93%) had a melting point, 52°C , and spectral characteristics coincident with those of the starting azomethine Ia.

Reaction of 2-methoxybenzal-4'-methylaniline with NaBH_4 . A similar procedure gave *N*-4-methylphenyl-2'-methoxybenzylamine VI ($\text{R}^1 = \text{OCH}_3$, $\text{R}^2 = 4\text{-CH}_3\text{C}_6\text{H}_4$, $\text{R}^3 = \text{H}$) in 89% yield. Large colourless plates, m.p. 67°C (from hexane). ^1H NMR (CCl_4): 2.10 (s, 3H, CH_3), 3.62 (s, 1H, NH), 3.67 (s, 3H, OCH_3), 4.13 (s, 2H, CH_2), 6.26–7.16 (m, 8H, arom.). Found: C 78.9, H 7.2. $\text{C}_{15}\text{H}_{17}\text{NO}$ calc: C 79.3, H 7.5%.

2-(Mesityliminomethinyl)phenyltellurenyl bromide (IId). To a solution of 13.5 g (0.03 mol) (2-formylphenyl)butyl tellurium dibromide in 100 ml of benzene was added 4.1 g (0.03 mol) mesidine and 0.02 ml of CF_3COOH . The mixture immediately became turbid because of the elimination of water, which was distilled off azeotropically with benzene until 40 ml of the solution remained. The residue was diluted with 20 ml of warm hexane. Azomethine IId (in 98% yield) precipitated immediately as bright-yellow crystals. M.p. $229\text{--}230^\circ\text{C}$ (from toluene/hexane). ^1H NMR (CDCl_3): 2.08 (s, 6H, *ortho*- CH_3), 2.30 (s, 3H, *para*- CH_3), 6.96–8.81 (m, 6H, arom.), 9.17 (s, 1H, $\text{CH}=\text{N}$). Found: C 44.5, H 3.8. $\text{C}_{16}\text{H}_{16}\text{BrNTe}$ calc: C 44.7, H 3.8%.

The other azomethine derivatives of phenyltellurenyl bromide were similarly prepared in almost quantitative yields.

2-(4'-Iodophenyliminomethinyl)phenyltellurenyl bromide (IIe), m.p. $201\text{--}202^\circ\text{C}$, ^1H NMR (CDCl_3): 7.10–8.75 (m, 8H, arom.), 9.27 (s, 1H, $\text{CH}=\text{N}$). Found: C 29.9, H 1.9. $\text{C}_{13}\text{H}_9\text{BrINTe}$ calc: C 30.2, H 1.8%.

2-(tert-Butyliminomethinyl)phenyltellurenyl bromide (IIf), m.p. $177\text{--}178^\circ\text{C}$, ^1H NMR (CDCl_3): 1.58 (s, 9H, $\text{C}(\text{CH}_3)_3$), 7.23–8.70 (m, 4H, arom.), 9.28 (s, 1H, $\text{CH}=\text{N}$). Found: C 36.3, H 4.0. $\text{C}_{11}\text{H}_{14}\text{BrNTe}$ calc: C 35.9, H 3.8%.

2-(4'-Methylphenyliminomethinyl)phenyltellurenyl bromide (IIa), m.p. $174\text{--}176^\circ\text{C}$, and *2-(4'-methoxyphenyliminomethinyl)phenyltellurenyl bromide (IIc),* m.p. 153°C , whose spectral characteristics were identical with those of the compounds obtained previously by halogenolysis of the appropriate 2-butyltellurobenzalanilines [1,2].

2-Acetoxytellurenylbenzal-4'-methylaniline (IXa).

1. *By exchange reaction.* Solutions of 11.5 g (0.0286 mol) azomethine IIa in 100 ml of CHCl_3 and 4.8 g (0.0286 mol) silver acetate in 60 ml of water were mixed in a separating funnel and shaken during 15 min. The silver bromide sediment was filtered off, the organic layer was collected, and dried azeotropically. After evaporation of CHCl_3 by exposure to air 10.4 g (95%) of crystalline IXa were obtained. Large yellow plates with m.p. $186\text{--}188^\circ\text{C}$ (from acetonitrile). ^1H NMR (CD_2Cl_2): 2.12 (s, 3H, OCOCH_3), 2.38 (s, 3H, CH_3), 7.32–8.45 (m, 8H, arom.), 9.26 (s, 1H, $\text{CH}=\text{N}$). IR: 1618, 1583, 1532, 1511, 1435, 1307, 1255, 1200, 1160, 1120, 1040, 1020, 963, 947, 927, 871, 839, 760, 720, 660 cm^{-1} . Found: C 50.9, H 4.6. $\text{C}_{16}\text{H}_{15}\text{NO}_2\text{Te}$ calc: C 50.5, H 4.0%.

2. *By the reaction of arenetellurenic acid anhydride (XIIIa) with acetic acid.* To a solution of 6.6 g (0.01 mol) 2-(4'-methylphenyliminomethinyl)phenyl tellurenic acid anhydride, XIIIa in 50 ml of toluene 1.16 g (0.02 mol) of CH_3COOH was added and the mixture was refluxed with a Dean–Stark trap until separation of water (0.35 ml) was complete. The color of the mixture changed from red-orange to lemon-yellow, a portion of the solvent (25 ml) was distilled off, the residue was diluted with 10 ml of

hexane, and cooled to 0°C to give compound IXa as yellow plates (yield 6.0 g, 80%). M.p. 186–188°C.

The other compounds IX were obtained similarly.

2-Acetoxytellurenylbenzal-4'-methoxyaniline (IXc), 84% yield, m.p. 124–126°C (from acetonitrile), ¹H NMR (CDCl₃): 2.17 (s,3H,OCOCH₃), 3.78 (s,3H,OCH₃), 6.80–8.35 (m,8H,arom.), 9.14 (s,1H,CH=N). Found: C 48.3, H 3.6. C₁₆H₁₅NO₃Te calc: C 48.4, H 3.8%.

2-Acetoxytellurenylbenzal-2',4',6'-trimethylaniline (IXd), 69% yield, m.p. 210–213°C (from acetonitrile), ¹H NMR (CDCl₃): 2.05 (s,6H,*ortho*-CH₃), 2.12 (s,3H,OCOCH₃), 2.29 (s, 3H,*para*-CH₃), 6.92–8.56 (m,6H,arom.), 9.06 (s,1H,CH=N). Found: C 52.5, H 4.4. C₁₈H₁₉NO₂Te calc: C 52.9, H 4.7%.

2-Azidotellurenylbenzal-4'-methylaniline (Xa). To a solution of 0.4 g (0.001 mol) 2-bromotellurenylbenzal-4'-methylaniline, IIa, in 30 ml of acetone, was added a solution of 0.13 g (0.001 mol) sodium azide in 20 ml of water with stirring and keeping the temperature below 5°C. Cold water (10 ml) was added dropwise until the solution became slightly turbid. The solution was cooled to –7°C and the precipitated bright-yellow needles were filtered off, washed with cold water and dried in air. Yield of Xa 0.3g (82%). M.p. 95°C. ¹H NMR: (acetone-*d*₆): 2.32 (s,3H,CH₃), 7.22–8.71 (m,8H,arom.), 9.56 (s,1H,CH=N). IR: 2033 (*ν*(N₃)), 1580,1527,1500,1313,1267,1251,1189,1013,925,905,810,754,707 cm⁻¹. Found: C 46.3, H 3.2. C₁₄H₁₂N₄Te calc: C 46.2, H 3.3%.

2-Azidotellurenylbenzal-aniline Xb, enriched with ¹⁵N isotope (50%), was obtained similarly in 73% yield. Orange-yellow crystals, m.p. 145–148°C (dec.) (from acetone). IR: 2040 (*ν*(N₃)). Found: C 44.2, H 2.8. C₁₃H₁₀N₄Te. calc: C 44.6, H 2.9%.

Methyl ester of 2-[(4'-methoxyphenyl)iminomethinyl]phenyltellurenic acid (XIIC). To a solution of 8.35 g (0.02 mol) 2-bromotellurenylbenzal-4'-methoxyaniline, IIc, in 60 ml of CHCl₃ (purified from ethanol) was added a solution of sodium methoxide (obtained from 0.5 g (0.02 g-a) of sodium metal and 20 ml of methanol) dropwise with vigorous stirring. Most of the part solvent was distilled off, 60 ml of hexane was added to the residue and remaining methanol was removed azeotropically using Dean–Stark trap. Sodium bromide was filtered off and the yellow filtrate was cooled to –7°C. The yellow rhombic crystals of the ester XIIC were separated off and dried in vacuo. Yield 5.4g (76%). ¹H NMR (CDCl₃): 3.72 (s,3H,OCH₃), 4.02 (s,3H,TeOCH₃), 6.80–8.22 (m,8H,arom.), 8.90 (s,1H,CH=N). IR: 1596,1575,1527,1493,1295,1240,1189,1153,1100,1011,900,820,747,712 cm⁻¹. Found: C 49.2, H 3.9. C₁₅H₁₅NO₂Te calc: C 48.8, H 4.1%.

2-[(4'-methylphenyl)iminomethinyl]phenyltellurenic acid anhydride (XIIIa). To a solution of 40.1 g (0.1 mol) 2-bromotellurenyl-4'-methylaniline IIa in 250 ml of CHCl₃ was added a solution of sodium methoxide (prepared from 2.3 g (0.1 g-a) sodium metal and 50 ml of methanol) dropwise with stirring. To the reaction mixture was added 200 ml of water and the mixture was stirred until the suspension of NaBr initially formed had completely dissolved. The red, organic layer, was separated off, dried with CaCl₂ and most of the solvent was distilled off. The residue was treated with ether until the mixture became slightly turbid. The mixture was cooled to –7°C to give 27.7 g (80%) of XIIIa as red-orange crystals, m.p. 202–204°C. ¹H NMR (CD₂Cl₂): 2.36 (s,3H,CH₃), 7.26–8.55 (m,8H,arom.), 9.02 (s,1H,CH=N). IR: 1593,1580,1500,1432,1351,1312,1247,1231,1193,1150,1108,1036,

1016,950,898,755,713 cm^{-1} . Mass spectra (m/e): 338,322,282,270,258,209,194,180, 165,152,106,91,77,65. Found: C 50.5, H 3.4. $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O Te}_2$ calc: C 51.0, H 3.7%. The other compounds XIII were obtained similarly.

2-[(4'-Methoxyphenyl)iminomethinyl]phenyltellurenic acid anhydride (XIIIc), 92% yield, orange crystals, m.p. 202–203°C (from $\text{CHCl}_3/\text{CH}_3\text{CN}$), $^1\text{H NMR}$ (CDCl_3): 3.80 (s,3H, OCH_3), 6.81–8.60 (m,8H,arom.), 8.91 (s,1H, $\text{CH}=\text{N}$). Found: C 48.4, H 3.7. $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_3\text{Te}_2$ calc: C 48.6, H 3.5%.

2-[(2',4',6'-Trimethylphenyl)iminomethinyl]phenyltellurenic acid anhydride (XIII d), 73% yield, yellow-orange crystals with m.p. 160–163°C, $^1\text{H NMR}$ (CDCl_3): 2.07 (s,6H,*ortho*- CH_3), 2.27 (s,3H,*para*- CH_3), 6.90–8.60 (m,6H,arom.), 8.71 (s,1H, $\text{CH}=\text{N}$). Found: C 53.4, H 4.2. $\text{C}_{32}\text{H}_{32}\text{N}_2\text{OTE}_2$ calc: C 53.7, H 4.5%.

2-[(4'-Iodophenyl)iminomethinyl]phenyltellurenic acid anhydride (XIII e), 95% yield, red crystals with m.p. 143–145°C (from CHCl_3), $^1\text{H NMR}$ (CDCl_3): 6.79–8.28 (m,8H,arom.), 8.77 (s,1H, $\text{CH}=\text{N}$). Found: C 35.0, H 1.8. $\text{C}_{26}\text{H}_{18}\text{I}_2\text{N}_2\text{OTE}_2$ calc: C 35.3, H 2.1%.

2-(*tert*-Butyliminomethinyl)phenyltellurenic acid anhydride (XIII f), 82% yield, yellow powder with m.p. 148–150°C (from octane), $^1\text{H NMR}$ (CDCl_3): 1.44 (s,9H, $\text{C}(\text{CH}_3)_3$), 7.19–8.58 (m,4H,arom.), 8.81 (s,1H, $\text{CH}=\text{N}$). Found: C 44.2, H 4.5. $\text{C}_{22}\text{H}_{28}\text{N}_2\text{OTE}_2$ calc: C 44.6, H 4.8%.

Di[2-(4'-bromophenyl)iminomethinyl]phenyl ditelluride (XIg), containing 50% of ^{15}N isotope. To 5.0 g (0.021 mol) of fused $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was added 1.42 g (0.00336 mol) of powdered 2-chlorotellurenylbenzal-4'-bromoaniline- ^{15}N in small portions, and the mixture was kept at 100°C during 2h. Then the mixture was diluted with 20 ml of water and orange-red suspension of XIg was filtered off, washed with water and dried in vacuo. Yield of XIg 1.23 g (95%). Orange crystals, m.p. 204°C (from CHCl_3 /ether). $^1\text{H NMR}$ (CDCl_3): 7.15–7.65 (m,8H,arom.), 8.85 (s + d,1H, $\text{CH}=\text{N}$). Found: C 40.8, H 2.6. $\text{C}_{26}\text{H}_{18}\text{Br}_2\text{N}_2\text{Te}_2$ calc: C 40.3, H 2.3%.

Di[2-(4'-methylphenyl)iminomethinyl]phenyl ditelluride (XIa). To a solution of 4.0 g (0.0086 mol) di(2-formylphenyl) ditelluride in 50 ml of CHCl_3 was added a solution of 1.85 g (0.0173 mol) *p*-toluidine in 10 ml of CHCl_3 and 0.02 ml of CH_3COOH . After 30 min of reflux, 40 ml of solvent was distilled off, the residue was diluted with 20 ml of pentane and cooled to -5°C . The precipitated product was filtered off and washed with pentane. Yield 5.25 g (82%). Orange needles, m.p. 175–176°C (from CHCl_3 /pentane). $^1\text{H NMR}$ (CDCl_3): 2.38 (s,3H, CH_3), 7.07–8.22 (m,8H,arom.), 8.77 (s,1H, $\text{CH}=\text{N}$). Mass spectra (m/e): 422,410,388,322,297,282, 267,258,232,194,178,165,152,118,106,91, Found: C 51.9, H 3.5. $\text{C}_{28}\text{H}_{24}\text{N}_2\text{Te}_2$ calc: C 52.2, H 3.8%.

Some of the other ditellurides XI were prepared by the reaction of di(2-formylphenyl) ditelluride with primary amines.

Di[2-(4'-methoxyphenyl)iminomethinyl]phenyl ditelluride (XIc), 89% yield, orange crystals, m.p. 176–178°C (from CHCl_3 /hexane), $^1\text{H NMR}$ (CDCl_3): 3.80 (s,3H, OCH_3), 6.88–8.24 (m,8H,arom.), 8.68 (s,1H, $\text{CH}=\text{N}$). Found: C 49.4, H 3.3. $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2\text{Te}_2$ calc: C 49.8, H 3.6%.

Di[2-(2',4',6'-trimethylphenyl)iminomethinyl]phenyl ditelluride (XI d), 94% yield, light-orange needles, m.p. 120–121°C (from hexane), $^1\text{H NMR}$ (CDCl_3): 2.25 (s,6H,*ortho*- CH_3), 2.33 (s,3H,*para*- CH_3), 6.98–8.32 (m,6H,arom.), 8.52 (s,1H, $\text{CH}=\text{N}$). Found: C 55.1, H 4.8. $\text{C}_{32}\text{H}_{32}\text{N}_2\text{Te}_2$ calc: C 54.9, H 4.6%. Synthesis of the compound XI d was successful only when CF_3COOH was used as catalyst.

Di[2-(4'-iodophenyl)iminomethinyl]phenyl ditelluride (XIe), 98% yield, orange crystals, m.p. 183–184°C (from CHCl_3), ^1H NMR (CDCl_3): 7.05–8.18 (m, 8H, arom.), 8.67 (s, 1H, CH=N). Found: C 35.6, H 1.9. $\text{C}_{26}\text{H}_{18}\text{I}_2\text{N}_2\text{Te}_2$ calc: C 36.0, H 2.1%.

Di(2-tert-butyliminomethinyl)phenyl ditelluride (XI f), 76% yield, yellow crystals, m.p. 150–152°C (from CCl_4), ^1H NMR (CDCl_3): 1.47 (s, 9H, $\text{C}(\text{CH}_3)_3$), 7.00–8.17 (m, 4H, arom.), 8.53 (s, 1H, CH=N). Found: C 46.3, H 5.2. $\text{C}_{22}\text{H}_{28}\text{N}_2\text{Te}_2$ calc: C 45.9, H, 4.9%.

N-(4-Methylphenyl)benzoisotellurazolium perchlorate. (XVII; X = CH, R = H, R' = 4- $\text{CH}_3\text{C}_6\text{H}_4$) To a solution of 10.72 g (0.03 mol) 2-chlorotellurenyl-4'-methyl-aniline in 300 ml of dry acetone was added a solution of 9.95 g (0.03 mol) $\text{AgClO}_4 \cdot 3\text{CH}_3\text{CN}$ in 40 ml of dry acetone dropwise with stirring during 5 min. Stirring was then continued at ambient temperature for 1 h until the liquid phase became clear. Silver chloride was filtered off and the filtrate was concentrated to a volume of 100 ml. The residue was diluted with 200 ml of dry ether and then cooled to 0°C, to give XVII 10.6 g (84%). Orange crystals, M.p. 125–130°C (explosive). ^1H NMR (acetone- d_6): 2.18 (s, 3H, CH_3), 7.02–8.56 (m, 8H, arom.), 9.82 (s, 1H, CH=N). IR: 1100 cm^{-1} ($\nu(\text{ClO}_4)$). Found: C 39.7, H 3.0. $\text{C}_{14}\text{H}_{12}\text{ClNO}_4\text{Te}$ calc: C 39.9, H 2.9%.

Some of the other salts XVII were prepared similarly.

N-Phenylbenzoisotellurazolium perchlorate (XVII; X = CH, R = H, R' = C_6H_5 ; containing 50% of ^{15}N isotope), 65% yield, yellow crystals, m.p. 135°C (explosive), ^1H NMR (acetone- d_6): 7.52–8.38 (m, 9H, arom.), 9.92 (s + d, 1H, CH=N). IR: 1091 ($\nu(\text{ClO}_4)$). Found: C 38.0, H 2.3, $\text{C}_{13}\text{H}_{10}\text{ClO}_4\text{Te}$ calc: C 38.8, H 2.5%.

N-4'-Bromophenylbenzoisotellurazolium perchlorate (XVII; X = CH, R = H, R' = 4- BrC_6H_4 ; containing 50% of ^{15}N isotope), 72% yield, yellow-orange crystals, m.p. 144–148°C (explosive), ^1H NMR ($\text{DMSO}-d_6$): 7.80–8.67 (m, 8H, arom.), 10.30 (s + d, 1H, CH=N). IR: 1133 cm^{-1} ($\nu(\text{ClO}_4)$). Found: C 31.8, H 1.9. $\text{C}_{13}\text{H}_9\text{BrClNO}_4\text{Te}$ calc: C 32.1, H 1.8%.

Starting from 4,4'-dimethyl-2-chlorotellurenylazobenzene [11], *6-methyl-2-N-(4'-methylphenyl)benzotelluradiazolium perchlorate* (XVII; X = N, R = CH_3 , R' = 4- $\text{CH}_3\text{C}_6\text{H}_4$) was prepared in 65% yield described by a procedure previously. Red crystals, m.p. 139–141°C (explosive), ^1H NMR (CF_3COOD): 1.95 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 6.79–8.26 (m, 7H, arom.). IR: 1100 cm^{-1} ($\nu(\text{ClO}_4)$). Found: C 38.9, H 2.7. $\text{C}_{14}\text{H}_{13}\text{ClN}_2\text{O}_4\text{Te}$ calc: C 38.5, H 3.0.

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