Insertion of an Oxygen Atom between Tellurium Atoms upon Oxidation of a Diaryl Telluride with $NOBF_4$ or $(CF_3SO_2)_2O/O_2$: Dicationic Bis[diaryltellurium(IV)] Oxide**

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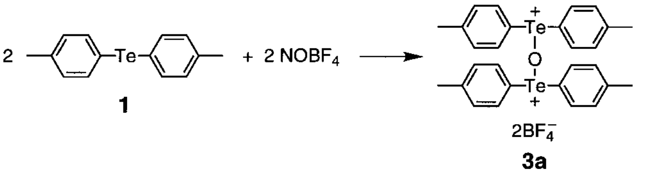
Despite the large body of information on σ-bonded dichalcogen dications formed by intramolecular reactions through transannular effects,[1] bond formation by intermolecular reactions has received much less attention. Musker et al. pointed out that the radical cation prepared from 1,5-dithiacyclooctane and one equivalent of nitrosyl tetrafluoroborate ($NOBF_4$) would be dimerized in the solid state to form an intermolecular dithia dication.[2] As part of our aim to synthesize an intermolecularly formed ditellurium dication and multitellurium dications,[3] we report here on the preparation, crystal structure, and properties of the bis[diaryltellurium(IV)] oxide dication in **3**,[4, 5] which was apparently produced for the first time by insertion of the oxygen atom of nitrogen monoxide or an O_2 molecule between two tellurium atoms by various chemical oxidations of diaryl telluride.

Treatment of bis(4-methylphenyl) telluride (**1**) with one equivalent of $NOBF_4$ in dry CH_2Cl_2/CH_3CN at $-40\,^\circ C$ under an Ar atmosphere for 30 min afforded bis[bis(4-methylphenyl)tellurium(IV)] oxide bis(tetrafluoroborate) (**3a**) in quantitative yield (Scheme 1). The ^{125}Te NMR spectrum of **3a** in CD_3CN shows a peak at $\delta = 1301.3$, that is, shifted downfield by 646 ppm relative to the signal for **1**. This remarkable downfield shift is characteristic of a cationic species. The FAB-MS spectrum of **3a** exhibits a parent peak at $m/z = 655$ for M^+ $[M^+ = (M - 2BF_4^- + F^-)^+]$. Compound **3a** reacted with four equivalents of thiophenol under an Ar atmosphere to give **1** and diphenyl disulfide in quantitative yields. Treatment of **3a** with aqueous NaOH quantitatively afforded bis(4-methylphenyl) telluroxide (**2**). These results undoubtedly support the formation of **3a** with the dicationic Te-O-Te bond, in which the Te atoms are threefold coordinated (Scheme 1).

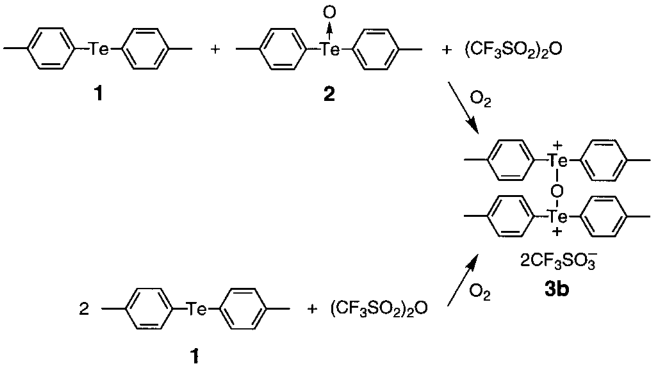


Scheme 1. Synthesis of **3a** from **1** and $NOBF_4$.

Bis[(halo)diaryltellurium(IV)] oxides having tetracoordinate Te atoms are generally prepared by the thermal dehydration of diaryltellurium hydroxy halides and their derivatives.[4–6] The present reaction is not of this type. It proceeds instantaneously at $-40\,^\circ C$ under anhydrous and anaerobic conditions. In the presence of two equivalents of $H_2{}^{18}O$, the reaction gave **3a**, whose FAB-MS spectrum showed no incorporation of an ^{18}O atom. These results suggest that nitrogen monoxide (NO), which is generated from the redox reaction of **1** with $NOBF_4$, would be a source of the oxygen atom in **3a**. Thus, a radical cation of **1** or the corresponding ditellurium dication formed by dimerization would react with NO to give **3a**.[7, 8]

The hypothesis that NO is the oxygen source was partly confirmed by the reaction of **1** with one equivalent of ethyl nitrite (10 wt% in ethanol) as a synthetic equivalent of NO in the presence of one equivalent of $Cu(ClO_4)_2 \cdot 6H_2O$ as an oxidizing agent in CH_3CN under an Ar atmosphere. A similar dicationic Te-O-Te bonded species was formed in quantitative yield.

The similar dicationic bis[diaryltellurium(IV)] oxide ditriflate (**3b**) was quantitatively obtained by the reaction of a 1:1 mixture of **1** and **2** with one equivalent of triflic anhydride (Tf_2O) in dry CH_3CN between $-40\,^\circ C$ and room temperature under an O_2 atmosphere for 1 h (Scheme 2).[9] Treatment of **1** with 0.5 equivalents of Tf_2O under the same conditions also afforded **3b** in quantitative yield. In solution, the triflate as a counterion is not expected to be coordinated to the Te atoms, because the chemical shift of **3b** in the ^{125}Te NMR spectrum ($\delta = 1288.4$) is almost the same as that of **3a**. Under an Ar atmosphere neither of the reactions shown in Scheme 2 afforded **3b**; hence, molecular oxygen is essential for the formation of **3b**.[10] The following mechanism seems to be plausible. The reaction of **2** with Tf_2O may lead to a diaryl(trifluoromethanesulfonyloxy)telluronium salt[11] or diaryltellurium ditriflate,[12] which reacts with **1** to afford an intermolecular ditellurium dication and two molecules of triflate. Insertion of O_2 into the resulting ditellurium dication would produce **3b**. In the other case, the reaction of **1** with Tf_2O leading to a diaryl(trifluoromethanesulfonyl)telluronium salt[13] and the subsequent reaction with the second molecule of **1** may afford the ditellurium dication and trifluoromethanesulfinate, both of which would be oxidized by O_2 to produce **3b**.



Scheme 2. Synthesis of **3b**.

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The crystal structure of **3b** was determined by X-ray diffraction analysis (Figure 1).[14] An inspection reveals several important points: 1) Molecules of **3b** associate in pairs across a center of symmetry located between the atoms O1 and O1′ (Figure 1b; the primed atoms refer to the respective symmetry-related atoms at $1-x, -y, -z$). Each of the four counterions interacts with the Te atoms of the paired dications through their O atoms in the range of 2.64–2.98 Å. These contacts are considerably shorter than the sum of the van der Waals radii (3.60 Å) of the two elements. 2) Each Te atom has a pseudo-octahedral geometry. 3) The pairs of bis[diaryltellurium(IV)] oxide dications are stacked in columns that run approximately parallel to the *a* axis. The resulting channels created by the dications are occupied by two columns of the triflate counterions.

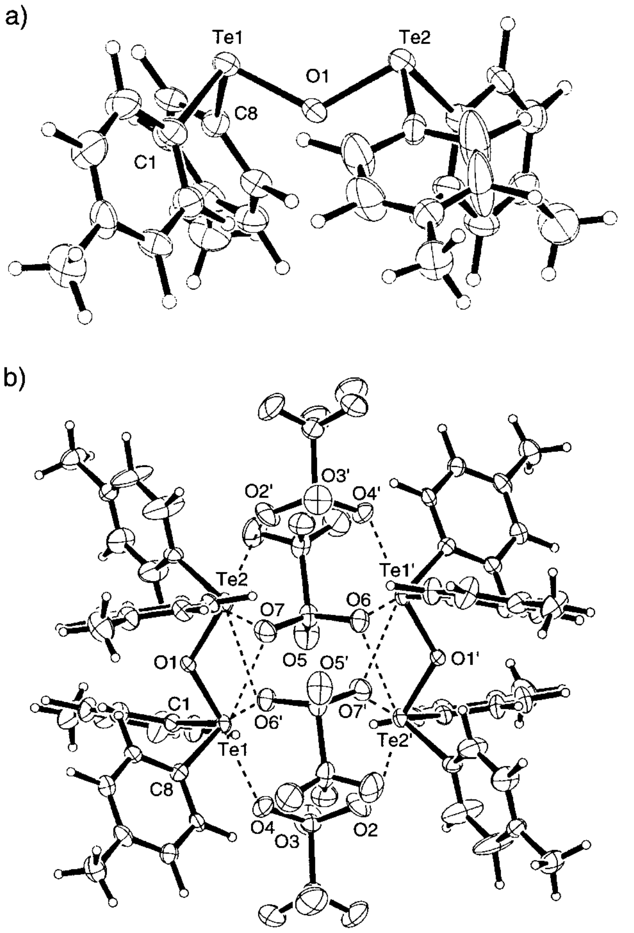

Figure 1. a) ORTEP drawing of the structure of **3b** (thermal ellipsoids represent the 30% probability level); for clarity the counterions have been removed. b) A pair of **3b** molecules with counterions. Selected bond lengths [Å] and angles [°]: Te1–O1 1.937(6), Te1 ··· O4 2.639(7), Te1 ··· O6′ 2.901(7), Te1 ··· O7 2.898(7), Te2–O1 1.957(6), Te2 ··· O2′ 2.680(7), Te2 ··· O6′ 2.977(7), Te2 ··· O7 2.922(8); Te1-O1-Te2 123.8(3), O1-Te1-C1 90.0(3), O1-Te1-C8 90.9(3), C1-Te1-C8 98.3(4), O4 ··· Te1-O1 174.4(2), O7 ··· Te1-C8 161.4(2), O6′ ··· Te1-C1 160.2(2).

In the present study we have demonstrated that NO and O_2 molecules can be the oxygen source to afford the dicationic Te-O-Te bonded species by chemical oxidations of diaryl telluride.[15]

Experimental Section

3a: To a solution of **1** (0.56 mmol) in dry CH_2Cl_2 (2 mL) at −40 °C under an Ar atmosphere was added a solution of $NOBF_4$ (0.67 mmol) in dry CH_3CN (4 mL). The resulting deep red solution was stirred for 30 min at the same temperature, during which time it became pale yellow. The reaction mixture was evaporated in vacuo to give **3a** as a white powder in quantitative yield. Recrystallization of **3a** from CH_3CN/benzene gave colorless crystals. M.p. 155–160 °C (decomp); ^1H NMR (400 MHz, CD_3CN, 25 °C): $\delta = 2.42$ (s, 6 H), 7.45, 7.65 (AB q, $J = 7.9$ Hz, 8 H); ^{13}C NMR (100 MHz, CD_3CN, 25 °C): $\delta = 21.5$, 131.0, 131.9, 133.7, 145.0; ^{19}F NMR (254 MHz, CD_3CN, 25 °C): $\delta = -150.7$; ^{125}Te NMR (126 MHz, CD_3CN, 25 °C): $\delta = 1301.3$; FAB-MS (2-nitrophenyl octyl ether matrix): m/z: 655 $[M^+]$ ($M^+ = (M - 2BF_4^- + F^-)^+$); elemental analysis calcd for $C_{28}H_{28}OTe_2 \cdot 2BF_4$: C 41.55, H 3.49; found: C 41.53, H 4.08.

3b: To a suspension of **1** (0.12 mmol) and **2** (0.12 mmol) in dry CH_3CN (2 mL) at −40 °C under an O_2 atmosphere was added triflic anhydride (0.12 mmol). The resulting homogeneous deep red solution was stirred at room temperature for 1 h, during which time it became pale orange. The reaction mixture was evaporated in vacuo to give **3b** as a white powder in quantitative yield. Recrystallization of **3b** from CH_3CN at −20 °C gave colorless single crystals that were suitable for an X-ray analysis. M.p. 273–274 °C (decomp); ^1H NMR (400 MHz, CD_3CN, 25 °C): $\delta = 2.42$ (s, 6 H), 7.45, 7.66 (AB q, $J = 7.9$ Hz, 8 H); ^{13}C NMR (100 MHz, CD_3CN, 25 °C): $\delta = 21.4$, 121.2 ($^1J_{C,F} = 317.3$ Hz), 131.0, 131.6, 133.6, 144.8; ^{19}F NMR (254 MHz, CD_3CN, 25 °C): $\delta = -79.7$; ^{125}Te NMR (126 MHz, CD_3CN, 25 °C): $\delta = 1288.4$; elemental analysis calcd for $C_{28}H_{28}OTe_2 \cdot 2CF_3SO_3$: C 38.59, H 3.02; found: C 38.40, H 2.93.

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[6] The only exception is reported by E. A. Meyers et al. The reaction of phenoxatellurine with its dinitrate in CH_2Cl_2 at room temperature gives bis(phenoxatelluronium) dinitrate: M. M. Mangion, M. R. Smith, E. A. Meyers, *J. Heterocycl. Chem.* **1973**, *10*, 543–549.

[7] The fate of the N atom of NO remains uncertain at this stage. The ESR spectrum of the reaction mixture under the same conditions did not show any signals probably owing to instability of a radical cation of **1** or a very fast reaction. For the related isolable Te^{III} radical cation of $Te[N(SiMe_3)_2]_2$, see M. Björgvinsson, T. Heinze, H. W. Roesky, F. Pauer, D. Stalke, G. M. Sheldrick, *Angew. Chem.* **1991**, *103*, 1671–1672; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1677–1678.

[8] We reported that 1,5-ditelluracyclooctane, in which the two Te atoms are juxtapositioned, reacts with two equivalents of $NOBF_4$ to give the stable ditellurium dication (H. Fujihara, T. Ninoi, R. Akaishi, T. Erata, N. Furukawa, *Tetrahedron Lett.* **1991**, *32*, 4537–4540). By dimerization of two radical cations of **1**, the present reaction may also form an intermolecular ditellurium dication which, in marked contrast, would be very unstable owing to a flexible conformation and may therefore react with NO to give **3a**.

[9] The reaction of **2** with 0.5 equivalents of Tf_2O gave **3b** in very low yield (ca. 16%). This difference may be partly explained by the

possibility that the reactivity of **2** with respect to a diaryl(trifluoromethanesulfonyloxy)telluronium salt which could be initially formed is lower than that of **1**.

[10] Both reactions in the absence of O_2 in CH_3CN were monitored by ESR spectroscopy. However, no ESR signals were detected. Even if a radical cation is formed, its concentration would be quite low.

[11] Diphenyl sulfoxide reacts with Tf_2O to form a diphenyl(trifluoromethanesulfonyloxy)sulfonium salt: B. A. Garcia, J. L. Poole, D. Y. Gin, *J. Am. Chem. Soc.* **1997**, *119*, 7597–7598.

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[13] Dimethyl sulfide reacts with Tf_2O to produce a dimethyl(trifluoromethanesulfonyl)sulfonium salt: V. G. Nenajdenko, P. V. Vertelezkij, A. B. Koldobskij, I. V. Alabugin, E. S. Balenkova, *J. Org. Chem.* **1997**, *62*, 2483–2486.

[14] Crystal structure analysis of **3b**: crystal dimensions $0.15 \times 0.25 \times 0.30$ mm, monoclinic, space group $P2_1/n$, $a = 13.318(4)$, $b = 18.319(7)$, $c = 14.871(4)$ Å, $\beta = 104.01(2)^\circ$, $V = 3520(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.76$ g cm^{-3}, $2\theta_{max} = 51.9^\circ$. Rigaku AFC-7R four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $\omega/2\theta$ scan mode, $T = 253$ K, 5330 measured reflections, Lorentzian and polarization corrections, absorption coefficient 18.5 cm^{-1}, semi-empirical absorption correction (Ψ scans; transmission factors 0.60–1.00), structure solution with direct methods (SIR92), package teXsan (1992), full-matrix least-squares refinement based on F, 2893 observed reflections ($I > 3.0\sigma(I)$), 424 parameters, hydrogen atoms included but not refined, $R = 0.036$, $R_w = 0.039$, residual electron density 0.51 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100642. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[15] For elements of Group 15 (E = Sb, Bi), insertion of O_2 molecules into E–E bonds occurs: a) F. Calderazzo, R. Poli, G. Pelizzi, *J. Chem. Soc. Dalton Trans.* **1984**, 2365–2369; b) H. J. Breunig, T. Krüger, E. Lork, *Angew. Chem.* **1997**, *109*, 654–655; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 615–617.

Enhanced Electronic Conjugation in Anthracene-Linked Porphyrins

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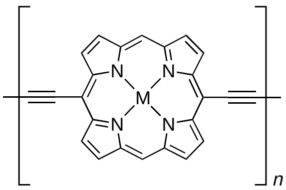
Porphyrin polymers such as **1** (side chains omitted for clarity) exhibit exceptionally strong third-order nonlinear optical (NLO) behavior[1] because of their extensive electronic conjugation. This is potentially useful for fabricating electro-optic modulators for telecommunications. However even in **1** the NLO coefficient $\chi^{(3)}$ is not high enough for practical devices, so we are exploring routes to more conjugated porphyrin polymers. Müllen et al. have shown that the incorporation of 9,10-anthrylene units in conjugated polymers reduces the band-gap by reducing the energy difference between the aromatic and quinoidal resonance structures.[2] Thus the anthracene/porphyrin polymer **2** might be expected to be more conjugated than **1** because the anthrylene units stabilize the quinoidal/cumulenic resonance structure **3**. 9,10-Diethynylanthracene units are also interesting because of their intense fluorescence and potential electroluminescence; several conjugated polymers containing these units have been synthesized.[3] Here we demonstrate, using model oligomers, that 9,10-diethynylanthracene spacers enhance the conjugation between *meso*-linked porphyrins better than butadiyne, 1,4-diethynylbenzene or 1,4-diethynylthiophene bridges.



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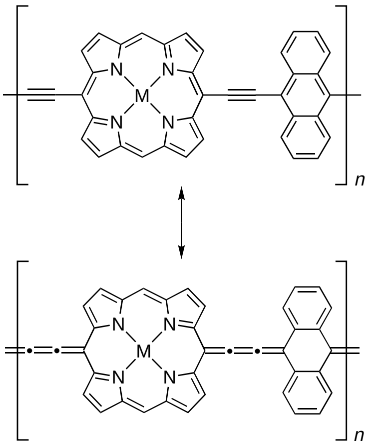

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3

There are numerous examples of molecules containing porphyrins and anthracenes linked either directly[4] or through saturated bridges,[5] polyenes,[6] and aromatic linkages.[7] Few of these exhibit much porphyrin–anthracene conjugation, because most unsaturated bridges twist out of plane with the porphyrin to avoid steric clashes. Alkynyl substituents are the only effective way of making conjugated connections to the *meso* position of a porphyrin. Marx and Breitmaier[8] have reported a porphyrin connected through alkynyl substituents to the 1-position of anthracene, but this does not allow resonance of the type postulated for **2** ↔ **3**.

To develop a synthetic route to conjugated anthracene/porphyrin oligomers we first synthesized **4** by the two routes shown in Scheme 1. Condensation of aldehyde **5**[9] with 3,5-

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