Triple-helix formation is also photoregulated when an azobenzene is included within the oligo(T) block. As shown in Table 1, [*trans*-**TXT$_{10}$/t/a**] is more stable than [*cis*-**TXT$_{10}$/t/a**] ($\Delta T_m = 9.2\,^{\circ}C$). In this case, however, the triple helices (even of the *trans*-isomer) are less stable than either [**T$_{11}$/t/a**] or [**T$_{12}$/t/a**]. The intercalation of the *trans*-azobenzene to form the triple helix is less efficient here, mainly because it accompanies partial breakdown of the adjacent Hoogsteen-type base-pairs.

Experimental Section

The modified oligonucleotides (**XT$_{13}$**, **XT$_{11}$**, and **TXT$_{10}$**) were synthesized as described in ref. [3a]. The ratio of the *trans* to the *cis*-isomer in the reaction mixtures was determined by reversed-phase HPLC. In order to isomerize the azobenzene, the solutions were irradiated for 30 min by light from a 150 W xenon lamp through an appropriate filter (UV-D36C and L-42 filters from Asahi Technoglass Corporation for the *trans* → *cis* and *cis* → *trans* isomerization, respectively). The T_m value was determined from the maximum in the first derivative of the melting curve. The absorbance at 280 nm, which is the isosbestic point of the *trans*- and the *cis*-azobenzene, was monitored at pH 7.0 (10 mM 2-[4-(2-hydroxylethyl)-1-piperazinyl] ethanesulfonic acid (HEPES) buffer) on a JASCO model V-530 spectrophotometer equipped with a programmable temperature controller. The temperature ramp was $1.0\,^{\circ}C\,min^{-1}$. The concentrations of **t**, **a**, and the modified oligo(T) were 2.2, 2.0, and 2.4 μM, respectively.[10] In the T_m measurement of the *cis* isomer, intermittent UV irradiation was used in order to suppress the thermal *cis* → *trans* isomerization. The fraction of the *cis* isomer was kept almost constant (at 70%) throughout the measurement.

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[1] a) J. W. Szewczyk, E. E. Baird, P. B. Dervan, *Angew. Chem.* **1996**, *108*, 1596–1598; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1487–1489; b) U. Asseline, N. T. Thuong, C. Hélène, *New J. Chem.* **1997**, *21*, 5–17, and references therein; c) A. Ferdous, H. Watanabe, T. Akaike, A. Maruyama, *Nucleic Acids Res.* **1998**, *26*, 3949–3954; d) S. Bevers, T. P. O'Dea, L. W. McLaughlin, *J. Am. Chem. Soc.* **1998**, *120*, 11004–11005; e) U. Sehlstedt, P. Aich, J. Bergman, H. Vallberg, B. Nordén, A. Gräslund, *J. Mol. Biol.* **1998**, *278*, 31–56; f) F. Godde, J.-J. Toulmé, S. Moreau, *Biochemistry* **1998**, *37*, 13765–13775; g) F. D. Lewis, Y. Zhang, X. Liu, N. Xu, R. L. Letsinger, *J. Phys. Chem. B* **1999**, *103*, 2570–2578; h) F. M. Orson, J. Klysik, D. E. Bergstrom, B. Ward, G. A. Glass, P. Hua, B. M. Kinsey, *Nucleic Acids Res.* **1999**, *27*, 810–816.

[2] a) C. Giovannangeli, L. Perrouault, C. Escudé, N. Thuong, C. Hélène, *Biochemistry* **1996**, *35*, 10539–10548; b) S. A. Ciftan, H. H. Thorp, *J. Am. Chem. Soc.* **1998**, *120*, 9995–10000; c) P. Aich, S. Ritchie, K. Bonham, J. S. Lee, *Nucleic Acids Res.* **1998**, *26*, 4173–4177; d) F.-X. Barre, C. Giovannangeli, C. Hélène, A. Harel-Bellan, *Nucleic Acids Res.* **1999**, *27*, 743–749.

[3] a) H. Asanuma, T. Ito, M. Komiyama, *Tetrahedron Lett.* **1998**, *39*, 9015–9018; b) H. Asanuma, T. Ito, T. Yoshida, X. Liang, M. Komiyama, *Angew. Chem.* **1999**, *111*, 2547–2549; *Angew. Chem. Int. Ed.* **1999**, *38*, 2393–2395.

[4] For other studies on the introduction of azobenzene to oligonucleotides, see: a) K. Yamana, A. Yoshikawa, H. Nakano, *Tetrahedron Lett.* **1996**, *37*, 637–640; b) K. Yamana, A. Yoshikawa, R. Noda, H. Nakano, *Nucleosides Nucleotides* **1998**, *17*, 233–242.

[5] The modified oligonucleotides **XT$_{13}$**, **XT$_{11}$**, and **TXT$_{10}$** were used as mixtures of the two diastereomers with respect to the chirality of the **X** residue. The attempts to separate these two diastereomers by HPLC have been unsuccessful.

[6] Nordén et al. concretely correlated the sign and magnitude of the CD, induced on the binding of small molecules to DNA, to the manner of the binding: a) M. Kubista, B. Åkerman, B. Nordén, *J. Phys. Chem.* **1988**, *92*, 2352–2356; b) R. Lyng, A. Rodger, B. Nordén, *Biopolymers* **1992**, *32*, 1201–1214; c) P. Pradhan, B. Jernström, A. Seidel, B. Nordén, A. Gräslund, *Biochemistry* **1998**, *37*, 4664–4673.

[7] The rotatory strength of the [*trans*-**XT$_{13}$/t/a**] triple helix was determined to be −0.15 Debye–Bohr magnetons (DBM). This is in marked contrast with the large positive values for the well-known groove binders dibutylproflavine (+1.77 DBM) and netropsin (+1.31 DBM) (data from ref. [6]).

[8] The middle point of the λ_{max} versus T plot is 25 °C (Figure 3B), which is identical with the T_m of the triple helix, within experimental error.

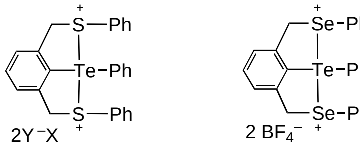
[9] J. M. Robertson, *J. Chem. Soc.* **1939**, 232–236.

[10] The **t**:**a** ratio was kept at 1:1 in order to ensure that there exists no free **a**, which should form a duplex with the modified oligo(T) and perturb the T_m measurement.

Synthesis of Dicationic Telluranes by Remote Oxidation through a π-Conjugated System**

Katsutoshi Kobayashi, Soichi Sato, Ernst Horn, and Naomichi Furukawa*

Recently, we synthesized a sulfanyl-substituted tellurium cation as a bis-tetrafluoroborate (**1a**) and a bis-trifluoromethanesulfonate salt (**1b**) and the analogous selenyl-substituted tellurium cation as bis-tetrafluoroborate salt (**2**) by the reaction of tellurides or telluroxides having heteroatoms at the 2,6-positions of the benzene ring with oxidizing agents such as $NOBF_4$ and $NOPF_6$, or with $(CF_3SO_2)_2O$. In these reactions, the tellurium atom should be directly oxidized by the oxidizing agent to form the corresponding dicationic tellurane.[1] Furthermore, we have reported on remote oxygen migration between sulfur atoms in the monooxide of 1,4-bis(methylsulfanyl)benzene in the presence of CF_3CO_2H. This reaction is proposed to proceed not via a quinoid-type intermediate but via the bis(dithia dication) dimer.[2]



1a (X= BF_4^-)
1b (X= $CF_3SO_3^-$)

2

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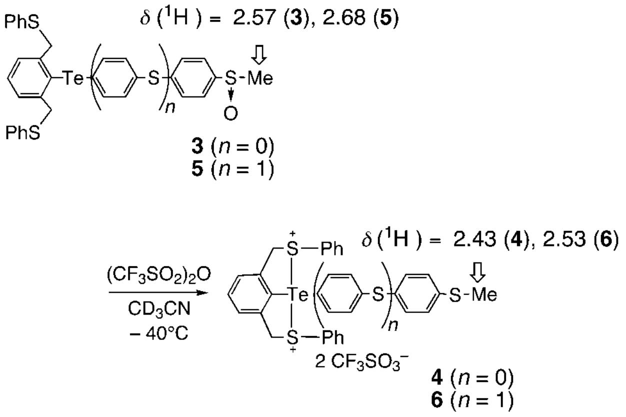
On the basis of these results, we treated the tellurides with a sulfinyl substituent at the 4-position of the tellurophenyl ring with $(CF_3SO_2)_2O$ with the aim of obtaining the corresponding dicationic telluranes. Apparently, deoxygenation of the sulfinyl group is promoted by the telluride group and the (phenylsulfanyl)methyl groups in 2,6-position by the concerted donation of electrons. We propose that this process involves a novel remote oxidation reaction with electron transfer through π-conjugated bonds, similar to the domino effect. Here we report the synthesis of dicationic telluranes and the reaction mechanisms of these novel remote oxidation reactions.

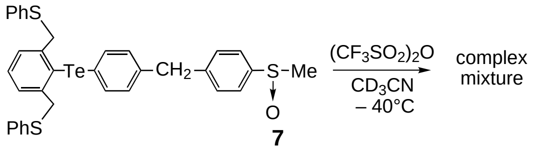
The telluride **3** was prepared by the oxidation of the dicationic tellurane derived from 2,6-bis[(phenylsulfanyl)methyl]phenyl 4-(methylsulfanyl)phenyl telluride with *m*-chloroperbenzoic acid (*m*-CPBA) and then reduction of the dicationic part with PhSH.[3] Treatment of **3** with 1.2 equivalents of $(CF_3SO_2)_2O$ (Tf_2O) at −40 °C in CD_3CN readily afforded the corresponding stable dicationic tellurane **4** (Scheme 1). In the ^1H NMR spectrum of **4**, the benzylic methylene protons give rise to two sets of AB quartet signals at $\delta = 4.42, 5.26$ ($J = 18$ Hz) and 4.90, 5.24 ($J = 17$ Hz) in a 1:1 ratio. These signals were assigned to the asymmetric bicyclic form of the dicationic tellurane. These results demonstrate that the two sulfur atoms are directly coordinated to the central tellurium atom. The ^1H NMR signal of the methyl protons is shifted upfield from $\delta = 2.57$ to 2.43 on adding Tf_2O. This indicates that the sulfur atom of the methylsulfinyl substituent is reduced to form a methylsulfanyl substituent. The ^{125}Te chemical shift of **4** is $\delta = 1343$, which is similar to that of the corresponding dicationic tellurane **1b** ($\delta = 1331$) without a *p*-sulfanylmethyl group. The dicationic tellurane **4** was characterized by elemental and spectroscopic (EI-MS; ^1H, ^{13}C, and ^{125}Te NMR) analyses, and the structure was determined by X-ray crystallographic analysis.[4]



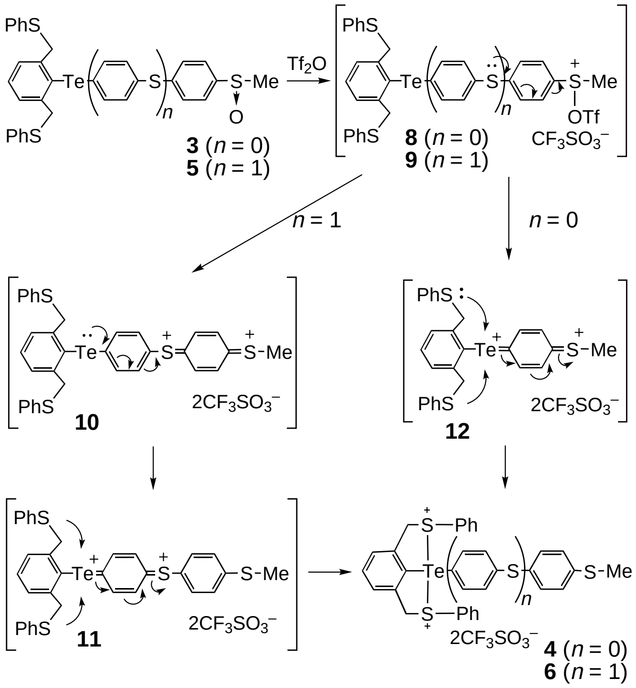
Scheme 1. Reaction of **3** or **5** with Tf_2O.

The telluride **5**, which has an extended π-conjugated system, was prepared similarly to **3** and treated with Tf_2O to give the corresponding dicationic tellurane **6** with a methylsulfanyl substituent (Scheme 1). The structure of this dicationic tellurane was assigned by EI-MS and ^1H, ^{13}C, and ^{125}Te NMR spectroscopy. The ^1H NMR spectrum of **6** also shows two sets of AB quartet signals that are shifted downfield relative to those of **5**. The ^{125}Te NMR signal of **6** was observed at $\delta = 1339.7$.

To determine the mechanism of this type of reaction, the telluride **7**, without a π-conjugated system between the tellurium atom and the sulfinyl substituent, was treated with Tf_2O. This reaction gave only a complex mixture, and no dicationic tellurane was observed. This result supports the notion that the π-conjugated system is necessary to transfer electrons from the tellurium atom to the sulfur atom of the sulfinyl group and also rules out intermolecular electron transfer between two molecules of the telluride.



On the basis of this result, the reaction is considered to proceed by the mechanism shown in Scheme 2. In the case of **3**, the formation of the intermediate sulfonium salt **8** may be followed by reaction with Tf_2O, and the corresponding dicationic compound **4** could be produced by the conformational change of the two (phenylsulfanyl)methyl groups via the dicationic quinoid-type compound **12** as an intermediate or a transition state, formed by electron transfer from the tellurium atom to the sulfur atom of the methylsulfinyl group. The reaction proceeds too rapidly to observe **8** or **12** by NMR spectroscopy.



Scheme 2. Proposed mechanism for the reaction of **3** or **5** with Tf_2O.

A similar mechanism is predicted for the reaction of the telluride **5** with Tf_2O. As shown in Scheme 2, electron transfer occurs from the tellurium atom to the sulfur atom of the methylsulfinyl group by means of intramolecular π-conjugation between the benzene rings and the sulfur atom. This sulfur atom is important in connecting the π-conjugated system on the tellurium atom with the sulfur atom of the methylsulfinyl group.

In summary, we have found a new remote oxidation reaction through π-conjugated bonds for the formation of dicationic telluranes.

Experimental Section

4: Tf_2O (4 μL, 0.024 mol) was added to a solution of **3** (14 mg, 0.02 mol) in dry CH_3CN at −40 °C under an argon atmosphere. The resulting solution was stirred for 12 h at room temperature, and the solvent was then evaporated to give **4** (15 mg, 86%) as the residue. M.p. 118–123 °C (decomp); ^1H NMR (270 MHz, CD_3CN): $\delta = 2.43$ (s, 3H), 4.42, 5.26 (AB q, $J = 18$ Hz, 2H), 4.90, 5.24 (AB q, $J = 17$ Hz, 2H), 6.86–8.23 (m, 17H, Ar-H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 14.5$, 39.1, 39.9, 124.2, 124.9, 127.6, 128.7, 130.0, 131.0, 131.5, 132.2, 132.3, 132.8, 132.9, 134.8, 136.2, 147.5, 147.9, 150.5; ^{125}Te NMR (126 MHz, CD_3CN, 25 °C): $\delta = 1343.2$ (relative to Me_2Te); EI-MS: m/z: 574 $[M^+ - 2\,TfO^-]$; elemental analysis calcd for $C_{29}H_{24}F_6O_6S_5Te$: C 40.02, H 2.78; found: C 39.79, H 2.99.

6: M.p. 145–150 °C (decomp); ^1H NMR (400 MHz, CD_3CN): $\delta = 2.53$ (s, 3H), 4.45, 5.15 (AB q, $J = 18$ Hz, 2H), 5.03, 5.22 (AB q, $J = 17$ Hz, 2H), 6.81–8.16 (m, 21H, ArH); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 15.0$, 39.5, 40.3, 120.1, 122.3, 123.3, 124.6, 125.3, 127.7, 128.3, 129.0, 130.3, 131.0, 131.6, 132.1, 132.5, 132.8, 132.9, 135.3, 136.2, 136.5, 143.2, 147.7, 148.1, 150.0; ^{125}Te NMR (126 MHz, CD_3CN): $\delta = 1339.7$ (relative to Me_2Te); FAB-MS: m/z: 831 $[M^+ - TfO^-]$.

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[1] a) A. B. Bergholdt, K. Kobayashi, E. Horn, O. Takahashi, S. Sato, N. Furukawa, M. Yokoyama, K. Yamaguchi, *J. Am. Chem. Soc.* **1998**, *120*, 1230–1236; b) N. Furukawa, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2571–2591.

[2] a) K. Kobayashi, T. Obinata, N. Furukawa, *Chem. Lett.* **1997**, 1175–1176; b) K. Kobayashi, E. Koyama, K. Namatame, T. Kitaura, C. Kono, M. Goto, T. Obinata, N. Furukawa, *J. Org. Chem.* **1999**, *64*, 3190–3195.

[3] Since 2,6-bis[(phenylsulfanyl)methyl]phenyl 4-(methylsulfanyl)phenyl telluride has four chalcogen atoms which are susceptible to oxidation, it is difficult to selectively oxidize the S atom of the methylsulfanyl group. Therefore, the compound was initially converted to the corresponding dicationic tellurane, which was then treated with *m*-CPBA to oxidize the sulfur atom of the methylsulfanyl group. The telluride **3** was obtained by reduction of the dicationic tellurane with two equivalents of thiophenol.

[4] X-ray structure analysis of **4**: Selected bond lengths [Å] and angles [°]: Te1-S1 2.637(1), Te1-S2 2.730(1), S1-Te1-S2 160.60(3). Crystal data: $C_{29}H_{26}F_6O_7S_5Te$, crystal dimensions $0.75 \times 0.30 \times 0.25$ mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.822(3)$, $b = 16.531(3)$, $c = 10.187(2)$ Å, $\alpha = 99.65(1)$, $\beta = 103.81(2)$, $\gamma = 92.63(2)°$, $V = 1737.7(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.70\ g\,cm^{-3}$, $2\theta_{max} = 60.0°$. Rigaku AFC-7R four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $\omega/2\theta$ scan mode, $T = 296$ K, 11109 measured reflections, Lorentzian and polarization corrections, absorption coefficient 12.3 cm^{-1}, semiempirical absorption correction (ψ scans; transmission factors 0.93–1.00), structure solution with direct methods, program package teXsan(1992), full-matrix least-squares refinement on F, 7190 observed reflections ($I > 3.0\sigma(I)$), 440 parameters, hydrogen atoms included but not refined, $R = 0.041$, $R_w = 0.053$, residual electron density 1.07 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-136391. 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).

Pyrone-Like Structures as Novel Oxygen-Based Organic Superbases[**]

Dimas Suárez, J. Angel Menéndez, Enrique Fuente, and Miguel A. Montes-Morán[*]

The concept of strong organic basicity is generally associated with proton sponge compounds.[1] An unexpectedly high pK_a value was reported for the parent compound of this class, 1,8-bis(dimethylamino)naphthalene (DMAN) by Alder et al. more than 30 years ago.[2] This high thermodynamic basicity arises from the interaction of basic groups in close proximity to each other. In contrast, the hydrophobic shielding of the basic centers in DMAN derivatives results in a weak nucleophilic character and low rates of proton transfer,[3] attributes which ultimately will decide the utilization of the organic superbases as proton scavengers in chemical and biochemical processes.[4]

The term "pyrone-like structures" (as used in this communication) was originally adopted by Voll and Boehm[5] to define a type of oxygen-containing functionality capable of acting as a basic center on carbon surfaces.[6] According to their definition[5] these pyrone-like compounds are combinations of non-neighbouring carbonyl and ether oxygen atoms at the edges of a graphene layer. Thus, this generic designation would include not only γ-pyrone derivatives but also structures where the two oxygen atoms are located in different rings. Although there are no reported data, within our knowledge, for these latter pyrone-like systems, we have recently demonstrated using ab initio calculations that they show a broad spectrum of base strength (around 12 pK_a units).[7]

Herein we report a systematic ab initio study of the gas-phase proton affinities (PAs) of mono- and polycyclic pyrone-like structures **1**–**7**. The structural and energetic results for compounds **1**–**7** will be compared with those of the prototypical proton sponge DMAN **8**, and thus support the title proposal of pyrone-like structures as organic superbases. In addition, some specific aspects justify the novelty of and interest shown in the comparison of these relatively simple organic compounds with conventional proton sponges. First, the proton acceptor atom corresponds to a neutral carbonyl oxygen atom in contrast to the predominance of amine and imine functionalities in the nitrogenated superbases. Second-

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