

Synthesis and X-ray crystal structure of 1-cyano-3,3-bis(trifluoromethyl)-1,3-dihydro-1 λ^3 ,2-benziodoxole, a stable cyanoiodolane

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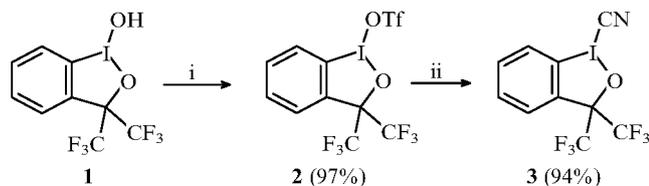
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Stable, crystalline cyanoiodolane **3** has been prepared in two steps by sequential reactions of 1-hydroxy-3,3-bis(trifluoromethyl)-1,3-dihydro-1 λ^3 ,2-benziodoxole **1** with trimethylsilyltriflate and then with cyanotrimethylsilane; X-ray structure analysis reveals a distorted T-shaped structure for iodine with an endocyclic I–O bond distance of 2.117 Å, which is significantly shorter than usual in C-substituted benziodoxole derivatives.

The cyano derivatives of polyvalent iodine, especially phenyl(cyano)iodonium triflate PhI(CN)OTf and (dicyano)iodonium triflate (CN)₂IOTf, have found synthetic application as efficient iodonium transfer reagents useful in the synthesis of various alkynyl-, alkenyl-, aryl-, and heteroaryl- iodonium salts.^{1–5} However, only few examples of cyanoiodinanes have been reported in the literature and details of their structure remain unknown because of the low thermal stability and air-sensitivity of these compounds. In this communication we wish to report the preparation and X-ray structure determination of the novel cyanoiodolane **3**, in which polyvalent iodine is

stabilized due to incorporation into a five-membered heterocycle.

Cyanoiodolane **3** can be prepared in two steps starting from 1-hydroxy-3,3-bis(trifluoromethyl)-1,3-dihydro-1 λ^3 ,2-benziodoxole **1** (Scheme 1). In the first step, benziodoxole **1** was converted in high yield into triflate **2** by treatment with trimethylsilyltriflate in CH₂Cl₂ at room temperature. Compound **2** was isolated as a moderately hygroscopic, but thermally stable yellow microcrystalline product and identified by spectral data and elemental analysis.[†] In the second step, triflate **2** was treated with cyanotrimethylsilane to afford



Scheme 1 Reagents and conditions: i, Me₃SiOTf, CH₂Cl₂, 25°C, 10–20 min; ii, Me₃SiCN, MeCN, 0°C, 10–12 min.

[†] Preparation and characterization of **2**. To a stirred suspension of 3,3-bis(trifluoromethyl)-1,3-dihydro-1 λ^3 ,2-benziodoxol-1-ol **1**⁹ (0.200 g, 0.52 mmol) in dry CH₂Cl₂ (15 ml), trimethylsilyltriflate (0.11 ml, 0.57 mmol) was added under nitrogen at room temperature. After stirring 10–20 min, the resulting clear yellow solution was evaporated and product **2** was collected and dried under vacuum; yield (0.260 g, 97%), mp 143–145°C; IR (KBr)/cm⁻¹: 3089 (Ar), 1377, 1258, 1185, 1105, 1037, 952; ¹H NMR (CDCl₃) δ : 7.93 (m, 2H), 7.77 (m, 2H); ¹⁹F NMR (CDCl₃) δ : -75.50 (s, CF₃) and 78.60 (s, CF₃SO₃⁻); (Found: C, 22.45; H, 1.14; I, 23.76. Calc. for C₁₀H₄IF₉O₄S·H₂O: C, 22.40; H, 1.13; I, 23.67%.)

cyaniodolane **3** in high yield.[‡] Cyaniodolane **3** was isolated as a thermally stable, non-air-sensitive, white, crystalline solid and identified by spectral data and elemental analysis.[§] Particularly characteristic were ¹³C NMR spectra displaying all the respective signals of the carbon skeleton and the cyano carbon at $\delta = 87.47$ ppm. In the case of previously reported cyaniodolanes, signals of the cyano carbons were observed at $\delta = 68.3$ ppm for PhI(CN)OTf,³ $\delta = 124.75$ ppm for PhI(CN)₂⁶ and at $\delta = 32.1$ ppm for (NC)₂IOTf.⁵ The IR absorption of the cyano group was observed at 2154 cm^{-1} , which is close to the CN absorption of previously reported cyaniodolanes.

To elucidate the structural features for this novel cyaniodolane **3**, an X-ray investigation was carried out on a single crystal grown from chloroform.[¶] The ORTEP and the key structural parameters for compound **3** are shown in Figure 1. The structural data revealed the distorted T-shaped geometry expected for hypervalent iodine with an endocyclic C(2)–I–O bond angle of 78.2° and a C(1)–I–O bond angle of 169.5° . The lengths of the bonds to the iodine atom, I–C(1) (2.167 Å), I–O (2.117 Å) and I–C (2) (2.112 Å) are within the range of typical single covalent bond lengths in non-cyclic organic derivatives of polyvalent iodine.[†] However, these parameters are substantially different from the literature data on structure of the known cyclic, C-substituted benzoiodoxole derivatives.^{7,8} In particular, the endocyclic I–O bond in **3** is significantly shorter than usual in C-substituted benzoiodoxoles, while the I–C(1) bond is slightly longer. For example, in 1-alkynyl-1,3-dihydro-1 λ^3 ,2-benzoiodoxole-3(1*H*)-

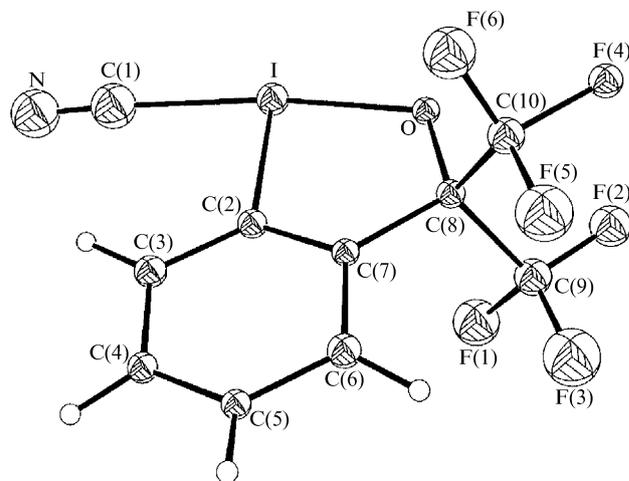


Figure 1 ORTEP representation of the molecular structure of cyaniodolane **3**. Selected bond lengths (Å) and bond angles ($^\circ$): I–O 2.117(4), I–C(1) 2.167(6), I–C(2) 2.112(5), N–C(1) 1.128(8), O–C(8) 1.369(7), C(7)–C(8) 1.538(8), C(8)–C(9) 1.60(3), C(8)–C(10) 1.48(3); O–I–C(1) 167.7(3), O–I–C(2) 78.9(2), C(1)–I–C(2) 89.3(2), I–O–C(8) 116.9(4), I–C(1)–N 175.0(3), I–C(2)–C(3) 122.7(4), I–C(2)–C(7) 113.9(4), O–C(8)–C(7) 111.5(5), C(2)–C(7)–C(8) 118.0(4), O–C(8)–C(9) 114.0(2), O–C(8)–C(10) 102.0(2).

one the endocyclic I–O bond has a length of 2.34 Å and the I–C(1) bond length is 2.03 Å.⁷ An even greater difference in I–O (2.478 Å) and I–C (2.105 Å) bond distances is observed in 1-phenyl-1,3-dihydro-1 λ^3 ,2-benzoiodoxol-3-one.⁸

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[‡] *Preparation of 3*. To a stirred solution of 1-trifluoromethanesulfonyloxy-3,3-bis(trifluoromethyl)-1,3-dihydro-1 λ^3 ,2-benzoiodoxole (**2**; 1.0 g, 1.95 mmol) in dry MeCN (25 ml), cyanotrimethylsilane (0.5 ml, 3.5 mmol) was added under nitrogen at 0°C . After stirring 10–20 min, two drops of pyridine were added and the reaction mixture was concentrated under reduced pressure. The resulting clear, colourless oil was redissolved in ether and filtered through a short silica gel plug. The ether solution was evaporated, and the product collected and dried under vacuum. The product was recrystallized from ether–hexane; yield (0.727 g, 94%). X-ray quality single crystals were obtained by slowly evaporating a solution of **3** in CHCl_3 in an open air container.

[§] *Characterization data for 3*: mp $161\text{--}164^\circ\text{C}$; IR (KBr)/ cm^{-1} : 3089 (Ar), 2154 (CN), 1466, 1384, 1268, 1187, 1144, 1129, 1113, 970; ¹H NMR ($\text{CDCl}_3/\text{CD}_3\text{CN}$, 10:1) δ : 8.22 (m, 1H), 7.83 (m, 3H); ¹³C NMR ($\text{CDCl}_3/\text{CD}_3\text{CN}$, 10:1) δ : 134.20, 132.17, 129.86, 129.36 (Ar), 122.71 [q, $J = 290\text{ Hz}$, $\text{C}(\text{CF}_3)_2$], 110.69, 87.47 (CN), 82.39 [septet, $J = 30.5\text{ Hz}$, $\text{C}(\text{CF}_3)_2$]. (Found: C, 30.02; H, 1.18. Calc. for $\text{C}_{10}\text{H}_4\text{IF}_6\text{ON}\cdot\text{H}_2\text{O}$: C, 30.40; H, 1.02%.)

[¶] *Crystal data for 3*. $\text{C}_{10}\text{H}_4\text{F}_6\text{ION}$, $M_r = 395.04$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 8.562(2)$, $b = 16.259(4)$, $c = 8.575(2)$ Å, $V = 1193.67\text{ Å}^3$, $Z = 4$, $D_c = 2.198\text{ g cm}^{-3}$, $F(000) = 744$. Crystal dimensions $0.43 \times 0.32 \times 0.29\text{ mm}$. Data were collected at 291 K on an Enraf-Nonius CAD-4 diffractometer, $\text{MoK}\alpha$ -radiation, $\lambda = 0.71073\text{ Å}$. The intensities of 1146 non-zero reflections were measured; 983 of the unique reflections in the range $4.0 < 2\theta < 50.0^\circ$ were used for the structure analysis (scan technique $\theta/2\theta$, scan width $0.800 + 0.340(\tan\theta)\text{ deg}$, data collection position: bisecting with $\omega = 0$). No decay correction was applied. Absorption correction: empirical. Minimum % transmission: 88.5. Maximum % transmission: 99.9. Average % transmission: 95.4. Highest peak in final difference Fourier 0.862 e/Å^3 . Summary of final least squares refinement: weighting scheme - non-Poisson contribution; ignorance factor, $P = 0.05$; data rejected if $I < 3.00\sigma(I)$; 981 observations; 172 variables; data to parameter ratio 5.70; shift to error ratio 0.028; error in an observation of unit weight (GOF) 1.1660; R factor 0.0271; weighted R factor 0.0330. All hydrogen atoms were calculated and included in the final least-squares refinements. All calculations were carried out using the MOLEN software distributed by Enraf-Nonius. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *Mendeleev Communications*, Issue 1.