J. Am. Chem. Soc. 1993, 115, 9808-9809

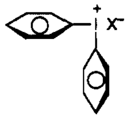
Preparation and Characterization of a Macrocyclic Tetraaryltetraiodonium Compound, cyclo$(Ar_4I_4)^{4+}\cdot 4X^-$. A Unique, Charged, Cationic Molecular Box†

Peter J. Stang* and Viktor V. Zhdankin

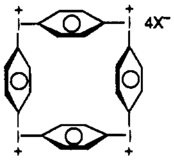
Department of Chemistry
The University of Utah
Salt Lake City, Utah 84112

Received June 9, 1993

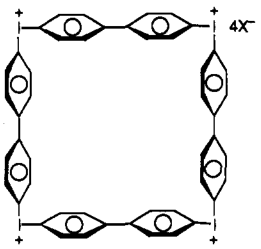
The rich chemistry of multicoordinated iodine compounds with at least one organic ligand continues to fascinate chemists since the discovery of $PhICl_2$ by Willgerodt over 100 years ago.[1-3] The T-shaped geometry of iodine(III) compounds, with circa 90° bond angles as exemplified by the classical diaryliodonium species **1**, described as 8-I-2 (for monocationic salts **1**) or as 10-I-3 (for neutral) species in the Martin–Arduengo formalism,[4] predicts the existence[5] and likely formation of novel macrocyclic tetraiodonium salts, as illustrated by **2**–**4**. Such charged molecular boxes are inherently interesting as well as of considerable potential use as anion hosts,[6] in molecular electronics,[7] in nanoscale machinery,[8] and in providing insight into noncovalent bonding interactions.[9] In this communication we report the synthesis and characterization of the first example of a macrocyclic tetraaryltetraiodonium salt (**3**).



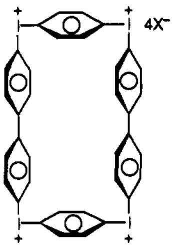
1



2



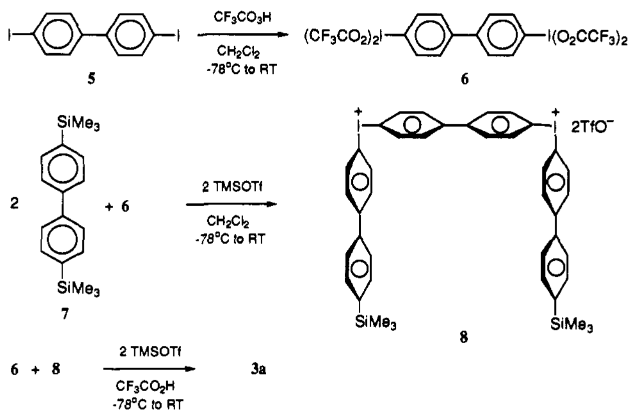
3



4

3a: X = TfO; **3b**: X = BPh_4;
3c: X = Cl; **3d**: X = I

Scheme I



Tetraiodonium triflate **3a** was prepared as outlined in Scheme I. Oxidation of commercial 4,4′-diiodobiphenyl (**5**) with CF_3CO_3H (prepared[10] from $(CF_3CO)_2O$ and 80% H_2O_2) gave **6** in 77% yield.[11] Reaction of **6** with 2 equiv of **7** and Me_3SiOTf, respectively, gave bisiodonium triflate salt **8** in 86% isolated yield.[12] Reaction of **8** with **6** in CF_3CO_2H followed by slow addition of Me_3SiOTf gave, after workup, a yellow oil consisting of **3a** and acyclic oligomers. When this yellow oil was dissolved in CH_3OH, addition of CH_2Cl_2 resulted in the precipitation of the acyclic oligomeric material. Addition of diethyl ether to the residual mother liquor precipitated crude **3a** (40%). Recrystallization of crude **3a** from methanol/ether (2–3 times) yielded analytically pure **3a**[13] in 10–15% isolated yield as a stable, off-white, microcrystalline solid.

Cyclotetraaryltetraiodonium triflate **3a** is characterized by spectral, analytical, and chemical means.[13] Specifically, the elemental analysis is consistent with the composition of **3a**. The FAB mass spectrum shows a small (0.6%) peak at $m/z = 1563$ that corresponds to the molecular ion of the cationic portion $[M - 1TfO^-]^+$ of **3a**. Likewise, the peak at 707 (5%) corresponds to the doubly charged cation $^1/_2[M - 2TfO^-]^{2+}$ with a correct HRMS.[13] The ^1H NMR spectrum consists of two broad doublets in a 1:1 ratio at 8.05 and 7.56 ppm, respectively, where the downfield signal corresponds to the ortho hydrogens and the signal at 7.56 ppm to the meta hydrogens of the biphenyl units. The ^{13}C NMR displays four signals, corresponding to the *ipso*-C–I$^+$, 116.2 ppm, *m*-C, 130.2 ppm, *o*-C, 135.9, and *p*-C, 141.6 ppm of the biphenyl units, as well as a quartet at 120.8 ppm due to the fluorine-coupled signal of the C of the CF_3SO_3 counterions. The

---

† Dedicated to the memory of Paul G. Gassman.

(1) Willgerodt, C. *J. Prakt. Chem.* **1886**, *33*, 155.

(2) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH Publishers, Inc.: New York, 1992.

(3) Reviews: Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274. Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365. Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431. Merkushev, E. B. *Russ. Chem. Rev.* **1987**, *56*, 826. Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. Ochiai, M.; Nagao, Y. *Kyokai Yuki Gosie Kagaku Kyeokaishi* **1986**, *44*, 660. Varvoglis, A. *Synthesis* **1984**, 7099. Koser, G. F. In *The Chemistry of Functional Groups, Suppl. D*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1983; Chapters 18 and 25, pp 721–811 and 1265–1351.

(4) Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(5) Boldyrev, A. I.; Zhdankin, V. V.; Simons, J.; Stang, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 10569.

(6) Reviews: *Host Guest Complex Chemistry/Macrocycles*; Vögtle, F., Webber, E., Eds.; Springer-Verlag: Berlin, 1985. *Inclusion Phenomena and Molecular Recognition*; Atwood, J. L., Ed.; Plenum: New York, 1990.

(7) *Molecular Electronic Devices*; Carter, F., Ed.; Marcel Dekker: New York, 1987.

(8) Bradley, D. *Science* **1993**, *259*, 890. Amato, I. *Ibid.* **1993**, *260*, 753. Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304; **1988**, *27*, 89.

(9) Lindsey, J. S. *New J. Chem.* **1991**, *15*, 153. Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vincent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193. Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795.

(10) Yagupolskii, L. M.; Maletina, I. I.; Kondratenko, N. V.; Orda, V. V. *Synthesis* **1978**, 835.

(11) **6**: mp 195–200 °C dec. IR (CCl_4, cm^{-1}): 3095, 3061, 1693, 1564, 1371, 1211, 1217, 1153, 993. ^1H NMR (δ, $CF_3CO_2H/CDCl_3$ 1/1): 8.42 (d, $J = 8.3$, 4H), 7.88 (d, $J = 8.4$, 4H). ^{19}F NMR (δ, $CF_3CO_2H/CDCl_3$ 1/1): −78.9 (s, CF_3CO_2). Anal. Calcd for $C_{20}H_8I_2O_8F_{12}$: C, 28.00; H, 0.94; I, 29.58. Found: C, 27.59; H, 1.02; I, 29.14.

(12) **8**: mp 255–260 °C dec. IR (CCl_4, cm^{-1}): 3090, 3064, 2958, 1474, 1384, 1235, 1168, 1026, 990. ^1H NMR (δ, DMSO-d_6/$CDCl_3$ 1/3): 8.05 (d, $J = 8.2$, 4H), 8.00 (d, $J = 8.3$, 4H), 7.6–7.45 (m, 16H), 0.21 (s, 18H, $2Me_3Si$). ^{19}F NMR (δ, DMSO-d_6/$CDCl_3$ 1/3): −78.3 (s, CF_3SO_3). Mass spectrum (FAB) *m/z*: 1005 (55) $[M - TfO^-]^+$, 428 (21) $1/2[M - 2TfO^-]^{2+}$; HRMS for $C_{43}H_{42}SSi_2I_2O_3F_3$ $[M - TfO^-]^+$ calcd 1005.043 239, found 1005.039 139. Anal. Calcd for $C_{44}H_{42}S_2Si_2I_2O_6F_6$: C, 45.76; H, 3.67. Found: C, 45.25; H, 3.58.

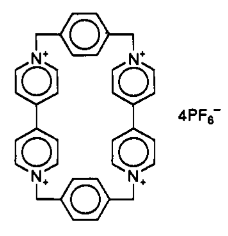
(13) **3a**: mp 274–276 °C dec. IR (CCl_4, cm^{-1}): 3086, 3057, 1471, 1383, 1240, 1158, 1025, 985. ^1H NMR (δ, DMSO-d_6/$CDCl_3$ 1/3): 8.05 (d, $J = 8.7$, 16H), 7.56 (d, $J = 8.7$, 16H). ^{13}C NMR (δ, DMSO-d_6/$CDCl_3$ 1/3): 141.6, 135.9, 130.2, 116.2 (all Ar), 120.8 (quart, $J = 319$ Hz, CF_3). ^{19}F NMR (δ, DMSO-d_6/$CDCl_3$ 1/3): −78.13 (s, CF_3SO_3). Mass spectrum (FAB) *m/z*: 1563 (0.6) $[M - TfO^-]^+$, 1415 (0.6) $[M - 2TfO^- + H^+]^+$, 707 (5) $1/2[M - 2TfO^-]^{2+}$; HRMS for $C_{50}H_{32}S_2I_4O_6F_6$ $[M - TfO^-]^{2+}$ calcd 1413.767 20, found 1413.771 86. Anal. Calcd for $C_{52}H_{32}S_4I_4O_{12}F_{12}$: C, 36.47; H, 1.88; I, 29.64; S, 7.49. Found: C, 36.34; H, 1.92; I, 29.66; S, 7.42.

0002-7863/93/1515-9808$04.00/0

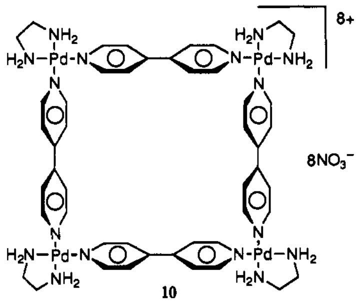
presence of the ionic $CF_3SO_3^-$ counterions is confirmed by the signal at −78 ppm in the ^{19}F NMR, as well as characteristic IR absorptions at 1240, 1158, and 1025 cm^{-1}.

Anion exchange of **3a** with $NaBPh_4$, NaCl, or NaI in methanol results in species **3b–d**, respectively. Unfortunately, **3c** is completely insoluble in all common solvents, and **3b,d** are only sparingly soluble. Nevertheless, treatment of **3c** with CF_3SO_3H regenerates **3a** that is identical in all respects with authentic material. Compound **3b** has spectral and physicochemical properties consistent with the proposed structure and similar to **3a**.[14]

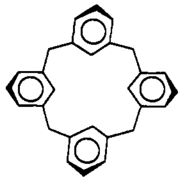
These novel charged molecular boxes **2–4** are related to the recently reported[15] cyclobis(paraquat-*p*-phenylene) macrocycle **9** and the macrocyclic polynuclear Pd complex[16] **10** as well as the more traditional, neutral cyclophanes[17] as exemplified by **11**.[18]



9



10



11

In summary, the first example of a unique, charged molecular box, a tetraaryltetraiodonium salt (**3a**), was prepared in three steps starting from commercial 4,4′-diiodobiphenyl. The properties and uses of **3a** as well as the syntheses of other members (such as **2**, **4**, and others) of this novel family of cyclic polyiodonium-based, charged molecular boxes is under active investigation and will be the subject of future reports.

Acknowledgment. This work was supported by the NCI of NIH (2RO1CA16903).

Supplementary Material Available: ^1H NMR, ^{13}C NMR, and mass spectra for **3a** (4 pages). Ordering information is given on any current masthead page.

---

(14) **3b**: (75%), mp 235–240 °C dec. IR (CCl_4, cm^{-1}): 3052, 1578, 1551, 1467, 981. ^1H NMR (δ, DMSO-d_6): 7.95 (d, J = 8.6 Hz, 16H), 7.41 (d, J = 8.6 Hz, 16H), 7.19 (m, 32H), 6.82 (m, 32H), 6.69 (m, 16H). **3c**: (82%), mp 200–205 °C dec. IR (CCl_4, cm^{-1}): 3070, 3042, 1558, 1471, 985. **3d**: (91%), mp 155–160 °C dec. IR (CCl_4, cm^{-1}): 3045, 3020, 1557, 1471, 1379, 988. ^1H NMR (δ, DMSO-d_6): 8.1 (d, J = 8.5 Hz, 16H), 7.6 (d, J = 8.5 Hz, 16H).

(15) Benniston, A. C.; Harriman, A.; Philp, D.; Stoddard, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 5298. Ashton, P. R.; Reder, A. S.; Spencer, N.; Stoddard, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 5286. Benniston, A. C.; Harriman, A. *Synlett* **1993**, 223. Ashton, P. R.; Bissell, R. A.; Spencer, N.; Stoddard, J. F.; Tolley, M. S. *Ibid.* **1992**, 914. Anelli, P. L.; Spencer, N.; Stoddard, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 5131. Philp, D.; Stoddard, J. F. *Synlett* **1991**, 445.

(16) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645. Fujita, M.; Yazaki, J.; Ogura, K. *Chem. Lett.* **1991**, 1031. Fujita, M.; Yazaki, J.; Ogura, K. *Tetrahedron Lett.* **1991**, *32*, 5589.

(17) Diederich, F. In *Cyclophanes*; Monographs in Supramolecular Chemistry 2; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, 1991. Gutsche, C. D. In *Calixarenes*; Monographs in Supramolecular Chemistry 1; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, 1989. *Cyclophanes*; Keehn, P. M., Rosenfield, R. S., Eds.; Academic Press: New York, 1983.

(18) Cram, D. J.; Tanner, M. E.; Keipert, S. J.; Knobler, C. B. *J. Am. Chem. Soc.* **1991**, *113*, 8909.