Polymorphism of ((Tosylimino)iodo)-*o*-toluene: Two New Modes of Polymeric Association for ArINTs

Ronald L. Cicero, Dong Zhao, and John D. Protasiewicz*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7078

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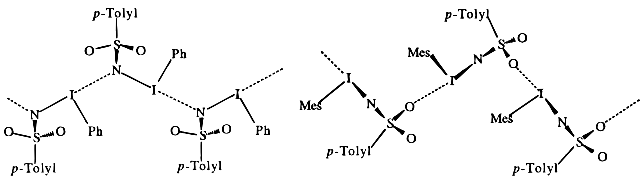
Organoiodine(III) reagents in organic and inorganic chemistry are increasingly being utilized as selective oxidants for a variety of transformations.[1−6] Amongst these reagents are iodosylbenzene (PhIO) and (tosyliminoiodo)benzene (PhINTs, Ts = $p\text{-}O_2SC_6H_4CH_3$),[7] which serve as primary oxo and tosylimino sources for many transition metal catalyzed reactions.[8] These two organoiodine(III) reagents display many similarities. Neither dissolve to any appreciable extent in nonreactive organic media, and both reversibly solvolyze in methanol forming $PhI(OMe)_2$.[9,10] Results from X-ray powder diffraction studies of PhINTs determined that the structure of PhINTs to be polymeric with asymmetric I−N···I linkages for the backbone of the polymer.[11] EXAFS data for iodosylbenzene suggested a similar structure.[11] Very recently single crystal diffraction studies of PhINTs and MesINTs (mes = 2,4,6-trimethylbenzene) were reported by Power and coworkers, which not only detailed the polymeric nature of these substances but also revealed that while PhINTs is comprised of a zigzag polymer having I−N···I connectivity (Chart 1, left), MesINTs contains a backbone assembled of O···I−N units (Chart 1, right).[12]

Chart 1



The reasons for such a dramatic shift in the intermolecular association were not clear, but did establish the potential diversity for molecular aggregation of ArINTs. Herein we report detailed structural studies of *o*-TolylINTs (**1**) which have revealed two new forms for polymeric aggregation of ArINTs in the solid state and demonstrate that the aggregation of these polymeric materials can be dramatically influenced by aromatic substitutions and by choice of particular crystal.

o-TolylINTs (**1**) was prepared analogously to PhINTs[7,13] in 65% yield.[14,15] Crystals of **1** suitable for study were grown from $MeOH/H_2O$ at 0 °C, and both triclinic (**A**) and monoclinic (**B**) forms were isolated.[16] Figure 1 (right) shows the resulting ORTEP representation for each polymorph of **1**. The I−N distances are 2.011(2) and 2.013(3) Å for **A** and **B** respectively, intermediate of the corresponding values for PhINTs and MesINTs (2.039(2) and 2.008(4) Å) and consistent with single bond values.[17] The C1−I−N angles in forms **A** and **B** are 100.3(1) and 98.7(1)° respectively, while I−C1 and N−S bond distances are 2.114(3), 2.107(3) Å and 1.604(3), 1.601(4) Å, respectively. Each iodine atom may be considered quasi-two-coordinate. The greatest difference between the two monomers lies in the orientation of the two aromatic rings of the two polymorphs. In species **A** the angle between the least squares

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(1) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365.

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

(3) Oae, S.; Uchida, Y. *Acc. Chem. Res.* **1991**, *24*, 202.

(4) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244.

(5) Koser, G. F., In *The Chemistry of the Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1983; pp 721.

(6) Varvoglis, A. *Synthesis* **1984**, 709.

(7) Yamada, Y.; Yamamoto, T.; Okawara, M. *Chem. Lett.* **1975**, 361.

(8) Lead references for ArINR as nitrene source: (a) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889. (b) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326. (c) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742. (d) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* **1991**, *56*, 6744. (e) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726. (f) Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6728. (g) Breslow, R.; Gellman, S. H. *J. Chem. Soc. Chem. Comm.* **1982**, 1400. (h) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *New. J. Chem.* **1989**, *13*, 651. (i) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc. Perkin Trans. 2* **1988**, 1517. (j) Mahy, J.-P.; Battioni, P.; Bedi, G.; Mansuy, D.; Fischer, J.; Weiss, R.; Morgenstern-Badarau, I. *Inorg. Chem.* **1988**, *27*, 353. (k) Mahy, J. P.; Bedi, G.; Battioni, P.; Mansuy, D. *Tetrahedron Lett.* **1988**, *29*, 1927. (l) Mahy, J.-P.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1986**, *108*, 1079. (m) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc. Chem. Comm.* **1984**, 1161. (n) Noda, K.; Hosoya, N.; Irie, R.; Ito, Y.; Katsuki, T. *Synlett* **1993**, 469. (o) O'Conner, K. J.; Wey, S.-J.; Burrows, C. J. *Tetrahedron Lett.* **1992**, *33*, 1001. (p) Lowenthal, R. E.; Masamune, S. *Tetrahedron Lett.* **1991**, *32*, 7373. Use of ArIO as oxo source: (q) Palucki, M.; Pospisil, P. J.; Zhang, W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 9333. (r) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571. (s) Collman, J. P.; Zhang, X.; Lee, V. J.; Uffelman, E. S.; Brauman, J. I. *Science* **1993**, *261*, 1404. (t) Ostovic, D.; Bruice, T. C. *Acc. Chem. Res.* **1992**, *25*, 314. (u) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801. (v) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (w) McMurry, T. J.; Groves, J. T., In *Cytochrome P-450: Structure, Mechanism and Biochemistry*; P. R. Ortez de Montello, Ed.; Plenum Press: New York, 1986; pp 1−28 and references therein. (x) Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9.

(9) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563.

(10) White, R. E. *Inorg. Chem.* **1987**, *26*, 3916.

(11) Carmalt, C. J.; Crossley, J. G.; Knight, J. G.; Lightfoot, P.; Martin, A.; Muldowney, M. P.; Norman, N. C.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1994**, 2367.

(12) Mishra, A. K.; Olmstead, M. M.; Ellison, J. J.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 3210.

(13) (Diacetoxyiodo)-*o*-toluene was prepared as described in: McKillop, A.; Kemp, D. *Tetrahedron* **1989**, *45*, 3299.

(14) ^{1}H-NMR (300 MHz, dmso-d_6): δ 2.23 (s, 3H), 2.41 (s, 3H), 6.95 (d, H = 7.7 Hz, 2H), 7.02 (m, 1H), 7.24 (d, J = 7.1 Hz, 1H), 7.30 (d, J = 7.8 Hz, 2H), 7.37 (m, 1H), 7.70 (d, J = 7.8 Hz, 1H). Mp: 92−96 °C dec. Anal. Calcd C, 43.42; H, 3.64; N, 3.62. Found: C, 43.47; H, 3.78; N. 3.65.

(15) Other reported ArINR: ((tosylimino)iodo)-*p*-toluene and ((tosylimino)iodo)-*p*-chlorobenzene: see ref 7; (((trifluoroacyl)imino)iodo)benzene, see ref 8m; ((tosylimino)iodo)-6-^{t}Bu,2,3,4-trimethylbenzene, see ref 8a; ((((2,5-diisopropylphenyl)sulfonyl)imino)iodo)benzene see ref 8f; (((methanesulfonyl)imino)iodo)benzene see: Abramovitich, R. A.; Bailey, T. D.; Takaya, T.; Uma, V. *J. Org. Chem.* **1974**, *39*, 340. ((Tosylimino)iodo)-*p*-fluorobenzene: Mironova, A. A.; Maletina, I. I.; Yagupolskii, L. M.; Orda, V. V.; Iksanova, S. V. *Zh. Org. Khim.* **1989**, *25*, 306.

(16) X-ray data for *o*-TolylINTs (**1**): polymorph **A**, T = 198 K, a = 7.0831(7) Å, b = 7.9520(8) Å, c = 13.2724(10) Å, α = 100.657(7)°, β = 102.558(7)°, γ = 101.635(9)°, Z = 2, triclinic, space group $P\bar{1}$, R1 = 0.0231, wR2 = 0.0655 for 2335 unique data and 207 parameters; polymorph **B**, T = 207 K, a = 12.4623(9) Å, b = 7.0343(9) Å, c = 15.706(2) Å, β = 93.131(7)°, Z = 4, monoclinic, space group $P2_1/c$, R1 = 0.0277, wR2 = 0.0739 for 1929 unique data and 215 parameters.

(17) Longer I−N distances of 2.06−2.14 Å have been noted for heterocyclic benziododazoles having at most single bonds: (a) Prout, K.; Stevens, N. M.; Coda, A.; Tazzoli, V.; Shaw, R. A.; Demir, T. *Z. Naturforsch.* **1976**, *31B*, 687. (b) Naae, D. G.; Gougoutas, J. Z. *J. Org. Chem.* **1975**, *40*, 2129. (c) Balthazor, T. M.; Godar, D. E.; Stults, B. R. *J. Org. Chem.* **1979**, *44*, 1447.

0020-1669/96/1335-0275$12.00/0

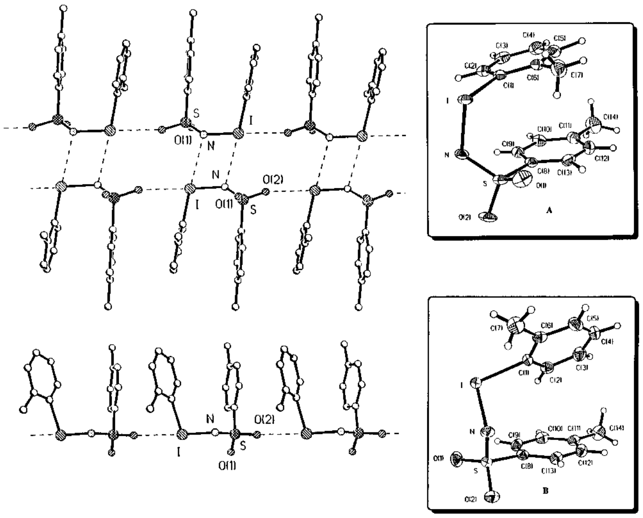


Figure 1. Top right: ORTEP of asymmetric unit of *o*-TolylINTs (**1**) triclinic form (**A**). Selected intramolecular bond distances (Å) and angles (deg): I−N, 2.011(2); I−C1, 2.114(3); N−S, 1.604(3); S−O1, 1.449(2); S−O2, 1.453(2); C1−I−N, 100.3(1); I−N−S, 114.1(1). Top left: Polymer derived by aggregation of *o*-TolylINTs (**1**) triclinic form (**A**) in the crystal lattice. Selected intermolecular bond distances (Å) and angles (deg): I···N, 3.140(2); I···O2, 2.849(2); N-I···O2, 170.23(9), N-I···N′, 7). Bottom right: ORTEP of asymmetric unit of *o*-TolylINTs (**1**) monoclinic form (**B**). Selected intramolecular bond distances (Å) and angles (°): I−N, 2.013(3); I−C1, 2.107(3); N−S, 1.601(4); S−O1, 1.443(3); S−O2, 1.439(3); C1−I−N, 98.7(1); I−N−S, 111.4(2). Bottom left: Polymer derived by aggregation of *o*-TolylINTs (**1**) monoclinic form (**B**) in the crystal lattice. Selected intermolecular bond distances (Å) and angles (deg): I···O1, 2.826(3); N−I···O2, 168.7(1); C1−I···O2, 76.8(1).

plane formed by the two aromatic rings is 9.78(5)°, while in polymorph **B** this value is 43.38(9)°.

This subtle structural difference results in a dramatic effect in the manner in which the polar ArI$^+$N$^-$Ts units aggregate in the solid state. Figure 1 (left) depicts the polymeric nature of **A** and **B**. Monomers of **1** in **A** pair into centrosymmetric dimers through long I···N interactions at 3.140(2) Å, appreciably longer than the I···N distances of 2.482(2) Å found in PhINTs. A unique ladder polymer is fabricated by association of the dimers of **1** along the a axis of the crystal via I···O interactions (2.849(2) Å). Similar I···O associations for MesINTs were determined to occur at 2.857(4) Å. The geometry at the nitrogen atoms within this environment is distorted pyramidal with values of 102.05(9), 114.1(1), and 97.9(1)° for the I···N−I, S−N−I, and I···N−S angles respectively.

Monomers of **1** within polymorph **B** lack any appreciable I···N interactions (no I···N distances <5 Å), and instead, a chain polymer more similar in nature to that of MesINTs is formed. The units of **1** are bound together along the *b* axis of the crystal by I···O contacts at 2.826(3) Å. Additionally, polymorph **B** does not form a zigzag chain polymer as in MesINTs, but a nearly linear polymer with an N−I···O2 angle of 168.7(1)° is realized. Polymorph **B** may closely be related to **A** by dimerization of the chains of **B**, but such a process would require substantial movement of the chains of **B** in the lattice, and suggests that the interchain interactions in polymorph **A** are relatively weak.

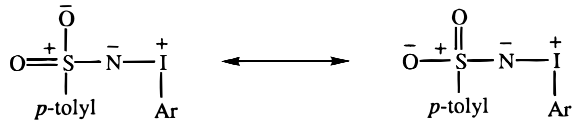
Table 1. Structural Comparisons between ArINTs

angles (deg)[a]	Ph-INTs	*o*-TolylINTs A	*o*-TolylINTs B	Mes-INTs
N−I−C1−C2 dihedral	−67.2	69.8(2)	88.3(3)	−109.7
N−I−C1−C6 dihedral	110.0	−109.6(2)	−91.2(3)	67.9
C1−I−N−S dihedral	83.1	75.2(2)	−108.0(2)	71.2
I−N−S−C dihedral	−106.4	−77.5(2)	71.7(2)	−82.9
between aromatic rings[b]	47.1	9.78(5)	43.38(9)	19.6

[a] Numbering of iodoarene ring used to match **1**. [b] Least squares plane through six carbon atoms.

Reasons for such structural diversity upon such small perturbations of the iodoarene ring probably do not lie solely in the steric hindrance of the iodine center to approach by N or O atoms of neighboring ArINTs molecules.[18] A single methyl group would not seem such a barrier to preventing **1** from adopting a structure similar to PhINTs or inflict a shift from the zigzag polymer of MesINTs to the forms described here. In all of the four structures (**A**, **B**, PhINTs and MesINTs) it is noted that the two aromatic residues favor the same sides of the molecule (in other words, all four describe a distorted U-shaped molecule). Table 1 relates some pertinent torsion angles and the angles formed between the planes of the two aryl rings. The latter values show that attractive forces between aromatic groups may be important in **1A** and MesINTs. No correlation is readily apparent between these data to explain the differing structures, however.

Preliminary calculations at both the Fenske−Hall and ab intio (STO 3-21G*) levels on ArINTs show pronounced charge localization on the I,N, S, and O atoms consistent with the resonance forms.[19]



Bond orders for both I−N and S−N were essentially the same, and close to unity. The aromatic residues may thus find it most favorable to segregate themselves away from this polar array as much as possible resulting in the observed U-shaped structures. This arrangement also allows maximal intermolecular I$^+$···O$^-$ and I$^+$···N$^-$ interactions. We are in the progress of characterizing further ArINTs compounds to determine the importance of the role that added alkyl substituents could serve to *attenuate* the electrophilicity of the iodine(III) center, and hence the degree of molecular association. Cyclic voltammetry of PhINTs, *o*-TolylINTs, and MesINTs in DMSO (Pt disk electrode, Et$_4$NClO$_4$ supporting electrolyte) exposes irreversible reduction potentials which are reduced by 70 mV across the series and that the potentials are nearly identical to those reported for Ph(OAc)$_2$, thus indicating the NTs^{2-} group to be electrochemically equivalent to two OAc$^-$ groups.[19,20]

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Supporting Information Available: Text describing the experimental details of the X-ray structures of **A** and **B**, and tables of atomic coordinates, crystallographic data, bond lengths and angles, and isotropic and anisotropic thermal parameters (13 pages). Ordering information is given on any current masthead page.

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(18) Large substituents at *ortho* positions of ArICl$_2$ inhibit, but do not prevent, intermolecular I···Cl contacts. See ref 12 and: Protasiewicz, J. D. *J. Chem. Soc. Chem. Comm.* **1995**, 1115.

(19) Zhao, D.; Ren, T.; Protasiewicz, J. to be detailed in a full report.

(20) Kokkinidis, G.; Papadopoulou, M.; Varvoglis, A. *Electrochem. Acta* **1989**, *34*, 133.