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Hypervalent Iodine Compounds

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trans Influences on Hypervalent Bonding of Aryl λ^3-Iodanes: Their Stabilities and Isodesmic Reactions of Benziodoxolones and Benziodazolones**

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Aryl λ^3-iodanes ArILL′ (L, L′: heteroatom ligands and others) adopt T-shaped geometries with a nearly linear L−I−L′ triad. It has been generally accepted that electronegative axial ligands stabilize the aryl λ^3-iodanes because of the inherent nature of the linear three-center four-electron (3c–4e) L−I−L′ bonding that places more electron density at the ends (L, L′) than at the center.[1] This idea is in a good agreement with the fact that triphenyl-λ^3-iodane, which decomposes even at −10 °C,[2] is less stable than (diacetoxyiodo)benzene, but not compatible with the labile nature of (dihydroxyiodo)benzene and the derivatives $PhI(OMe)_2$, PhI(OH)OMe,[3] and $PhI(OTf)_2$.[4a] We report herein that mutual ligand influence (*trans* influence) in hypervalent aryl λ^3-iodanes probably plays an important role in their stabilities. The structural *trans* influence of the ligands is responsible for the oxo-bridged polymeric structure of iodosylbenzene as opposed to the monomeric structure of (dihydroxyiodo)benzene,[5] the facile isomerization of phenyl-λ^3-iodanes **6** (L = L′ = NO_3, OTf, ClO_4) to the oxo-bridged dimers,[4] and the smooth rearrangement of some benziodazolones **3a** (L = RO, RCONH) to iminiobenziodoxoles **4**.[6]

The *trans* influence of a ligand in a transition-metal complex is a well-known, much argued phenomenon, defined as the extent to which that ligand weakens the bond *trans* to itself in the equilibrium state of the complex.[7] Therefore, *trans* influence is a thermodynamic concept and directly associated with the stability of the complex. Calculations by Shustorovich and Buslaev indicated that in aryl λ^3-iodanes strengthening of the I−L bond and weakening of the I−L′ bond, which are *trans* to each other, will occur monotonically with increasing donor ability of ligand L.[8] In linear L−I−L′

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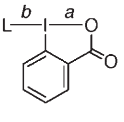

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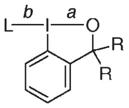
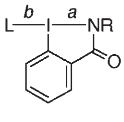
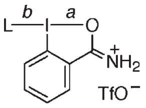


2a: R = Me
2b: R = CF$_3$



3a: R = H; **3b**: R = Cl
3c: R = CH$_2$CO$_2$Me
3d: R = CHMeCO$_2$Me



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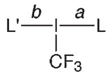

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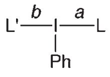

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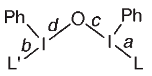

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hypervalent bonding in which the central iodine atom retains the 5s^2 lone pair, the influence of the σ-bonded ligand L is transmitted through the 5p$_\sigma$ orbital of the iodine atom, and the resulting *trans* influence is exclusively inductive in nature.

The *trans* influences are experimentally accessible by crystallographic bond-length determination, vibrational (IR) and NMR spectroscopy, and other measurements on stable complexes.[7] In conjunction with the recent increasing use of hypervalent organo-λ^3-iodanes in organic synthesis, a large number of their solid-state structures are available, and this makes it possible to evaluate the magnitude of the *trans* influence of the ligands attached to iodine(III). Comparison of I$^{\mathrm{III}}$–O (N, L, or L′) bond lengths in a variety of organo-λ^3-iodanes **1**–**7** (Tables 1–3) provides an order of structural *trans* influence of the ligands (Scheme 1). For instance, significant differences in the endocyclic I–O bond lengths *a* of **1** (L = Ph, 2.478 Å; L = cyclohexylethynyl, 2.34 Å; L = OH, 2.30 Å; Table 1, entries 2–4) illustrate a quantitative measure of the relative *trans* influence of these groups, which decreases in the order Ph > C≡C-*c*-C$_6$H$_{11}$ > OH. A similar order (C≡CPh > OCOC$_6$H$_4$-*m*-Cl > OCOCF$_3$ > NO$_3$) was reported for platinum(II) hydride complexes.[7b]

Table 1: Selected bond lengths in hypervalent λ^3-iodanes **1**–**4**.

Entry	λ^3-Iodane (L)	Bond *a* [Å]	Bond *b* [Å]	σ_I	Ref.
1	**1** (C(=PPh$_3$)CO$_2$Me)	2.484(2)	2.056(3)		[16]
2	**1** (Ph)	2.478(4)	2.105(4)	0.12	[17]
3	**1** (C≡C-*c*-C$_6$H$_{11}$)	2.34(1)	2.03(2)	0.29	[18]
4	**1** (OH)	2.30	2.00	0.33	[19]
5	**1** (CF$_3$)	2.283(2)	2.219(4)	0.38	[20]
6	**1** (OMe)	2.22(4)	1.98(4)	0.29	[21]
7	**1** (OO*t*Bu)	2.181(5)	2.039(5)		[13a]
8	**1** (OOCMe$_2$C≡CSiMe$_3$)	2.153(7)	2.032(6)		[22]
9	**1** (OAc)	2.13(2)	2.11(2)	0.42	[23]
10	**1** (OCOC$_6$H$_4$-*m*-Cl)	2.11	2.13		[24]
11	**1** (Cl)	2.091(3)	2.461(1)	0.42	[25]
12	**2a** (Br)	2.050(5)	2.6927(8)	0.45	[26]
13	**2b** (CF$_3$)	2.2014(15)	2.229(2)	0.38	[20]
14	**2b** (N$_3$)	2.130(5)	2.182(7)	0.48	[27]
15	**2b** (Br)	2.118(6)	2.5945(11)	0.45	[26]
16	**2b** (Cl)	2.110(5)	2.438(2)	0.42	[25]
17	**3a** (OAc)	2.101(5)	2.234(4)	0.42	[6a]
18	**3b** (Cl)	2.06	2.56	0.42	[12]
19	**3c** (Cl)	2.113	2.563	0.42	[28]
20	**3d** (Ph)	2.455(6)	2.133(7)	0.12	[29]
21	**4** (NHCO*i*Pr)	2.323(3)	2.010(4)	0.21	[6b]
22	**4** (O*i*Pr)	2.271(2)	1.986(2)	0.34	[6a]

Table 2: Selected bond lengths in hypervalent λ^3-iodanes **5** and **6**.

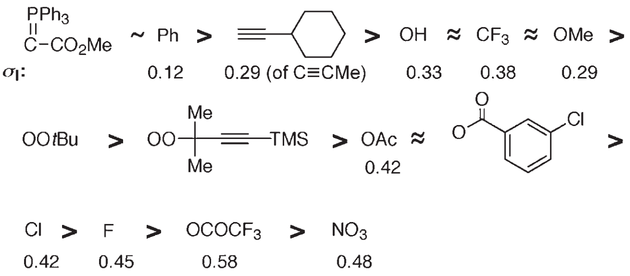
Entry	λ^3-Iodane (L, L′)	Bond *a* [Å]	Bond *b* [Å]	Ref.
1	**5** (OMe, OMe)	2.053[a]	2.053[a]	[30]
2	**5** (OMe, Cl)	1.980[a]	2.579[a]	[30]
3	**5** (Cl, Cl)	2.468[a]	2.468[a]	[31]
4	**5** (Cl, F)	2.412(3)	2.023(6)	[32]
5	**5** (Cl, OCOCF$_3$)	2.398(2)	2.219(6)	[33]
6	**5** (F, F)	1.982(2)	1.982(2)	[34]
7	**5** (OCOCF$_3$, OCOCF$_3$)	2.127[a]	2.127[a]	[35]
8	**6** (Ph, I)	2.099[b]	3.437[b]	[36]
9	**6** (Ph, Br)	2.083[b]	3.250[b]	[36]
10	**6** (Ph, Cl)	2.087[b]	3.085[b]	[36]
11	**6** (Ph, BF$_4$)	2.03[a]	2.97[a]	[37]
12	**6** (OCOCF$_3$, OCOCF$_3$)	2.162[a]	2.162[a]	[38]

[a] Average. [b] Average in halogen-bridged dimers.

Table 3: Selected bond lengths in hypervalent λ^3-iodanes **7**.

Entry	λ^3-Iodane (L, L′)	Bond *a* [Å]	Bond *b* [Å]	Bond *c* [Å]	Bond *d* [Å]	Ref.
1	**7** (OCOCF$_3$, OCOCF$_3$)	2.273[a]	2.273[a]	2.016[a]	2.016[a]	[39]
2	**7** (OCOCF$_3$, NO$_3$)	2.264(14)	2.354(15)	2.012(14)	1.999(16)	[40]
3	**7** (NO$_3$, NO$_3$)	2.32[a]	2.32[a]	2.01[a]	2.01[a]	[41]

[a] Average.

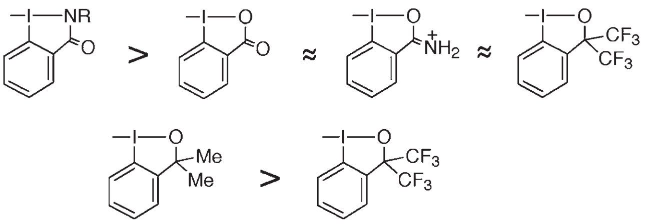


Scheme 1. Ligand order of decreasing *trans* influence in aryl λ^3-iodanes and Hammett inductive constants σ_I. TMS = SiMe$_3$.

The relative *trans* influence of halogens (I > Br ≈ Cl > F) is also determined by comparison of isomorphous pairs of λ^3-iodanes **2b** (L = Br, Cl: Table 1, entries 15 and 16), **5** (L = L′ = Cl and L = Cl, L′ = F: Table 2, entries 3 and 4), and **6** (L = Ph, L′ = I, Br, and Cl: Table 2, entries 8–10) in which the *trans* ligand is the same for both members of each pair. This ordering of halogens is in good agreement with that observed for thiourea complexes of phenyltellurium halides.[8b,9] The order of *trans* influences shown in Scheme 1 seems to correlate with Hammett inductive constants σ_I and to decrease with increasing σ_I, which is in accord with expectations based on the theory.[8] Note that some hypervalent bonds are weak and probably influenced by lattice forces.[9] The intermolecular contacts involving I$^{\mathrm{III}}$ centers that are observed frequently in the crystal structures of λ^3-iodanes will also affect the bond lengths.

The phenyl-λ^3-iodanes **6** with two strong *trans*-influencing ligands on iodine(III) (L = L′ = Ph, OH, OMe, OO*t*Bu) are predicted to be labile, because of the unfavorable mutual influences of the ligands: in fact, $PhI(OO\textit{t}Bu)_2$ decomposes even at −80 °C in dichloromethane,[10] $PhI(OMe)_2$ decomposes explosively,[11] and $PhI(OH)_2$ has never been synthesized.

The exocyclic I−OAc bond lengths *b* [2.11 Å for **1** (L = OAc) and 2.234 Å for **3a** (L = OAc); Table 1, entries 9 and 17] of five-membered λ^3-iodanyl heterocycles apparently reflect a significantly greater *trans* influence of the benziodazolone group compared to the benziodoxolone ring, as shown in Scheme 2. Furthermore, differences in I−O distances of **1** (L = MeO) and **4** (L = *i*PrO), and in I−Cl bond lengths of **1** (L = Cl) and **2b** (L = Cl), illustrate that the magnitude of the effects for the iminiobenziodoxole group and the Martin ligand are comparable to that for the benziodoxolone ring (Table 1, entries 6, 22, 11, and 16). As expected, the *trans* influence in the Martin ligand **2b** is smaller than that in the dimethyl analogue (Table 1, entries 12 and 15).

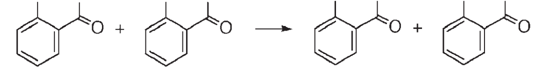


Scheme 2. The *trans* influence in iodazoles and iodoxoles.

The benziodoxolyl unit in **1**, associated with a moderate *trans* influence, accommodates *trans* ligands L with various degrees of *trans* influence, such as Ph, CCR, OH, CF_3, OMe, OO*t*Bu, OAc, Cl, $OCOCF_3$, OTs, OTf, and so on, and all of these λ^3-iodanes have been synthesized as stable compounds. On the other hand, the benziodazolyl unit in **3a**, with a larger *trans* influence, is applicable only to *trans* ligands L with weak or moderate influence, such as OAc, Cl, OTs, OTf, and so on.[6,12] Thus, alkylperoxy benziodoxolone **1** (L = OO*t*Bu) was prepared from hydroxy-λ^3-iodane **1** (L = OH) through BF_3-catalyzed ligand exchange with *tert*-butyl hydroperoxide under mild conditions,[13] while the attempted ligand exchange of (triflyloxy)benziodazolone **3a** (L = OTf) with *tert*-butyl hydroperoxide in acetonitrile did not afford peroxybenziodazolone **3a** (L = OO*t*Bu) at all, but instead produced the rearranged alkylperoxy iminiobenziodoxole **4** (78%) selectively. The highly *trans*-influencing *t*BuOO ligand probably prefers to bind to iminiobenziodoxolyl units with a moderate influence rather than to benziodazolonyl units. The rearrangement of benziodazolones to iminiobenziodoxoles, probably directed on the basis of a preferred combination of *trans* influences, was originally described by Zhdankin and coworkers in 1997.[6] They reported selective formation of rearranged iminiobenziodoxoles **4** from benziodazolone **3a** (L = TfO) by ligand exchange with the highly *trans*-influencing alkoxyl (MeO and *i*PrO) and amido (EtCONH and *i*PrCONH) groups.

To assess the energetic effect of *trans* influence in benziodoxolones **1** and benziodazolones **3a**, the isodesmic (homodesmic)[14] ligand-exchange reaction energies listed in Table 4 were calculated (see also Table S1 in the Supporting Information). Use of isodesmic reactions helps to eliminate systematic errors in ab initio calculations.[15] Stabilization in this ligand exchange can be taken as an indicator of the preferred combination, mostly controlled by *trans* influences. Large stabilization energies (> 3 kcal mol^{-1}) were obtained for combinations of a strongly *trans*-influencing group (OH or OMe) that prefers to attach to the benziodoxolone ring with a weaker one (NO_3) that prefers to bind to the benziodazolone ring. Interestingly, the stabilization energy seems to decrease with a decreasing difference in magnitude of the *trans* influences of the ligands; thus, combinations of OH/OMe and OAc/Cl groups showed small isodesmic reaction energies. These isodesmic reaction energies tend to correlate with the differences in inductive parameters σ_I of the two ligands X and Y with a correlation coefficient of $r = 0.91$ (Figure 1), but not with those in electronegativities.

Table 4: Isodesmic reaction energies for ligand exchange between benziodoxolones and benziodazolones in kcal mol^{-1} at the MP2/6-311 + G(2d, p) level of theory.



X↓ Y→	OH	OMe	OAc	Cl	F
NO_3	−3.15	−3.24	−1.83	−1.56	−0.80
F	−2.35	−2.44	−1.03	−0.76	
Cl	−1.59	−1.68	−0.27		
OAc	−1.32	−1.42			
OMe	+0.10				

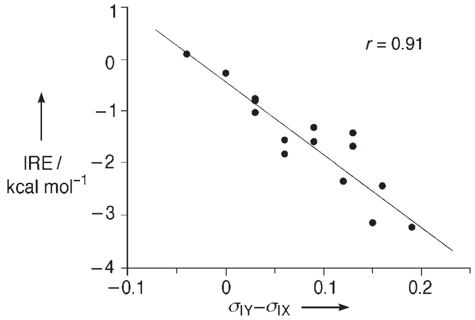


Figure 1. Calculated isodesmic reaction energies (IRE) for ligand exchange between benziodoxolones and benziodazolones versus $\sigma_{IY}-\sigma_{IX}$.

Phenyl-λ^3-iodanes **6** (L = L′ = NO_3, OTf, ClO_4) with two very weakly nucleophilic ligands on iodine(III) are generally labile and extremely moisture-sensitive,[1c,4] probably because of the unfavorable combination of *trans* influences. They have a pronounced tendency to isomerize to the more stable yellow solids of μ-oxo-λ^3-iodanes **7**, which are useful oxidants for alkenes and alkynes. A greater structural *trans* influence of μ-oxo-λ^3-iodanyl groups OI(Ph)L compared to the ligand L (NO_3, OTf, ClO_4) is responsible for this facile dimerization (Scheme 3, left). In fact, the $I-OCOCF_3$ bond lengths *trans* to

Scheme 3. *trans* influences in μ-oxo-λ^3-iodanyl groups.

the trifluoroacetoxy group of bis(trifluoroacetate) **6** (L = L′ = OCOCF$_3$) and *trans* to the μ-oxo-λ^3-iodanyl group of its μ-oxo analogue **7** are 2.162 and 2.273 Å, respectively, which indicates a greater *trans* influence of OI(Ph)OCOCF$_3$ group than of OCOCF$_3$ (Table 2, entry 12 and Table 3, entry 1). On the other hand, it seems reasonable to assume that the μ-oxo-λ^3-iodanyl group OI(Ph)L shows a reduced *trans* influence compared to the ligand L itself when L (OH, OR, Ph) is a high-*trans*-influence ligand (Scheme 3, right). These considerations seem to account for the fact that iodosylbenzene adopts a μ-oxo-bridged zigzag polymer structure,[5] as opposed to (dihydroxyiodo)benzene, which is monomeric.

In conclusion, we have shown that 3c–4e hypervalent bonding in aryl λ^3-iodanes is greatly affected by *trans* influences, which play an important role in their stability, whereby combinations of ligands with large and small *trans* influences, as in Koser's reagent Ph[I(OH)OTs], or of two moderately *trans*-influencing ligands, as in (diacetoxyiodo)benzene, are favored.

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Keywords: hypervalent compounds · iodine · iodosylbenzene · substituent effects · *trans* influence

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