

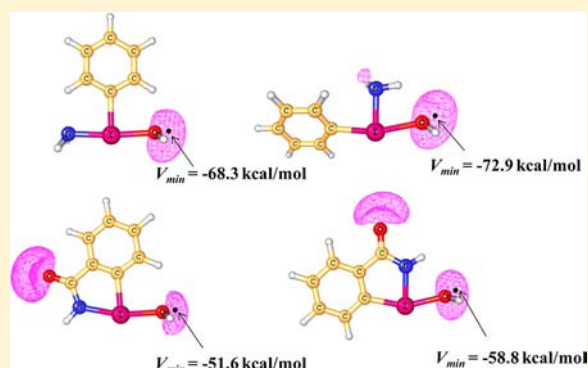
## Trans and Cis Influences in Hypervalent Iodine(III) Complexes: A DFT Study

P. K. Sajith and Cherumuttathu H. Suresh\*

Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum, India 695 019

## Supporting Information

**ABSTRACT:** Trans and cis influences of various X ligands in two isomeric structures of acyclic hypervalent compound Ph[XI(OH)] and heterocyclic  $\lambda^3$ -iodane Ph[(heterocycle)I(OH)] have been investigated on the basis of I–OH bond distance ( $d$ ), electron density at I–OH bond critical point ( $\rho$ ), I–OH stretching frequency ( $\nu$ ), and molecular electrostatic potential minimum ( $V_{\min}$ ) at the OH lone pair.  $d$ ,  $\rho$ ,  $\nu$ , and  $V_{\min}$  are found to be good parameters for quantifying trans and cis influences, and among them,  $V_{\min}$  is the most sensitive parameter. Heterocyclic  $\lambda^3$ -iodanes showed a smaller trans influence than acyclic  $\lambda^3$ -iodanes. All systems showed higher trans influence than cis influence while relative order of both is in accordance with the inductive nature of the ligands. Among the heterocyclic  $\lambda^3$ -iodanes, strong trans/cis influence is observed with N or B in the ring while P gave moderate and S gave weak trans/cis influence. Among the substituents on the cis-positioned phenyl ring in heterocyclic  $\lambda^3$ -iodanes, electron withdrawing ortho substitution significantly strengthened the hypervalent I–OH bond. The stability of a product resulting from the nucleophilic attack of  $\text{Cl}^-$  on a  $\lambda^3$ -iodane is directly correlated with the trans/cis influence of the ligands. This relationship is helpful to make good prediction on the interaction energy of a nucleophile in trivalent hypervalent iodine complex and hence useful in designing stable acyclic and heterocyclic hypervalent complexes.



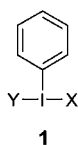
## INTRODUCTION

Hypervalent iodine complexes are well-known as versatile oxidizing agents to conduct organic transformation reactions involving the formation of new C–C and C–heteroatom bonds.<sup>1–8</sup> These complexes are environmentally friendly, mild, stable, not very toxic, and highly selective reagents.<sup>9–16</sup> Among various hypervalent iodine complexes, iodine(III) complexes are plentiful and are called  $\lambda^3$ -iodanes according to IUPAC nomenclature.<sup>15,17–21</sup> In general,  $\lambda^3$ -iodanes have a T-shaped structure wherein two electronegative ligands in the axial positions participate in a linear three-center four-electron (3c–4e) bond called the hypervalent bond while an electropositive ligand in the equatorial position experiences a normal covalent bond.<sup>10,22–26</sup> Selected examples of commonly used  $\lambda^3$ -iodanes and its derivatives are shown in Figure 1. Acyclic  $\lambda^3$ -iodanes with two heteroatom ligands as in **1** are extensively used for the functionalization of carbonyl derivatives at the  $\alpha$ -carbon atom.<sup>27–30</sup> The reaction pathways of acyclic  $\lambda^3$ -iodanes with two carbon ligands as in **2** are comparable to that of metal catalyzed reactions and are found highly useful in C–C bond formation reactions.<sup>2,31</sup> For the 3–8 systems, the heterocyclic  $\lambda^3$ -iodanes exhibit higher stability and versatile reactivity than acyclic  $\lambda^3$ -iodanes.<sup>3,32,33</sup> In almost all heterocyclic  $\lambda^3$ -iodanes, carbon atom occupies the equatorial position while hetero-

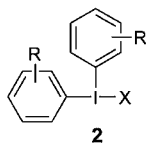
atoms (oxygen/nitrogen) occupy the axial positions,<sup>9,34</sup> and the axial and equatorial positions are connected through a five-membered ring. This geometric preference is attributed to strong orbital overlap between the aromatic ligand and the lone pair of iodine.<sup>8,35</sup> Heterocyclic  $\lambda^3$ -iodanes of the type **3** are called “benziodoxoles” wherein oxygen and iodine incorporated five-membered ring are fused to a phenyl ring. These systems have received much attention compared to the iodine–nitrogen analogue, benziodazoles (**4**).<sup>1,10,36,37</sup> A wide variety of benziodoxoles and benziodazoles derivatives have been synthesized by introducing substituents at the phenyl ring and also by incorporating various elements and various substituents in the five-membered ring (Figure 1).<sup>17,34</sup> The inclusion of other heteroatoms is represented by benziodoxathioles<sup>35</sup> **5**, cyclic phosphonate<sup>38</sup> **6**, benziodoxaborol<sup>39</sup> **7**, and benziodathiazole<sup>40</sup> **8**. Modifications on heterocycles and proper substitutions have a profound influence on the activity of hypervalent mediated reactions.<sup>36,41</sup> A recent study showed that the rate of catalytic heterocyclic  $\lambda^3$ -iodane based  $\alpha$ -tosyloxylation reaction can be enhanced drastically by steric hindrance at the ortho position of the phenyl group.<sup>42</sup>

Received: February 15, 2013

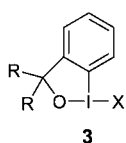
Published: May 8, 2013

Acyclic  $\lambda^3$ -iodanes

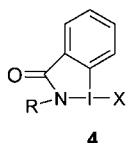
X = OTs, OH, OCOCF<sub>3</sub>, OAc, Cl, Br  
Y = OTs, OCOCF<sub>3</sub>, OSO<sub>2</sub>R, NTs<sub>2</sub>, Cl, Br



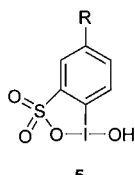
X = Cl, Br, I, OTs, OTf  
R = H, Me, etc

Heterocyclic  $\lambda^3$ -iodanes

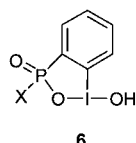
X = OH, OTs, Br, Cl, OAc, N<sub>3</sub>, CF<sub>3</sub>  
2R = O, R = CF<sub>3</sub>, Me



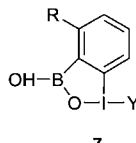
X = OAc, Cl  
R = H, Ac



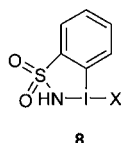
R = H, Me



X = OH, Me



R = F, H  
Y = OH, Cl, OCOCF<sub>3</sub>



X = Cl, OH, OAc

**Figure 1.** Representative examples of hypervalent iodine(III) compounds.

The stability of the hypervalent iodine complexes is directly related to the mutual trans influence of the trans ligands X and Y present at the axial positions (Figure 1).<sup>29,43–45</sup> Ochiai et al. proposed that a trans combination of X and Y is preferred if both are moderate trans influencing or one is a strong and the other is a weak trans influencing ligand.<sup>44</sup> Thus, the stability of Ph[I(OH)OTs] and Ph[I(OAc)<sub>2</sub>] can be explained on the basis of these principles wherein the ligands OH, OAc, and OTs are examples for strong, moderate, and weak trans influencing ligands.<sup>10,15,45</sup> The benzodiazolyl unit in 4 exhibits a strong trans influence which means that it can form stable compounds if trans ligand X is a moderate or weak trans influencing ligand. The benzodioxolyl unit in 3 shows moderate trans influence which can form stable complexes with X having a wide range of trans influence.

Recently we have shown that bond dissociation energies of various ligands in acyclic  $\lambda^3$ -iodanes are significantly influenced by the trans influence and mutual influence of trans ligands.<sup>45</sup> Even though both trans and cis influences can affect the ground state properties of hypervalent iodine complexes, previous studies have focused only on trans influence.<sup>44,45</sup> The present study will focus on both trans and cis influences in acyclic and heterocyclic  $\lambda^3$ -iodanes given in Figure 1. The general formula used for acyclic  $\lambda^3$ -iodanes is Ph[XI(OH)], and that of heterocyclic  $\lambda^3$ -iodanes is Ph[(heterocycle)I(OH)], and in the later, the heterocycle shares a CC bond with the phenyl ring (Figure 1). In all the systems, I–OH bond is retained because the majority of the hypervalent compounds contain I–O bond.<sup>46</sup> Further, the OH ligand will help us to monitor the trans/cis influence of various X ligands in terms of the effect it

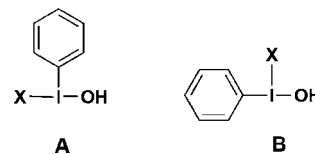
has on the properties of the I–OH bond. In the case of Ph[(heterocycle)I(OH)], structural changes as well as incorporation of other elements in the heterocycle can significantly affect the trans influence while substituents on the equatorial phenyl group can tune the cis influence. As in our previous paper,<sup>45</sup> we will utilize the atoms-in-molecule (AIM)<sup>47</sup> and molecular electrostatic potential (MESP) analysis<sup>48</sup> to understand both cis and trans influences along the 3c–4e bond. Further, stretching frequency of I–OH bond ( $\nu$ ) will be analyzed to evaluate these influences.

## COMPUTATIONAL METHODS

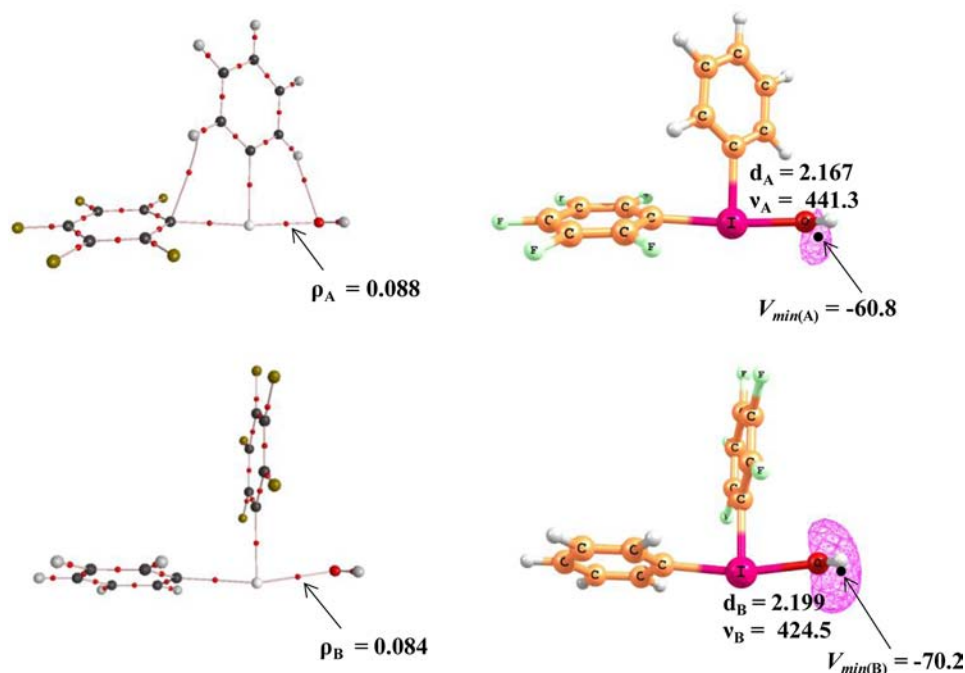
All the calculations were performed at B3LYP<sup>49,50</sup> level of DFT method by using Gaussian09<sup>51</sup> suite of quantum chemical programs. The triple- $\zeta$  basis set 6-311++G(d,p) was employed for all the atoms except iodine. Iodine is treated with the DGDZVP<sup>52</sup> basis set. This mixed basis set used for a molecule is denoted as BS1. Previous studies<sup>45,53</sup> have shown that B3LYP/BS1 level of theory can reproduce the bond length variations in iodine complexes. The wave function generated from the B3LYP/BS1 method was used for the calculation of molecular electrostatic potential (MESP).<sup>54–56</sup> Further, absolute minimum of the MESP ( $V_{\min}$ ) at the oxygen lone pair of I–OH bond was determined.<sup>57</sup> The atoms-in-molecule (AIM) analysis<sup>47</sup> was performed at B3LYP/BS1 level using AIM2000<sup>58</sup> program. A bond critical point (bcp) of the nature (3, –1) was located for I–OH bond of all  $\lambda^3$ -iodanes, and the electron density value  $\rho(r)$  at the bcp was determined.

## RESULTS AND DISCUSSIONS

**Trans and Cis Influences in Acyclic  $\lambda^3$ -Iodanes.** To compare the trans and cis influences<sup>59–66</sup> of the ligand X on the electronic properties of OH group, model systems A and B are useful (Scheme 1). In A, X has trans influence on OH while in

Scheme 1. Systems Used To Investigate the Trans and Cis Influence in Acyclic  $\lambda^3$ -Iodanes

B it has cis influence. The trans/cis influence can be monitored by I–OH bond length ( $d_A$  for A and  $d_B$  for B), the electron density at the bcp ( $\rho_A$  for A and  $\rho_B$  for B), I–OH stretching frequency ( $\nu_A$  for A and  $\nu_B$  for B), and  $V_{\min}$  at the lone pair region ( $V_{\min(A)}$  for A and  $V_{\min(B)}$  for B). In Ph[PhI(OH)], phenyl groups occupy cis and trans positions, and hence, this system can be used as a reference to monitor trans/cis influence of other ligands. An illustration of the AIM molecular graph and MESP distribution of a representative case (X = C<sub>6</sub>F<sub>5</sub>) is depicted in Figure 2. For A,  $\rho$  is larger than B which indicates that phenyl group has more influence on I–O bond in the trans position than cis position. Also, the I–OH bond of A is shorter (2.167 Å) than B (2.199 Å) meaning that iodine accepts more electron density from the OH group when C<sub>6</sub>F<sub>5</sub> is at the trans position rather than the cis position. As a result, less negative  $V_{\min}$  is observed for OH group in A than B. The quantities  $\Delta d = d_A - d_B$ ,  $\Delta\rho = \rho_A - \rho_B$ ,  $\Delta\nu = \nu_A - \nu_B$ , and  $\Delta V_{\min} = V_{\min(A)} - V_{\min(B)}$  are –0.032 Å, 0.004 au, 16.8 cm<sup>–1</sup>, and 9.4 kcal/mol, respectively, for X = C<sub>6</sub>F<sub>5</sub>. This indicates that  $V_{\min}$  is the most sensitive parameter to measure trans/cis influence. The  $d_A$ ,  $\rho_A$ ,  $\nu_A$ ,  $V_{\min(A)}$ ,  $d_B$ ,  $\rho_B$ ,  $\nu_B$ , and  $V_{\min(B)}$  values for all the systems are



**Figure 2.** QTAIM topological plot of two isomeric structures of Ph[XI(OH)] with X = C<sub>6</sub>F<sub>5</sub>. Big circles correspond to attractors, and small red circles correspond to bond critical points. The  $\rho(r)$  value (au) at the bond critical point of I–OH bond is also shown. The MESP isosurface at  $-53.3$  kcal/mol and the  $V_{\min}$  value in kcal/mol are depicted for the corresponding complexes along with I–OH bond distance (in Å) and stretching frequency of I–OH bond (in  $\text{cm}^{-1}$ ).

**Table 1.** I–OH Bond Length (in Å), Electron Density at bcp (in au), I–OH Stretching Frequency (in  $\text{cm}^{-1}$ ), and  $V_{\min}$  on the O Atom of OH (in kcal/mol) for the Structures A and B<sup>a</sup>

ligand (X)	$d_A$	$\rho_A$	$\nu_A$	$V_{\min(A)}$	$d_B$	$\rho_B$	$\nu_B$	$V_{\min(B)}$	$\Delta E_{AB}$
Et	2.249	0.076	380.3	−81.7	2.253	0.075	392.1	−77.6	−5.2
Me	2.248	0.076	382.9	−79.8	2.247	0.076	398.5	−75.9	−2.6
Ph	2.237	0.078	389.2	−77.5	2.237	0.077	389.2	−77.5	0.0
CH <sub>2</sub> Cl	2.210	0.081	403.5	−71.2	2.234	0.078	402.7	−77.2	0.4
NH <sub>2</sub>	2.188	0.085	442.2	−68.3	2.235	0.078	409.4	−72.9	9.6
CCPh	2.179	0.086	437.3	−71.2	2.187	0.086	432.3	−74.5	11.8
CCH	2.173	0.086	446.0	−65.6	2.183	0.086	429.1	−74.4	12.4
CF <sub>3</sub>	2.172	0.087	437.1	−60.9	2.188	0.085	430.4	−70.0	7.3
C <sub>6</sub> F <sub>5</sub>	2.167	0.088	441.3	−60.8	2.199	0.084	424.5	−70.2	8.9
OMe	2.144	0.092	461.0	−59.4	2.183	0.085	424.1	−64.2	17.3
CN	2.138	0.092	471.3	−51.4	2.159	0.090	459.7	−61.7	17.3
Br	2.135	0.093	466.4	−47.4	2.164	0.088	433.1	−62.2	24.4
Cl	2.122	0.095	481.3	−45.7	2.156	0.089	436.1	−59.4	26.2
OTs	2.090	0.101	505.8	−41.7	2.139	0.093	444.9	−49.0	25.6

<sup>a</sup>Energy difference between B and A ( $\Delta E_{AB}$ ) is also given in kcal/mol.

given in Table 1 along with the energy difference between the structures B and A ( $\Delta E_{AB}$ ).

On the basis of decreasing  $d_A$  values, a decreasing order of trans influence of various ligands can be obtained, *viz.*, Et  $\sim$  Me  $>$  Ph  $>$  CH<sub>2</sub>Cl  $>$  NH<sub>2</sub>  $>$  CCPh  $>$  CF<sub>3</sub>  $\sim$  CCH  $>$  C<sub>6</sub>F<sub>5</sub>  $>$  OMe  $>$  CN  $\sim$  Br  $>$  Cl  $>$  OTs.  $d_B$  values suggest an almost similar order for cis influence. The trend in the values of  $\rho_A$  and  $\rho_B$  is parallel to that of  $d_A$  and  $d_B$ , respectively, and the strong linear correlation between I–OH distance and  $\rho$  at the bcp confirms this.<sup>45</sup> The  $\nu_A$  and  $\nu_B$  also showed good correlations with I–OH distance with correlation coefficients 0.990 and 0.929, respectively (Supporting Information, Figures S1 and S2).  $d_A$  range 2.090–2.249 Å suggests a variation of 0.159 Å while  $d_B$  range 2.139–2.253 Å suggests a variation of 0.114 Å, and in

terms of electron density,  $\rho_A$  (0.076–0.101 au) values are higher than the  $\rho_B$  (0.075–0.093 au) values. Further, variation in  $\nu_A$  (380.3–505.8  $\text{cm}^{-1}$ ) is higher than  $\nu_B$  (392.1–459.7  $\text{cm}^{-1}$ ). This means that trans influence is higher than cis influence. Since trans influence is mainly affected by the inductive nature of a ligand,<sup>44,45</sup> and the relative ordering of trans and cis influences is the same for the ligands, the origin of cis influence can also be linked with the inductive effect of the X ligand.

In structure B, secondary effects such as through space interactions and steric interactions between OH and X can affect cis influence, while in A, such an effect is a constant as phenyl is always cis to OH group.  $V_{\min}$  is very sensitive to secondary effects compared to I–OH bond distance and  $\rho$  on

the I–O bond. Hence,  $V_{\min(A)}$  showed a good linear correlation<sup>45</sup> with trans bond length  $d_A$  ( $r = 0.967$ ) while  $V_{\min(B)}$  showed a poor correlation with  $d_B$  ( $r = 0.864$ ). The poor correlation of the cis systems can be attributed to the repulsive interaction between the lone pair region of OH and the lone pair region of ligands present in the cis position as well as increased steric effects in cis complexes.  $V_{\min(A)}$  fall in a broader range (–81.7 to –41.7 kcal/mol) than  $V_{\min(B)}$  values (–77.6 to –49.0 kcal/mol), indicating that trans influence is greater than cis influence. The variation in the values is 40.0 kcal/mol for **A** and 28.6 kcal/mol for **B** systems.

Compared to the reference Ph[PhI(OH)] system, only alkyl groups have showed an increase in  $d$  or decrease in  $\rho$  or  $\nu$  values and an increase in the negative character of  $V_{\min}$  while all the others showed the reverse trend. This means that alkyl group is more trans influencing than phenyl while the rest are less trans influencing than phenyl.

Negative sign of  $\Delta E_{AB}$  for  $X = \text{Me}$  and  $\text{Et}$  indicates that isomer **B** is more stable than **A**. In all other cases, isomer **A** is more stable than **B** meaning that more trans influencing phenyl group prefers the equatorial position. Since trans and cis influences show almost a parallel trend,  $\Delta E_{AB}$  shows a good linear correlation with the parameters  $d_A$ ,  $d_B$ ,  $\rho_A$  and  $\rho_B$  (Figure 3 and Supporting Information). Since the inductive effect is

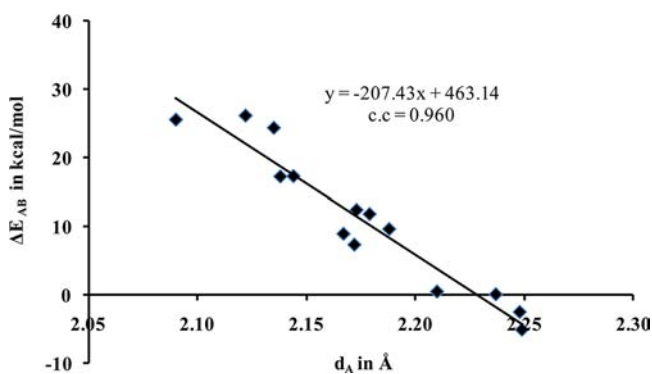


Figure 3. Plot of  $d_A$  against  $\Delta E_{AB}$  for acyclic  $\lambda^3$ -iodanes.

mainly responsible for the trans/cis influence, it is safe to say that, in acyclic  $\lambda^3$ -iodanes, the more electronegative ligand tends to occupy the axial position,<sup>5</sup> and the best examples for this are structures with F, Cl, Br, O, and N as coordinating trans atoms.

**Trans and Cis Influence in Heterocyclic  $\lambda^3$ -Iodanes.** In Figures 4 and 5, heterocyclic  $\lambda^3$ -iodanes in the categories benziodoxoles, benziodazoles, benziodoxathioles, cyclic phosphonate, and benziodoxaborol are depicted along with some six-membered systems. Structures depicted in Figure 4 have a phenyl group in the cis position, and those in Figure 5 are the corresponding trans isomers. In complex **9**, cis and trans positions are fulfilled by phenyl group, and hence it can be used as a reference system to monitor trans/cis influence of other systems. The isomer with heteroatom in the trans position is designated as **a**, and that with heteroatom in the cis position is designated as **b**. For **a** isomer, the notations  $d_a$ ,  $\rho_a$ ,  $\nu_a$ , and  $V_{\min(a)}$  are used to indicate I–OH distance,  $\rho$  at the bcp of I–OH bond, stretching frequency of I–OH bond, and  $V_{\min}$  at the OH group, respectively. Similarly the notations used for **b** isomer are  $d_b$ ,  $\rho_b$ ,  $\nu_b$ , and  $V_{\min(b)}$ . The numbers 2, 3, 4, 5, 6, 7 are used to represent the position of substituent on the phenyl ring with respect to the central iodine atom (see **9** in Figure 4).

An illustration of the AIM molecular graph and MESP distribution of a representative case **10a** and its isomer **10b** are depicted in Figure 6. The ordered quadruple (I–OH bond distance,  $\rho$ ,  $\nu$ ,  $V_{\min}$ ) for **10a** and **10b** are (2.099 Å, 0.100 au, 505.9  $\text{cm}^{-1}$ , –41.4 kcal/mol) and (2.112 Å, 0.098 au, 465.7  $\text{cm}^{-1}$ , –46.9 kcal/mol), respectively, meaning that the phenyl group in the trans position displays a high trans influence. Going from **10a** to **10b**, an increase in I–O distance reduces  $\rho$  at the I–OH bcp and  $\nu$  value as well as increases the negative character of  $V_{\min}$ . In all the cases except **13a** and **13b**, I–OH distance of **a** is smaller than that of **b** isomer (Table 2). Similarly  $\rho_a$  values are higher than  $\rho_b$  while  $V_{\min(a)}$  values are less negative than  $V_{\min(b)}$ .  $d_a$  values fall in the range 2.079–2.220 Å with a variation of 0.141 Å while variation in  $d_b$  is 0.131 Å.  $\rho_a$  values are in the range 0.080–0.103 au and  $\rho_b$  values are in the range 0.080–0.102 au.

Among the complex **9–29a**, in terms of  $d_a$ , **9** exhibits the highest trans influence (2.220 Å) and benziodoxathiole (**16a**) the lowest (2.079 Å). Similarly, in terms of  $d_b$ , the highest and lowest cis influence is exhibited by **9** and **16b** (2.089 Å), respectively. For benziodoxazole (**17a**), cyclic phosphonate (**18a**), and benziodoxaborol (**20a**),  $d_a$  is 2.139, 2.097, and 2.109 Å, respectively, while cis isomers **17b**, **18b**, and **20b** show  $d_b$  values 2.185, 2.106, and 2.126 Å, respectively. The higher trans/cis influence of benziodazolyl derivatives compared to benziodoxolyl derivatives is also evident from the compounds **10a** and **22a** where  $d_a$  values are 2.099 and 2.128 Å, respectively, and the corresponding  $d_b$  values are 2.112, and 2.172 Å, respectively.

For compounds **11a–15a**,  $-\text{CH}_2$ ,  $-\text{CF}_2$ ,  $-\text{CMe}_2$ ,  $-\text{C}(\text{CF}_3)_2$ , and  $-\text{Cyc}$  are, respectively, incorporated at position 7 in the heterocycle, and the corresponding  $d_a$  values are 2.124, 2.091, 2.128, 2.098, and 2.126 Å. Compared to **10a** where position 7 is fulfilled by a CO group, I–OH bond distances of  $-\text{CH}_2$ ,  $-\text{CMe}_2$ , and  $-\text{Cyc}$  incorporated systems are elongated by 0.025, 0.029, 0.027 Å, respectively, while that of  $-\text{CF}_2$  and  $-\text{C}(\text{CF}_3)_2$  incorporated systems are shrunken by 0.008 and 0.001 Å, respectively. Similar observations are noted for other isomers (**11b–15b**) too. When  $-\text{CO}$  group in **22a** and **22b** is replaced by  $-\text{CH}_2$  group (**24a** and **24b**), the  $d_a$  and  $d_b$  are increased by 0.046 and 0.021 Å, respectively, whereas when  $-\text{Me}$  at P atom of **18a** and **18b** is replaced by electron withdrawing  $-\text{OH}$  group (**19a** and **19b**),  $d_a$  and  $d_b$  are decreased by 0.009 and 0.008 Å, respectively. Similarly, Me substitution at N-center (**23a** and **23b**) increases  $d_a$  and  $d_b$  by 0.013 Å respectively compared to **22a** and **22b**. Compared to five-membered heterocycles, six-membered phosphate moieties in **28a** and **28b** show lower trans and cis influences, respectively, while Me substitution in six-membered **29a** and **29b** suggests strong trans and cis influences. These results clearly suggest that the nature of substituents, particularly electron releasing on the ring, significantly affects the strength of hypervalent I–OH bond.<sup>45</sup> On the basis of decreasing trans influence, various heterocyclic  $\lambda^3$ -iodanes can be arranged in the order **9** > **24a** > **26a** ~ **27a** > **29a** ~ **17a** > **23a** > **13a** ~ **22a** > **15a** ~ **11a** > **25a** > **21a** ~ **20a** > **10a** ~ **14a** ~ **18a** > **12a** > **19a** > **28a** > **16a**. An almost similar order is observed for cis influence. Similar conclusions can be obtained with  $\rho$ ,  $\nu$ , and  $V_{\min}$  data as all these correlate linearly with I–OH distance data (Supporting Information). In fact, the correlation of I–OH distance and  $\rho$  is almost perfect (correlation coefficient,  $cc > 0.99$  for **a** and **b**). The I–OH distance showed a good correlation with  $\nu$  with correlation coefficients 0.973 and 0.985,

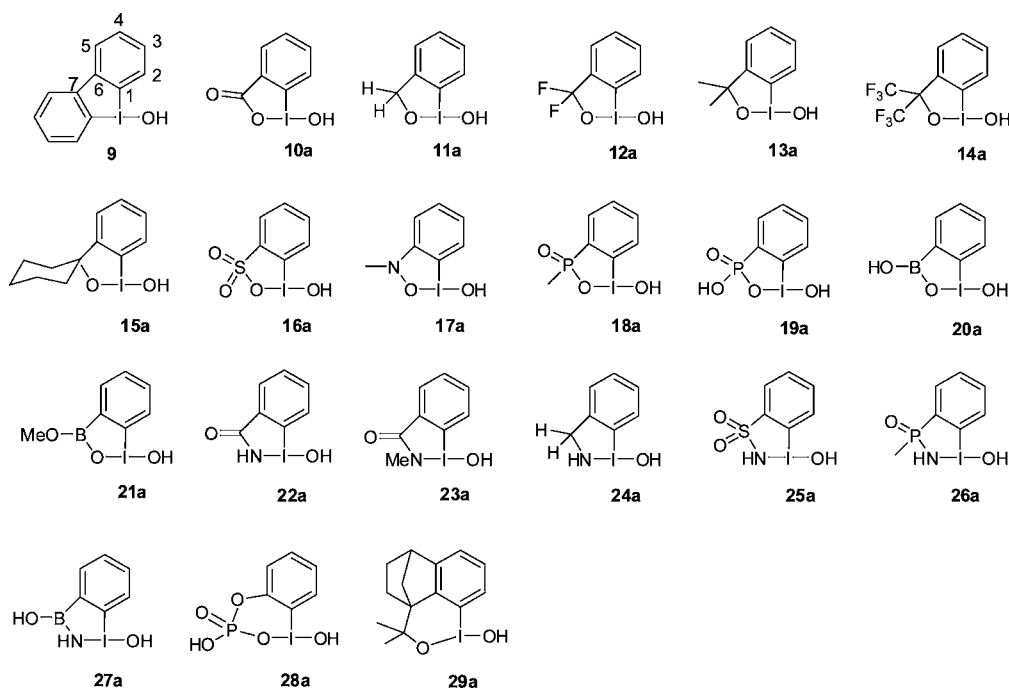


Figure 4. Heterocyclic  $\lambda^3$ -iodanes selected to study the trans influence of various heterocyclic moieties.

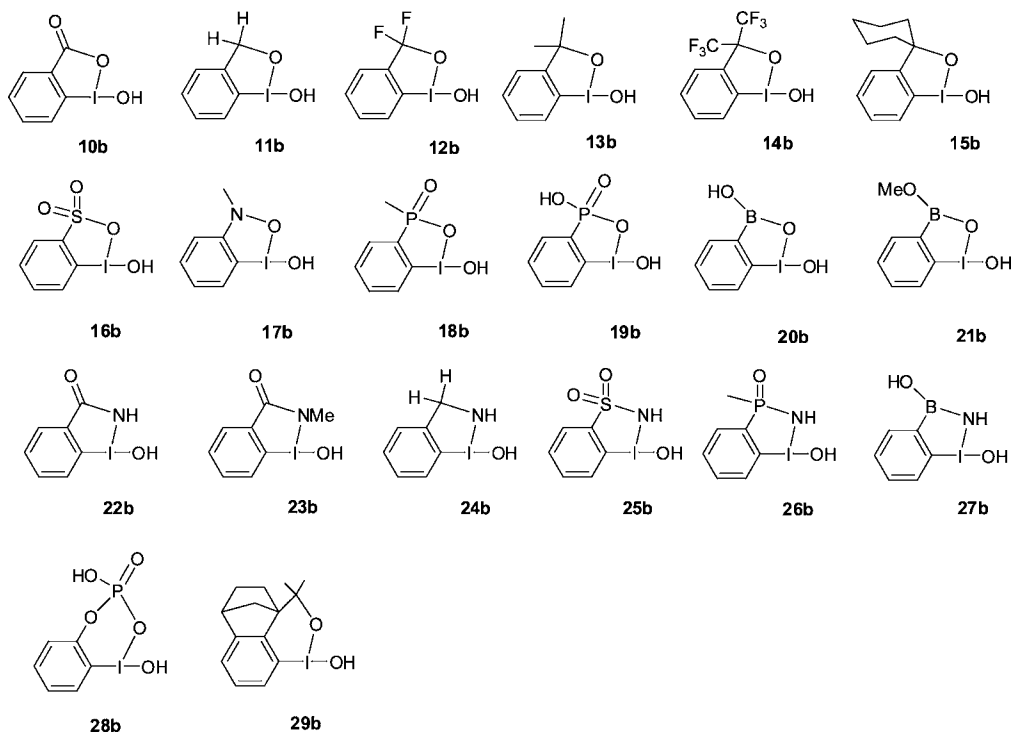
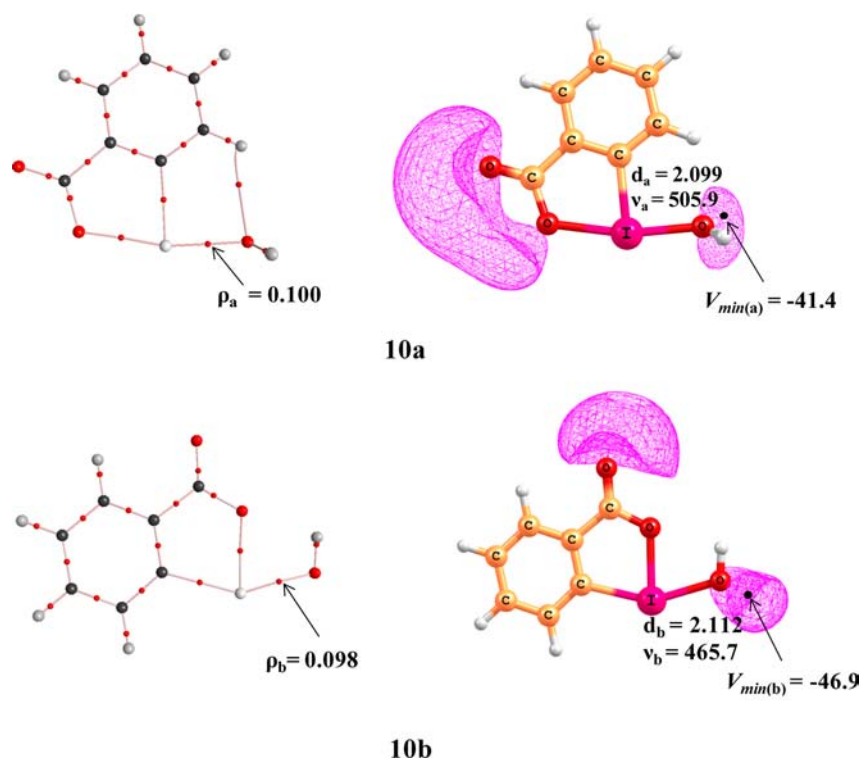


Figure 5. Heterocyclic  $\lambda^3$ -iodanes selected to study the cis influence of various heterocyclic moieties.

respectively, for **a** and **b** while that between I–OH distance and  $V_{\min}$  is 0.939 for **a** and 0.875 for **b**. Relatively large deviation from linearity shown by  $V_{\min}$  can be attributed to through space interaction of the lone pair of OH group with adjacent moieties. Compared to  $d$  and  $\rho$  data,  $\nu$  and  $V_{\min}$  show a wide range of values. The  $\nu$  range is 402–511  $\text{cm}^{-1}$  for **a** and 402–490  $\text{cm}^{-1}$  for **b** while  $V_{\min}$  range is –32.6 to –74.9 kcal/mol for **a** and –39.7 to –74.9 kcal/mol for **b** isomers indicating high sensitivity of these two properties to indicate subtle variations in the ligand atmosphere. The use of  $\nu$  (the I–OH bond

stretch) as a measure of cis/trans influences is highly useful as an experimental measure because this stretch usually appeared as the most intense peak in acyclic and heterocyclic  $\lambda^3$ -iodanes.

The energy differences between the **b** and **a** isomers, designated as  $\Delta E_{ab}$ , are reported in Table 2.  $\Delta E_{ab}$  values are positive (0.0–24.8 kcal/mol) indicating higher stability of **a** isomer than **b** and suggesting the preference of heteroatom at the axial position. In fact, all the reported heterocyclic  $\lambda^3$ -iodanes are **a** isomers. As in acyclic  $\lambda^3$ -iodanes, I–OH values show good correlation with  $\Delta E_{ab}$  (Figure 7). This again



**Figure 6.** QTAIM topological plot of compounds **10a** and **10b** showing the bond critical point (small red circles) and the  $\rho(r)$  value (au) at the bond critical point of I–OH bond along with the representation of MESP isosurface of the corresponding complexes at  $-28.0$  kcal/mol. The deepest value ( $V_{\min}$  in kcal/mol), the I–OH bond distance (in Å), and the I–OH stretching frequency ( $\nu$  in  $\text{cm}^{-1}$ ) are also shown.

**Table 2.** I–OH Bond Distance ( $d$  in Å), Electron Density ( $\rho$  in au) at the bcp of I–OH Bond, Stretching Frequency of I–OH Bond ( $\nu$  in  $\text{cm}^{-1}$ ), and the Deepest MESP Value ( $V_{\min}$  kcal/mol) for the Compounds Used To Study the Trans and Cis Influences of Various Heterocyclic Moieties in  $\lambda^3$ -Iodanes<sup>a</sup>

complex	$d_a$	$\rho_a$	$\nu_a$	$V_{\min(a)}$	complex	$d_b$	$\rho_b$	$\nu_b$	$V_{\min(b)}$	$\Delta E_{ab}$
<b>9</b>	2.220	0.080	402.2	−74.9	<b>9</b>	2.220	0.080	402.2	−74.9	0.0
<b>10a</b>	2.099	0.100	505.9	−41.4	<b>10b</b>	2.112	0.098	465.7	−46.9	21.9
<b>11a</b>	2.124	0.095	484.7	−55.9	<b>11b</b>	2.126	0.096	462.2	−59.0	17.6
<b>12a</b>	2.091	0.101	502.1	−40.0	<b>12b</b>	2.097	0.101	489.7	−44.0	21.4
<b>13a</b>	2.128	0.094	471.5	−57.3	<b>13b</b>	2.128	0.095	458.5	−60.7	17.4
<b>14a</b>	2.098	0.100	503.6	−42.0	<b>14b</b>	2.102	0.100	475.1	−46.1	19.6
<b>15a</b>	2.126	0.094	472.6	−57.1	<b>15b</b>	2.132	0.095	452.5	−60.7	17.4
<b>16a</b>	2.079	0.103	511.4	−32.6	<b>16b</b>	2.089	0.102	485.8	−39.7	24.8
<b>17a</b>	2.139	0.093	449.7	−55.8	<b>17b</b>	2.185	0.084	418.3	−68.8	10.2
<b>18a</b>	2.097	0.100	495.7	−42.7	<b>18b</b>	2.106	0.099	474.7	−48.9	22.7
<b>19a</b>	2.088	0.101	506.2	−38.3	<b>19b</b>	2.098	0.101	481.6	−43.4	24.3
<b>20a</b>	2.109	0.097	489.1	−50.8	<b>20b</b>	2.126	0.096	456.7	−54.9	22.6
<b>21a</b>	2.111	0.097	488.5	−52.1	<b>21b</b>	2.127	0.095	462.3	−56.3	22.4
<b>22a</b>	2.128	0.094	481.9	−51.6	<b>22b</b>	2.172	0.088	435.6	−58.8	14.5
<b>23a</b>	2.132	0.094	466.6	−53.1	<b>23b</b>	2.185	0.085	423.1	−56.9	17.0
<b>24a</b>	2.174	0.087	443.6	−67.2	<b>24b</b>	2.193	0.084	412.2	−69.0	6.9
<b>25a</b>	2.120	0.096	467.9	−44.7	<b>25b</b>	2.135	0.094	452.6	−53.5	17.7
<b>26a</b>	2.146	0.091	456.5	−54.3	<b>26b</b>	2.174	0.087	436.4	−61.6	14.2
<b>27a</b>	2.145	0.091	466.1	−61.7	<b>27b</b>	2.206	0.083	411.4	−68.2	12.5
<b>28a</b>	2.083	0.102	510.6	−35.0	<b>28b</b>	2.096	0.101	488.4	−42.2	23.8
<b>29a</b>	2.140	0.092	463.0	−60.6	<b>29b</b>	2.154	0.091	445.2	−66.5	18.8

<sup>a</sup>The energy difference between the isomers **b** and **a** ( $\Delta E_{ab}$  in kcal/mol) are also given.

confirms our earlier conclusion that trans/cis influence mainly depends on the inductive effect of the substituent.

**Influence of Substituent on Phenyl Group on Hyper-valent Bond.** Several heterocyclic  $\lambda^3$ -iodanes with various substituents on the equatorial phenyl group have been

reported.<sup>8,10,20</sup> We used electron donating Me and electron withdrawing F group on phenyl group (**30a–43a** in Figure 8) to study their influence of the I–OH bond. Since phenyl group prefers equatorial position, its substituent will have cis influence on the I–OH bond.  $d_a$ ,  $\rho_a$ ,  $\nu_a$  and  $V_{\min(a)}$  of all systems are

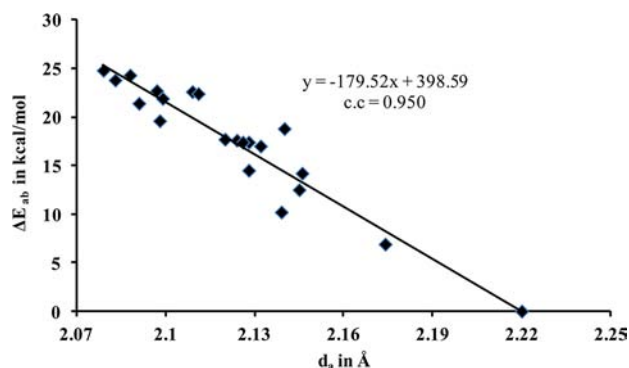


Figure 7. Plot of  $d_a$  values against relative energy of the isomers a and b in heterocyclic  $\lambda^3$ -iodanes.

given in Table S1 of Supporting Information. In complexes **30a–34a**, compared to benziiodoxoles (**10a**), F at the ortho position (position 2, **30a**) leads to significant decrease (0.028 Å) in  $d_a$  value whereas only a marginal decrease in  $d_a$  is observed for **31a**, **32a**, and **33a**. Though all positions are substituted by F in **34a**, the decrease in  $d_a$  (0.030 Å) is comparable to that of **30a**. Similar observation is found for **40a** and **42a** as they show shorter I–OH bonds than **16a** and **22a**, respectively. In **35a–39a**, **41a**, and **43a**,  $d_a$  is nearly unchanged with Me substitution. These results clearly suggest that F substituent at the ortho position significantly stabilizes the 3c–4e bond in heterocyclic  $\lambda^3$ -iodanes while such an effect is not seen when an electron donating Me group is present at the ortho position. This phenomenon can be explained on the basis of steric effect that operates between OH group and the ortho substituent. The steric effect causes an elongation of the I–C<sub>phenyl</sub> bond (for both F and Me) and suggests an increase in the electron sharing at the I–OH bond meaning that F or Me at the ortho position can strengthen the I–OH bond. This ortho effect is more pronounced in the case of F because the electron withdrawing character of F also contributes to the strength of the I–OH bond whereas Me with electron donating character favors elongation of the I–OH bond.

**Significance of Trans and Cis Influence Parameters.** The oxidizing power of  $\lambda^3$ -iodanes is based on the higher

electrophilic nature of the central iodine atom.<sup>3,27,67,68</sup> A nucleophile ( $\text{Nu}^-$ ) can directly coordinate to the iodine atom of tri-coordinated hypervalent  $\text{Ph}[\text{IX}_2]$  complexes, which results in the formation of a square planar species of the type  $[\text{PhIX}_2\text{Nu}^-]$ .<sup>3,13,29</sup> This is followed by isomerization and elimination reactions depending upon the nature of the nucleophile.<sup>3,69</sup> Electrophilic character of iodine atom can be assessed by studying the interactive behavior of hypervalent system with a nucleophile. To investigate this and its relationship to trans and cis influences, we have studied the reaction of both the isomers of acyclic and heterocyclic  $\lambda^3$ -iodanes with  $\text{Cl}^-$  nucleophile. In Figure 9, representative examples of four such product complexes are shown. For acyclic  $\lambda^3$ -iodanes, the interaction energy of  $\text{Cl}^-$  ( $E_{\text{Cl}^-}$ ) is in the range  $-13.2$  to  $-38.9$  kcal/mol, and that of heterocyclic  $\lambda^3$ -iodanes is in the range  $-18.5$  to  $-43.6$  kcal/mol (Tables S2 and S3). It is obvious that  $\text{Cl}^-$  ligand in the product complex will experience both cis and trans influences from other ligands. Hence, we use the sum of trans and cis influence parameters of the ligands to correlate with  $E_{\text{Cl}^-}$  values. As shown in Figure 10, good linear relationships with correlation coefficient values 0.965 and 0.936 are found, respectively, for acyclic and heterocyclic  $\lambda^3$ -iodanes when  $E_{\text{Cl}^-}$  is plotted against sum of  $V_{\text{min}}$  based trans and cis parameters. The other trans/cis parameters, viz.,  $d_{\text{trans/cis}}$ ,  $\rho_{\text{trans/cis}}$  and  $\nu_{\text{trans/cis}}$  too give similar trends. Points that show significant deviations from the linear plot suffer from strong secondary effects such as hydrogen bonding and other through space interactions. These linear plots suggest that the lower the cis and trans influences of the ligands is, the higher the stability will be of the tetracoordinated iodine complexes. The analysis of tetracoordinate hypervalent iodine complexes is also helpful to understand the self-assemblies in hypervalent iodine systems because  $\lambda^3$ -iodanes can exist as tetra- and pentacoordinated structures in the solid state through secondary bonding interactions leading to polymeric structures.<sup>34,70–73</sup>

## CONCLUSION

Quantum chemical analysis has been carried out to understand the trans and cis influence in acyclic  $\lambda^3$ -iodanes of the type  $\text{Ph}[\text{XI}(\text{OH})]$  and heterocyclic  $\lambda^3$ -iodanes. The relative energy

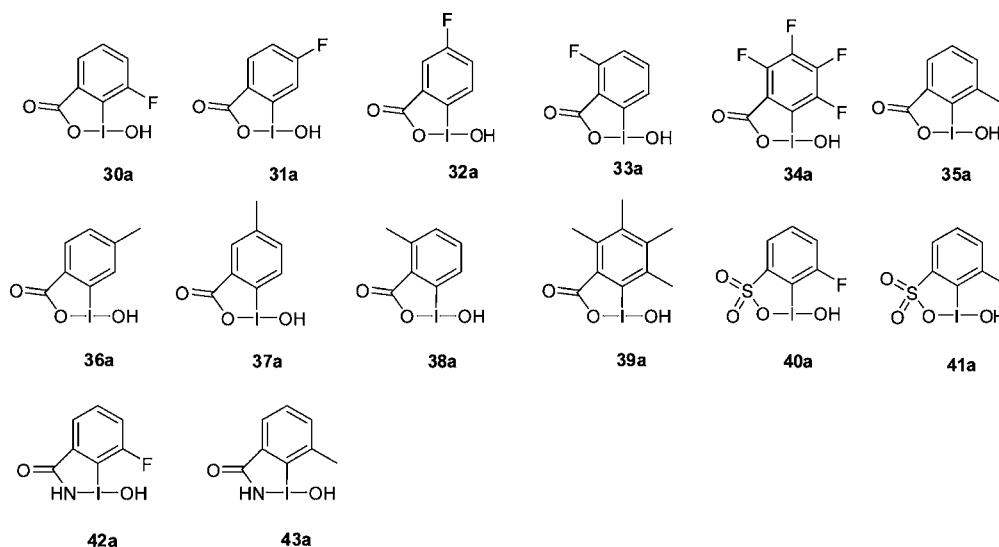
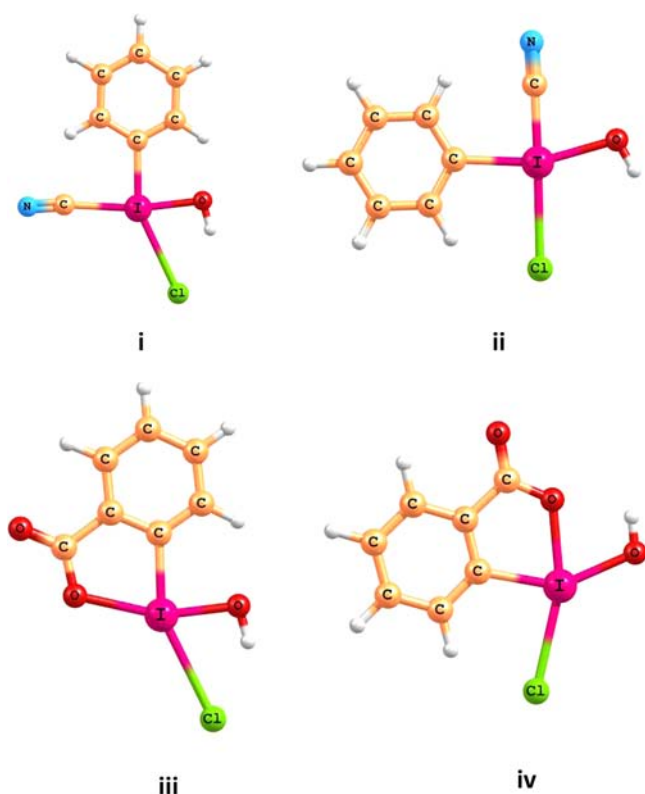
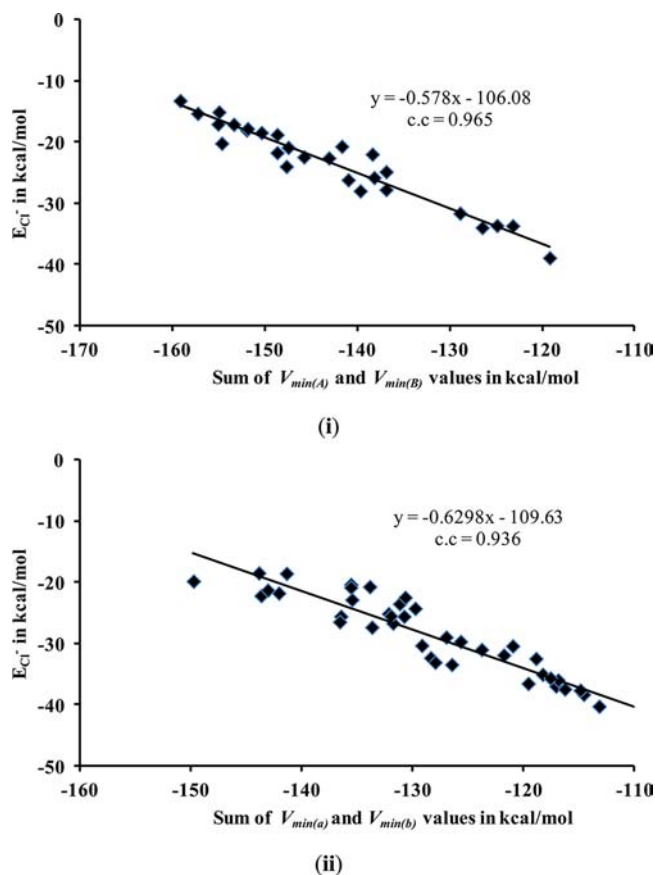


Figure 8. Heterocyclic  $\lambda^3$ -iodanes selected for the study of substituent effects of phenyl ring.



**Figure 9.** Representative examples of optimized geometries of the tetracoordinated hypervalent iodine complexes. (i and ii) Coordination of  $\text{Cl}^-$  to the complexes of the type  $\text{Ph}[\text{XI}(\text{OH})]$  (where  $\text{X} = \text{CN}$ ). (iii and iv) Coordination of  $\text{Cl}^-$  to the heterocyclic  $\lambda^3$ -iodanes.

of trans and cis isomers of  $\text{Ph}[\text{XI}(\text{OH})]$  as well as that of heterocyclic  $\lambda^3$ -iodanes is directly related with the trans/cis influence parameters. Both trans and cis influences originate from the inductive nature of the ligand X. This study also helped us to arrange a variety of heterocyclic  $\lambda^3$ -iodanes as well as a variety of ligands in the increasing order of their trans and cis influences. Though the order of trans influence is same as that of cis influence, the former shows more magnitude than the latter. An electron withdrawing substituent at the ortho position to the phenyl ring significantly stabilizes hypervalent I–OH bond in heterocyclic  $\lambda^3$ -iodanes. Analysis of interaction energies of  $\text{Cl}^-$  on  $\lambda^3$ -iodanes reveals that the proposed  $V_{\text{min}}$  parameter for the trans and cis influence of various ligands is a good descriptor to assess the tetracoordinating power of iodine atom. Both I–OH bond distance and  $\rho$  at the I–OH bond critical point can be used as good parameters for trans/cis influence, and these two quantities show almost a perfect linear correlation. However, these parameters are insensitive to through space effect of ligands around the OH group. Compared to  $d$  and  $\rho$ ,  $\nu$  and  $V_{\text{min}}$  show a wide range of values and suggest highly sensitivity nature of these quantities to the subtle variations in the ligand environment. We feel that trans/cis influence parameters proposed in this study are useful to explain the reaction mechanisms of hypervalent mediated reactions and ortho substituent effect; additionally, they may find use in designing stable acyclic and heterocyclic hypervalent complexes. Stretching frequency of the I–OH bond will be useful as a simple experimental parameter to measure trans/cis influence.



**Figure 10.** Correlations between interaction energy of  $\text{Cl}^-$  and sum of cis and trans  $V_{\text{min}}$  values (i) for acyclic  $\lambda^3$ -iodanes and (ii) for heterocyclic  $\lambda^3$ -iodanes.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Cartesian coordinates of all  $\lambda^3$ -iodanes. Correlation diagrams,  $d_a$ ,  $\rho_a$ ,  $\nu_a$  and  $V_{\text{min}(a)}$  values for the compounds 30a–43a, and  $E_{\text{Cl}^-}$  values. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [sureshch@gmail.com](mailto:sureshch@gmail.com).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the Council of Scientific and Industrial Research (CSIR), India, for the support through the CSIR MSM Project CSC0129. P.K.S. is thankful to University Grants Commission (UGC), Government of India, for a fellowship.

## ■ REFERENCES

- (1) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press: London, 1997.
- (2) Stang, P. J. *J. Org. Chem.* **2003**, *68*, 2997.
- (3) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123.
- (4) Moriarty, R. M.; Prakash, O. *Hypervalent Iodine in Organic Chemistry: Chemical Transformations*; Wiley-Interscience: New York, 2008.



- (5) Ochiai, M. *Chemistry of Hypervalent Compounds*; Wiley-VCH: New York, 1999.
- (6) Ochiai, M. *Chem. Rec.* **2007**, *7*, 12.
- (7) Richardson, R. D.; Wirth, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 4402.
- (8) Zhdankin, V. V. *Curr. Org. Synth.* **2005**, *2*, 121.
- (9) Wirth, T. *Hypervalent Iodine Chemistry; Topics in Current Chemistry*; Springer: Berlin, 2003; Vol. 224.
- (10) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299.
- (11) Merritt, E. A.; Olofsson, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 9052.
- (12) Uyanik, M.; Akakura, M.; Ishihara, K. *J. Am. Chem. Soc.* **2009**, *131*, 251.
- (13) Ochiai, M. *Top. Curr. Chem.* **2003**, *224*, 5.
- (14) Paintner, F. F.; Allmendinger, L.; Bauschke, G. *Synthesis* **2001**, 2113.
- (15) Zhdankin, V. V. *ARKIVOC* **2009**, 1.
- (16) Thoma, H.; Kita, Y. *Adv. Synth. Catal.* **2004**, *346*, 111.
- (17) Zhdankin, V. V.; Stang, P. J. *J. Chem. Rev.* **2002**, *102*, 2523.
- (18) Deprezand, N. R.; Sanford, M. S. *Inorg. Chem.* **2007**, *46*, 1924.
- (19) Phippsand, R. J.; Gaunt, M. J. *Science* **2009**, *323*, 1593.
- (20) Brand, J. P.; Gonzalez, D. F.; Nicolai, S.; Waser, J. *Chem. Commun.* **2011**, 47, 102.
- (21) Souto, J. A.; Zian, D.; Muniz, K. *J. Am. Chem. Soc.* **2012**, *134*, 7242.
- (22) Musher, J. I. *Angew. Chem., Int. Ed.* **1969**, *8*, 54.
- (23) Reed, R. E.; von Rague Schleyer, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 1434.
- (24) Kutzelnigg, W. *Angew. Chem., Int. Ed.* **1984**, *23*, 272.
- (25) Weinhold, F.; Landis, C. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: New York, 2005.
- (26) Silva, L. F., Jr.; Olofsson, B. *Nat. Prod. Rep.* **2011**, *28*, 1722.
- (27) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487.
- (28) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3656.
- (29) Norrby, P.-O.; Petersen, T. B.; Bielawski, M.; Olofsson, B. *Chem.—Eur. J.* **2010**, *16*, 8251.
- (30) Ghosh, H.; Baneerjee, A.; Rout, S. K.; Patel, B. K. *ARKIVOC* **2011**, 209.
- (31) Merritt, E. A.; Olofsson, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 9052.
- (32) Martin, J. C.; Perozzi, E. F. *Science* **1976**, *191*, 154.
- (33) Wang, X.; Ye, Y.; Zhang, S.; Feng, J.; Xu, Y.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 16410.
- (34) Kiprof, K.; Zhdankin, V. *ARKIVOC* **2003**, 170.
- (35) Koser, G. F.; Sun, G.; Porter, C. W.; Youngs, W. J. *J. Org. Chem.* **1993**, *58*, 7310.
- (36) Niedermann, K.; Welch, J. M.; Koller, R.; Cvengros, J.; Santschi, N.; Battaglia, P.; Togni, A. *Tetrahedron Lett.* **2010**, *66*, 5753.
- (37) Kikugawa, Y.; Kawase, M. *Chem. Lett.* **1990**, 581.
- (38) Balthazar, T. M.; Miles, J. A.; Stults, B. R. *J. Org. Chem.* **1978**, *43*, 4538.
- (39) Nemykin, V. N.; Maskavev, A. V.; Geraskina, M. R.; Yusubov, M. S.; Zhdankin, V. V. *Inorg. Chem.* **2011**, *50*, 11263.
- (40) Jaffe, H.; Leffler, J. *Eur. J. Org. Chem.* **1975**, *40*, 797.
- (41) Su, J. T.; Goddard, W. A. *J. Am. Chem. Soc.* **2005**, *127*, 14146.
- (42) Guilbault, A. A.; Legault, C. Y. *ACS Catal.* **2012**, *2*, 219.
- (43) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.
- (44) Ochiai, M.; Sueda, K.; Miyamoto, T.; Kiprof, P.; Zhdankin, V. V. *Angew. Chem., Int. Ed.* **2006**, *45*, 8203.
- (45) Sajith, P. K.; Suresh, C. H. *Inorg. Chem.* **2012**, *51*, 967.
- (46) Kiprof, P. *ARKIVOC* **2005**, 19.
- (47) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.
- (48) Gadre, S. R.; Shirsat, R. N. *Electrostatics of Atoms and Molecules*; Universities Press: Hyderabad, India, 2000.
- (49) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (50) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision C.01*, Gaussian, Inc.: Wallingford, CT, 2009.
- (52) Sosa, C.; Andzelm, J.; Elkin, B. C.; Wimmer, E.; Dobbs, K. D.; Dixon, D. A. *J. Phys. Chem. A* **1992**, *96*, 6630.
- (53) Yurieva, A. G.; Kh, P. O.; Filimonov, V. D. *J. Struct. Chem.* **2008**, *49*, 548.
- (54) Politzer, P.; Truhlar, D. G. *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Plenum Press: New York, 1981.
- (55) Mathew, J.; Suresh, C. H. *Inorg. Chem.* **2010**, *49*, 4665.
- (56) Sayyed, F. B.; Suresh, C. H. *J. Phys. Chem. A* **2012**, *116*, 5723.
- (57) Suresh, C. H.; Alexander, P.; Vijayalakshmi, K. P.; Sajith, P. K.; Gadre, S. R. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6492.
- (58) König, F. B.; Schönbohm, J.; Bayles, D. J. *Comput. Chem.* **2001**, *22*, 545.
- (59) Sajith, P. K.; Suresh, C. H. *Dalton Trans.* **2010**, 39, 815.
- (60) Sajith, P. K.; Suresh, C. H. *J. Organomet. Chem.* **2011**, *696*, 2086.
- (61) Sajith, P. K.; Suresh, C. H. *Inorg. Chem.* **2011**, *50*, 8085.
- (62) Anastasi, A. E.; Deeth, R. J. *J. Chem. Theory Comput.* **2009**, *5*, 2339.
- (63) Deeth, R. J. *J. Chem. Soc., Dalton Trans.* **1993**, 3711.
- (64) Rigamonti, L.; Rusconi, M.; Manassero, C.; Manassero, M.; Pasini, A. *Inorg. Chim. Acta* **2010**, *363*, 3498.
- (65) Rigamonti, L.; Manassero, C.; Rusconi, M.; Manassero, M.; Pasini, A. *Dalton Trans.* **2009**, 1206.
- (66) Rigamonti, L.; Forni, A.; Manassero, M.; Manassero, C.; Pasini, A. *Inorg. Chem.* **2010**, *49*, 123.
- (67) Zefirov, N. S.; Zhdankin, V. V.; Dañkov, Y. V.; Sorokin, V. D.; Semerikov, V. N.; Kožmin, A. S.; Caple, R.; Berglund, B. A. *Tetrahedron Lett.* **1986**, *27*, 3971.
- (68) Gately, D. A.; Luther, T. A.; Norton, J. R.; Miller, M. M.; Anderson, O. P. *J. Org. Chem.* **1992**, *57*, 6496.
- (69) Oae, S.; Uchida, Y. *Acc. Chem. Res.* **1991**, *24*, 202.
- (70) Ochiai, M.; Suefuji, T.; Miyamoto, K.; Shirob, M. *Chem. Commun.* **2003**, 1438.
- (71) Ochiai, M.; Kitagawa, Y.; Takayama, N.; Takaoka, Y.; Shiro, M. *J. Am. Chem. Soc.* **1999**, *121*, 9233.
- (72) Montanari, V.; DesMarteau, D. D.; Pennington, W. T. *J. Mol. Struct.* **2000**, *337*, 550.
- (73) Edwards, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1723.