Inorganic Chemistry
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Quantification of the Trans Influence in Hypervalent Iodine Complexes

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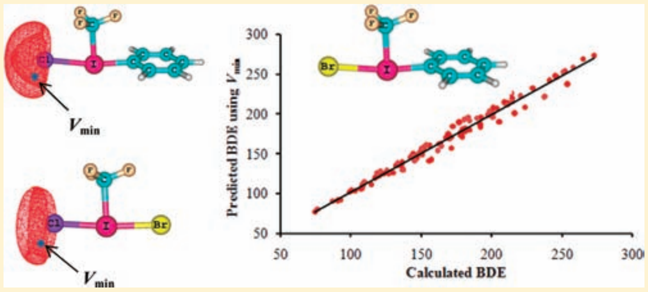
Supporting Information

ABSTRACT: The trans influence of various X ligands in hypervalent iodine(III) complexes of the type $CF_3[I(X)Cl]$ has been quantified using the trans I−Cl bond length (d_X), the electron density $\rho(\mathbf{r})$ at the (3, −1) bond critical point of the trans I−Cl bond, and topological features of the molecular electrostatic potential (MESP). The MESP minimum at the Cl lone pair region (V_{min}) is a sensitive measure of the trans influence. The trans influence of X ligands in hypervalent iodine(V) complexes is smaller than that in iodine(III) complexes, while the relative ordering of this influence is the same in both complexes. In $CF_3[I(X)Y]$ complexes, the mutual trans influence due to the trans disposition of the X and Y ligands is quantified using the energy E_{XY} of the isodesmic reaction $CF_3[I(X)Cl] + CF_3[I(Y)Cl] \rightarrow CF_3[I(Cl)Cl] + CF_3[I(X)Y]$. E_{XY} is predicted with good accuracy using the trans-influence parameters of X and Y, measured in terms of d_X, $\rho(\mathbf{r})$, or V_{min}. The bond dissociation energy (E_d) of X or Y in $CF_3[I(X)Y]$ is significantly influenced by the trans influence as well as the mutual trans influence. This is confirmed by deriving an empirical equation to predict E_d using one of the trans-influence parameters (d_X, $\rho(\mathbf{r})$, or V_{min}) and the mutual trans-influence parameter E_{XY} for a large number of complexes. The quantified values of both the trans influence and the mutual trans-influence parameters may find use in assessing the stability of hypervalent iodine compounds as well as in the design of new stable hypervalent complexes. Knowledge about the I−X bond dissociation energies will be useful for explaining the reactivity of hypervalent iodine complexes and the mechanism of their reactions.



INTRODUCTION

During the past few decades, hypervalent iodine compounds have received considerable attention as versatile oxidizing agents in organic synthesis.[1−16] Preparations, structural studies, and synthetic applications of various hypervalent iodine(III) and iodine(V) derivatives have been recently reviewed by Zhdankin and Stang.[17] One of the characteristic features which distinguish hypervalent compounds from others is the presence of a 3-center 4-electron (3c-4e) bond formed by the interaction of the orbitals of three collinear atoms.[18] In T-shaped iodine(III) complexes, the interaction of the filled 5p orbital of the central iodine atom and the half-filled orbitals of two ligands (X and Y) trans to each other leads to formation of three molecular orbitals, viz. bonding, nonbonding, and antibonding (Figure 1).[18−24] Because the highest occupied molecular orbital (HOMO) contains a node at the central iodine, the hypervalent bonds show a highly polarized nature; hence, more electronegative atoms tend to occupy the axial positions.[1,10]

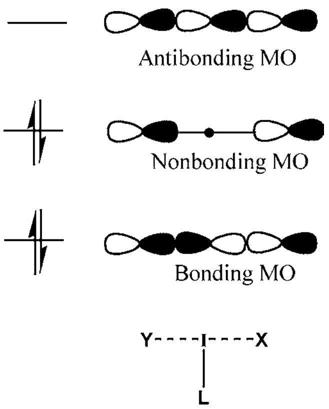


Figure 1. MOs of the 3c-4e bond formed in the hypervalent iodine(III) complexes.

The focus of the present study is to understand the phenomenon of the trans influence in hypervalent iodine complexes. The trans influence is defined as the ability of a ligand (Y) to weaken the metal−ligand bond (M−X) trans to it.[25−32] The trans influence is well known in transition metal complexes and even extended to the main group elements and lanthanides.[33−44] The mutual influence of ligands in main group coordination complexes was theoretically studied by Shustorovich and Buslaev, who found that the trans influence

Received: September 20, 2011
Published: December 28, 2011

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between two ligands X and Y is always present when the central atom retained the *ns*^{2} lone pair.[41] In T-shaped iodine(III) complexes, the iodine atom preserves the 5s^2 lone pair and the σ-donating ability of ligand Y will influence the trans I−X bond through the 5p orbital of the central iodine and hence the mutual trans influence caused through the 3c-4e bond is solely resulting from the inductive effect of the trans ligands X and Y.[41] Ochiai et al.[42] analyzed various crystal structures of iodine(III) complexes, classified various ligands in the order of their trans influence, and concluded that the mutual trans influence of ligands plays an important role in the stability of these complexes. On the basis of theoretical investigations using isodesmic reactions,[42] Ochiai et al. proposed that the ligands with a large and small trans influence in the axial positions are favored over the combinations of two strong and two weak ligands in the trans positions; otherwise, two moderately trans-influencing ligands are favored. Thus, the phenomenon of the trans influence can explain the stability of Ph[I(OH)OTs] and Ph[I(OAc)$_2$] complexes as well as the instability of Ph[I(OH)$_2$], Ph[I(OOtBu)$_2$], and Ph[I(OMe)$_2$] complexes.[17]

The trans bond length data from X-ray crystal structures are frequently used for the study of the trans influence of various ligands. In many cases, the packing interactions in the crystal structure as well as influence from cis ligands also affect the trans bond.[45,46] Structural parameters are not very sensitive to subtle electronic variations, and theoretically derived molecular properties have been used as powerful descriptors for explaining the reactivity and stabilities of hypervalent complexes. In our recent studies,[31,47,48] applying Bader's quantum theory of atoms in molecules (QTAIM),[49] we have shown that the electron density at the bond critical point of the trans M−Cl bond (M = Pd(II) and Pt(II)) in [MCl$_3$X]$^{n-}$ complexes) can be used as a good measure of the trans influence of various ligands. Moreover, the contributions of the trans-influence terms in the bond dissociation energy of various ligands in the square planar complexes were quantified using the electron density-based approach.[48]

In the present study, the trans influence of various ligands in hypervalent iodine complexes of the type CF$_3$[I(X)Cl] is considered. The selected X ligands are F, Cl, Br, CPPh$_3$COOMe, CPPh$_3$COMe, Et, Ph, Me, O*i*Pr, CCSiMe$_3$, CH$_2$Cl, CCH, CCPh, C$_6$F$_5$, CF$_3$, 2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene, CF$_2$CF$_2$CF$_3$, NH$_2$, OMe, NHTf, OO*t*Bu, OH, OAc, NO$_2$, OCOCOOMe, OTs, OSO$_2$Me, OCOCCl$_3$, NO$_3$, OCOCF$_3$, OTf, and BF$_4$. Most of the selected ligands are located from the X-ray crystal structure of various hypervalent iodine complexes, retrieved from the Cambridge Structural Database (CSD).[50] The trans influence will be analyzed using the QTAIM approach. Further, the subtle electronic variations surrounding the coordinated ligands due to 3c-4e bond will be analyzed in terms of the molecular electrostatic potential (MESP).[51]

COMPUTATIONAL DETAILS

All electronic structure calculations were performed at the B3LYP[52,53] level of the DFT method using the Gaussian 03[54] package of programs. It has been proposed that all electron basis sets correctly reproduce the bond length in iodine compounds,[55] and hence, the full electron basis set DGDZVP[56] was chosen to describe the iodine atom, and for all other atoms the basis set 6-311++G(d,p) was selected. The combined basis set is denoted as BS1.Vibrational frequency analysis at B3LYP/BS1 was performed to confirm that all the optimized geometries are minima (zero imaginary frequencies).

For topological analysis of electron density, B3LYP/BS1 wave functions were used as input in the AIM2000 program.[57] The AIM parameters such as electron density $\rho(\mathbf{r})$, the Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$, and the total electron energy density $H(\mathbf{r})$ and its components potential electron energy density $V(\mathbf{r})$ and kinetic electron energy density $G(\mathbf{r})$ were calculated at the (3,−1) bond critical point (bcp) of the trans I−Cl bonds in CF$_3$[I(X)Cl] complexes. The $\rho(\mathbf{r})$ at the bcps can be used as a measure of the strength of bonding interactions.[49] The negative value of $\nabla^2\rho(\mathbf{r})$ shows the charge concentration due to shared interactions (covalent), while the positive $\nabla^2\rho(\mathbf{r})$ shows the charge depletion due to closed-shell (ionic) interactions.[58] The total electron energy density at the bcp $H(\mathbf{r})$ is yet another parameter to assess the bonding interactions.[59−61] A negative $H(\mathbf{r})$ indicates a covalent bond, while a positive value indicates ionic interactions.

The B3LYP/BS1 level of theory was used for calculation of molecular electrostatic potential (MESP). MESP is a physical property of a molecule, $V(\mathbf{r})$ at a point $\mathbf{r}$, that can be calculated using its electron density, $\rho(\mathbf{r})$, with eq 1, where Z_A is the charge on the nucleus A, located at R_A.[51,62]

$$V(\mathbf{r}) = \sum_{A}^{N} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \qquad (1)$$

Equation 1 shows that for electron-dense regions, the electronic terms will dominate over the nuclear term and hence these regions are characterized by negative MESP values, whereas the electron-deficient regions show positive MESP values.[51,62] The deepest MESP minimum ($V_{\min}$) was obtained from the MESP topography calculations by generating cube files using Gaussian 03.

RESULTS AND DISCUSSIONS

Trans Influence from the Trans Bond Length. The T-shaped CF$_3$[I(X)(Y)] systems are the simplest stable hypervalent systems showing a 3c-4e bond.[63] The crystal structures of many such complexes with highly electronegative atoms at the axial positions have been reported.[64,65] The CF$_3$[I(X)Cl] complexes are modeled in such a way that the axial positions of the T-shaped structure are occupied by the ligands Cl and X. The trans I−Cl distances (d_X) for 32 complexes are given in Table 1. Short d_X shows a weak trans-influencing X ligand, while long d_X shows a strong trans-influencing X ligand, which means that BF$_4$ has the lowest trans influence (d_X = 2.440 Å) while C(PPh$_3$)COMe has the highest (d_X = 2.740 Å) trans influence. On the basis of d_X values, the following order of trans influence is obtained: CPPh$_3$COOMe ≈ CPPh$_3$COMe > Et > Ph ≈ Me > CH$_2$Cl > CCPh > CCSiMe$_3$ ≈ NH$_2$ > CCH ≈ C$_6$F$_5$ ≈ CF$_3$ ≈ CF$_2$CF$_2$CF$_3$ > 2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene > O*i*Pr ≈ NO$_2$ > OMe ≈ Br ≈ OO*t*Bu > OH > Cl > NHTf > OAc ≈ OCOCOOMe > F ≈ OTs ≈ OSO$_2$Me ≈ OCOCCl$_3$ ≈ NO$_3$ ≈ OCOCF$_3$ > OTf > BF$_4$ (series i).

This order of trans influence given in series (i) is almost similar to the experimentally reported order for hypervalent iodine complexes.[42] Some minor deviations are noted because the experimental values are also affected by packing forces and interactions from the ligands in the neighboring molecules.

Quantification of the Trans Influence Using Electron Density Values. The QTAIM parameters, viz. the electron density ($\rho(\mathbf{r})$), the Laplacian of electron density ($\nabla^2\rho(\mathbf{r})$), total electron energy density ($H(\mathbf{r})$), and the ratio of potential and kinetic electron energy density ($k(\mathbf{r})$) at the bond critical point (bcp) of the trans I−Cl bond, are reported in the Table 1. A long trans I−Cl bond, indicative of the strong trans influence of X, is observed with a small $\rho(\mathbf{r})$ value, while a short I−Cl bond,

Table 1. QTAIM Parameters at the (3,−1) Bond Critical Points of the Trans I−Cl Bond in $CF_3[I(X)Cl]$ Complexes along with the Trans I−Cl Bond Length

			AIM parameters			
Sl no.	trans ligand X	trans I−Cl bond length d_X (Å)	$\rho(\mathbf{r})$ (au)	$\nabla^2 \rho(\mathbf{r})$ (au)	$H(\mathbf{r})$ (au)	$k(\mathbf{r})$
1	$C(PPh_3)COMe$	2.740	0.048	0.075	−0.007	−1.28
2	$C(PPh_3)COOMe$	2.738	0.048	0.075	−0.007	−1.28
3	Et	2.709	0.051	0.075	−0.008	−1.30
4	Ph	2.691	0.052	0.076	−0.009	−1.32
5	Me	2.690	0.052	0.076	−0.009	−1.32
6	CH_2Cl	2.647	0.057	0.077	−0.011	−1.36
7	CCPh	2.627	0.058	0.079	−0.012	−1.38
8	$CCSiMe_3$	2.624	0.059	0.079	−0.012	−1.38
9	NH_2	2.622	0.059	0.077	−0.012	−1.39
10	$CF_3CF_2CF_2$	2.613	0.060	0.077	−0.013	−1.40
11	CF_3	2.612	0.061	0.077	−0.013	−1.40
12	C_6F_5	2.611	0.061	0.077	−0.013	−1.41
13	CCH	2.609	0.060	0.079	−0.013	−1.40
14	$C_6F_4(CF_3)^a$	2.602	0.062	0.077	−0.014	−1.41
15	O*i*Pr	2.571	0.065	0.077	−0.015	−1.45
16	NO_2	2.568	0.066	0.074	−0.015	−1.45
17	OMe	2.561	0.066	0.077	−0.016	−1.45
18	Br	2.560	0.066	0.078	−0.015	−1.43
19	OO*t*Bu	2.560	0.066	0.076	−0.016	−1.46
20	OH	2.551	0.067	0.077	−0.017	−1.47
21	Cl	2.537	0.068	0.079	−0.016	−1.45
22	NHTf	2.525	0.071	0.076	−0.018	−1.49
23	OAc	2.521	0.071	0.078	−0.018	−1.48
24	OCOCOOMe	2.517	0.072	0.075	−0.019	−1.50
25	F	2.500	0.073	0.076	−0.020	−1.52
26	OTs	2.499	0.074	0.075	−0.020	−1.52
27	$OCOCCl_3$	2.498	0.074	0.075	−0.020	−1.52
28	OSO_2Me	2.497	0.074	0.075	−0.020	−1.52
29	$OCOCF_3$	2.496	0.074	0.074	−0.020	−1.52
30	NO_3	2.495	0.074	0.074	−0.021	−1.53
31	OTf	2.465	0.078	0.073	−0.023	−1.56
32	BF_4	2.440	0.082	0.071	−0.025	−1.59

[a] 2,3,5,6-Tetrafluoro-4-(trifluoromethyl)benzene.

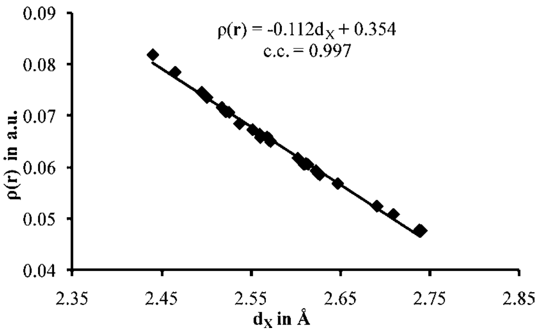


Figure 2. Correlation between the electron density at the bond critical point of the trans I−Cl bond and the trans I−Cl distance in $CF_3[I(X)Cl]$complexes.

indicative of the weak trans influence of X, is seen with a high $\rho(\mathbf{r})$ value. For instance, the $CPPh_3COMe$ ligand showed the lowest $\rho(\mathbf{r})$ (0.048 au), while the BF_4 ligand exhibited the highest $\rho(\mathbf{r})$ (0.082 au). The $\rho(\mathbf{r})$, often used as an indicator of the strength of a bond,[49] shows a strong linear correlation with the trans bond length data (Figure 2), suggesting the use of this quantity as an electronic parameter to measure the trans influence.

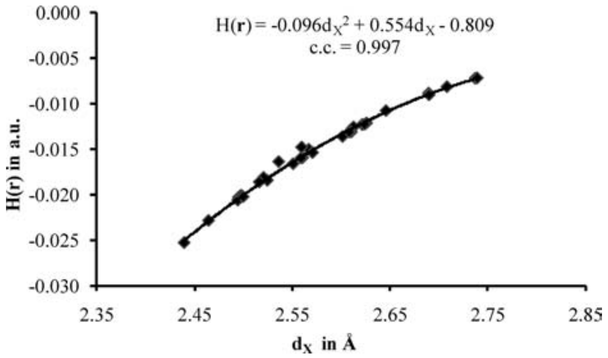


Figure 3. Correlation between the total electron energy density and the trans I−Cl bond length in $CF_3[I(X)Cl]$complexes.

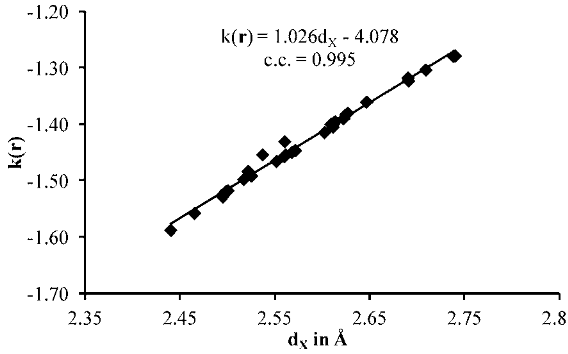


Figure 4. Correlation between $k(\mathbf{r})$ and the trans I−Cl bond length in $CF_3[I(X)Cl]$ complexes.

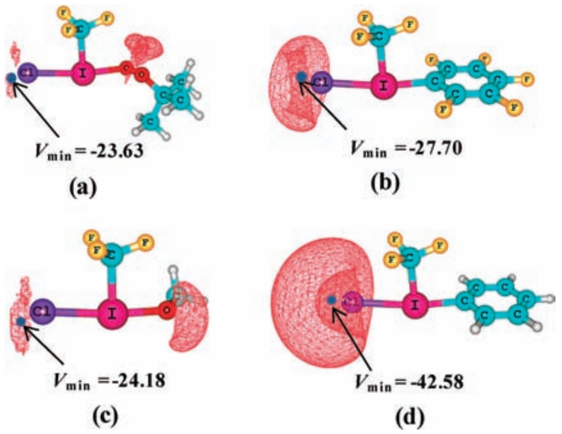


Figure 5. Representation of MESP isosurface in $CF_3[I(X)Cl]$ complexes at −23 kcal/mol along with V_{min} in kcal/mol. The ligands X are (a) OO*t*Bu, (b) C_6F_5, (c) OMe, and (d) Ph.

Trans Influence and Covalent Nature of Hypervalent Bonds. All $\nabla^2\rho(\mathbf{r})$ values are positive (0.071−0.079 au), whereas $H(\mathbf{r})$ values are negative (from −0.007 to −0.025 au). The positive $\nabla^2\rho(\mathbf{r})$ indicates the ionic nature of the I−Cl bond, while the negative $H(\mathbf{r})$ suggests covalent character. Therefore, like metal−ligand bonds,[66−68] the hypervalent I−Cl bonds can be considered as bonds with partial ionic and partial covalent characters. $\nabla^2\rho(\mathbf{r})$ showed no correlation with d_X, while $H(\mathbf{r})$ correlated remarkably well with it on a second

Table 2. V_{min} Values of $CF_3[I(X)Cl]$ Complexes

Sl no.	trans ligand X	V_{min} on trans Cl (kcal/mol)
1	$C(PPh_3)COMe$	−54.32
2	$C(PPh_3)COOMe$	−56.60
3	Et	−43.22
4	Ph	−42.58
5	Me	−40.95
6	CH_2Cl	−33.36
7	CCPh	−35.39
8	$CCSiMe_3$	−34.28
9	NH_2	−33.38
10	$CF_3CF_2CF_2$	−25.11
11	CF_3	−25.51
12	C_6F_5	−27.70
13	CCH	−30.69
14	$C_6F_4(CF_3)^a$	−25.14
15	O*i*Pr	−26.21
16	NO_2	−14.74
17	OMe	−24.18
18	Br	−16.58
19	OO*t*Bu	−23.63
20	OH	−21.97
21	Cl	−14.38
22	NHTf	−13.94
23	OAc	−17.04
24	OCOCOOMe	−13.35
25	F	−12.13
26	OTs	−12.55
27	$OCOCCl_3$	−8.50
28	OSO_2Me	−12.43
29	$OCOCF_3$	−7.11
30	NO_3	−7.67
31	OTf	−1.32
32	BF_4	2.35

[a] 2,3,5,6-Tetrafluoro-4-(trifluoromethyl)benzene.

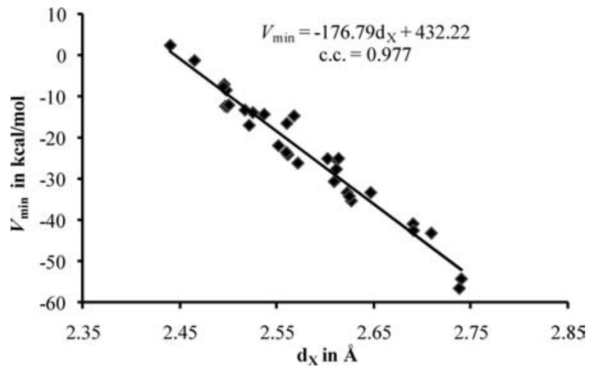


Figure 6. Correlation between V_{min} and the trans I−Cl bond length in $CF_3[I(X)Cl]$ complexes.

degree polynomial equation for the distance range 2.44−2.74 Å (Figure 3). It should be noted that d_X and $H(\mathbf{r})$ show a good linear correlation with a correlation coefficient of 0.988, while the ligands with the highest and lowest trans influence show a tendency to deviate from the linear plot. The (d_X, $H(\mathbf{r})$) correlation suggests that an increase in the trans influence of the X ligand leads to a decrease in the covalent character of the I−Cl bond.

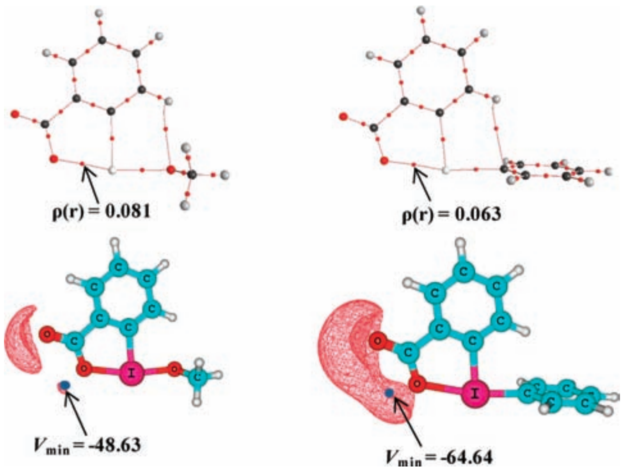


Figure 7. (Top) AIM topological plot of λ^3-aryl iodanes with X = OMe and Ph. Big circles corresponds to attractors (atomic nuclei), and small red circles indicate bond critical points. (Bottom) Representation of the MESP isosurface at −46 kcal/mol along with the V_{min} value in kcal/mol.

Table 3. Trans-Influence Parameters of λ^3-Aryl Iodanes

trans ligand	d_X (Å)	$\rho(\mathbf{r})$ (au)	V_{min} (kcal/mol)
Et	2.366	0.060	−65.44
Me	2.349	0.062	−63.49
Ph	2.344	0.063	−64.64
C_6F_5	2.265	0.073	−51.90
CF_3	2.260	0.074	−49.39
OMe	2.208	0.081	−48.63
Br	2.202	0.082	−40.85
OH	2.199	0.082	−46.94
Cl	2.181	0.085	−39.09
OAc	2.174	0.086	−42.48
F	2.147	0.090	−37.51
OTs	2.145	0.091	−38.15
OSO_2Me	2.138	0.092	−35.77
NO_3	2.137	0.093	−31.88
BF_4	2.092	0.101	−21.72

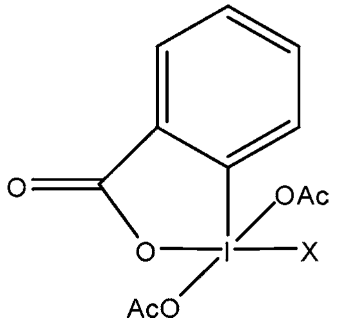


Figure 8. System considered for the study of the trans influence in iodine(V) compounds, where X indicates the trans ligand.

The covalent character of the I−Cl bond can also be assessed using the $V(\mathbf{r})/G(\mathbf{r})$ ratio (denoted as $k(\mathbf{r})$).[31] In general, the value of $|k(\mathbf{r})| < 1$ at the bcp indicates the closed-shell nature of the bond, while $|k(\mathbf{r})| > 1$ shows the covalent nature. It is clear from the Table 1 that all the trans I−Cl bonds showed $|k(\mathbf{r})| > 1$ at the bcp with $k(\mathbf{r})$ values ranges between −1.28 and −1.59. Figure 4 presents the linear relationship between $k(\mathbf{r})$ and the I−Cl distance parameter which nicely complement the conclusion obtained from the (d_X, $H(\mathbf{r})$) correlation.

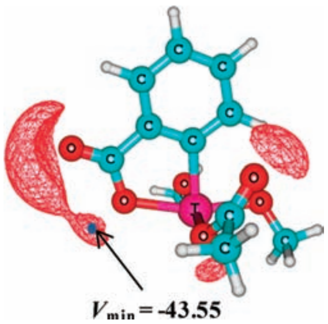
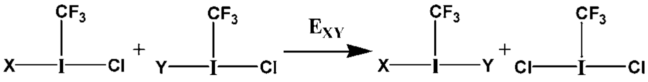


Figure 9. Representation of the MESP isosurface at −37 kcal/mol when X = OMe. Corresponding V_{min} (kcal/mol) is also given.

Table 4. Trans-Influence Parameters of λ^5-Aryl Iodanes

trans ligand	d_X (Å)	$\rho(\mathbf{r})$ (au)	V_{min} (kcal/mol)
Et	2.368	0.063	−60.68
Me	2.345	0.066	−57.99
Ph	2.336	0.067	−59.50
CF_3	2.253	0.078	−44.93
C_6F_5	2.246	0.079	−46.00
OMe	2.186	0.088	−43.55
Br	2.169	0.091	−36.29
OH	2.185	0.088	−41.42
Cl	2.147	0.095	−34.03
OAc	2.138	0.096	−34.58
F	2.113	0.100	−32.71
OTs	2.112	0.101	−34.42
OSO_2Me	2.106	0.102	−31.19
NO_3	2.103	0.103	−28.12
BF_4	2.004	0.116	−20.10

Scheme 1. Isodesmic Reactions Used To Study the Mutual Trans Ligand Influence due to X and Y



MESP Minimum As a Measure of the Trans Influence.

Recently, we have shown that critical features of MESP can be used as good descriptors for study of the inductive effect.[69,70] Further, the subtle variations of electronic features induced by substituents on organic molecules as well as ligands in complexed systems can be quantified by studying the topographical features of MESP.[71,72] For instance, the minimum value of MESP in the lone pair region of phosphine[73] and carbene ligands[74] can be used as a good measure of the donating power of these ligands in coordination complexes. Hence, it is felt that MESP can provide valuable insight on the highly polarized 3c-4e bonding in hypervalent iodine complexes as this bond is largely influenced by the inductive effect of the X ligands. In MESP studies, it is convenient to select an electron-rich region in the molecule for monitoring the changes in the electron density distribution. The chloro ligand in $CF_3[I(X)Cl]$ shows the most electron-rich lone pair region, and therefore, the MESP minimum (designated as V_{min}) observed for this region is used for monitoring the trans influence of X.

In Figure 5, V_{min} at the Cl lone pair region is depicted along with an electrostatic representation of the molecule using an MESP isosurface of value −23 kcal/mol for a representative set of four molecules. Table 2 depicts the V_{min} of all the systems. For X = $CPPh_3COOMe$, the chloro ligand shows the most negative V_{min} (−56.60 kcal/mol), while for X = BF_4, V_{min} has the highest value (2.35 kcal/mol). The chloro ligand trans to BF_4 is devoid of negative V_{min}, which can be attributed to the very weak trans influence of BF_4, resulting in strong I−Cl bond formation. When going from electron-donating to -withdrawing ligands, a gradual decrease in the negative value of V_{min} is observed. In general, a weak I−Cl bond is characterized by highly negative V_{min}. Because the weak I−Cl bond is due to the strong trans influence of X, the high negative MESP surrounding the chloro ligand can be attributed to the increased ionic character or the decreased covalent character of the I−Cl bond.

Figure 6 gives a good linear relation between V_{min} and the trans I−Cl distance parameter d_X. It suggests that V_{min} can be used as a sensitive measure of the trans influence. The trans bond length, a structural measure of the trans influence, is less sensitive than the one electron property which is immediately noted in the wide range of V_{min} values (from 2 to −57 kcal/mol) observed for the 32 ligands considered in this study. Further, V_{min} is useful as an energetic measure of the trans influence because its value also represents the energy required to bring a unit test positive charge from infinity to that location.[62] On the basis of V_{min} values, ligands are classified into four groups, viz.

(1) *Very strong trans influencing:* V_{min} values more negative than −30 kcal/mol. The ligands are $CPPh_3COOMe$, $CPPh_3COMe$, Et, Ph, Me, CCPh, $CCSiMe_3$, CH_2Cl, CCH, and NH_2.
(2) *Strong trans influencing:* V_{min} values ranges from −30 to −20 kcal/mol. The ligands are CF_3, C_6F_5, 2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene, $CF_2CF_2CF_3$, OO*t*Bu, O*i*Pr, OMe, and OH.
(3) *Moderate trans influencing:* V_{min} values from −20 to −10 kcal/mol. The ligands are Br, NO_2, Cl, OAc, NHTf, OSO_2Me, OTs, OCOCOOMe, and F.
(4) *Weak trans influencing:* V_{min} values less negative values than −10 kcal/mol. The ligands are $OCOCCl_3$, NO_3, $OCOCF_3$, OTf, and BF_4.

Trans Influence in λ^3-Iodanes.

To assess the trans influence of X in another ligand environment, various X ligands in benziodoxoles are considered for a representative set of 15 ligands. QTAIM topological plots of two representative examples are given in Figure 7 along with an MESP isosurface representation of the same structures. The probe to measure V_{min} is the lone pair region of the oxygen atom that is trans to the X ligand. The I−O bond length d_X, $\rho(\mathbf{r})$ value for the I−O bond, and V_{min} are reported in Table 3. All three trans-influence parameters (d_X, $\rho(\mathbf{r})$, and V_{min}) correlate strongly with the corresponding values obtained for $CF_3[I(X)Cl]$ systems. Therefore, the trans-influence order presented in series (i) is taken as a general order of the trans influence in hypervalent iodine(III) complexes.

Trans Influence in Iodine(V) Compounds.

A model of the iodine(V) complex selected for this study is shown in Figure 8, which can be considered as a derivative of Dess−Martin periodane (DMP) wherein one of the OAc groups trans to the O atom of the aryl group is replaced by the X ligand. These λ^5-iodanes complexes are characterized by two orthogonal 3c-4e bonds because the central iodine atom is coordinated to four different ligands through two hypervalent bondings while the fifth ligand occupies the apical position of the square pyramidal structure through a normal covalent

Table 5. Calculated and Predicted E_{XY} (kcal/mol)

isodesmic reactions	ligands in the trans positions		calcd E_{XY}	predicted E_{XY}		
	X	Y		d_X	$\rho(\mathbf{r})$	V_{min}
1	F	Br	0.34	−1.53	−1.67	−0.11
2	F	F	−0.68	0.37	0.29	0.47
3	$OCOCCl_3$	OH	−2.58	−1.37	−1.47	−2.09
4	OTs	Ph	−6.51	−6.44	−5.37	−3.22
5	OH	Br	0.67	1.08	1.20	0.93
6	OTs	CF_3	−3.61	−3.65	−3.16	−1.12
7	Br	$CCSiMe_3$	1.73	2.06	3.28	0.24
8	$CF_2CF_2CF_3$	Me	9.23	9.93	10.90	6.34
9	OMe	O*i*Pr	2.60	1.69	1.88	3.87
10	OSO_2Me	Me	−6.38	−6.12	−5.68	−3.11
11	BF_4	Me	−16.22	−13.98	−15.19	−14.14
12	F	$C(PPh_3)COOMe$	−0.67	−7.17	−6.18	−5.40
13	F	Me	−1.53	−5.66	−5.01	−3.34
14	NO_3	Ph	−5.59	−6.44	−6.25	−7.03
15	F	OMe	−1.57	−1.56	−1.57	−1.12
16	BF_4	$C(PPh_3)COOMe$	−24.96	−17.41	−18.60	−20.96
17	OTs	F	−0.73	0.31	0.29	0.42
18	OO*t*Bu	Me	4.70	2.52	3.69	5.24
19	Me	Et	20.44	22.30	22.35	19.24
20	OTf	Br	−1.61	−3.34	−3.93	−2.64
21	OH	$CCSiMe_3$	3.23	1.24	1.94	3.51
22	OTf	Et	−12.42	−11.56	−11.89	−12.22
23	NO_3	Me	−5.10	−6.43	−6.25	−6.67
24	OSO_2Me	Et	−6.73	−6.75	−6.13	−3.40
25	OTf	OSO_2Me	0.68	0.16	0.52	−1.15
26	OH	OMe	1.04	1.09	1.16	2.75
27	Et	$C(PPh_3)COOMe$	26.89	28.22	27.68	28.01
28	CF_3	CF_3	6.83	6.38	6.71	4.35
29	$OCOCCl_3$	OSO_2Me	1.74	0.42	0.43	−0.10
30	O*i*Pr	CCPh	5.31	3.15	3.99	6.25
31	NO_2	CCPh	−0.17	2.78	3.19	−0.96
32	OCOCOOMe	OCOCOOMe	−0.27	0.21	0.05	0.52
33	$OCOCCl_3$	$OCOCCl_3$	0.23	0.43	0.43	0.72
34	Br	Br	0.00	1.53	1.92	0.93
35	OMe	OMe	1.76	1.60	1.68	3.62
36	NO_3	OH	−1.80	−1.51	−1.65	−2.38
37	NO_3	OMe	−1.38	−1.85	−2.01	−2.87
38	Br	Ph	1.55	2.60	4.54	−0.08
39	NO_3	F	−0.21	0.31	0.28	−0.15
40	$C(PPh_3)COMe$	$C(PPh_3)COMe$	33.62	33.74	32.47	38.22
41	BF_4	BF_4	3.49	4.04	6.26	4.75
42	OTf	OMe	−4.45	−3.40	−3.73	−5.37

bond.[17] This model will help us to assess the effect of a 3c-4e bond (the AcO−I−OAc bonding) on the trans-influencing power of the X ligands. The I−O bond length (trans to X ligand) is the structural parameter, d_X for the trans influence, while the corresponding $\rho(\mathbf{r})$ is the electron density-based parameter. The MESP minimum on the oxygen lone pair, V_{min}, for the I−O bond (trans to the X ligand) will serve as the electrostatic measure of the trans influence. In Figure 9, the MESP isosurface is displayed for a representative system along with the corresponding V_{min} value. The trans-influence parameters for the 15 ligands are reported in Table 4.

All three trans-influence parameters of λ^5-iodanes almost strictly follow the order of trans influence observed in the case of λ^3-iodanes. d_X is less sensitive as a trans-influence parameter than $\rho(\mathbf{r})$ and V_{min} because from iodine(V) to iodine(III) complex the former shows only 1−2% decrease, whereas $\rho(\mathbf{r})$ increases by 5−12%, while V_{min} becomes less negative by 7−23%. These data also suggest that the presence of a second 3c-4e bond decreases the trans influence of the X ligand.

Isodesmic Reactions To Study Mutual Trans Influence of Two Ligands X and Y. Isodesmic reactions are hypothetical reactions in which the number of bonds of the given type is conserved. The reaction depicted in Scheme 1 is isodesmic as the number and type of bonds in the reactant side is equal to the number and type of bonds in the product side. However, the trans influence is not conserved in the reaction. Therefore, the energy of the reaction, E_{XY}, will mainly account for the difference between the trans influence at the product and the reactant sides. In the reactant side, the trans influence of X and Y is present, while the trans influence due to (X, Y) combination as well as the trans influence of Cl is present in the product side. Because the trans influence due to Cl in

Table 6. Isodesmic Reactions Used for the Test Set[a]

	ligands in the trans positions			predicted E_{XY}		
isodesmic reactions	X	Y	calcd E_{XY}	eq 2	eq 3	eq 4
1	BF_4	Ph	−17.52	−14.01	−15.21	−14.85
2	$C(PPh)_3COOMe$	$C(PPh)_3COOMe$	32.16	33.12	32.27	42.38
3	O*i*Pr	CCH	4.42	2.87	3.51	5.49
4	BF_4	$C(PPh)_3COMe$	−24.49	−17.56	−18.65	−19.97
5	NHTf	OH	−0.56	−0.13	−0.21	−0.20
6	OTs	OO*t*Bu	−2.16	−1.80	−1.62	−0.88
7	$C_6F_5CF_3$	CF_3	6.67	5.54	5.92	4.19
8	C_6F_5	$CCSiMe_3$	9.14	6.85	7.61	6.98
9	$CF_2CF_2CF_3$	Ph	9.85	9.95	10.91	6.57
10	OCOCOOMe	Br	−1.15	−0.68	−0.79	0.17
11	OCOCOOMe	CCH	−2.63	−1.69	−1.53	−1.33
12	$OCOCCl_3$	CH_2Cl	−4.11	−4.56	−4.43	−4.46
13	$OCOCF_3$	$OCOCF_3$	1.03	0.48	0.55	0.96
14	F	Ph	−1.84	−5.67	−5.02	−3.55
15	F	NH_2	−1.60	−3.50	−3.27	−2.33
16	$OCOCF_3$	OO*t*Bu	−2.25	−1.75	−1.87	−2.96
17	OAc	OH	0.16	−0.30	−0.24	0.88
18	Br	Me	1.47	2.57	4.56	−0.04
19	OMe	Ph	6.78	2.75	4.08	5.84
20	NO_2	OMe	−0.03	1.65	1.77	−0.09
21	OSO_2Me	CH_2Cl	−2.97	−4.63	−4.44	−2.16

[a] Calculated and predicted E_{XY} are given. All values in kcal/mol.

$[CF_3ICl_2]$ is constant for all reactions, the energy of the reaction E_{XY} can be used as a good measure of the mutual trans influence of the (X, Y) combination. In other words, E_{XY} values will indicate the stabilization/destabilization due to the trans disposition of the X and Y ligands around the I atom. From the 32 ligands selected in this study, we randomly picked 63 combinations of X and Y and studied the corresponding 63 isodesmic reactions. Out of the 63 reactions, the E_{XY} values of 42 reactions given in Tables 5 are used as a training set for statistical analysis (sample size, $n = 42$), while the remaining 21 reactions in Table 6 are used as test set ($n = 21$).

All E_{XY} values fall in the range from −24.96 to 33.62 kcal/mol (Tables 5 and 6). A positive E_{XY} corresponds to destabilization due to the mutual trans influence, while a negative E_{XY} indicates a stable trans combination. The ($C(PPh_3)COMe$, $C(PPh_3)COMe$) and ($CPPh_3COOMe$, $CPPh_3COOMe$) combinations show the highest E_{XY} values of 33.62 and 32.16 kcal/mol, respectively, and they correspond to highly unstable (very strong, very strong) trans-influencing pairs. Similarly, E_{XY} above 20 kcal/mol is observed for the (Me, Et) and (Et, $C(PPh_3)COOMe$) combinations. All very strong−very strong, very strong−strong, and strong−strong trans influencing pairs are unfavorable combinations. The weak−weak combinations (BF_4, BF_4) and ($OCOCF_3$, $OCOCF_3$) are also unstable, whereas the weak−weak combination, ($OCOCCl_3$, $OCOCCl_3$) is slightly unstable (E_{XY} = 0.23 kcal/mol). As suggested by Ochiai et al.,[42] moderate trans-influencing combinations are stable with most of the E_{XY} showing negative values. The most favorable combinations are the medium−strong, weak−strong, and weak−very strong trans-influencing pairs. For example, the lowest E_{XY} of −24.49 and −24.96 kcal/mol are shown by (BF_4, $CPPh_3COOMe$) and (BF_4, $CPPh_3COMe$), respectively, and they correspond to weak−very strong trans-influencing combinations.

The results presented herein suggest that the presence of electronegative atoms at the axial position is not an essential criterion for explaining the stability of hypervalent iodine compounds.[42] The electron-releasing groups such as Me, Et, Ph, and $CPPh_3COOMe$ can also make the system stable provided that the trans position is occupied by ligands with a small trans influence such as BF_4, OTf, and NO_3. Further, the mutual trans influence of X and Y strongly depends on the individual trans influence of X as well as Y. It is found that using the trans-influence parameter of X, the trans-influence parameter of Y, and the product of the trans-influence parameters of X and Y, empirical eqs 2−4 can be derived for predicting the values of E_{XY} using MLR analysis

$$E_{XY} = -1657.68d_X - 1700.66d_Y + 667.47d_Xd_Y + 4224.54 \tag{2}$$

where $n = 42$, $s = 2.05$, and $r = 0.976$.

$$E_{XY} = -6.75\rho_x(\mathbf{r}) - 6.33\rho_y(\mathbf{r}) + 0.146\rho_x(\mathbf{r})\rho_y(\mathbf{r}) + 293 \tag{3}$$

where the $\rho(\mathbf{r})$ values are expressed in kcal/mol, $n = 42$, $s = 1.91$, and $r = 0.980$.

$$E_{XY} = 0.115V_{\min(X)} + 0.387V_{\min(Y)} + 0.021V_{\min(X)}V_{\min(Y)} + 3.460 \tag{4}$$

where $n = 42$, $s = 1.95$, and $r = 0.980$. In these equations, the terms d_X, $\rho_x(\mathbf{r})$, and $V_{\min(X)}$ indicate, respectively, the trans I−Cl bond distance, $\rho(\mathbf{r})$, and $V_{\min}$ of the $CF_3[I(X)(Cl)]$ complex while d_Y, $\rho_y(\mathbf{r})$, and $V_{\min(Y)}$ are, respectively, the trans I−Cl bond distance, $\rho(\mathbf{r})$, and $V_{\min}$ of the $CF_3[I(Y)(Cl)]$ complex. Also, the trans influence of X ≤ the trans influence of Y. s and r are the standard deviation and correlation coefficient, respectively.

Table 7. Calculated and Predicted Bond Dissociation Energy Values of X and Y in $CF_3[I(X)(Y)]$ Complexes (kcal/mol)

ligands in the trans positions					
X	Y	calcd E_d for X	predicted E_d for X using V_{min}	calcd E_d for Y	predicted E_d for Y using V_{min}
F	Br	181.00	182.48	171.64	156.86
F	F	205.28	190.00	205.28	190.00
$OCOCCl_3$	OH	136.96	129.67	211.22	213.68
OTs	Ph	99.36	102.37	213.93	226.09
OH	Br	197.42	198.64	149.65	143.02
OTs	CF_3	119.43	124.46	177.05	189.75
Br	$CCSiMe_3$	119.58	123.09	179.12	180.61
$CF_2CF_2CF_3$	Me	127.11	125.04	201.17	208.03
OMe	O*i*Pr	177.71	176.15	178.16	173.68
OSO_2Me	Me	108.16	106.51	241.04	242.06
BF_4	Me	92.96	91.61	272.59	273.45
F	$C(PPh_3)COOMe$	123.37	124.93	223.78	208.22
F	Me	151.03	148.68	253.69	237.69
NO_3	Ph	100.74	103.73	229.26	232.33
F	OMe	177.72	173.27	216.32	200.88
BF_4	$C(PPh_3)COOMe$	74.91	77.39	252.28	253.51
OTs	F	155.70	141.17	176.75	189.43
OO*t*Bu	Me	147.05	144.72	208.74	214.68
Me	Et	171.09	170.40	181.15	178.18
OTf	Br	117.24	119.70	169.25	174.61
OH	$CCSiMe_3$	167.45	170.22	179.22	171.24
OTf	Et	90.67	91.46	264.78	268.77
NO_3	Me	107.27	105.62	244.93	247.76
OSO_2Me	Et	102.97	103.53	245.91	246.87
OTf	OSO_2Me	120.70	123.49	151.86	157.47
OH	OMe	191.86	187.18	192.06	183.90
Et	$C(PPh_3)COOMe$	147.91	148.88	135.59	135.39
CF_3	CF_3	156.03	160.43	156.03	160.43
$OCOCCl_3$	OSO_2Me	136.80	139.34	142.44	145.92
O*i*Pr	CCPh	150.21	154.57	163.91	162.54
NO_2	CCPh	120.29	125.15	172.39	184.75
OCOCOOMe	OCOCOOMe	144.26	150.00	144.26	150.00
$OCOCCl_3$	$OCOCCl_3$	143.11	146.58	143.11	146.58
Br	Br	148.73	150.70	148.73	150.70
OMe	OMe	184.54	179.96	184.54	179.96
NO_3	OH	137.41	130.11	210.82	214.14
NO_3	OMe	130.20	126.47	203.80	207.23
Br	Ph	108.31	111.12	211.19	212.20
NO_3	F	157.47	142.91	192.47	196.06
$C(PPh_3)COMe$	$C(PPh_3)COMe$	108.72	111.61	108.72	111.61
BF_4	BF_4	132.56	135.39	132.56	135.39
OTf	OMe	114.89	111.42	214.86	219.55

To test the reliability of the trans-influence parameters, the leave-one-out (LOO) cross-validation methodology is applied. In this test, one isodesmic reaction is removed from the data set and the corresponding E_{XY} value is predicted from the rest of the data. The process is repeated for each isodesmic reaction, and the cross-validated correlation coefficients (r^2_{cv}) of 0.940, 0.947, and 0.937 are obtained, respectively, for the trans-influence parameters d_X, $\rho_x(\mathbf{r})$, and $V_{min(X)}$. This is an indication of the high predictive power of this model. Further, eqs 2, 3, and 4 are validated using a set of 21 isodesmic reactions given in Table 6. The statistical parameters obtained for the test set are good, viz. s equal to 2.40, 2.01, and 2.85 for eqs 2, 3, and 4, respectively, and r equal to 0.977, 0.987, and 0.970 for eqs 2, 3, and 4, respectively. The predicted E_{XY} values for the training set and the test set are given in Tables 5 and 6, respectively.

Bond Dissociation Energy and Trans Influence. Ligands in the axial positions of a hypervalent iodine(III) complex can be cleaved heterolytically.[2] This reaction can be represented as either $CF_3[I(X)(Y)] \rightarrow [CF_3IY]^+ + X^-$ or $CF_3[I(X)(Y)] \rightarrow [CF_3IX]^+ + Y^-$. It is well known that the bond dissociation energy (BDE) of various ligands depends on the nature of the trans ligands.[47,48] In the present case, the dissociation of X^- or Y^- can be influenced by the trans influence of X or Y as well as the mutual trans influence of the (X, Y) combination. The trans (X, Cl) combination represents the $CF_3[I(X)(Cl)]$ system and is used herein as the reference structure to evaluate the trans parameters d_X, $\rho(\mathbf{r})$, and V_{min}. Therefore, the BDE of X in the $CF_3[I(X)(Cl)]$ system (designated as $E_{d(X)}$; all the values are given in the Supporting Information) is used as a reference value to estimate the mutual trans influence of the (X, Y) combination on the dissociation

Table 8. Calculated and Predicted Bond Dissociation Energy Values of X and Y for Compounds Used for the Test Set (kcal/mol)

ligands in the trans positions					
X	Y	calcd E_d for X	predicted E_d for X with eq 7	calcd E_d for Y	predicted E_d for Y with eq 7
BF_4	Ph	87.25	90.55	257.72	258.87
$C(PPh)_3COOMe$	$C(PPh)_3COOMe$	109.06	110.61	109.06	110.61
O*i*Pr	CCH	162.79	162.38	170.04	168.62
BF_4	$C(PPh)_3COMe$	76.43	80.28	250.93	252.24
NHTf	OH	137.48	130.19	198.76	203.77
OTs	OO*t*Bu	118.41	125.81	180.45	193.12
$C_6F_5CF_3$	CF_3	133.24	138.02	153.70	161.16
C_6F_5	$CCSiMe_3$	125.54	128.93	150.48	157.01
$CF_2CF_2CF_3$	Ph	119.47	122.07	184.38	191.53
OCOCOOMe	Br	144.10	146.17	150.91	156.59
OCOCOOMe	CCH	126.83	127.01	189.32	194.43
$OCOCCl_3$	CH_2Cl	109.97	114.54	220.50	222.88
$OCOCF_3$	$OCOCF_3$	148.75	149.65	148.75	149.65
F	Ph	144.31	146.64	237.83	222.11
F	NH_2	164.29	159.85	237.20	221.48
$OCOCF_3$	OO*t*Bu	121.39	128.74	201.02	201.16
OAc	OH	161.63	153.97	197.36	198.52
Br	Me	115.40	113.60	227.44	228.24
OMe	Ph	145.86	148.09	200.77	195.94
NO_2	OMe	145.40	141.45	183.35	195.58
OSO_2Me	CH_2Cl	109.67	114.24	214.56	216.00

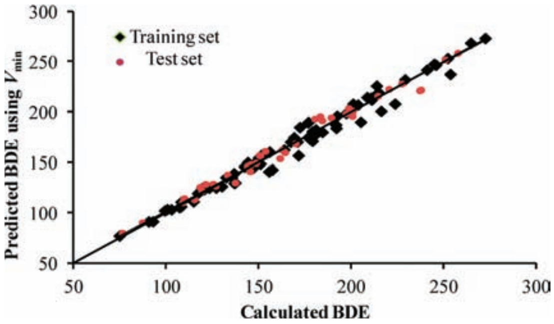


Figure 10. Agreement between calculated and predicted bond dissociation energy values. All values are in kcal/mol.

energy of either the X or the Y ligand in the $CF_3[I(X)(Y)]$ system. To make a reasonable prediction of the BDE of the X or Y ligand in the $CF_3[I(X)(Y)]$ complex (designated as E_d), MLR analysis is done with three variables, viz. $E_{d(X)}$, any one of the trans-influence parameters, and E_{XY}. The following equations are obtained from the 42 compounds considered in Table 5

$$E_d = 0.976E_{d(X)} - 258.574d_X - 0.992E_{XY} + 654.944 \quad (5)$$

where $n = 42$, $s = 6.59$, and $r = 0.989$.

$$E_d = 0.977E_{d(X)} + 3.651\rho(\mathbf{r}) - 0.995E_{XY} - 160.084 \quad (6)$$

where $n = 42$, $s = 6.80$, and $r = 0.988$.

$$E_d = 0.985E_{d(X)} + 1.463V_{min} - 0.993E_{XY} + 21.485 \quad (7)$$

where $n = 42$, $s = 6.44$, and $r = 0.989$.

The accuracy of the present model is assessed by the LOO cross-validation procedure, and excellent r^2_{cv} values of 0.976, 0.972, and 0.977 are obtained for d_X, $\rho_x(\mathbf{r})$, and $V_{min(X)}$, respectively, which show the high predictive nature of this model. Further, the obtained eqs 5, 6, and 7 are validated using the 21 complexes given in Table 6. The statistical parameters of the test set, respectively, for eqs 5, 6, and 7 are as follows: s = 5.88, 6.05, and 5.80; r = 0.992, 0.991, and 0.992. The calculated E_d values of these complexes are given in Tables 7 and 8 along with the predicted E_d values using eq 7. Similar results are also obtained using eqs 5 and 6 (Supporting Information). It can be seen that the above equations can predict the E_d values (in the range 74–272 kcal/mol) reasonably well. Figure 10 illustrates the agreement between the actual and the predicted E_d values as well as the predictive power of eq 7. There are 10 compounds in the training set and 4 compounds in the test set with a prediction error of more than 10 kcal/mol. If we remove these outliers and further considering the data set, the new regression equation obtained is

$$E_d = 0.988E_{d(X)} + 1.394V_{min} - 1.040E_{XY} + 18.521 \quad (8)$$

Equation 8 gives an s value of 3.56 and 3.80 for the training set and test set, respectively, and shows an improved r value of more than 0.99 for both sets. The outliers are mainly the complexes with the ligand F at the axial position; hence, it can be assumed that the through-space interactions arising from the F atom of the CF_3 ligand are stronger in such cases. Deviations are also expected due to steric interactions from bulky ligands. It may be noted that the constants in the above equations can vary depending on the level of theory used, while these equations firmly suggest that the trans influence as well as the mutual trans influence significantly affect the bond dissociation energy of ligands in hypervalent iodine complexes.

Using any of the above equations it is possible to predict the BDE values of any trans combinations (X and Y) and hence to predict the most facile dissociation of a 3c-4e bond. For example, in $CF_3[I(Br)(Ph)]$ complexes, the E_d values of trans combinations Br and Ph are 108.31 and 211.19 kcal/mol, respectively. Similarly, for $CF_3[I(F)(Br)]$ complexes, E_d values are 181.00 and 171.64 kcal/mol for trans combinations F and Br, respectively. Thus, the I−Br bond trans to the Ph ligand is 63.33 kcal/mol less stable than the I−Br bond trans to the F ligand. The predicted values also follow a similar order. It is generally observed that in hypervalent iodine-mediated reactions the I−X bond which is trans to a highly trans-influencing aryl ligand is cleaved regularly.[1−3] Hence, the understanding of the BDE of I−X bonds and the influence of the trans ligand Y can be utilized for explaining the mechanistic steps involved in cleavage of the I−X bond.

■ CONCLUSIONS

The trans I−Cl bond length, electron density at the (3,−1) bond critical point at the trans I−Cl bond, and MESP minimum (V_{min}) at the chloro ligand in $CF_3[I(X)(Cl)]$ complexes have been proposed as parameters for quantification of the trans influence of various ligands in hypervalent complexes. The V_{min} values of hypervalent iodine(III) as well as iodine(V) complexes are used as a sensitive measure of the trans influence of X. On the basis of trans-influence parameters, the ligands are classified into 4 groups, viz. very strong, strong, medium, and weak trans-influencing ligands. Simple isodesmic reactions of the type $CF_3[I(X)Cl] + CF_3[I(Y)Cl] \rightarrow CF_3[I(Cl)Cl] + CF_3[I(X)Y]$ are useful for understanding the preferred trans combination of a variety of X and Y ligands. The isodesmic reaction energy, E_{XY}, indicates the mutual trans influence between X and Y ligands. The medium−medium, medium−strong, weak−strong, and weak−very strong trans-influencing combinations are found to be preferred combinations, while the very strong−very strong, strong−strong, strong−very strong, and weak−weak combinations are found to be unstable combinations. The mutual trans influence of a large number of (X, Y) combinations is predicted with good accuracy using the trans-influence parameters of the X and Y ligands. Empirical equations using the trans influence and mutual trans-influence parameters have been derived for predicting the bond dissociation energy of either the X or the Y ligand in $CF_3[I(X)Y]$ complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates of all geometries, $E_{d(X)}$ values, and predicted bond dissociation energy using the trans-influence parameters d_X and $\rho(\mathbf{r})$. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the Council of Scientific and Industrial Research(CSIR), India, for support through a project NWP-53. P.K.S. is thankful to the University Grants Commission (UGC), Government of India, for a fellowship.

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