Electronic Structure and Bonding in Polycoordinated Iodine Compounds

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An investigation of the geometry and electronic structure of some hypervalent iodine compounds of type $PhIX_2$ by means of extended Hückel and CNDO/2 quantum chemical approaches was undertaken. The analysis of the bonding was made in terms of both the model of delocalized MOs on the basis of interactions between fragment molecular orbitals derived from EHMO-SCCC calculations, and that of localized MOs derived by the CNDO/2 method. The ability of these compounds to afford *cis*-addition products with ethylene double bonds *via* a synchronous molecular addition mechanism was found to be theoretically feasible.

A prominent feature of iodine is its marked tendency to form hypervalent compounds where it becomes polycoordinated by forming relatively weak bonds mostly with electronegative elements or groups.[1] Such compounds, in which iodine has a formal valency of 3, 5 or 7, have been known since the end of the nineteenth century.[2] However, the interest in the chemistry of polycoordinated iodine has recently flourished with the discovery of several new classes of compounds and notably with the development of synthetically important new reactions for several of their members. Among them, the bis haloiodanes, $PhIX_2$ (X = F, Cl), have been extensively used in a variety of reactions, such as ligand exchange by nucleophiles and halogenation or oxidation of anion substrates.[1,3] Bis haloiodanes are very similar to the known simple hypervalent halogen compounds, ClF_3 and BrF_3, which adopt a T-shaped structure. Accordingly, in these molecules there are two ligands *trans* to each other, attached to the central atom by a three-centre-four-electron bond, and one ligand attached by a conventional two-centre-two-electron bond.[4]

The electronic structure of hypervalent molecules has been described within valence bond (VB) theory[5] by the introduction of the concept of 'expanded valence shell'[6,7] or the use of hybridization schemes including d orbitals.[8,9] This has led to a controversy, mainly owing to the large promotion energies required for such a hybridization.[10,13] On the other hand, molecular orbital (MO) theory has provided a treatment of these molecules in terms of non-classical multicentre bonding using only s and p orbitals,[14,15] whereas the participation of charge transfer configurations in the molecular wave function has also been discussed.[16,17] However, as Moriarty *et al.* pointed out,[18] theoretical calculations on hypervalent iodine structures are possible and should yield important information about bonding. To this end, we here present the investigation of the electronic structure of $PhIF_2$ and $PhICl_2$ by means of extended Hückel and CNDO/2 quantum chemical methods. Although *ab initio* methods have been successfully used for the calculation of the ground state geometry of analogous hypervalent molecules,[19] in this work we have resorted to semi-empirical methods, which generally provide a valuable basis for a meaningful discussion of the most important bonding aspects of such molecules, rather than obtaining the full potential energy surface. The analysis of the orbital interactions responsible for both the bonding and the geometric features of the molecules was made on the basis of Hoffmann's extended Hückel approach within the fragment formalism, which has been proven an excellent tool for the interpretation of chemical bonding.[4] For the extraction of the natural hybrid orbitals involved in the hypervalent bonding, we have used the first-order density matrix obtained from CNDO/2 calculations, as in this approximation the basis orbitals are implicitly orthonormal, so that the calculations procedure is significantly simplified. Moreover, the ability of these compounds to form addition products with ethylene double bonds[1] *via* a synchronous molecular addition mechanism was also examined.

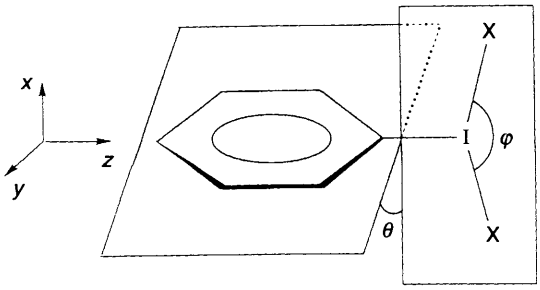
Table 1 Slater exponents and iteration parameters used for EHMO-SCCC calculations

Atom	AO	ζ	A/eV	B/eV	C/eV
H	1s	1.300	13.618	27.180	13.600
C	2s	1.625	0.000	11.900	20.400
	2p	1.625	0.000	11.900	10.600
F	2s	2.425	0.000	16.200	42.400
	2p	2.425	0.000	16.200	19.600
Cl	3s	2.033	0.000	10.660	25.930
	3p	2.033	0.000	10.660	13.820
	3d	1.633	0.000	10.660	8.000
I	5s	1.525	0.000	9.030	22.000
	5p	1.525	0.000	9.030	10.270
	5d	1.438	0.000	9.030	6.840

Computational Details

Calculations were carried out in the framework of the extended Hückel LCAO-MO method with self-consistent charge and configuration (EHMO-SCCC)[20–22] by using the FORTICON-8 computer program.[23] In these iterative calculations the so-called 'weighted H_{ij} formula' for the off-diagonal matrix elements (H_{ij}) was used in order to reduce the intriguing phenomenon of counterintuitive orbital mixing (COM).[24] The value of 1.75 was used for the parameter *k*. The orbital exponents for all atoms[25–27] and the charge iteration parameters[28] are given in Table 1.

In the SCF-LCAO-MO calculations implemented at the CNDO/2 level of approximation,[29] the AO basis set consisted of 1s AO for H, *n*s and *n*p AOs for C, F, Cl and I. The CNDO/2 wave function for $PhICl_2$ was analysed by natural hybrid orbital (NHO) analysis.[30] To this end, the full-density matrix was partitioned into atomic subblocks $\mathbf{P}_{AA}$ and $\mathbf{P}_{AB}$ associated with atomic orbitals on centre A or on centres A and B, respectively. The diagonalization of $\mathbf{P}_{AA}$ gave eigen values $n_i^{(A)} = 2.00$ whose eigen vector $\varphi_i^{(A)}$ corresponded to the lone-



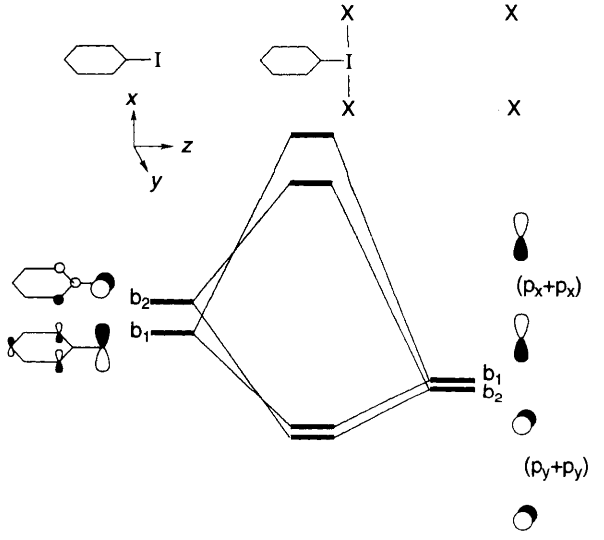
Scheme 1

pair localized orbitals $h_i^{(A)}$, and $n_i^{(A)} = 1.00$ with eigen vectors corresponding to half-filled orbitals available for covalent bonding. The natural bond orbitals $\varphi_i^{(AB)}$ for each bond A–B in the molecule were found by diagonalizing the '2 × 2' submatrices $\mathbf{P}_{AB}$ depleted of the lone-pair eigen vectors $\varphi_i^{(A)}$. Finally, the directed hybrids $h_i^{(A)}$ and $h_i^{(B)}$ in each centre, contributing to $\varphi_i^{(AB)}$, were symmetrical orthogonalized to obtain the final natural hybrid orbitals for each centre. The minimal occupancy, n_{min}, adopted was taken to be 1.900.

Results and Discussion

Geometry Optimization.—The first polyvalent iodine compound subjected to an X-ray structure analysis was $PhICl_2$.[31] Although imprecise by modern standards, the structure revealed the characteristic T-shape of iodanes, that is, the existence of an almost linear symmetrical Cl–I–Cl group nearly perpendicular (86 ± 1°) to the plane of the benzene ring. Thus, CNDO/2 geometry optimization calculations were carried out for both the $PhIF_2$ and $PhICl_2$ molecules in order to check the ability of the method to reproduce the experimental results in the case of $PhICl_2$, and to find the most crucial geometrical parameters for $PhIF_2$, as well. In these calculations the geometry of the benzene ring was kept constant. Furthermore, the C–I bond length was taken equal to that found for $PhICl_2$.[31] This is a valid assumption since the C–I bond length in $PhICl_2$ is almost equal to that of Ph–I,[32] implying that the formation of the triatomic group X–I–X has little effect on this bond. A preliminary series of calculations has also shown that the torsion angle θ (Scheme 1) adopts an optimal value of 90° for any reasonable value of the bond length d(I–X) and the angle φ, as well.

The potential energy surfaces for both the $PhICl_2$ and $PhIF_2$ molecules, obtained on the basis of the above assumptions under the C_{2v} symmetry constraint, show the variation of the energy of the molecules as a function of the remaining structural parameters, namely the bond length d(I–X) and the angle φ (Fig. 1). The minima located correspond to I–F = 1.95 Å and $\varphi = 200°$ for $PhIF_2$, and I–Cl = 2.45 Å and $\varphi = 190°$ for $PhICl_2$. The values for $PhICl_2$ are in excellent agreement with the experimental ones (I–Cl = 2.464 Å and $\varphi = 188°$), whereas the T-shaped structure of the molecules studied is in satisfactory agreement with those found for simple hypervalent compounds, such as ClF_3 and BrF_3.[33] In both molecules there is a distortion from the idealized T-shape, since the angle φ is somewhat greater than 180°, that is, the two halide ligands bend towards the benzene ring. This result can be explained in terms of the elementary valence-shell-electron-pair-repulsion model (VSEPR) or its recent version renamed as valence-shell-electron-pair-domain model (VSEPD).[34] Actually, there are five localized electron pair domains on the vertices of a trigonal bipyramid, **1**, in the valence shell of the iodine central atom. Three vertices are occupied by single bond domains, the other two being nonbonding ones. According to VSEPD, nonbonding domains being larger than the single bond ones, repel them more intensely than the latter repel each other. Thus, the halide ligands are pushed away from the nonbonding domains, leading to $\varphi > 180°$. Furthermore, the lengthening of the I–X bond in going from F to Cl is in line with both the larger atomic radius and the smaller electronegativity of the latter atom.



Scheme 2

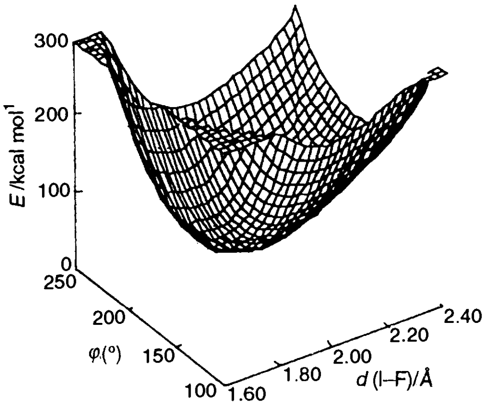
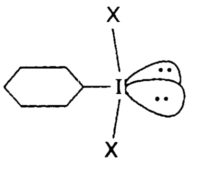


Fig. 1 CNDO/2 potential energy surface, $E = f[\varphi, d(\text{I–F})]$, for $PhIF_2$



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Electronic Structure of the Compounds.—In order to analyse the orbital interactions responsible for the formation of the C_{2v}–$PhIX_2$ molecule from its molecular fragment PhI and two slightly interacting halide ligands X, a fragment molecular orbital study was carried out at the extended Hückel level, with no inclusion of the d orbitals of iodine in the basis set, at first. However, the role of these orbitals will be discussed later in our analysis.

According to the calculations there is a set of orbitals of the two fragments either more or less perturbed or remaining nonbonding. The only interactions that have bonding consequences in both molecules are those between orbitals of b_1 and b_2 symmetry. Actually, the symmetrical combination of the two p_x orbitals of the halide ligands X interacts with the appropriate b_1 orbital of the PhI fragment. In fact, there is more than one orbital of b_1 symmetry in PhI, but owing to both overlap and

Table 2 One-electron energies and partial wave analyses of the most important frontier MOs for $PhIF_2$

	MO	Energy/eV	Charge (%)					Basis functions				
			I	2F	C[a]	5C[b]	5H	I	2F	C[a]	5C[b]	5H
NNLUMO	$3a_2$	−8.191	11	2	0	87	0	xy	y		x	
NLUMO	$6b_1$	−8.313	20	3	22	55	0	x,xz	z	x	x	
LUMO	$12a_1$	−9.510	92	0	3	4	1	s,z,x^2-y^2,z^2		z	y	s
HOMO	$7b_2$	−11.144	89	7	1	3	0	y,yz	y	y	z	
NHOMO	$11a_1$	−11.545	11	3	45	35	6	z	z	z	y,z	s
NNHOMO	$5b_1$	−12.277	3	2	30	65	0	xz	z	x	x	

[a] Carbon atom bonded to I. [b] Remaining carbon atoms.

Table 3 One-electron energies and partial wave analyses of the most important frontier MOs for $PhICl_2$

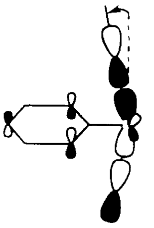
	MO	Energy/eV	Charge (%)					Basis functions				
			I	2Cl	C[a]	5C[b]	5H	I	2Cl	C[a]	5C[b]	5H
NNLUMO	$3a_2$	−8.462	20	49	0	31	0	xy	y,xy		x	
NLUMO	$6b_1$	−8.670	12	31	14	43	0	xz	z,xz	x	x	
LUMO	$12a_1$	−9.308	70	24	3	3	0	s,z,x^2-y^2,z^2	z,z^2,xz	z	y	
HOMO	$7b_2$	−10.455	50	50	0	0	0	y,yz	y,xy			
NHOMO	$11a_1$	−11.222	31	63	4	2	0	s,z,x^2-y^2	x,z,xz	z	y	
NNHOMO	$10a_1$	−11.615	5	22	38	30	5	s,z,z^2	x,z	z	z	s

[a] Carbon atom bonded to I. [b] Remaining carbon atoms.

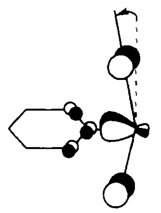
energy reasons the main interaction is that shown in Scheme 2. This interaction is a non-classical three-centre-two-electron one, present in MO analysis of other hypervalent molecules. The other stabilizing orbital interaction within the b_2 representation is quite similar. The symmetrical $p_y + p_y$ ligand group X···X orbital finds its counterpart in a b_2 orbital of PhI. The $(p_y + p_y)/b_2$ overlap is less than the one between $(p_x + p_x)$ and b_1, and thus, the stabilization gained from this interaction is smaller.

The calculated ground-state one-electron energies and partial wave analysis of the most important frontier MOs of $PhIF_2$ and $PhICl_2$ are given in Tables 2 and 3, respectively. For $PhIF_2$ both the HOMO, $7b_2$, and the LUMO, $12a_1$, are nonbonding orbitals localized on the iodine, whereas the NHOMO, $11a_1$, and the NNHOMO, $5b_1$, are π-MOs delocalized over the benzene ring. The NLUMO, $6b_1$, and NNLUMO, $3a_2$ are π*-MOs delocalized also over the benzene ring. Of particular interest is the lack of MOs delocalized within the linear trihalide group, which serves as a first indication of a significant ionic character of the I–F bond. On the other hand, the frontier orbitals of $PhICl_2$ differ substantially from those of $PhIF_2$. The LUMO, $12a_1$, HOMO, $7b_2$ and NHOMO, $11a_1$, are totally localized on the triatomic group Cl–I–Cl. The shape of these MOs is indicative of the enhanced covalency of I–Cl bond relative to I–F. Indeed, on going from Cl to F the energy gap between the frontier orbitals of the two fragments, shown in Scheme 2, increases due to the higher electronegativity of the latter atom, while the magnitude of the interactions decreases and the I–F bond becomes less covalent. This is reflected to the overlap populations calculated for the I–X bonds (0.631 for X = F and 1.319 for X = Cl). Finally, the overlap population of the C–I bond (0.971 and 0.915 for $PhIF_2$ and $PhICl_2$, respectively) shows a single carbon–iodine bond.

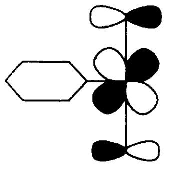
The inclusion of the d orbitals of iodine in the basis set, although it has a little effect in the energy of the b_1 and b_2 orbitals of PhI, perturbs their shape in an interesting way. Since d orbitals are at much higher energy, they mix in a bonding way with the aforesaid orbitals through a second order mixing and alter their shape. Now, it is clear that the maximum overlap between $(p_x + p_x)$ and b_1, **2**, is achieved when the two ligand atoms X bend towards the benzene ring leading to an angle $\varphi > 180°$. The same is also true for the b_2 interaction, where this distortion from the idealized T-shape increases the $(p_y + p_y)/b_2$ overlap, **3**. It must be mentioned, however, that owing to the high energy of the d orbitals, their coefficients in **2** and **3** are small. Thus, the bending produced is small, in line with the small deviation of the angle φ from 180° in both molecules. Finally, it should be mentioned that the orbitals of PhI, based on d_{xz} and d_{yz} of iodine, interact also with the $b_1:(p_z - p_z)$, **4**, and $a_2:(p_y - p_y)$, **5**, symmetry adapted combinations of X···X, respectively, which are mostly nonbonding when d orbitals are omitted. These interactions are very small due to the large energy gap between the orbitals involved, but result in a secondary charge transfer.


$b_1/(p_x+p_x)$

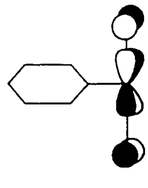
2


$b_2/(p_y-p_y)$

3


$b_1:d_{xz}/(p_z-p_z)$

4


$a_2:d_{yz}/(p_y-p_y)$

5

The results of the Mülliken population analysis for the halogens, given in Table 4, elucidate the mechanism of the bond

Table 4 Results of Mülliken population analysis for the molecules studied

	Atom	$\|s>$	$\|x>$	$\|y>$	$\|z>$	$\|x^2-y^2>$	$\|z^2>$	$\|xy>$	$\|xz>$	$\|yz>$
$PhIF_2$										
I	6.113 (5.283)[a]	1.489	0.284	1.763	1.101	0.398	0.131	0.221	0.300	0.425
F	7.463 (7.745)	1.713	1.970	1.879	1.901					
$PhICl_2$										
I	6.524 (5.477)	1.452	0.565	1.503	1.051	0.583	0.232	0.421	0.457	0.259
Cl	7.242 (7.671)	1.586	1.789	1.755	1.782	0.026	0.011	0.212	0.075	0.006

[a] Values in parentheses are the corresponding values without d AOs on I.

Table 5 Localized bond orbitals and NHOs for $PhICl_2$

	$n_1^{(I)}$ (1.9673) $\varphi_1^{(I)}$	$n_2^{(I)}$ (1.9599) $\varphi_2^{(I)}$	$n_1^{(C-I)}$ (1.9710) $\varphi_1^{(C-I)}$	$n_1^{(I-Cl)}$ (1.9526) $\varphi_1^{(I-Cl)}$	$n_2^{(I-Cl)}$ (1.9994) $\varphi_2^{(I-Cl)}$	$n_3^{(I-Cl)}$ (1.9996) $\varphi_3^{(I-Cl)}$	$n_4^{(I-Cl)}$ (1.9995) $\varphi_4^{(I-Cl)}$
I							
s	0.9202		0.2985	−0.0338	0.0239	−0.0009	
x				−0.6100	0.0017	−0.1086	
y		1.0000					
z	−0.3912		0.6995	−0.0796	0.0570	0.0026	
Cl							
s				−0.0308	0.2902	−0.9433	
x				0.7856	0.0765	−0.1034	
y							1.0000
z				−0.0470	0.9519	0.2959	
C							
s			0.3695				
x							
y							
z			−0.5339				
$h^{(I)}$	$sp^{0.18}$	p	$sp^{5.49}$	p	—	—	—
$h^{(Cl)}$	—	—	—	p	$sp^{10.76}$	$sp^{0.11}$	p
$h^{(C)}$	—	—	$sp^{2.08}$	—	—	—	—

formation within the triatomic group. Thus, the central iodine atom presents a decreased electron density at the 5s and 5p orbitals, whereas some electron density appears at the 5d atomic orbitals. The least electronic density is located on the $5p_x$ AO, which interacts with the np_x AO of the terminal halide ligands X. The appearance of electronic density in the initially empty 5d AO of the central atom must be mainly due to a transfer of electronic density from the terminal ligands. Of special interest are the values of the electron densities of the halogen atoms which resulted from calculations without the 5d AO of iodine in the basis set. In this case, the electron density decreases on iodine and increases on fluorine or chlorine. Thus, we conclude that the transfer of electronic density in the direction X ⟶ I must function according to the mechanism X: (*n*p) ⟶ I: (5d). Concerning the 3d AOs of the chlorine in $PhICl_2$, they present very low values since their participation in the bonding MOs is negligible.

According to perturbation theory,[35] the stabilization energy (ΔE) resulting from a charge (q) transferred from the filled p orbitals of the terminal halogens to the d AOs of iodine may be approximated as $\Delta E = q(\varepsilon_p - \varepsilon_d)$, where $(\varepsilon_p - \varepsilon_d)$ is the energy gap between these AOs. On the basis of the values of $(\varepsilon_p - \varepsilon_d)$ calculated from the diagonal Hückel matrix elements for the AOs involved in the charge transfer and the populations presented in Table 4, we calculated a ΔE value of 270 and 300 kcal mol^{-1} * for $PhIF_2$ and $PhICl_2$, respectively. These values correspond to 1–2% of the total energy of the molecules. Thus, the d AOs of the central iodine seem to serve as available acceptor orbitals in a second-order charge transfer, making a small contribution to the molecular binding energy. The above conclusions are in line with previous results concerning models for hypervalent bonding which do not require d orbital participation.[7,36–39] Furthermore, there is much experimental evidence that points in favour of models of hypervalency not requiring d orbital participation.[40–46]

The CNDO/2 wave functions for $PhICl_2$ were analysed in order to find the natural bond orbitals (NBO) and the natural hybrid orbitals (NHO). This method has produced NHOs of molecules with hybridizations that are qualitatively in accord with chemical intuition. The selection of the CNDO/2 method was made because of the orthonormal basis which is used in it, a fact that facilitates the calculations. Furthermore, it should be stressed that the atomic electron densities derived from this method agree to an adequate extend with the results obtained from the EHMO-SCCC method used for the above description of the electronic structure of the compounds. To check the validity of the conclusion that the d orbitals contribute a little to the bonding in the molecules under investigation, we have excluded these AOs from the basis set. The localized orbitals of one or two centres, $\varphi_i^{(A)}$ and $\varphi_i^{(AB)}$, the occupation numbers, $n_i^{(A)}$ and $n_i^{(AB)}$, as well as the NHOs of the atoms, I, Cl and C, into which they are analysed, are given in Table 5.

From the NBOs derived, the $\varphi_1^{(I)}$ and $\varphi_2^{(I)}$ are pure iodine NHOs, the first being a $sp^{0.18}$ hybrid and the second a pure p_y AO. Furthermore, $\varphi_2^{(I-Cl)}$, $\varphi_3^{(I-Cl)}$ and $\varphi_4^{(I-Cl)}$ are

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* 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

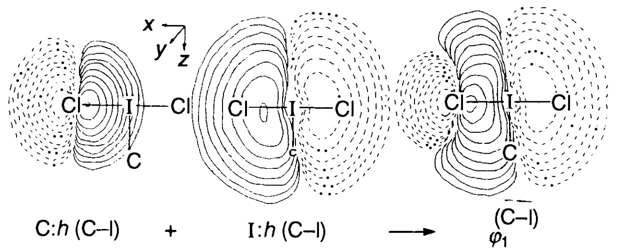


Fig. 2 Contour plots of localized bond orbital $\varphi_1^{(C-I)}$ and its analysis to the natural hybrid orbitals $h^{(Cl)}$ and $h^{(I)}$ for PhICl$_2$

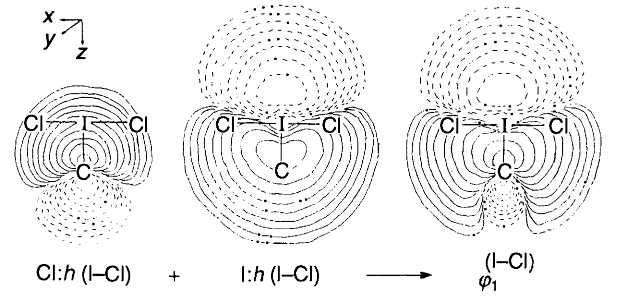
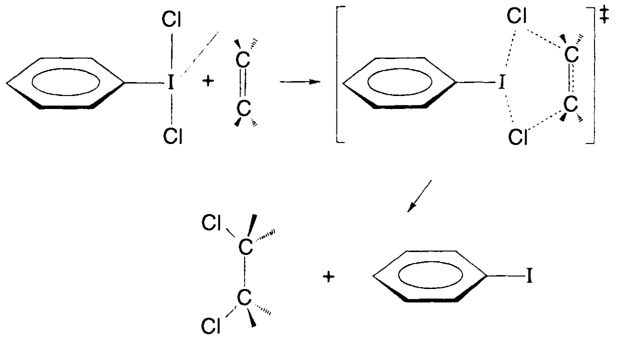
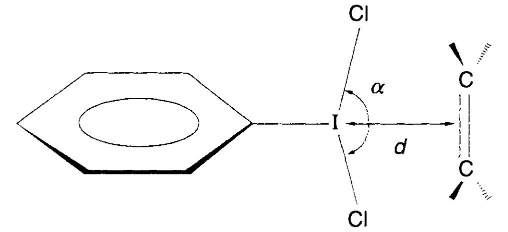


Fig. 3 Contour plots of localized bond orbital $\varphi_1^{(I-Cl)}$ and its analysis to the NHOs $h^{(Cl)}$ and $h^{(I)}$ for PhICl$_2$



Scheme 3



Scheme 4

the one-centre 'lone pair' NBOs analysed simply to unmixed chlorine NHOs. The hybridization of these NHOs are sp$^{10.76}$ and sp$^{0.11}$, whereas the last is pure p_y character. There are two two-centre 'bond' NBOs, $\varphi_1^{(C-I)}$ and $\varphi_1^{(I-Cl)}$, whose contour plots are given in Figs. 2 and 3, respectively. $\varphi_1^{(C-I)}$ is formed as a linear combination of two orthonormal NHOs and describes the carbon–iodine single bond. The hybridization of the carbon NHO is sp$^{2.08}$, very close to that expected, and that of the iodine NHO is sp$^{5.49}$. The $\varphi_1^{(I-Cl)}$ NBO describes the I–Cl bond and is formed from two NHOs of I and Cl which are pure p_x AOs. Finally, the success of the model of the localized MOs in the description of the electronic structure of PhICl$_2$ should be mentioned, even if the d orbitals of the central atom are not included in the basis set.

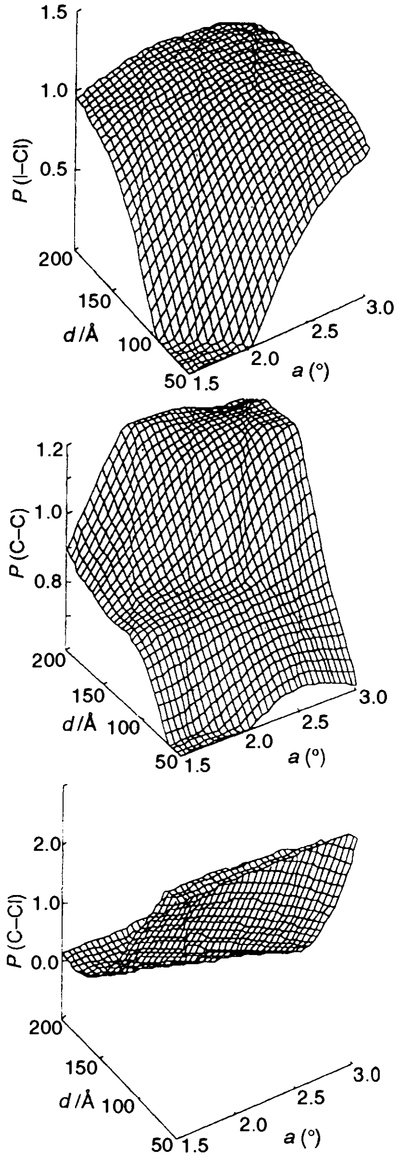


Fig. 4 Dependence of the overlap populations of I–Cl, Cl–C and C–C bonds on the parameters α and d for PhICl$_2$ (see Scheme 4)

Mechanism of Halogen Addition to Alkenes.—Dichloroiodobenzene, PhICl$_2$, is used in organic synthesis for the addition of chlorine to olefinic double bonds under mild conditions.[47–48] The yields of these reactions are usually higher than those achieved through other reagents of chlorination, while the geometric isomerism of the products is of some interest. Thus, the reaction of dichloroiodobenzene with cyclohexene leads to a selective *cis*-addition, while the same reaction with other reagents affords *trans*-addition products. In general, PhICl$_2$ has been used in the chlorination of terpenes and related compounds,[49,50] as well as steroids,[51] 1,3-cyclodienes,[52–54] and methylenecyclobutane.[55] Two possible mechanisms were proposed for the reaction of the double bond with the dichloroiodobenzene.[56] The first one constitutes an 'ionic mechanism', which takes place in the presence of water and leads mainly to the formation of *trans*-isomer, while the second one is a synchronous mechanism of 'molecular addition', which obviously leads to the formation of the *cis*-isomer (Scheme 3).

From these mechanisms, the most questionable is that of 'molecular addition' and that was the reason why we tried to ascertain whether this mechanism is feasible or not. Thus, extended Hückel calculations were carried out for the various stages of the approach of dichloroiodobenzene to an olefinic double bond, that is for a series of values of the distance d and the angle α (Scheme 4), since it is apparent that the formation of a transition state presupposes the deformation of the triatomic group Cl–I–Cl.

It is clear that the criterion for the formation or not of a transitional state must be sought in the overlap populations of those bonds, which are expected to be either strengthened or weakened during the gradual approach of the molecules. Therefore, the variation of the overlap populations of I–Cl, Cl–C and C–C bonds was investigated. From the variation of these overlap populations, given in Fig. 4, it is clear that, during the gradual approach of dichloroiodobenzene to the ethylenic double bond (decrease of the distance *d*), as well as the distortion of the Cl–I–Cl group to a more favourable arrangement (decrease of the angle α), the overlap population of the I–Cl bond decreases. The initially double C–C bond weakens and tends to values of overlap population typical of a single C–C bond, while an increase is observed for the overlap population of the Cl–C bond, a fact that confirms the formation of this bond. Therefore, our calculations confirm both the cleavage of the I–Cl bond and the creation of the Cl–C bond, as well as the transformation of the double C–C bond into a single one. Thus, it is apparent that the mechanism of the molecular addition is possible from a theoretical point of view.

References

1 A. Varvoglis, *The Organic Chemistry of Polycoordinated Iodine*, VCH Publishers, New York, 1992.
2 C. Willgerodt, *J. Prakt. Chem.*, 1886, **33**, 154.
3 M. Zupan and A. Pollak, *J. Fluorine Chem.*, 1976, **7**, 445.
4 T. A. Albright, J. K. Burdett and W. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, 1985.
5 L. Pauling, *The Nature of Chemical Bond,* Cornell University Press, Ithaca, New York, 1960.
6 G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, Chemical Catalog, New York, 1927.
7 N. V. Sidgwick, *The Electronic Theory of Valency*, Clarendon Press, Oxford, 1927.
8 L. Pauling, *J. Am. Chem. Soc.*, 1931, **53**, 1367.
9 G. E. Kimball, *J. Chem. Phys.*, 1940, **8**, 188.
10 C. A. Coulson, *J. Chem. Soc.*, 1964, 1442.
11 K. A. R. Mitchell, *Chem. Rev.*, 1969, **69**, 157.
12 R. Bersohn, *J. Chem. Phys.*, 1963, **38**, 2913.
13 C. A. Coulson and F. A. Gianturco, *J. Chem. Soc. A*, 1968, 1618.
14 J. G. Malm, H. Selig, J. Jortner and S. A. Rice, *Chem. Rev.*, 1965, **65**, 199.
15 R. E. Rundle, *J. Am. Chem. Soc.*, 1963, **85**, 112.
16 C. A. Coulson, *J. Chem. Phys.*, 1968, **44**, 468.
17 K. S. Pitzer, *Science*, 1963, **139**, 414.
18 R. M. Moriarty and O. Prakash, *Acc. Chem. Res.*, 1986, **19**, 244.
19 A. I. Boldyrev, V. Z. Zhdankin, J. Simons and P. J. Stang, *J. Am. Chem. Soc.*, 1992, **114**, 10569.
20 R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.
21 A. Viste and H. B. Gray, *Inorg. Chem.*, 1964, **3**, 1113.
22 C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 111.
23 QCPE 344, FORTICON-8, Indiana University, Bloomington, IN.
24 J. H. Ammeter, H. B. Burgi, J. C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 3686.
25 C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory*, W. Benjamin, New York, 1964.
26 J. W. Richardson, W. C. Nieuwpoort, R. R. Powell and W. F. Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.
27 J. W. Richardson, R. R. Powell and W. C. Nieuwpoort, *J. Chem. Phys.*, 1963, **38**, 796.
28 S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita and D. G. Carrol, *Introduction to Applied Quantum Chemistry*, Holt, Rinehart and Winston, New York, 1972.
29 J. Pople and D. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
30 J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.*, 1980, **162**, 7211.
31 E. M. Archer and T. G. D. van Schalkwyk, *Acta Crystallogr.*, 1953, **6**, 88.
32 *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Suppl. 1956–1959, ed. L. E. Sutton, The Chemical Society, London, 1965.
33 D. W. Magnuson, *J. Chem. Phys.*, 1957, **27**, 223.
34 R. J. Gillespie, *Can. J. Chem.*, 1992, **70**, 742.
35 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735.
36 J. I. Musher, *Angew. Chem.*, 1969, **81**, 68.
37 G. C. Pimentel, *J. Chem. Phys.*, 1951, **19**, 446.
38 R. E. Rundle, *Rec. Chem. Progr.*, 1962, **23**, 195.
39 R. E. Rundle, *Survey Progr. Chem.*, 1963, **1**, 81.
40 C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, 1957, **27**, 1060.
41 R. S. Yamasaki and C. D. Cornwell, *J. Chem. Phys.*, 1959, **30**, 1265.
42 C. K. Jorgensen, *Struct. Bonding (Berlin)*, 1969, **6**, 95.
43 E. A. C. Lucken, *Struct. Bonding (Berlin)*, 1969, **6**, 1.
44 B. S. Ehrlish and M. Kaplan, *J. Chem. Phys.*, 1971, **54**, 612.
45 J. C. Martin and E. F. Perozzi, *Science*, 1976, **191**, 154.
46 J. C. Martin, *Science*, 1983, **221**, 509.
47 D. Banks, *Chem. Rev.*, 1966, **66**, 243.
48 A. Varvoglis, *Synthesis*, 1984, 709.
49 S. Masson and A. Thuillier, *Bull. Soc. Chim. Fr.*, 1969, 4368.
50 S. Masson and A. Thuillier, *Bull. Soc. Chim. Fr.*, 1971, 3508.
51 A. Zarecki, J. Wicha and M. Kocor, *Tetrahedron*, 1976, **32**, 559.
52 M. C. Lasne and A. Thuillier, *Bull. Soc. Chim. Fr.*, 1974, 1142.
53 S. Uemura, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1437.
54 V. L. Heasley, K. D. Rold, D. B. McKee and G. E. Heasley, *J. Org. Chem.*, 1976, **41**, 1287.
55 K. L. Erickson, J. Markstein and K. Kim, *J. Org. Chem.*, 1971, **36**, 1024.
56 D. H. R. Barton and E. Miller, *J. Am. Chem. Soc.*, 1950, **72**, 370.

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