Ion-Pair Strain as the Driving Force for Hypervalent Adduct Formation between Iodide Ions and Substituted Iodobenzenes: Structural Alternatives to Meisenheimer Complexes

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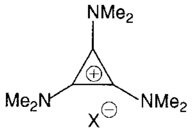
Abstract: The combination of an electron-rich cation with an electron-rich anion creates electronic strain within the corresponding ion pair through increased closed-shell repulsion. This effect reduces the ion-pairing energy and results in an increased nakedness of these ions. This situation is realized in tris(dimethylamino)cyclopropenium iodide. As a consequence, this salt represents a source of naked iodide ions of unprecedented coordinative power. Thus, iodide ions from this source are shown to form stable 1:1 adducts to substituted iodoarenes. As shown by a series of X-ray structures, a near-linear C-I-I arrangement of hypervalent nature is characteristic of these adducts. The heats of formation of these n→σ* adducts are a sensitive function of inductive (I) and mesomeric (M) effects of the ring substituents. They increase with the number of −I/M substituents in *o*/*p* positions much in the same way as expected for the heats of formation of the isomeric Meisenheimer complexes. This was corroborated by model calculations. Additionally, it is demonstrated both experimentally and from calculations that the σ* acidity of iodobenzene can be increased by additional iodine substituents in *ortho*, *meta*, and *para* positions. These unprecedented observations can be rationalized on the basis of through-bond coupling effects in the σ framework. The coordinative power of iodide in conventional sources of this ion, like the corresponding tetraphenylphosphonium and tetraethylammonium salts, is unsufficient for hypervalent adduct formation with the above-mentioned substrates. As a unique exception tetraethylammonium iodide forms a novel hypervalent adduct with two moles of picryliodide as the strongest σ* acceptor employed. In this adduct an iodide ion is complexed in a linear fashion by two C–I bonds. Factors responsible for this unprecedented bonding mode are discussed.

Keywords: electrostatic interactions · hypervalent compounds · iodo compounds · ion-pair strain · structure elucidation

Introduction

Some time ago we reported that anions X^- in salts of type **1** exhibit an unprecedented degree of nakedness, resulting in a remarkable tendency to coordinate even to very weak acceptor systems.[1]



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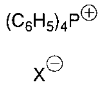

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X = I: a
X = Br: b
X = Cl: c

This effect could be traced back to the particular electronic structure of tris(dialkylamino)cyclopropenium systems. Whereas cations in general, and carbeniumions in particular, have to be classified as electron-deficient systems, tris(dialkylamino)cyclopropenium ions have long been known as true electron-surplus π systems. This is evidenced by their facile oxidation to stable dication radicals,[2] as well as by charge transfer (CT) interactions with both electron-deficient π systems[3] and inorganic complex anions[4] as acceptor components. This unusual behavior of what is generically still a carbeniumion has its origin in a high-lying HOMO, which derives from antibonding coupling of the totally symmetric group orbital of the NR_2 ligands with the aromatic doublet of the cyclopropenium core, as shown in Scheme 1.

As a result of this the electrostatic attraction of the electron-rich component ions in salts **1** is strongly counteracted by their closed-shell repulsion. We reasoned that this conflict should induce strain within the ion pair (ion-pair strain), which could be reduced or annihilated by coordination of the electron-rich anions to suitable acceptor systems.

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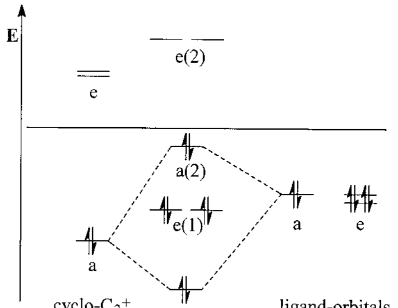
Therefore, in a given solvent, halide ions in **1** should appear much more naked—and thus prone to various coordination types—than halide counterions of conventional cations. This we indeed could demonstrate for two important interaction categories. As an example for unprecedented hard–hard interactions chlorides **1c** form an otherwise unobtainable series of stable hydrogen-bridged adducts with various weak Brønsted acids.[1a] With structurally novel hypervalent 1:1 adducts between iodides **1a** and iodoacetylenes we have contributed examples for soft–soft interactions induced by ion-pair strain.[1b]



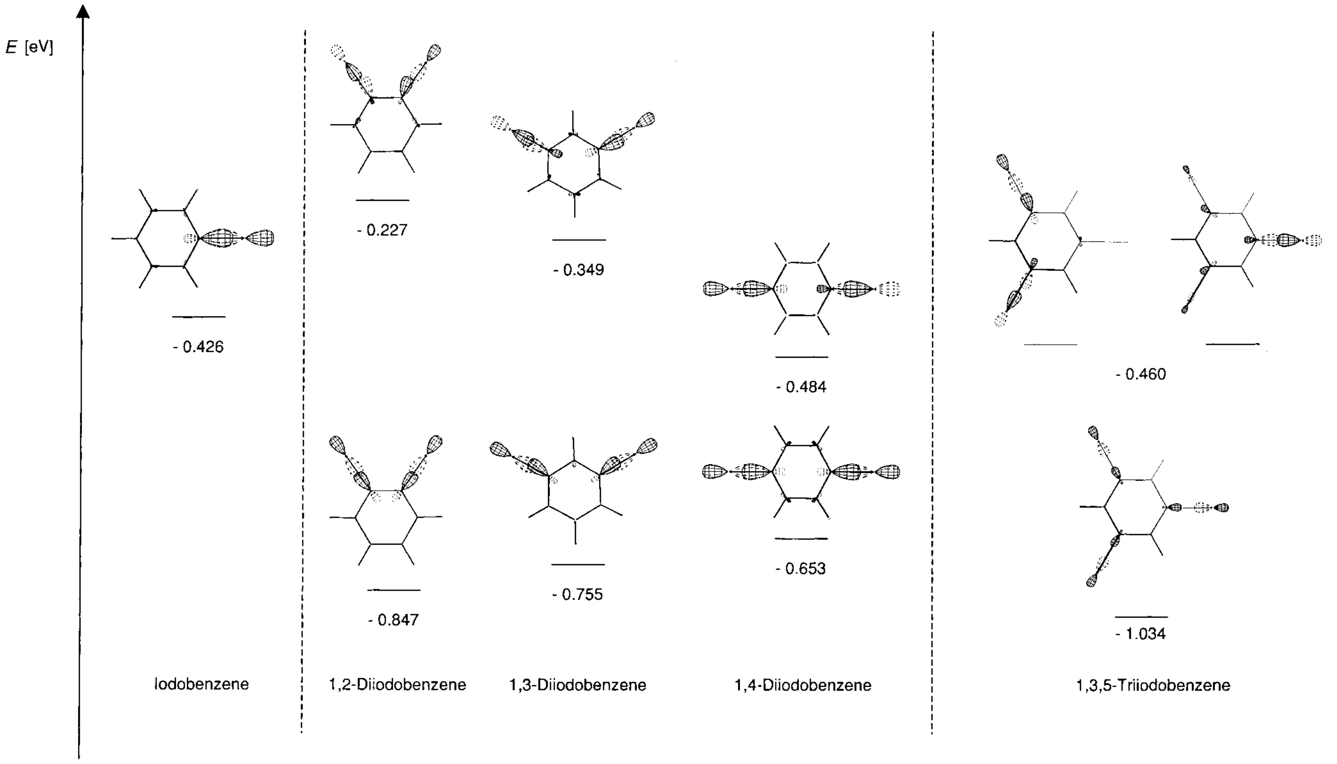
Scheme 1. Antibonding coupling of the totally symmetric group orbital of the NR$_2$ ligands with the aromatic doublet of the cyclopropenium core.

Recently, Dehnicke et al. reported that both tetraphenylphosphonium chloride **2c** and bromide **2b** form weak 1:1 complexes with iodobenzene.[5] The near-linear arrangement of the Hal-I-C sequence in these adducts is in formal agreement with a hypervalent bonding mode of halide ions to a halogenoarene. Surprisingly, the corresponding iodide adduct could not be obtained, contrary to what is expected according to the HSAB principle. Together with the long halide–iodine distances this latter observation would classify these adducts as ion-dipole complexes, whose stability for electrostatic reasons should decrease with increasing radius of the halide ion.

Motivated by these results of Dehnicke et al.[5] we have put our concept of ion-pair strain to a further test. Subsequently, we report that hypervalent adduct formation between the naked iodide in **1a** and various iodoarenes can for the first time be realized, if the latter fulfill certain structural requirements.

Results and discussion

We found that the inherent σ* acidity of iodobenzene itself is insufficient for adduct formation with **1a**. Using semiempirical calculations (PM3[15]) as a guide line, we then investigated which structural features would impart a more pronounced σ* acidity to iodoarenes. One group of compounds that emerged from these studies are the polyiodoarenes. As an example, the structural and energetic features of the C–I-derived σ* orbitals of the isomeric diiodobenzenes and of 1,3,5-triiodobenzene are shown in Scheme 2 together with those of the parent's C–I σ* orbital. In the series of the diiodobenzenes symmetrical and unsymmetrical coupling of the component C–I σ* orbitals leads to a considerable splitting of the resulting molecular orbitals, with the symmetrical combination emerging always lower in energy.



Scheme 2. C–I-derived σ* orbitals (PM3[15]) of selected polyiodobenzenes.

This coupling is achieved through direct overlap in the case of the *o* isomer, through a methine carbon in the *meta* case and through the intervening C–C σ bond in the *para* case.[6] The splitting of the two levels decreases in the same order. For 1,3,5-triiodobenzene a large splitting into a degenerate (e) set and a totally symmetric low-energy C–I σ*-orbital (a) is observed. The energies of the lowest C–I σ* orbitals of the iodobenzenes in Scheme 2 qualitatively decrease as the number of their C–I bonds increases. In each case, these orbitals represent the LUMO of the iodobenzenes under consideration. Very little mixing with C–C- or C–H-fragment orbitals is observed. Altogether, these orbital characteristics indicate that the tendency of iodobenzenes to form hypervalent adducts with nucleophiles should increase with the number of iodine substituents. This view is additionally supported by the calculated increase of positive charge on the iodine substituents on going from iodobenzene to 1,3,5-triiodobenzene (cf. Table 1). The LUMO structures of the di- and triiodobenzenes in Scheme 2 also suggest that these systems could function as bi- and tridentate σ* acids, respectively.

Table 1. Semiempirical calculations (PM3[15]) of polyiodoarenes.

	LUMO = σ*(C–I) [eV]	Charge (I)
Iodobenzene	– 0.426	0.018
1,2-Diiodobenzene	– 0.847	0.063
1,3-Diiodobenzene	– 0.755	0.034
1,4-Diiodobenzene	– 0.653	0.030
1,3,5-Triiodobenzene	– 1.034	0.048

Following this theoretical lead, we have treated the isomeric diiodobenzenes and 1,3,5-triiodobenzene with our source of naked iodide, **1a**. Irrespective of the relative molar ratios, stable 1:1 adducts were obtained for the three diiodobenzenes, whereas in the case of triiodobenzene an adduct of 2:3 stoichiometry resulted. These adducts were obtained in pure form and high yields (80–90%). So far all attempts to obtain crystals suitable for X-ray structural analysis from these compounds failed. However, an important conclusion can be drawn from the 2:3 stoichiometry of the 1,3,5-triiodobenzene adduct. This composition is only in line with formation of a hypervalent 2D polymer, in which the iodide ions act as bifunctional lone-pair (lp) donors and the triiodobenzene component as trifunctional σ* acids. For the 1:1 adducts of the diiodobenzenes similary a corresponding 1D polymer seems more likely than a monomeric structure, particularly in view of the 1D-polymeric structure of the 1:1 adduct of **1a** with diiodoacetylene established by us earlier.[1a]

Semiempirical investigations further suggested that the σ* acidity of iodoarenes should also be enhanced by the influence of strong – I/M substituents (I = inductive, M = mesomeric) such as the CN or NO_2 groups, as indicated by a lowering of the C–I σ* orbital and an increase of positive charge on the iodine substituent relative to the parent iodobenzenes (cf. Table 2).

Table 2. Semiempirical calculations (PM3[15]) of acceptor-substituted iodoarenes.

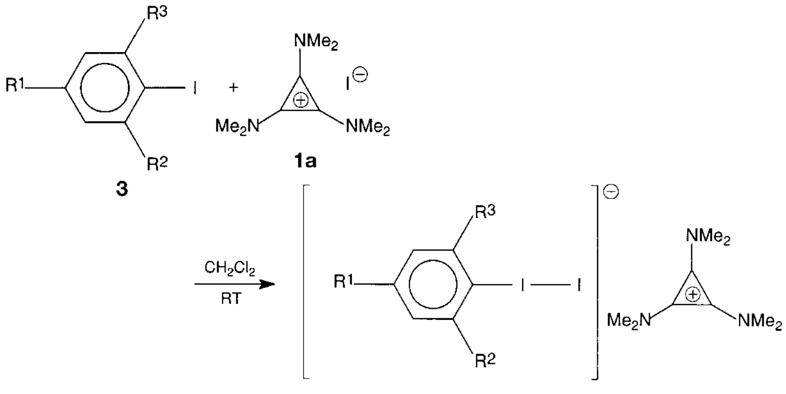
	σ*(C–I) [eV]	Charge (I)
Iodobenzene	– 0.43	0.018
4-Cyano-iodobenzene	– 0.81	0.047
1-Iodo-4-nitrobenzene	– 1.07	0.067
2-Iodo-1,3-dinitrobenzene	– 1.47	0.224
4-Iodo-1,3-dinitrobenzene	– 1.55	0.170
Picryliodide	– 2.02	0.265

In line with these predictions 4-cyanoiodobenzene **3a** and 1-iodo-4-nitrobenzene **3b** formed stable 1:1 adducts with **1a** in high yields. By contrast, the corresponding *o* and *m* isomers did not form analogous adducts with our source of naked iodide. This observation, while somewhat unexpected on the basis of the above-mentioned calculational results (cf. Table 2), indicates that adduct stabilities are not, as one might expect, exclusively determined by inductive and field effects of the electron withdrawing substituents (cf. discussion below).

Our calculations further predict that additional electron-withdrawing groups in the above-mentioned iodoarenes should further increase their σ* acidity. This was borne out experimentally in the nitro series: 4-iodo-1,3-dinitrobenzene **3c** and 2-iodo-1,3,5-trinitrobenzene (picryliodide) **3d** formed 1:1 adducts of increasing stability with respect to **3b**. This conclusion is based on competition experiments as well as on the solid-state structure of the corresponding adducts **4b–d** (cf. discussion below). All these reactions are summarized in Scheme 3.

Crystal structures of all three hypervalent adducts **4b–d** were determined; relevant structural data of these compounds are collected in Table 3 together with available literature data for reactant systems **3b** and **3d** for comparison. As a typical example, the structure of **4d** is shown in Figure 1.

The C-I-I sequence in adducts **4b–d** is almost linear, as is to be expected for hypervalent three-center four-electron sys-



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3a, 4a: $R^1 = CN; R^2 = R^3 = H$ **3b, 4b**: $R^1 = NO_2; R^2 = R^3 = H$

3c, 4c: $R^1 = R^2 = NO_2; R^3 = H$ **3d, 4d**: $R^1 = R^2 = R^3 = NO_2$

Scheme 3. Reaction scheme for the fomration of **4a–d**.

Table 3. Relevant structural data of **3b**, **3d** and of the adducts **4b–d**.

	d(C–I) [pm]	*d*(I–I) [pm]	Angle C-I-I [°]
3b[7]	209.7	–	–
3d[8]	208.3	–	–
4b	209.9	353.5	172
4c	211.7	343.1	178
4d	214.7	332.8	176

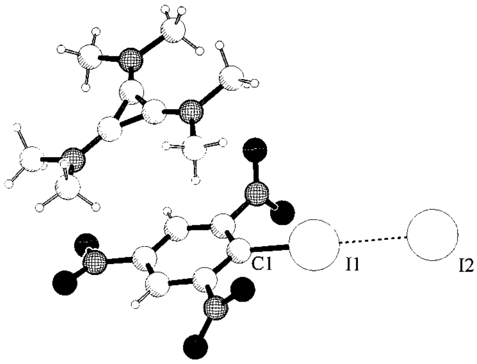
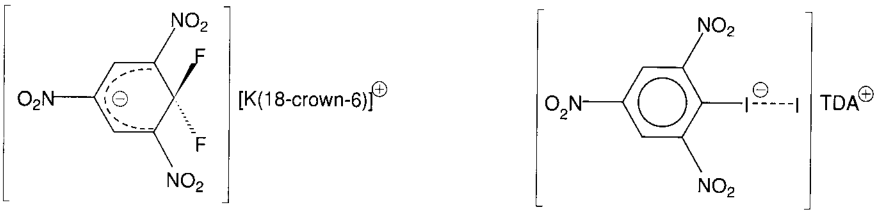


Figure 1. X-ray structure of **4d**.

tems of this kind. The I–I bonding distances in these compounds decrease distinctly with an increasing number of nitro functions in the *o* and *p* positions (cf. Table 3), indicating a corresponding increase in the I–I bonding energies, as predicted by our model calculations. By comparison, the concomitant widening of the C–I bonds as a consequence of C–I σ^* population by the coordinating iodide is only weakly developed, albeit into the expected direction (cf. Table 3).

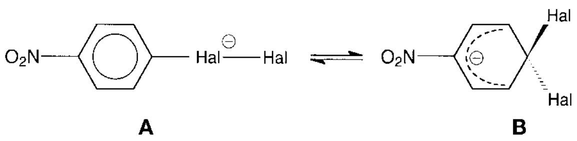


5 4d

Figure 2. The hypervalent adduct **4d** and the Meisenheimer adduct **5**.

All measured I···I bonding distances in **4b–d** are well below the sum of the components' van der Waals radii of 435 pm.[9] The shortest measured I···I contact in this series found is in **4d**, in which it reaches 333 pm, a value that we have also found in a (donor-stabilized) iodocarbenium iodide.[10a] Nearly the same I···I bonding distance (335 pm) was found by Kuhn et al. in the crystal structure of 1,3-diethyl-2-iododimethylimidazolium iodide.[10b] However, in the latter cases hypervalent I···I contacts derive an additional thermodynamic benefit from the electrostatic attraction of oppositely charged ions, such that **4d** seems to be the most stable adduct so far observed of iodide to any neutral C_{sp^2}–I σ^* acceptor.

Our experimental results show that hypervalent adducts of type **A** are stabilized by the same structural features as the corresponding structurally isomeric σ complexes of the Meisenheimer type **B** with a geminal dihalogen arrangement (Scheme 4).[11] The relative stabilities of the structurally isomeric adduct types depend strongly on the nature of the halogen, as exemplified by model calculations for the equilibrium shown in Scheme 4 (PM3[15] results in Table 4).



Scheme 4. Equilibrium between **A** and **B**.

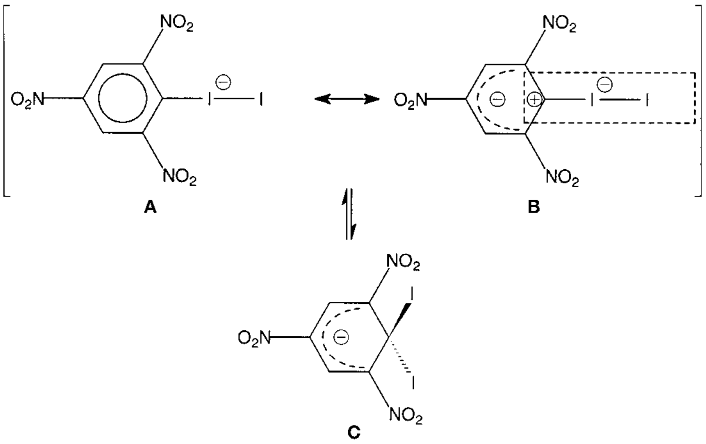
Table 4. Results of semiempirical calculations (PM3[15]) concerning the equilibrium shown in Scheme 4.

	F	Cl	Br	I
ΔH^R [kcal mol^{-1}]	– 69.82	– 0.98	14.32	31.30

According to these calculations structural-type **A** should be more stable for the heavier halogens, whereas structural-type **B** should be more stable for the lighter halogens chlorine and, especially, fluorine. This is in accord with the HSAB principle and the well-known tendency of heavier elements to form part of hypervalent structural elements. In view of the rather limited quality of the calculational method employed the results in Table 4 can only be taken to indicate a qualitative trend. There, the stable hypervalent adduct **4d** has to be contrasted with the Meisenheimer adduct **5** of fluoride to picrylfluoride (Figure 2).[12]

According to their nature as – I/M-acceptor functions the electronic role of the nitro groups in stabilizing the hypervalent adducts **4b–d** should be twofold. The – I effect is operative in the σ-framework and should enhance the adduct stability by withdrawal of σ-electron density from the central iodine towards the adjacent ring carbon. This traditional inductive effect should decrease with increasing distance of the nitro group(s). As we have shown that only 1-iodo-4-nitrobenzene, but not its *o* and *m* isomers, is capable of forming an $n \rightarrow \sigma^*$ complex with iodide, it becomes clear that factors other than the – I effect of the nitro groups are also contributing to the stability of these adducts. On the molecular level this must be the – M effect of the nitro groups, which comes into play in an indirect fashion, as subsequently demonstrated for **4d**.

The π-electron distribution of **4d** can be conceived as resulting from a resonance of type **A/B** in Scheme 5. Resonance structure **B** contains a bipolarized aromatic sextett, in which a tris acceptor-stabilized hexadienyl anion as a subunit stabilizes an iodocarbenium iodide subunit by donation. Both subunits are known as separate stable entities: the first is present in the corresponding Meisenheimer complexes **B** of picryl systems, and the latter in (donor-stabilized) iodocarbenium iodides.[10] However, the electronic parallelism between type **C** and type **B**, as far as the stabilizing effect of the acceptor groups is concerned, holds only in a rather attenuated form, because the *ortho* nitro groups in **A/B** are



Scheme 5. Resonance and equilibrium structures **A–C** of the picryl system.

severely rotated out of the benzene ring plane (33.7° and 84.4°). This arises, because the in-plane lone pair of the ring-bound iodine in **4d** would interact repulsively with both adjacent *o*-nitro groups were they coplanar. By contrast, the *o*-nitro groups in Meisenheimer complexes of type **B** can be fully effective as acceptor functions, as they are not compelled to rotate out of the ring plane.

From these considerations it follows that in the series of the isomeric nitroiodobenzenes the *p*-isomer is optimal for adduct formation, as the nitro function can exert its $-$I/M effects to the full extent, whereas its $-$M effect is very much reduced in the *o* isomer (for reasons shown above) and nonexistent in the *m*-isomer.

To further investigate the influence of mesomeric and inductive effects on the stability of hypervalent iodide adducts in substituted iodobenzenes, we chose to replace the *p*-nitro group in picryliodide by a methoxy group. The latter combines a moderate +M effect with a strong $-$I effect. We found that this reactant, 4-iodo-3,5-dinitro-anisole (**6**), could also be successfully treated with **1a** to give a stable 1:1 adduct **7**. Its structure is shown in Figure 3.

The I···I bonding distance in **7** is 4 pm longer than in the corresponding picryliodide adduct **4d**. This is expected in view of the electronic effects discussed above, but the effect is surprisingly small. Probably the very pronounced $-$I effect of the methoxy group compensates partially for the loss in hypervalent bonding energy introduced by the +M substituent. A number of further model compounds will have to considered before the relative importance of inductive and mesomeric effects in the hypervalent bonding of substituted iodoarenes can be reliably assessed.

Does the nature of the countercation influence the ability of iodide to form $n \rightarrow \sigma^*$ complexes with nitroiodoarenes? The answer to this question is of considerable importance with respect to our concept of ion-pair strain. We tested two conventional sources of iodide: a) tetraphenylphosphonium iodide (**2a**) and b) tetraethylammonium iodide (**8**). The first-mentioned iodide source did not form complexes in detectable amounts with the σ^*-acidic iodoarenes **3a–d**, whereas the latter gave only an adduct with picryliodide **3d** as the strongest σ^* acceptor in the series. Irrespective of the molar ratio used, this compound proved to be a 2:1 complex (**9**) of picryliodide **3d** to **8**. The crystal structure of this adduct is shown in Figure 4, the corresponding crystallographic data are contained in Table 5.

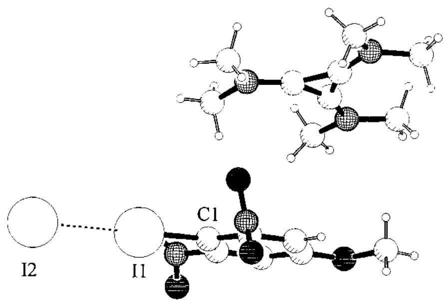


Figure 3. X-ray structure of **7**. Relevant distances [pm] and angles [°]: C1–I1 213.6, I1–I2 336.8, C1-I1-I2 177.8.

Figure 4 reveals a linear coordination of an iodide ion by the two σ^*-acidic C–I bonds of two picryliodide molecules, a novel structural feature in hypervalent bonding of iodide ions.

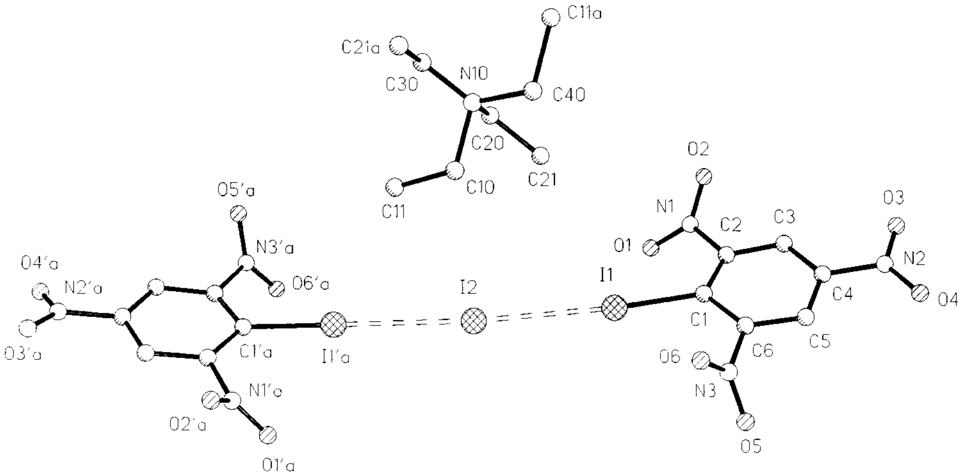


Figure 4. X-ray structure of **9**. Relevant distances [pm] and angles [°]: C1′a–I1′a 212, I1–I2 332, C1-I1-I2 176.2 C1′a–I1′a-I2 173.9 I1–I2-I1′a 170.3.

By contrast, the attempt to add a further mole of picryliodide to the 1:1 adduct **4d** was unsucesful. Obviously the countercation of iodide has a decisive influence on this ion's hypervalent coordination chemistry. Our model of ion-pair strain offers a simple explanation:

1) Ion-pair strain of the above-defined type is only present in **1a** and not in **8**.
2) As a consequence iodide ions in **1a** should be driven into a stronger coordination with the σ^* acceptor than those in **8**.
3) Therefore the terminal iodine center in the (hypothetical) 1:1 adduct of **8** with picryliodide should be more nucleo-

Table 5. Crystal data.

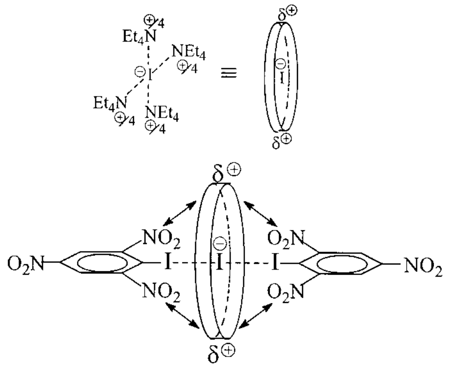
	3d	**4b**	**4c**	**4d**	**7**	**9**
formula	$C_6H_2N_3O_6I$	$C_{15}H_{22}N_4O_2I_2$	$C_{15}H_{21}N_5O_4I_2$	$C_{15}H_{20}N_6O_6I_2$	$C_{16}H_{23}N_5O_5I_2$	$C_{20}H_{24}N_7O_{12}I_3$
M_r	339.01	544.17	589.17	634.17	619.19	935.16
crystal system	tetragonal	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P4(3)2(1)2$	$P2(1)/m$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	7.0553(10)	7.736(4)	8.9161(8)	9.815(2)	8.3660(11)	8.0517(9)
b [Å]	7.0553(10)	10.200(4)	10.0648(6)	12.980(2)	9.8398(14)	13.560(1)
c [Å]	19.675(4)	13.016(5)	13.1406(8)	17.660(2)	14.906(3)	15.402(2)
α [°]	90	90	79.228(1)	90	94.23(2)	69.680(9)
β [°]	90	99.16(4)	81.904(1)	94.97(1)	94.77(2)	75.711(11)
γ [°]	90	90	70.758(1)	90	111.100(12)	86.371(9)
V [Å^3]	979.4(3)	1014.0(8)	1089.73(13)	2241.4(6)	1133.7(3)	1527.8(3)
Z	4	2	2	4	2	2
$F(000)$	640	524	568	1224	600	896
ρ_{calcd} [g cm^{-3}]	2.299	1.782	1.796	1.879	1.814	2.033
crystal size [mm]	0.30 × 0.30 × 0.30	0.50 × 0.40 × 0.40	0.40 × 0.40 × 0.30	0.30 × 0.20 × 0.20	0.30 × 0.30 × 0.10	0.35 × 0.30 × 0.30
2Θ scan range	3.07–26.98	2.67–26.29	2.49–25.97	2.61–25.02	2.49–24.97	2.50–23.97
refl.collected	1209	3980	4269	7863	4266	4786
indep. refl.	1063	2119	4269	3939	3970	4786
indep. obs. refl. $F_\sigma \leq 4_\sigma(F_\sigma)$	982	1894	3121	2613	3199	3674
$wR(F^2)$, all data	0.1365	0.1944	0.0830	0.0816	0.1615	0.1397
goodness-of-fit	1.105	1.127	1.803	1.012	1.107	1.043

philic than the one in 1:1 adduct **4d**, resulting in an increased tendency to coordinate a second σ* acceptor.

4) The concept of ion-pair strain entails an active role for the electron-rich countercation in **1a** vis-á-vis the electron-deficient nitroiodoarenes as reaction partners. Thus, all n→σ* adducts of **1a** reported in this paper contain, as a common structural element, a near-coplanar cofacial arrangement of the electron-rich cationic π system and the electron-deficient neutral π system; this is indicative of an attractive π→π* interaction between these components. Thus, both ionic donor subsystems present in **1a** have found their natural electronic counterparts in the nitroiodoarenes employed, facilitating the considerable cation–anion separation observed for the adducts of **1a**.
5) Naturally, a corresponding role for the countercation in **8** can not be envisaged. As a consequence, the tetraethylammonium ion in adduct **9** remains in close contact with iodide as is evident from Figure 4. A closer inspection of the X-ray structure of **9** reveals that the iodide ion is surrounded by four tetraethylammonium ions in a distorted square planar arrangement. The additional coordination of two picryliodide systems in the axial positions complements an octahedral coordination sphere of iodide (in strong contrast to this, iodide ions in corresponding adducts of **1a** are only monocoordinated). This arrangement allows additional electrostatic attractions between the nitrosubstituents with their negative partial charges and the countercations, as qualitatively shown in Scheme 6.

This additional electrostatic attraction would shorten the I⋯I distances in **9** beyond what would be expected on the basis of the hypervalent contacts alone. In view of this, almost identical I⋯I bond lengths in **4d** and **9** find a plausible explanation.

In summary, the experimental results presented in this paper definitely support our concept of ion-pair strain. In salts of type **1a** a π-donor cation is electrostatically coupled with a lone-pair-donor anion. Neutral substrates that offer complementary acceptor sites are best suited to relieve the resulting ion-pair strain. Substituted iodoarenes as presented in this paper are but one class of compounds satisfying this condition. Many others can be envisaged.



Scheme 6. Important nearest neighbor electrostatic attractions in the X-ray structure of **9**.

It seems very likely that electronic factors determining the stability of RI/I$^-$ complexes are also operative in reactions of RI with stronger nuclephiles, such as R–Li. Therefore the structures reported in this paper possess some model character for intermediate ate complexes in transmetallation reactions that have been observed in a very limited number of cases in solution.[14]

Experimental Section

General techniques: All reactions were carried out under dry nitrogen with standard vacuum-line techniques. Dichloromethane was destilled under nitrogen from calcium hydride, and diethyl ether from sodium-benzophenone. IR spectra werde obtained with a Bruker IFS25 FTIR spectrometer (Opus 2.0). ^1H NMR and ^{13}C NMR spectra were recorded at room temperature on a Jeol JNM GX 400 spectrometer and chemical shifts are reported in ppm downfield of tetramethylsilane.

General procedure for the synthesis of the hypervalent compounds with TDAI: A solution of tris(dimethylamino)cyclopropenium iodide TDAI (295 mg, 1.0 mmol) in dichloromethane (5 mL) was added dropwise to a solution of the aryliodide (1.0 mmol) in dichloromethane (20 mL). After 2 h of stirring diethyl ether (50 mL; in which the iodoarenes are soluble) was added. The resulting solid was isolated by vacuum filtration, washed twice with diethylether (10 mL) and dried in vacuo.

1:1 Adduct of 1,2-diiodobenzene to TDAI: Yield: 81 % (white solid); ^{1}H NMR ($CDCl_3$): $\delta = 7.90$ (m, 2H), 7.06 (m, 2H), 3.21 (s, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 139.1$, 128.9, 117.7, 107.7, 42.7; MS: *m/z* (%): 330 (100) $[C_6H_4I_2^+]$, 203 (55) $[C_6H_4I^+]$, 76 (70) $[C_6H_4^+]$; $C_{15}H_{22}N_3I_3$ (625.06): calcd C 28.82, H 3.55, N 6.72; found C 29.00, H 3.78, N 7.00.

1:1 Adduct of 1,3-diiodobenzene to TDAI: Yield: 82 % (white solid); ^{1}H NMR ($CDCl_3$): $\delta = 8.05$ (d, 1H), 7.66 (dd, 2H), 6.87 (t, 1H), 3.21 (s, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 145.1$, 136.6, 131.7, 118.1, 95.0, 43.0; MS: *m/z* (%): 330 (100) $[C_6H_4I_2^+]$, 203 (35) $[C_6H_4I^+]$, 127 (10) $[I^+]$, 76 (70) $[C_6H_4^+]$; $C_{15}H_{22}N_3I_3$ (625.06): calcd C 28.82, H 3.55, N 6.72; found C 28.63, H 3.42, N 6.48.

1:1 Adduct of 1,4-diiodobenzene to TDAI: Yield: 88 % (white solid); ^{1}H NMR ($CDCl_3/CD_3CN$): $\delta = 7.47$ (s, 4H), 3.13 (s, 18H); ^{13}C NMR ($CDCl_3/CD_3CN$): $\delta = 138.8$, 116.1, 92.9, 42.3; MS: *m/z* (%): 330 (100) $[C_6H_4I_2^+]$, 203 (45) $[C_6H_4I^+]$, 76 (80) $[C_6H_4^+]$; $C_{15}H_{22}N_3I_3$ (625.06): calcd C 28.82, H 3.55, N 6.72; found C 28.73, H 3.87, N 6.68.

2:3 Adduct of 1,3,5-triiodobenzene to TDAI: Yield: 75 % (brown solid); ^{1}H NMR ($CDCl_3$): $\delta = 8.05$ (m, 6H), 3.21 (s, 54H); ^{13}C NMR ($CDCl_3$): $\delta = 144.3$, 118.1, 95.5, 43.0; IR (Nujol): $\tilde{\nu} = 3030$ (w), 2930 (w), 1600 (m), 1560 (vs), 1395 (vs), 1200 (s), 1090 (w), 1020 (m), 779 (m), 680 cm^{-1} (w); MS: *m/z* (%): 456 (100) $[C_6H_3I_3^+]$, 329 (75) $[C_6H_3I_2^+]$, 202 (45) $[C_6H_3I^+]$; $C_{39}H_{60}N_9I_9$ (1796.68): calcd C 26.06, H 3.37, N 7.01; found C 26.25, H 3.37, N 7.28.

1:1 Adduct of 4-cyano-iodobenzene to TDAI: Yield: 79 % (light brown solid); ^{1}H NMR ($CDCl_3$): $\delta = 7.87$ (d, 2H), 7.38 (d, 2H), 3.22 (s, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 138.6$, 133.2, 118.2, 118.1, 111.6, 100.6, 43.0; IR (KBr): $\tilde{\nu} = 3020$ (w), 2910 (w), 2200 (s), 1575 (s), 1555 (sh), 1550 (vs), 1530 (sh), 1460 (m), 1400 (vs), 1370 (m), 1250 (w), 1210 (s), 1100 (w), 1020 (m), 990 (m), 825 (s), 775 cm^{-1} (s); MS: *m/z* (%): 2429 (100) $[C_7H_4NI^+]$, 127 (2) $[I^+]$, 102 (90) $[C_7H_4N^+]$, 76 (20) $[C_6H_4^+]$; $C_{16}H_{22}N_4I_2$ (524.19): calcd C 36.66, H 4.23, N 10.67; found C 36.78, H 4.53, N 11.28.

1:1 Adduct of 1-iodo-4-nitrobenzene to TDAI: Yield: 78 % (orange solid); ^{1}H NMR ($CDCl_3$): $\delta = 7.93$ (m, 4H), 3.22 (s, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 147.6$, 138.6, 124.7, 118.2, 102.7, 42.9; IR (KBr): $\tilde{\nu} = 3080$ (w), 3050 (w), 2940 (w), 1570 (vs), 1520 (s), 1410 (vs), 1340 (s), 1220 (m), 1100 (m), 1030 (m), 1000 (m), 845 (m), 780 (m), 740 cm^{-1} (m); MS: *m/z* (%): 249 (100) $[C_6H_4NO_2I^+]$, 203 (28) $[C_6H_4I^+]$, 127 (5) $[I^+]$, 76 (60) $[C_6H_4^+]$; $C_{15}H_{22}N_4O_2I_2$ (544.17): calcd C 33.11, H 4.08, N 10.30; found C 33.11, H 4.28, N 10.25.

1:1 Adduct of 4-iodo-1,3-dinitrobenzene to TDAI: Yield: 85 % (orange solid); ^{1}H NMR ($CDCl_3$): $\delta = 8.60$ (d, 1H), 8.39 (d, 1H), 8.17 (dd, 1H), 3.24 (s,18H); ^{13}C NMR ($CDCl_3$): $\delta = 153.2$, 147.5, 143.7, 127.1, 119.8, 117.9, 100.4, 43.0; IR (KBr): $\tilde{\nu} = 3060$ (w), 2940 (w), 1590 (sh; m), 1560 (s), 1525 (m), 1405 (s), 1345 (s), 1220 (m), 1030 (m), 1020 (m), 835 (w), 790 (w), 730 cm^{-1} (m); MS: *m/z* (%): 294 (100) $[C_6H_3N_2O_4I^+]$, 254 (8) $[I_2^+]$, 248 (12) $[C_6H_3NO_2I^+]$, 202 (15) $[C_6H_3I^+]$, 127 (3) $[I^+]$, 75 (35) $[C_6H_3^+]$, 30 (5) $[NO^+]$; $C_{15}H_{21}N_5O_4I_2$ (589.17): calcd C 30.58, H 3.59, N 11.89; found C 31.57, H 3.80, N 11.84.

1:1 Adduct of 2-iodo-1,3,5-trinitrobenzene to TDAI: Yield: 82 % (bright red solid); ^{1}H NMR ($[D_6]DMSO$): $\delta = 8.60$ (s, 2H), 3.04 (s, 18H); ^{13}C NMR ($D_6]DMSO$): $\delta = 160.6$, 141.7, 125.1, 124.2, 117.9, 41.9; IR (KBr): $\tilde{\nu} = 2983$ (w), 1549(s), 1404 (s), 1341 (s), 1216 (m), 1025 (w), 933 (w), 720 cm^{-1} (m); MS: *m/z* (%): 339 (100) $[C_6H_2N_3O_6I^+]$, 254 (70) $[I_2^+]$, 247 (13) $[C_6H_2NO_2I^+]$, 212 (72) $[C_5H_2N_3O_6^+]$, 201 (18) $[C_6H_2I^+]$, 166 (5) $[C_6H_2N_2O_4^+]$, 127 (11) $[I^+]$, 75 (55) $[C_6H_2^+]$, 30 (32) $[NO^+]$; $C_{15}H_{20}N_6O_6I_2$ (634.17): calcd C 28.41, H 3.18, N 13.25; found C 28.30, H 3.08, N 13.73.

1:1 Adduct of 3,5-dinitro-4-iodoanisole to TDAI: Yield: 80 % (yellow solid); ^{1}H NMR ($D_6]DMSO$): $\delta = 7.82$ (s, 2H), 3.88 (s, 3H), 3.60 (s, 18H); ^{13}C NMR ($D_6]DMSO$): $\delta = 160.1$, 156.0, 117.9, 112.8, 74.6, 57.1, 41.9; IR (KBr): $\tilde{\nu} = 2928$ (m), 2796 (w), 1541 (s), 1466 (w), 1433 (w), 1400 (s), 1353 (m), 1294 (s), 1264 (s), 1224 (m), 1133 (m), 1051 (s), 1032 (m), 917 (s), 876 (s), 787 (s), 723 cm^{-1} (s); MS: *m/z* (%): 324 (100) $[C_7H_5N_2O_5I^+$, 232 (10) $[C_7H_5OI^+]$, 205 (20), 105 (25) $[C_7H_5O^+]$, 62 (35); $C_{16}H_{23}N_5O_5I_2$ (619.19): calcd C 31.04, H 3.74, N 11.31; found C 31.54, H 3.99, N 11.31.

2:1 Adduct of 2-iodo-1,3,5-trinitrobenzene to NEt_4I: Tetraethylammonium iodide (2.0 mmol; 514.3 mg) was suspended in dichloromethane and stirred, and a solution of 2-iodo-1,3,5-trinitrobenzene (1.0 mmol; 339 mg) was added dropwise. While adding the 2-iodo-1,3,5-trinitrobenzene the suspension changed into an orange solution. After 1 h of stirring diethyl ether (50 mL) was added and the resulting solid was isolated by vacuum filtration, washed twice with diethyl ether (10 mL) and dried in vacuo. Yield: 75 % (yellow solid); ^{1}H NMR ($D_6]DMSO$): $\delta = 8.58$ (s, 4H), 3.20 (q, 8H), 1.15 (t, 12H); ^{13}C NMR ($D_6]DMSO$): $\delta = 160.7$, 141.8, 125.1, 124.1, 51.4, 7.0; IR (KBr): $\tilde{\nu} = 3079$ (m), 1596 (m), 1541 (vs), 1483 (w), 1392 (w), 1346 (vs), 1172 (w), 1102 (w), 999 (w), 916 (m), 821 (m), 783 (w), 719 cm^{-1} (s); MS: *m/z* (%): 339 (100) $[C_6H_2N_3O_6I^+]$, 201 (12) $[C_6H_2N_3O_6^+]$, 74 (30) $[C_6H_2^+]$; $C_{20}H_{24}O_{12}N_7I_3$ (935.16): calcd C 25.69, H 2.58, N 10.48; found C 25.37, H 2.61, N 10.22.

Crystal structure analysis: Crystal data collection and refinement parameters are given in Table 5. Suitable crystals for single-crystal X-ray diffraction were obtained by crystallization from CH_2Cl_2/Et_2O. The single-crystal X-ray diffraction experiments were carried out on a Nonius Mach 3 diffractometer with monochromatic $Mo_{K\alpha}$ radiation at 293(2) K (**4b** at 200(2) K). The structures were solved by direct methods (SHELXS 6[14]), completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures (SHELXS 93[14]). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100587 (**4b–d** and **9**) and no. CCDC-102486 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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