Hypervalent iodine compounds derived from *o*-nitroiodobenzene and related compounds: syntheses and structures

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Abstract

A series of compounds possessing polyvalent iodine groups was prepared from o-nitroiodobenzene. Single crystal X-ray investigation revealed a strong interaction between iodine atom and one of the oxygen atoms of the nitro group. This interaction is strongest in trifluoroacetate of hydroxy(*o*-nitrophenyl)iodonium salt, which is formed from an iodosylarene and an acid being the first example of this new class of compounds. These compounds are also characterized by NMR-spectroscopy.

Keywords: o-Nitroiodobenzene, hypervalent iodine compounds, 1,2-benziodox-3-azolin-3-onium ion

Introduction

Abnormally high reactivity of o-nitrohaloarenes compared to p-substituted ones in a number of reactions, such as Ullmann coupling[1], Cu(I) catalysed substitution of one halogen by another[2], dehalogenation with Cu in boiling acetic acid[3], has no clear explanation in the literature. We supposed that the enhanced reactivity of o-nitrohaloarenes could be a result of formation of a strong hypervalent donor-acceptor bond between oxygen of a nitro group and a halogen atom in a transition state or in an intermediate. This hypothetical moiety would contain a five-atom heterocycle, condensed with the benzene ring. One of the driving forces for its formation can be a relief of steric hindrance between halogen and nitro group. Additionally, conjugation between nitro group and aromatic ring would be favored by their coplanar disposition. Structural fragment of the same geometry is well known for polyvalent iodine compounds, the best example is

iodoxole, an isomer of the hypothetical o-iodosylbenzoic acid[4]. One should notice that the anion of iodoxole and o-nitroiodobenzene are isoelectronic compounds.

On the other hand, the hypervalent donor-acceptor bond, included into a 5-member cycle is known for a number of S, Se or Te containing compounds[5], which are, in turn, isoelectronic to 2-NO_2-C_6H_4-I^+-X type of compounds.

Thus our assumptions led us to a search for compounds, in which formation of a bond between halogen and o-nitro group is plausible. The positive charge on halogen atom is obviously favorable for this hypothetical interaction; therefore derivatives of o-nitroiodobenzene with polyvalent iodine appeared to be promising candidates to study at first. Chemistry of polyvalent iodine compounds has enlarged very fast in the past three decades.[6,7] Literature search has shown that a number of such compounds were described, but structural investigation had not been made at all, and their characterizations in many cases were insufficient.

A number of o-nitrodiphenyliodonium salts is known for years – iodide,[8,11] bromide,[9,11] chloride,[11] fluoride,[10] nitrate,[11] tetrafluoroborate[12] and hexachloroplatinate.[12,13]. They are characterized by melting points and, in one case, by [127]I NQR study.[12] One bromonium salt – o-nitrodiphenylbromonium triiodomercurate has also been prepared.[13] Other compounds are o-iodosyl-[9] and o-iodylnitrobenzenes,[9,14] o-nitroiodobenzene dichloride,[15] difluoride[16] and diacetate.[17] Two very interesting compounds had been reported, but also without investigation on their structure – betaines from nitramide[18] and from Meldrum's acid[19].
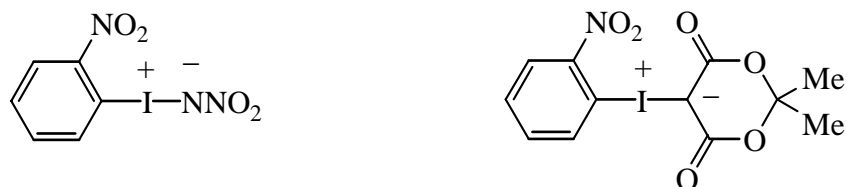
In spite of lack of structural data, some authors noticed and tried to explain the abnormal behavior of these o-nitrocompounds. Lyalin et al. observed decomposition of o-nitroiodobenzene difluoride above its melting point with elimination of fluorine and formation of parent o-nitroiodobenzene.[16] Gakovic and Morgan suggested that dipolar interaction of NO_2 and IO_2 groups in o-nitroiodylbenzene is responsible for longer wavelength of the band in its UV-spectrum.[14] Most interestingly, to explain faster dissociation of o-nitroiodobenzene dichloride Jeffery, Andrews and Keefer suggested contribution of the o-$NO2$ group in providing for transition state stabilization, as depicted below.[15]
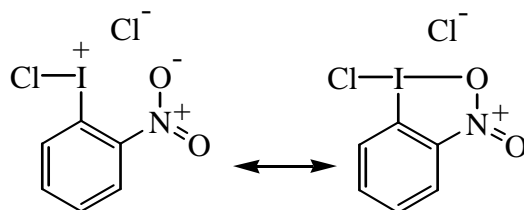
Therefore the goal of our work was to synthesize a number of derivatives of *o*-iodonitrobenzene, to study their structure and to attempt to find an evidence for existence of a bond between iodine and nitro group.

Results and Discussion

Syntheses

We were able to prepare a series of hypervalent iodine compounds from *o*-nitroiodobenzene **1** using methods, described for derivatives of unsubstituted iodobenzene. The *o*-dichloriodonitrobenzene **2**, *o*-iodylnitrobenzene **3**, *o*-yodosylnitrobenzene **4**, *o*-diacetoxyiodonitrobenzene **5** and *o*-di(chloroacetoxy)iodonitrobenzene **6** were prepared, as well as *o*-nitrodiphenyliodonium iodide **7**. However, all attempts to prepare *o*-nitrohydroxy-(tosyloxy)iodobenzene or *o*-dimethoxyiodonitrobenzene failed. Also failed several attempts to prepare *o*-nitrophenyliodine bis(trifluoroacetate). Instead, we managed to isolate a crystalline compound, which was later found to be 1:1 adduct of *o*-nitroiodosylbenzene and trifluoroacetic acid **8**, its unique structure will be discussed below. The synthetic sequence is given on Figure 1.
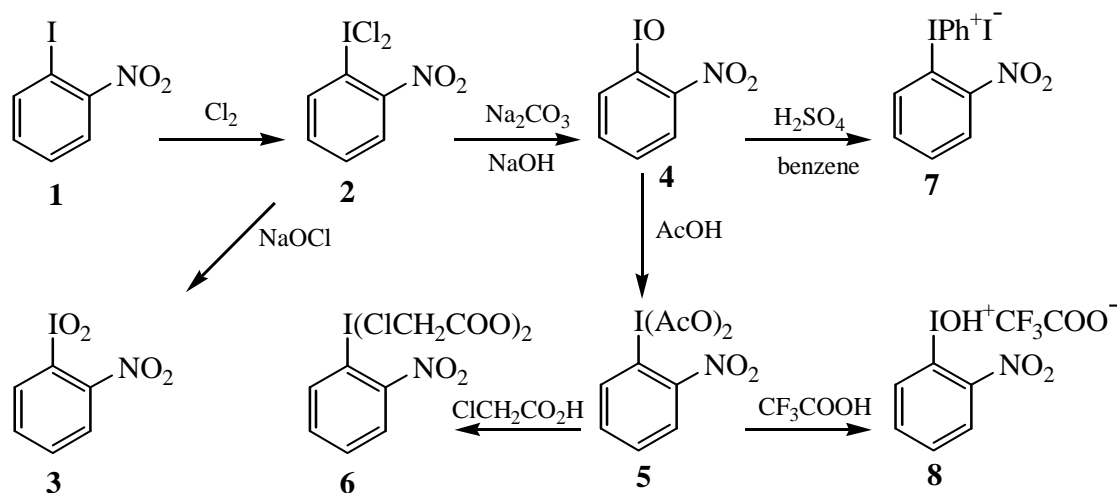

Figure 1. Syntheses of derivatives of o-nitroiodobenzene.

All compounds are stable in crystalline form, with exception of o-nitrophenyliododichloride **2**. It slowly decomposes on standing. In solutions, all compounds slowly form *o*-nitroiodobenzene **1**, therefore NMR measurements were made immediately after preparation of a sample. Availability and sufficient stability of these compounds makes them prospective candidates for testing as oxidants for various synthetic purposes.

p-Nitroiodobenzene dichloride, *p*-nitroiodylbenzene and *p*-nitrodiphenyliodonium bromide were also synthesized by the same known methods for comparison of their NMR spectra and crystal structure.

Crystallography

Five out of seven synthesized compounds formed good quality crystals for crystallographic study. All attempts to prepare crystals of o-nitroiodosobenzene **4** failed. We had good crystals of 2,4-dinitroiodobenzene (DNIB) and this compound was taken instead of o-iodonitrobenzene **1** for comparison. Detailed discussion on the crystalline structure of the compounds is beyond the scope of this article. Only key feature – interaction between nitro group and iodine-containing group will be considered. The ORTEP drawings are given on Fig. 1 and key parameters of molecular structure are given in Table 1.
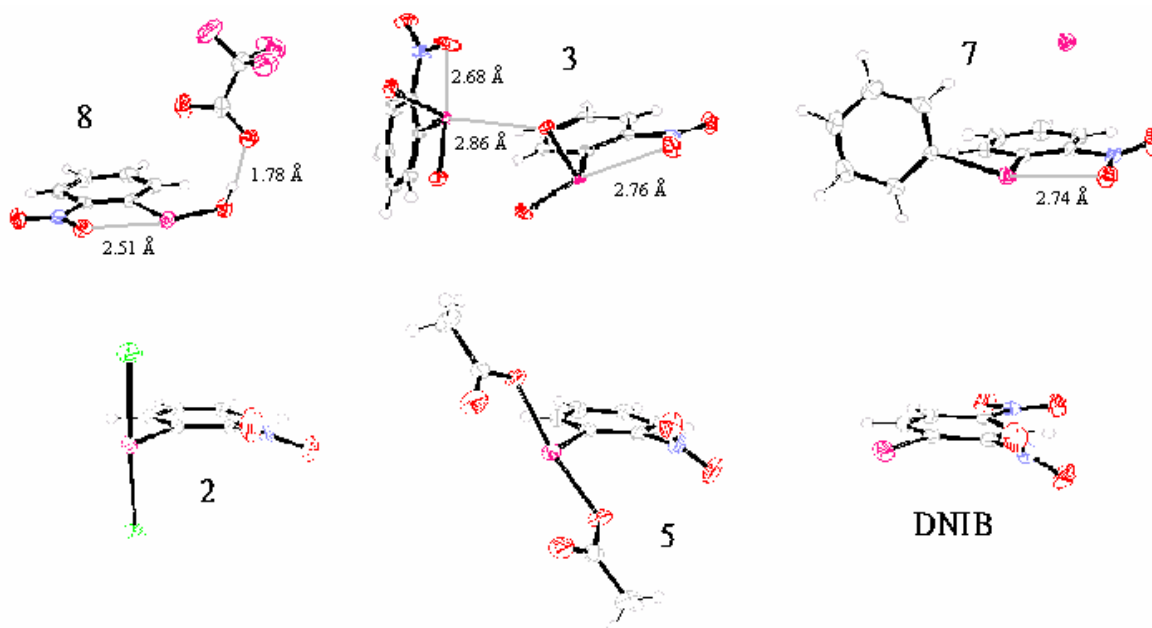

Figure 2. ORTEP plot (50% probability thermal ellipsoids) of **2**, **3**, **5**, **7**, **8**, DNIB. Hypervalent donor-acceptor bonds are indicated with grey lines. CCDC-168279, 207066 – 207071.

Table 1. Interatomic distances and angles in 5-membered ring (C-C-I-O-N) fragment of 2-NO_2-C_6H_4-X

No (Fig.1)	X	Distance O-I (Å)	Mean torsion angle	C-C-N angle	C-C-I angle
8	$^+$IOH $^-$OOCCF$_3$	2.51	1.7	119.4	120.3
3	IO$_2$(1)*	2.77	4.1	120.3	124.8
3	IO$_2$(2)*	2.68	13	119.3	122.4
7	$^+$IPh I$^-$	2.74	10	120.9	121.7
2	ICl$_2$	3.00	17	122.8	124.6
5	I(AcO)$_2$	3.11	30	122.1	123.2
	I (in DNIB)	3.16	33	121.2	123.1

* The crystal contains molecules of two types.

To our great satisfaction, three of the studied compounds (**3**, **7**, **8**) demonstrated strong interaction between nitro group and iodine (Fig. 2). This bond is included into a T-shaped hypervalent formation with I-C bond and a bond between iodine and a substituent at it.

o-Nitroiodobenzene dichloride **2** and diacetate **5** have no "vacancy" for formation of a T-shaped structure and therefore no bond between nitro group and iodine is formed.

The hypervalent iodine derivatives of *o*-nitroiodobenzene thus can be referred to two structural types: one – compounds **3**, **7**, **8** with covalent bond between O and I and a 5-ring geometry close to coplanar; another – compounds **2** and **5** with no or little covalent interaction between O and I and non-coplanar geometry, structurally similar to dinitroiodobenzene.

The strongest interaction between nitro group and iodine is in o-nitrophenylhydroxyiodonium trifluoroacetate **8**. This compound, in our opinion deserves a special attention. Bond O-I of 2.51 Å is only slightly (~ 0.2 Å) longer than in iodoxole (2.30 Å)[20]. The 5-membered ring is nearly coplanar (the biggest dihedral angle N-C-C-I is 3.0°). C-C-N and C-C-I angles are close to 120°. Like in iodoxole, C-I-O angle is distorted from optimal 90° and is 71.2°. In a crystalline state protonated iodosyl group and trifluoroacetate anion form a hydrogen bond (distance O-H = 1.78 Å, ∠O-H-O = 170°).

This compound has structural features of three different classes of compounds and the question should be raised - what is the correct chemical name for it?

It's a salt of *o*-nitroiodosylbenzene and trifluoroacetic acid, therefore we can call it o-nitrophenyliodosylium trifluoroacetate. The support for this name would be preparation of structurally similar salts from *o*-nitroiodosobenzene with other acids like trichloroacetic, other perfluorocarboxylic, toluenesulfonic, nitric, *etc*.

It's a compound with two radicals and a positive charge at iodine atom, therefore we can call it hydroxy(*o*-nitrophenyl)iodonium trifluoroacetate. This name would be supported by conversion of this compound to salts with other anions without exchange of a proton of HO-group or by HO-transfer reactions, similar to aryl transfer in diaryliodonium salts. However, it seems impossible to distinguish between the two names. Formation of other salts would support both, and HO-transfer can be explained as well-known oxidation by iodosyl compounds.

Most interestingly, it's a heterocyclic compound of a new type; therefore we can call it benziodoxazolium trifluoroacetate. To support this name, an exchange of substituents at 5-ring would be decisive factor – like substitution of HO to MeO or substitution of the second oxygen in a nitro group to another moiety, for instance PhN=.

Crystals of *o*-nitroiodylbenzene **3**(benziodoxazol oxide?) are built of molecules of two types, both having nearly coplanar five-membered ring and intramolecular O-I distances of 2.77 Å and 2.68 Å, respectively (in benziodoxol oxide – 2.32 Å[21] or 2.26 Å[22]). The shortest distance between these two molecules is 2.86 Å, however, other O-I intermolecular distances are also short, the shortest is 2.52 Å in a flat rhombic fragment formed by two iodyl groups of type (1). The O-I distance in 2-nitrodiphenyliodonium iodide **7** (phenylbenziodoxazolonium iodide?) is 2.74 Å, also just slightly longer than in carbon analog (2.48 Å).[20] The difference between derivatives of *o*-nitroiodobenzene and corresponding isoelectronic derivatives of *o*-iodobenzoic

acid is smaller for **7** and **8**, than for **3**. As we anticipated in the introduction, positive charge favors formation of a hypervalent donor-acceptor bond.

After the work was completed we learned about very similar findings on the structure of o-t-butylsulphonyliodyl- and yodosylbenzenes and tosylimide of the latter[23,24]. In these compounds distance between Iodine atom and one of the Oxygen atoms of SO_2 group is ca. 2.7 Å, and 5 atoms (I-O-S-C-C) form nearly coplanar 5-membered ring. Crystals of o-t-butylsulphonyliodyl- and yodosylbenzenes contain a molecule of methylene chloride and deuterochloroform respectively, which are bound by a weak hydrogen bond to an Oxygen atom, thus forming a structure similar to the structure of o-nitrophenylhydroxyiodonium trifluoroacetate **8**.

NMR

It is noteworthy that *o*-nitroiodosylbenzene **4** is the second of only two known to us examples of iodosyl compounds, for which NMR spectra had been recorded[23], though we can't be sure in which form **4** exists in DMSO solution.

^{1}H NMR chemical shifts are given in Table 2. [1]H shifts for compounds (5-8) are not in good correlation with calculated values (by simple additive scheme), this is mainly due to non-coplanar position of the nitro group. Regarding this group, the difference between calculated and experimental values is smallest for *o*-nitroiodobenzene dichloride **2**(dihedral angle between aromatic plane and nitro group is 25°). The difference is higher for parent *o*-nitroiodobenzene **1** (dihedral angle ca. 40°) and its diacetate (38°). Moreover, for the former two compounds deviations in chemical shifts are similar for protons at the same positions. Experimental values for chemical shifts of H-3 (*ortho*- to nitro group) and H-5 (*para*- to nitro group) in o-nitroiodobenzene **1** and *o*-nitroiodobenzene diacetate **5** are significantly lower than calculated ones. This is due to direct shielding effect of the π-electrons of the nitro group (for H-3) and its reduced conjugation with the aromatic ring, as a result of non-coplanarity.

Correlation for *o*-nitroiodylbenzene **3** is good. Mean deviation for this compound is 0.06 ppm, similar to that for *p*-nitroiodylbenzene (0.05 ppm). This also can be explained by a position of the nitro group, which is close to coplanar in this case. In o-nitrophenyliodonium iodide **7** calculated values for H-3 and H-4 are also close to experimental ones. Additional shielding by aromatic electron current of the second aromatic ring is, likely, responsible for relatively low chemical shifts of H-6 and H-5. As can be seen from Fig. 2, the unsubstituted aromatic ring is orthogonal to the plane of the ring that contains a nitro group; H-5 and especially H-6 thus fall into the shielding zone of the substituent. The spectrum of *o*-nitroiodosylbenzene trifluoroacetate **8** is more similar to that of o-nitroiodylbenzene **3**, rather than to the spectra of dicarboxylates **5** or **6**.

^{13}C NMR chemical shifts are given in Table 3. Low solubility and fast decomposition of o-nitroiodosylbenzene **4** in solution did not allow us to detect signals of C-1 and C-2 or to assign other signals. Assignment of signals for *o*-nitroiodylbenzene **3** is not unequivocal, due to close values for both experimental and calculated chemical shifts for pairs of carbon atoms that can not be assigned from 2D experiments(C-1/C-2, C-3/C-6 and C-4/C-5).

Table 2. ^{1}H NMR chemical shifts of 2-NO_2-C_6H_4-X at 30 ^{o}C in $CDCl_3$ (δ/ppm from TMS). In brackets – differences between experimental and calculated values

No.	X	H-3	H-4	H-5	H-6	Other H
8	$^+$IOH $^-$OOCCF$_3$	8.53	7.88	8.17	8.27	
3	IO$_2$*	8.37(-0.07)	8.89(0.02)	8.19(0.13)	8.29(0.03)	
7	$^+$IPh I$^-$*	8.35(-0.01)	7.85(-0.08)	7.81(-0.17)	8.11(-0.40)	8.29(H2'/6') 7.59(H3'/5'), 7.74(H-4')
4	IO*	8.45	7.77	8.05	7.93	
2	ICl$_2$	8.33(-0.11)	7.77(-0.10)	7.84(-0.07)	8.55(0.09)	
5	I(AcO)$_2$	8.28(-0.19)	7.79(-0.09)	7.72(-0.22)	8.39(0.02)	CH$_3$ – 1.99
6	I(ClCH$_2$COO)$_2$	8.36	7.85	7.79	8.47	CH$_2$ - 5.20
	I	7.86(-0.22)	7.49(-0.12)	7.27(-0.28)	8.05(0.06)	

*in DMSO-d$_6$.

Table 3. ^{13}C NMR chemical shifts of 2-NO_2-C_6H_4-X at 30 ^{o}C in $CDCl_3$ (δ/ppm from TMS). In brackets – differences between experimental and calculated values

X	C-1	C-2	C-3	C-4	C-5	C-6
$^+$IOH $^-$OOCCF$_3$	113.23	143.11	127.17	132.32	138.80	129.40
IO*	-	-	126.36, 127.38, 129.51, 136.24			
IO$_2$*	143.69	144.04	124.81	132.87	136.60	125.05
	(1.6)	(-2.9)	(-1.5)	(-3.1)	(-0.7)	(-2.8)
$^+$IPh I$^-$*	112.65	147.00	126.65	132.74	136.86	136.24
	(-1.1)	(-7.8)	(0.0)	(0.4)	(-0.6)	(0.4)
I(AcO)$_2$	113.51	147.69	125.85	132.96	135.13	139.19
	(-2.9)	(-6.9)	(0.1)	(0.6)	(-1.7)	(3.6)
I(ClCH$_2$COO)$_2$	113.64	146.89	126.24	133.83	135.72	139.33
I	86.15	153.11	125.39	129.02	133.32	141.91
	(-3.4)	(-4.0)	(0.3)	(0.7)	(-2.8)	(3.8)

*in DMSO-d$_6$.

^{13}C NMR chemical shifts show reasonable correlation with calculated values (unlike p-substituted hypervalent iodine compounds[25] that show good correlation). Spectra of diacetate **5** and of di(chloroacetate) **6** are almost identical. This fact confirms that **6**, despite the lack of X-ray data can be referred to the same structural type as **5**, without strong intramolecular O-I bond. Surprisingly, in contrast to proton spectra, there is little difference in chemical shifts of

trifluoroacetate **8** and of diacetate **5**, except for C-6 (where difference is ca. 10 ppm). On the other hand, there is no big difference between structurally similar trifluoroacetate **8** and o-nitroiodylbenzene **3**, except for a carbon atom C-1, bearing an iodine-containing substituent(30 ppm). Thus, different character of I(III) and I(V) influences on chemical shift of adjacent carbon only.

Conclusions

Indeed, our results confirm the existence of significant intramolecular O-I bond in certain derivatives of o-iodonitrobenzene. This bond is so strong in o-nitroiodosylbenzene trifluoroacetate, that the compound can be considered as the first example of a new class of heterocyclic compounds – benziodoxazolium salts.

   This finding is in agreement with our hypothesis that formation of similar bond is a key factor responsible for enhanced reactivity of o-nitrohaloarenes in selected reactions.

Experimental Section

Syntheses
o-**Nitroiodobenzene dichloride** (**2**). was prepared by passing chlorine into a solution of o-nitroiodobenzene **1** in chloroform or carbon tetrachloride. Precipitation started soon; when it stopped the reaction mixture was allowed to stand in the fridge overnight. The precipitate was filtered, washed with cold carbon tetrachloride and used for further reactions or crystallized from chloroform to obtain crystals for X-ray and NMR investigations. Several runs produced yields between 70 and 90%.
o-**Iodylnitrobenzene** (**3**). was prepared from o-nitroiodobenzene dichloride **2** by the method described for unsubstituted iodosylbenzene[26] by oxidation with sodium hypochlorite. Crude product was crystallized from 70% acetic acid to yield crystals suitable for X-ray and NMR measurements.
o-**Nitroiodosylbenzene** (**4**). This compound was prepared by the method described for unsubstituted iodosylbenzene[24] by grinding o-nitroiodobenzene dichloride **2** with sodium carbonate and sodium hydroxide. The orange powder was filtered, washed with water, dried, and washed with carbon tetrachloride several times. The resulting yellow powder contained no iodonitrobenzene **1** and less than 5% of o-iodylnitrobenzene **3** according to NMR.
o-**Nitroiodobenzene diacetate (5).** was prepared by mixing 5g of o-nitroiodosylbenzene **4** with 30 ml of glacial acetic acid with stirring. The colour disappeared immediately and clear solution formed; in a moment precipitation of the product started. The precipitate was filtered and recrystallized from glacial acetic acid. Yield 80%.
o-**Nitroiodobenzene di(chloroacetate) (6).** o-Nitroiodobenzene diacetate **5**(1.84 g, 0.5 mmol), chloroacetic acid (1 g, 10.6 mmol) and 10 ml of dry chlorobenzene were kept in a closed flask

for one week at ambient temperature. The solvent was evaporated off at reduced pressure. The residue was found to be o-nitroiodobenzene di(chloroacetate) **6**, containing less than 5% of the starting material.

***o*-Nitrodiphenyliodonium iodide (7).** 200mg of o-nitroiodosylbenzene **4** was added portion wise to a stirred mixture of 1ml of benzene and 1ml of concentrated sulfuric acid. After stirring at room temperature for 3 hours the mixture was poured into ice, filtered, and washed twice with methylene chloride. Then solution of KI was added to aqueous layer; the precipitate collected; washed with water and crystallized from acetone to yield small ruby crystals. Positive ion electrospray ionisation - time of flight (ESI-TOF) mass spectrum, which was calibrated with a raffinose sample, gave a molecular mass of 325.9651 for 2-nitrodiphenyliodonium ion (calculated 325.9678).

***o*-Nitrophenyliodosylbenzene trifluoroacetate (8).** 0.05 ml of trifluoroacetic acid was added to a solution of 100mg of o-nitroiodobenzene diacetate **5** in 1ml of chlorobenzene. On the next day the solution was evaporated in *vacuo*. Recrystallization of the semi-solid residue from carbon tetrachloride yielded lemon crystals of o-nitrophenyliodosylbenzene trifluoroacetate **8**(Mp 88 ^{o}C) suitable for X-ray analysis.

p-Nitroiodobenzene dichloride, p-iodylnitrobenzene and p-nitrodiphenyliodonium bromide were synthesized for comparison purposes, by the methods used for o-substituted compounds.

X-Ray Crystallography

Data were collected by Nonius Kappa CCD diffractometer using graphite monochromated radiation [λ(MoK$_{\alpha}$) = 0.71073 Å]. CCDC-168279, 207066 – 207071.

NMR Spectroscopy

^{1}H and ^{13}C NMR chemical shift assignments are based on Pulsed Field Gradient (PFG) ^{1}H,^{13}C Heteronuclear Multiple Quantum Coherence (HMQC) and Heteronuclear Multiple Bond Correlation (HMBC) measurements with a Bruker Avance DRX 500 spectrometer equipped with an inverse (proton) detection probehead and z-gradient accessory in CDCl$_{3}$ or DMSO-d$_{6}$ at 30 ^{o}C. Detailed lists of acquisition and processing parameters are available by E.K. on request.

Acknowledgements

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