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# $^{13}C$ NMR Study of 2-Iodoso- and 2-Iodoxy-benzoic Acids and Their Sodium Salts*

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**The $^{13}C$ NMR spectra for selected 2-iodosobenzoic acids, their sodium salts and the sodium salts of the corresponding iodoxybenzoic acids were measured and carbon assignments made using 2D and NOE experiments and relaxation times. Iodoso and iodoxy groups deshielded the *ipso*-carbon in these compounds by approximately 25 and 55 ppm, respectively, relative to the corresponding iodo compounds. The $^{13}C$ NMR spectra of the 2-iodosobenzoate anions were almost identical with those of the corresponding free acids, both possessing cyclic structures. The iodoxybenzoic acids are either insoluble in, or oxidize, suitable NMR solvents (i.e. DMSO-$d_6$, DMF-$d_7$). The cyclic structure postulated for iodoxybenzoate anions is supported by their $^{13}C$ chemical shifts.**

KEY WORDS $^{13}C$ NMR 2-Iodosobenzoic acids 2-Iodoxybenzoic acids Sodium 2-iodosobenzoates Sodium 2-iodoxybenzoates

## INTRODUCTION

2-Iodoso- (**3**) and 2-iodoxy-benzoic acids (**5**) and their derivatives constitute a separate class of polyvalent iodine compounds with distinct structures and properties.[1–3] A particularly interesting application of these compounds, discovered by Moss and co-workers, is their use as catalysts in the hydrolysis of phosphorus esters in micellar media.[4–9] The 2-iodoso- and 2-iodoxy-benzoic acids (IBA and IBX, respectively) have long been postulated[10] to exist as the cyclic tautomeric structures **3B** and **5B**. This has been demonstrated by x-ray crystallography for a few such acids by various workers authors[11–13] and confirmed for several anions **4B** and **6B** by our own results.[14] We now report and discuss the $^{13}C$ NMR spectra for a series of these compounds.

### Previously reported $^{13}C$ NMR spectra of related compounds

Except for the $^{13}C$ NMR spectra of some substituted IBA (**3**) and IBX (**5**) previously reported by us,[9] no $^{13}C$ NMR spectra of such compounds are available in the literature and certainly no systematic study has been undertaken. The only related study of analogous compounds is an NMR investigation of three diphenyliodonium-2-carboxylates.[15] In comparison with the chemical shifts of 2-iodobenzoic acid (**1a**), strong deshielding was observed at the carbon *ipso* to iodine (*ca.* 20 ppm) and a shielding at the *ortho* carbons (*ca.* 10 ppm).

We now report the $^{13}C$ NMR spectra for a series of substituted IBA and IBX and their sodium salts and discuss possible explanations for their characteristic aromatic carbon chemical shifts.

## RESULTS AND DISCUSSION

Most of the compounds investigated were prepared according to literature methods, as described in Part II.[9] The syntheses of the remaining compounds are described under Experimental.

The fact that polyvalent iodine compounds oxidize many of the usual NMR solvents (see Part III[1]) precluded the use of a common solvent for all measurements. Thus, DMSO-$d_6$ was used as an NMR solvent for the iodo- (**1**) and iodoso-benzoic acids (**3**) and the spectra of their sodium salts were measured in $D_2O$, DMSO-$d_6$ or a mixture of $D_2O$ and DMSO-$d_6$. We were unable to find an inert solvent for the free iodoxy acids. They dissolve in DMSO-$d_6$ and DMF-$d_7$ but react with them, being reduced to the corresponding iodo- and iodoso-benzoic acids, respectively. They dissolve in sulfolane on heating but are reduced to the corresponding iodo compounds. They are insoluble in $CDCl_3$ and they oxidize $CD_3OD$. Dissolution occurs in $CDCl_3$–$CF_3SO_3H$ or $CD_3COOD$, but the spectra obtained were complicated, probably owing to partial acetylation or triflation of the hydroxyl group, and/or addition to the I=O bond, and/or formation of the open structure. When NaOH or other bases in $D_2O$

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**Table 1. Selected $^{13}C$ NMR assignments for 2-iodobenzoic acids (1), 2-iodosobenzoic acids (2) and 2-iodoxybenzoic acids (3)**

| Compound | Form | $R^1$ | $R^2$ | M.p. (°C) | Literature m.p. (°C) | Ref. | Solvent | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C=O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1a** | Acid[a] | H | H | 160–162 | 163 | 3 | [b] | 136.9 | 94.0 | 140.6 | 132.5 | 128.2 | 130.2 | 168.1 |
| **2a** | Salt | H | H | — | — | — | [c] | 146.8 | 91.5 | 139.9 | 130.6 | 127.5 | 129.1 | 178.2 |
| **3a** | Acid | H | H | 223–225 | 231–232 | 3 | [b] | 131.5 | 120.4 | 134.5 | 131.1 | 126.3 | 130.4 | 167.7 |
| **4a** | Salt | H | H | — | — | — | [d] | 133.3 | 121.0 | 134.4 | 131.8 | 125.8 | 130.4 | 170.8 |
| **5a** | Acid | H | H | 176–178 | 222 | 16 | — | — | — | — | — | — | — | — |
| **6a** | Salt | H | H | — | — | — | [c] | 131.6 | 147.3 | 134.8 | 134.6 | 123.6 | 131.6 | 172.0 |
| **1b** | Acid | $OC_8H_{17}$ | H | 67–69 | 66–68 | 9 | [b] | 137.7 | 82.2 | 141.2 | 119.1 | 158.5 | 116.3 | 167.7 |
| **2b** | Salt | $OC_8H_{17}$ | H | — | — | — | [d] | 148.2 | 82.4 | 140.6 | 117.2 | 159.7 | 115.6 | 175.1 |
| **3b** | Acid | $OC_8H_{17}$ | H | 180–182 | 171–173 | 9 | [b] | 133.0 | 108.9 | 127.1 | 121.7 | 160.9 | 115.4 | 167.5 |
| **4b** | Salt | $OC_8H_{17}$ | H | — | — | — | [d] | 135.1 | 109.0 | 126.1 | 119.8 | 160.4 | 115.9 | 168.6 |
| **1c** | Acid[e] | $CH_3$ | H | 114–117 | 118–119 | 9 | [b] | 138.4 | 90.2 | 140.7 | 133.7 | 136.9 | 131.1 | 168.6 |
| **2c** | Salt | $CH_3$ | H | — | — | — | [d] | 147.4 | 89.2 | 139.2 | 130.4 | 137.8 | 129.4 | 173.7 |
| **3c** | Acid | $CH_3$ | H | 248–250 | 210–212 | 9 | [b] | 131.4 | 116.9 | 126.1 | 135.5 | 140.8 | 131.7 | 168.1 |
| **4c** | Salt | $CH_3$ | H | — | — | — | [d] | 133.4 | 116.9 | 125.3 | 134.6 | 140.0 | 131.8 | 169.8 |
| **5c** | Acid | $CH_3$ | H | 199–201 | 199–201 | 9 | — | — | — | — | — | — | — | — |
| **6c** | Salt | $CH_3$ | H | — | — | — | [c] | 131.9 | 146.1 | 123.7 | 135.1 | 144.1 | 132.0 | 172.1 |
| **1d** | Acid | H | $NO_2$ | 144–145 | 143 | 22 | [b] | 143.4 | 94.0 | 134.4 | 148.2 | 123.0 | 130.3 | 167.5 |
| **2d** | Salt | H | $NO_2$ | — | — | — | [b] | 154.5 | 92.3 | 133.6 | 146.1 | 123.0 | 128.3 | 170.6 |
| **3d** | Acid | H | $NO_2$ | 207–208 | 201 | 9 | [b] | 136.6 | 122.1 | 125.9 | 151.5 | 121.7 | 132.1 | 166.1 |
| **4d** | Salt | H | $NO_2$ | — | — | — | [c] | 137.5 | 121.7 | 125.7 | 151.8 | 120.9 | 132.4 | 170.3 |
| **5d** | Acid | H | $NO_2$ | 180–182 | 205 | 9 | — | — | — | — | — | — | — | — |
| **6d** | Salt | H | $NO_2$ | — | — | — | [c] | 137.3 | 149.4 | 129.3 | 151.4 | 119.2 | 132.7 | 169.8 |
| **1e** | Acid | $NO_2$ | H | 189–192 | 194 | 17 | [b] | 138.0 | 103.8 | 142.4 | 126.1 | 147.3 | 124.2 | 166.5 |
| **2e** | Salt | $NO_2$ | H | — | — | — | [b] | 149.1 | 101.9 | 142.2 | 124.8 | 148.8 | 122.5 | 175.4 |
| **3e** | Acid | $NO_2$ | H | 229–230 | 229–229.5 | 18 | [b] | 133.4 | 127.8 | 128.2 | 128.2 | 149.8 | 124.8 | 166.0 |
| **4e** | Salt | $NO_2$ | H | — | — | — | [d] | 135.9 | 129.9 | 127.3 | 126.8 | 149.6 | 124.5 | 167.3 |
| **5e** | Acid | $NO_2$ | H | 215 | 199–202 | 19 | — | — | — | — | — | — | — | — |
| **6e** | Salt | $NO_2$ | H | — | — | — | [c] | 134.1 | 153.5 | 128.9 | 126.2 | 151.7 | 125.0 | 169.7 |

[a] Lit.[15] data for compound **1a**, $\delta(CDCl_3)$: 142.0 (C-1), 94.1 (C-2), 141.6 (C-3), 132.9 (C-4), 128.3 (C-5), 131.3 (C-6).
[b] DMSO-$d_6$.
[c] $D_2O$.
[d] DMSO-$d_6$/$D_2O$.
[e] Lit.[15] data for compound **1c**, $\delta(CDCl_3)$: 141.7 (C-1), 90.6 (C-2), 141.7 (C-3), 134.6 (C-4), 138.2 (C-5), 132.9 (C-6).

were used to prepare the sodium salts (**6**) of the IBX they underwent facile reduction to IBA. The spectra of the sodium salts of IBX derivatives **6** were measured in NaOCl solution to avoid such reduction.

## $^{13}C$ NMR spectral assignments for selected 2-iodobenzoic acids (1), 2-iodosobenzoic acids (3) and 2-iodoxybenzoic acids (5)

In Table 1 the aromatic $^{13}C$ assignments for the 2-iodoso- (**3**) and 2-iodoxy-benzoic acids (**5**) and sodium salts used in this study are compared with those of the corresponding 2-iodobenzoic acid derivatives (**1**). A variety of standard techniques were utilized to assign the spectra, including $^{13}C$ substituent chemical shifts (SCS), INEPT, proton-coupled gated NOE experiments, relaxation times and 2D heteronuclear correlation spectroscopy (HETCOR). Carbon assignments for 2-iodobenzoic acids (**1**) were generally obtained by calculation of the expected chemical shifts from known SCS values. IBA (**3**) and IBX (**5**) derivatives normally required 2D-HETCOR experiments for unequivocal assignments.

The processes utilized to make more complex assignments can be exemplified by reference to 2-iodo-5-octyloxybenzoic acid (**1b**). The quaternary carbons C-1, C-2 and C-5 were readily identified as the less intense peaks (i.e. longer relaxation times) at $\delta$82.2, 137.7 and 158.5. The resonance at $\delta$82.2 could be assigned unambiguously to C-2, the upfield shift resulting from the iodine heavy-atom effect.[20a] The $\delta$158.5 peak was clearly due to C-5, the large downfield shift resulting from the large *ipso* SCS value for alkoxy groups (*ca.* +30);[20b] hence the peak at $\delta$137.7 can be assigned to C-1.

Methine carbons C-3, C-4 and C-6 could not be unequivocally assigned by the above process. However, the corresponding protons could be readily identified in the $^1H$ NMR spectrum as H-3 at $\delta$7.7 (d, $J = 9$ Hz; *ortho* coupling to H-4), H-6 at $\delta$7.3 (d, $J = 3$ Hz; *meta* coupling to H-4) and H-4 at $\delta$6.7 (dd, $J = 9$ Hz, 3 Hz; *ortho* coupling to H-3, *meta* coupling to H-6). A 2D HETCOR experiment (proton decoupled) was then carried out. The results clearly correlated H-3 with the carbon resonance at $\delta$141.2 (C-3), H-6 with the peak at $\delta$116.3 (C-6) and H-4 with that at $\delta$119.1 (C-4), thus completing the assignment.

## $^{13}C$ NMR chemical shift regularities of 2-iodoso- (3) and 2-iodoxy-benzoic acids (5)

The spectra listed in Table 1 show two striking general features: (a) the nearly identical chemical shifts of the

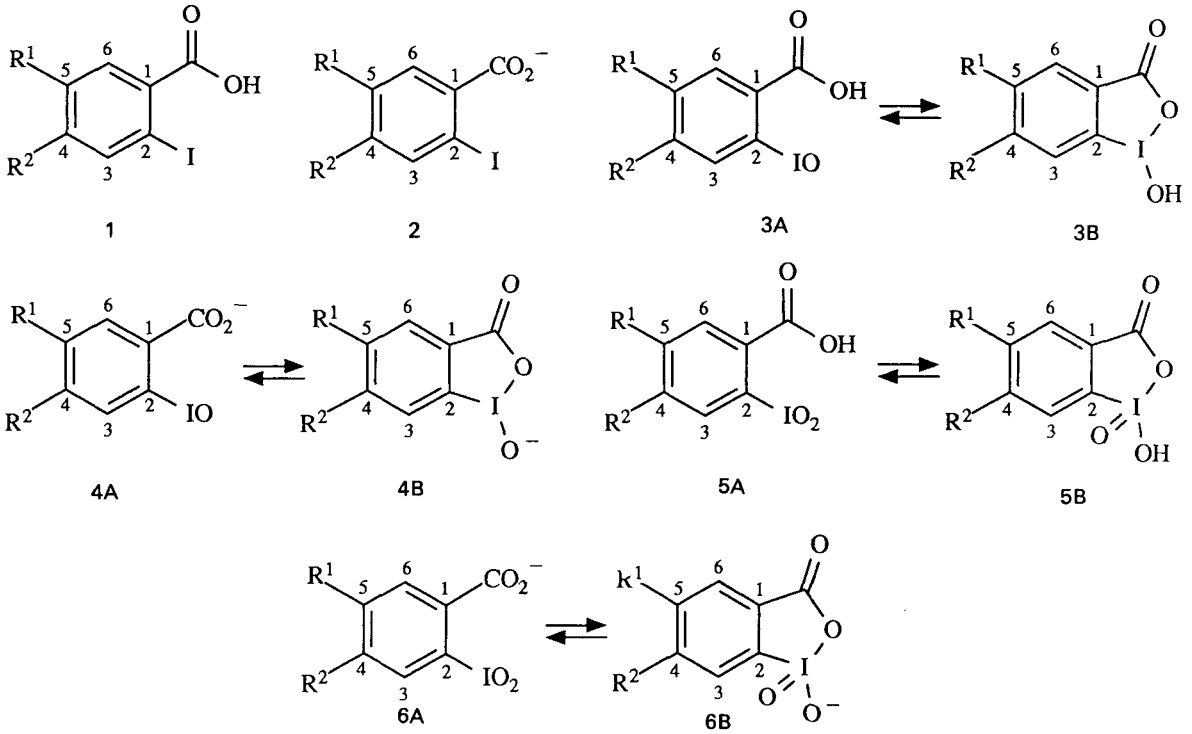


**Figure 1.** Structures of 2-iodobenzoic acids (**1**), 2-iodosobenzoic acids (**3**), 2-iodoxybenzoic acids (**5**) and the corresponding salts **2**, **4** and **6**.

iodosobenzoic acids (**3**) and their corresponding anions (**4**) and (b) the influence on the aromatic carbon resonances due to the change in the oxidation state of iodine(I) to iodine(III) and to iodine(V). Most noteworthy is the strong deshielding of C-2 [*ca.* 25 ppm for the iodosobenzoic acids (**3**) and salts (**4**) and *ca.* 55 ppm for the iodoxybenzoate salts (**6**)], relative to the corresponding iodo derivatives **1** or **2**.

The small differences in chemical shifts between the iodosobenzoic acids (**3**) and the corresponding salts (**4**) agree with other results[2,3,11–14] which show that both the free acids and salts exist in the cyclic forms **3B** and **4B**. Neither the results of previous workers nor those reported here give any evidence for the non-cyclized form, and if a tautomeric equilibrium exists it must greatly favor the cyclic form.

In the 2-iodobenzoic acid series (**1**), for which only the open structures can exist, significant chemical shift differences at C-1 are found between the acids (**1**) and their salts (**2**). The carboxylate anion deshields C-1 by about 10 ppm, an effect which cannot be attributed to solvent variance alone. Such an effect is not observed in the iodoso compounds **3** and **4**, again strongly implying that in solution the carboxylate group possesses the same (cyclic) structure in both the free acid **3B** and the anion **4B**. Evidently the negative charge of the anion (**4B**) is sufficiently distant from C-1 to minimize the effect of ionization. Further, the —IO$^-$ group does not significantly influence the *ipso* (C-2) carbon chemical shift compared with the corresponding —IOH group. This agrees with previously reported $^{13}$C NMR spectra of polyvalent iodine compounds (Part III[1]) and suggests that there is no linear correlation between the *ipso*-carbon chemical shift and the electron-withdrawing ability of the polyvalent-iodine substituent groups. Hence, for the iodoso compounds **3** and **4**, the chemical shift of the *ipso*-carbon depends predominantly on the oxidation state of the iodine atom and much less on the attached substituents, as discussed in Part III.[1]

The $^{13}$C NMR spectra of the IBX (**5**) are not available for comparison with those of their sodium salts (**6**). However, comparison of the C-1 (*ipso* to carboxyl group) chemical shifts of the iodo free acids (**1**), iodo salts (**2**) and IBX salts (**6**), and consideration of the previous conclusions, indicates that the IBX sodium salts also exist in the cyclic structure (**6B**). We are currently attempting to obtain x-ray structures to confirm this conclusion.[14]

In Part III,[1] it was concluded that (a) a change in the oxidation state of iodine from I to III causes changes of approximately +30 ppm for the carbon *ipso* to iodine, −4 ppm for the carbon *ortho* to iodine and +5 ppm for the *para* carbon; (b) a change from iodine(I) to iodine(V) causes changes of approximately +50 ppm for the carbon *ipso* to iodine, −10 ppm for the *ortho* carbon and +6 ppm for the *para* carbon and (c) the chemical shifts of the *meta* carbons are almost unaffected by the oxidation level of iodine.

Table 2 records the changes in chemical shifts (in ppm) from the change in the oxidation level of iodine(I → III → V) for the iodo derivatives of Table 1 and their sodium salts.

The general features discussed in part III[1] for the carbon spectral shifts of the organoiodine compounds are again encountered in the 2-carboxyphenyl derivatives.

The influence on C-4, C-5 and C-6 (*meta* and *para* carbons to iodine) due to the changes in iodine valency is minor and irregular. The combined interactions of the substituents, together with the cyclic structures of the

**Table 2. Changes in chemical shifts (in ppm) resulting from the change in the oxidation state of iodine(I → III → V) for the iodo derivatives (1–6a–e) and their sodium salts**

| Compound | Form | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 |
|---|---|---|---|---|---|---|---|
| **3a** | Acid | −5.4 | 26.4 | −6.1 | −1.4 | −1.9 | 0.2 |
| **4a** | Salt | −13.5 | 29.5 | −5.5 | 1.2 | −1.7 | 1.3 |
| **6a** | Salt | −15.2 | 56.8 | −5.1 | 4.0 | −3.9 | 1.4 |
| **3b** | Acid | −4.7 | 26.7 | −14.1 | 2.6 | 2.4 | −0.7 |
| **4b** | Salt | −13.1 | 26.6 | −14.5 | 2.6 | 0.7 | 0.3 |
| **3c** | Acid | −7.0 | 26.7 | −14.6 | 1.8 | 3.9 | 0.6 |
| **4c** | Salt | −14.0 | 27.7 | −13.9 | 2.6 | 0.7 | 0.3 |
| **6c** | Salt | −15.5 | 56.9 | −15.3 | 4.7 | 6.3 | 2.6 |
| **3d** | Acid | −6.8 | 28.1 | −8.5 | 3.3 | −1.3 | 1.8 |
| **4d** | Salt | −17.0 | 29.4 | −7.9 | 5.7 | −2.1 | 4.1 |
| **6d** | Salt | −17.2 | 57.1 | −4.3 | 5.3 | −3.8 | 4.4 |
| **3e** | Acid | −4.6 | 24.0 | −14.2 | 2.1 | 2.5 | 0.6 |
| **4e** | Salt | −13.2 | 28.0 | −14.9 | 2.0 | 0.8 | 2.0 |
| **6e** | Salt | −15.0 | 51.6 | −13.3 | 1.4 | 2.9 | 2.5 |

iodoso (**3B**, **4B**) and iodoxy compounds (**5B**, **6B**), significantly change the electronic environment of the aromatic carbons. This could be responsible for the observed deviations.

The carbons *ortho* to iodine (C-1 and C-3) are shielded by increasing the oxidation level of the iodine, in accordance with the general tendency for organoiodine compounds. In the 5-substituted derivatives C-3 is even more strongly shielded in both the iodoso and iodoxy compounds. This additional shielding could be attributed to the contribution of the additional substituent, which, together with the cyclic structure, alters the electron density on C-3.

## CONCLUSION

In this study we measured and assigned the $^{13}C$ chemical shifts of both acid and anionic forms of substituted 2-iodo-(**1**, **2**) and 2-iodoso-benzoic acids (**3**, **4**) and for the anionic form (**6**) of the 2-iodoxy analogs. In the trivalent-iodine series the *ipso* and carbonyl carbon atom resonances are similar in both the acid and salt forms. This is explained by the fact that both the acid and the salt exist in the cyclic form. The influence of the ionization charge is therefore remote from the ring carbon atoms. In contrast, the *ipso* and carbonyl carbon atoms of the corresponding iodobenzoic acid show a 10 ppm shift on ionization. As with other compounds containing this functional group, oxidation of iodine to its first polyvalent state (I → III) results in an incremental shift of *ca.* 30 ppm. Further oxidation to the second polyvalent state (III → V) results in an additional shift of *ca.* 25 ppm (measured as the anion). Ionization of the polyvalent iodine species, and additional substituents present on the aromatic ring, appear to have a minimal effect on the magnitude of these shifts. The dramatic shift at the *ipso* carbon atom thus becomes a major diagnostic tool for the assignment of the oxidation state of iodine in the polyvalent iodine compounds.

Because of the high oxidation power of IBX derivatives, great care should be exercized in the interpretation of spectra resulting from measurements obtained in common NMR solvents. Our study indicates the reaction between IBX derivatives and solvent (i.e. DMSO-$d_6$ or DMF-$d_7$) is rapid and gives the spectra of the corresponding reduced (I or III) derivatives. Anomalous results are also obtained when IBX derivatives are exposed to strong base.

## EXPERIMENTAL

### Methods

$^{13}C$ NMR spectra were obtained at 25 MHz on a JEOL FX-100 or at 50 MHz on a Varian XL-200 NMR spectrometer (FT mode), referenced either to solvent [$\delta(CDCl_3) = 77.0$; $\delta$(DMSO-$d_6$) = 39.5] or, when $D_2O$ was utilized, to added dioxane ($\delta$67.4), at ambient temperature. With mixtures of $CDCl_3$ and other solvents, $CDCl_3$ was used as reference. The 90° pulse widths were 13.5 μs and there was no pulse delay ($D_1 = 0$). The acquisition time was 0.998 s. The 2D-HETCOR spectra were obtained on either a Nicolet NT-300 or a Varian XL-200 spectrometer using the standard pulse sequence provided by Varian.

### Materials

Commercially available analytical-reagent grade solvents and reagents were used without further purification. All compounds, except those discussed below, were prepared according to literature methods.[9] 2-Iodosobenzoic acid (Sigma) and 2-iodobenzoic acid (Aldrich) were used as received.

The syntheses of 5-octyloxy-2-iodobenzoic acid, 5-octyloxy-2-iodosobenzoic acid, 5-octyloxy-2-iodoxybenzoic acid, 5-methyl-2-iodobenzoic acid, 5-methyl-2-iodosobenzoic acid, 5-methyl-2-iodoxybenzoic acid, 4-nitro-2-iodobenzoic acid, 4-nitro-2-iodosobenzoic acid and 4-nitro-2-iodoxybenzoic acid have been described elsewhere.[9]

The sodium salts of the iodo and iodoso compounds were not isolated but were prepared *in situ* using excess NaOH in $D_2O$ or $Na_2CO_3$ in $D_2O$ in the case of the 5-nitro-substituted compounds. The sodium salts of the iodoxy compounds were also not isolated but were prepared *in situ* using aqueous *ca.* 5% sodium hypochlorite (NaOCl) solution and added $D_2O$ as the internal lock.

**2-Iodoxybenzoic acid (5a).** Chlorine (dried by passing through $CaSO_4$) was bubbled into an ice-cold solution of 2-iodobenzoic acid (1.984 g, 8 mmol) in chloroform (20 ml) for 10 min. The yellow solid precipitate was collected by filtration, treated with 10 ml of commercial bleach (*ca.* 5% aqueous NaOCl) and the mixture stirred for 1 h at room temperature. The solution was acidified with concentrated sulfuric acid and the solid collected, washed with water and dried to give 2-iodoxybenzoic acid (**5a**) (2.222 g, 99%), m.p. 224–225 °C (lit.[16] m.p., 222 °C).

**5-Nitro-2-iodobenzoic acid (1e).** A mixture of 5-nitroanthranonitrile (16.3 g, 100 mmol) and 5% aqueous

sodium hydroxide (40 ml) was heated under reflux for 6 h and the resulting solution was acidified with acetic acid. The yellow microcrystals produced were collected by filtration, washed thoroughly with water and dried *in vacuo* to give 5-nitroanthranilic acid (15.5 g, 80%), m.p. 263–265 °C (lit.[21] m.p., 263 °C). Diazotization of 5-nitroanthranilic acid (9.1 g, 50 mmol) and reaction with potassium iodide according to the literature method[10] gave 5-nitro-2-iodobenzoic acid (4.5 g, 51%), m.p. 189–192 °C (lit.[17] m.p., 194 °C).

**5-Nitro-2-iodosobenzoic acid (3e).** A solution of 5-nitro-2-iodobenzoic acid (1.0 g, 3.4 mmol) in 90% fuming nitric acid (10 ml) was stirred for 6 h at room temperature. The reaction mixture was poured into water (200 ml), the resulting solid collected, washed with water and dried *in vacuo*. After trituration with ethyl acetate the solid was collected, washed with ethyl acetate and diethyl ether and dried to give 5-nitro-2-iodosobenzoic acid (**3e**) (0.8 g, 76%), m.p. 228–230 °C (lit.[18] m.p., 229–229.9 °C).

**5-Nitro-2-iodoxybenzoic acid (5e).** A suspension of 5-nitro-2-iodosobenzoic acid (0.4 g, 1.3 mmol) in 15 ml of commercial bleach was stirred at room temperature until complete dissolution occurred. The solution was acidified with concentrated sulfuric acid and the solid precipitate was collected by filtration, washed with water and diethyl ether to give 5-nitro-2-iodoxybenzoic acid (0.15 g, 36%), m.p. 215 °C (lit.[19] m.p., 199–202 °C).

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