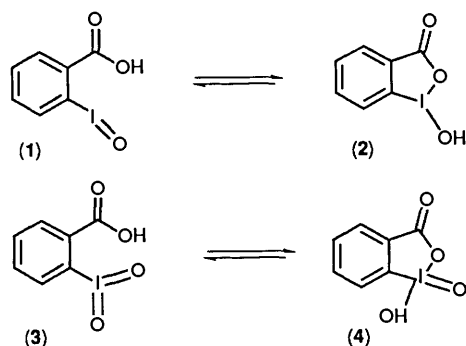


## A Structural Study of 3- and 4-Iodosylbenzoic Acids, 3- and 4-Iodylbenzoic Acids, and their Sodium Salts<sup>1</sup>

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The <sup>13</sup>C NMR, IR, and UV spectra of 3- and 4-iodobenzoic, 3- and 4-iodosylbenzoic, and 3- and 4-iodylbenzoic acids and their sodium salts have been measured and compared with those of the corresponding 2-isomers. Kinetic data for the catalytic microemulsion hydrolysis of 4-nitrophenyl diphenyl phosphonate in the presence of the iodosyl and iodyl compounds have been obtained. Catalytic efficiency of the 3- and 4-substituted isomers are measured to be three to six orders of magnitude less effective than the corresponding 2-substituted isomers. Possible structural configurations are suggested and discussed.

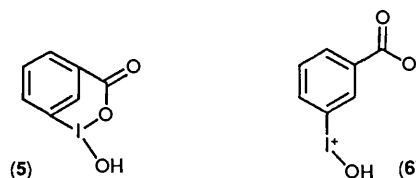
2-Iodosylbenzoic acid (1), and its derivatives, have long been postulated<sup>2,3</sup> to exist in the cyclic tautomeric form of 1-hydroxy-1,2-benziodoxolin-3-ones (2). A similar structure (4) can be drawn for derivatives of 2-iodylbenzoic acid (3). This postulation has been confirmed, in the solid state at least, by the X-ray crystallographic examination of a few such acids by various authors.<sup>4-9</sup> See Scheme.



Scheme.

The molecular structures of 3- and 4-iodosylbenzoic, and 3- and 4-iodylbenzoic acids, however, have not been fully elucidated. The only existing studies of these compounds are in the form of IR examinations by Bell and Morgan,<sup>10</sup> and Shenjie and co-workers<sup>11</sup> Both groups reported a low frequency carbonyl band for 3-iodosylbenzoic acid (Table 1). The latter group, however, did not observe the low frequency carbonyl band for 4-iodosylbenzoic acid. Bell and Morgan<sup>10</sup> reported a value of 1 625 cm<sup>-1</sup> for this band and also noted weak hydroxyl bands for 3- and 4-iodosylbenzoic, and 3- and 4-iodylbenzoic acids (at ca. 3 300 cm<sup>-1</sup>) which are characteristic of the cyclic 2-isomers. These data suggest that the structures of 3- and 4-iodosylbenzoic, and 3- and 4-iodylbenzoic acids also involve proton transfer from the carboxyl group to the iodosyl or iodyl group. Although an intramolecularly cyclized structure is impossible for the 4-isomer and highly unlikely for the 3-isomer, Shenjie and co-workers proposed the partial formation of structure (5) for the latter. Bell and Morgan favoured the

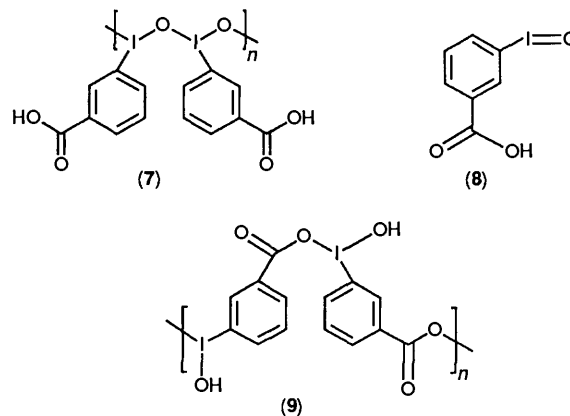
zwitterionic form (6) (*meta* shown) for the 3- and 4-iodosylbenzoic acids.



### Results and Discussion

To shed more light on this structural uncertainty, 3- and 4-iodosylbenzoic and 3- and 4-iodylbenzoic acids were prepared. The appropriate iodobenzoic acid was chlorinated with molecular chlorine to give the dichloroiodo compound. This was then either hydrolysed to the iodosylbenzoic acid or oxidatively hydrolysed (with aqueous sodium hypochlorite) to the iodylbenzoic acid.<sup>10,12</sup> The IR and UV adsorption values for the complete series are shown in Tables 1 and 2.

Among the plausible structures (6-9) for the iodosyl compounds, structures (7) and (8) are readily excluded by the low carbonyl frequency. Recent developments in organoiodine chemistry<sup>13-16</sup> suggest that the polymeric form (9), not con-



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sidered by Bell and Morgan, is more likely than their proposed zwitterionic structure (6). The amorphous character of these materials in the solid state also supports their polymeric nature.<sup>3</sup>

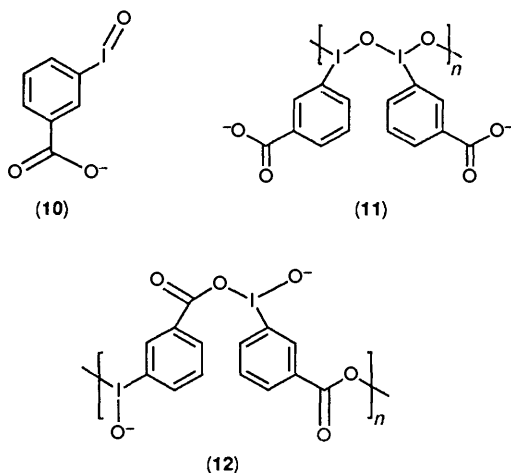
Three similar structures (10, 11, and 12) are conceivable for

**Table 1.** Absorption bands in the IR spectra (nujol) of iodo-, iododisyl-, and iodyl-benzoic acids ( $\text{cm}^{-3}$ ).

Compound	Present Work			Literature	
	$\nu(\text{OH})$	$\nu(\text{C=O})$	Other s or m bands	$\nu(\text{C=O})$ Ref. 11	$\nu(\text{C=O})$ Ref. 10
2- $\text{IC}_6\text{H}_4\text{CO}_2\text{H}$	3 000	1 670	1 575, 1 260, 1 010, 740	1 680	1 680
2- $\text{IC}_6\text{H}_4\text{CO}_2\text{Na}$	—	1 655	1 575, 1 525, 1 005, 735	—	—
2- $\text{OIC}_6\text{H}_4\text{CO}_2\text{H}$	3 000	1 612	1 565, 1 454, 1 342	1 605	1 620
2- $\text{OIC}_6\text{H}_4\text{CO}_2\text{Na}$	—	1 602	1 557, 742, 680	—	1 595
2- $\text{O}_2\text{IC}_6\text{H}_4\text{CO}_2\text{H}$	3 000	1 638	1 562, 1 337, 1 301, 779, 748	—	1 640
2- $\text{O}_2\text{IC}_6\text{H}_4\text{CO}_2\text{Na}$	—	1 600	1 555, 1 301, 970, 747	—	—
3- $\text{IC}_6\text{H}_4\text{CO}_2\text{H}$	3 000(w)	1 670	1 555, 1 305, 1 255, 935, 750	1 690	1 695
3- $\text{IC}_6\text{H}_4\text{CO}_2\text{Na}$	—	1 575	1 530, 745, 720	—	—
3- $\text{OIC}_6\text{H}_4\text{CO}_2\text{H}$	3 100	1 675	1 305, 935, 745	1 610	1 605
3- $\text{OIC}_6\text{H}_4\text{CO}_2\text{Na}$	—	1 585	1 540, 850, 750	—	1 595
3- $\text{O}_2\text{IC}_6\text{H}_4\text{CO}_2\text{H}$	3 400(w)	1 685	1 315, 770, 755, 740, 720	—	1 695
3- $\text{O}_2\text{IC}_6\text{H}_4\text{CO}_2\text{Na}$	—	1 595	1 130, 750, 715	—	—
4- $\text{IC}_6\text{H}_4\text{CO}_2\text{H}$	3 000	1 675	1 580, 1 315, 1 290, 1 005, 750	1 680	1 690
4- $\text{IC}_6\text{H}_4\text{CO}_2\text{Na}$	—	1 575	1 530, 1 010, 840, 760	—	—
4- $\text{OIC}_6\text{H}_4\text{CO}_2\text{H}$	3 400(w)	1 615	1 280, 830	1 680	1 624
4- $\text{OIC}_6\text{H}_4\text{CO}_2\text{Na}$	—	1 581	1 530, 723	—	—
4- $\text{O}_2\text{IC}_6\text{H}_4\text{CO}_2\text{H}$	3 300	1 685	1 275, 845, 755	—	—
4- $\text{O}_2\text{IC}_6\text{H}_4\text{CO}_2\text{Na}$	—	1 585	1 540, 770, 735	—	—

**Table 2.** UV Absorption maxima for iodo-, iododisyl- and iodyl-benzoic acids.

Compound	pH	$\lambda_{\text{max}}$	$\epsilon$
2- $\text{IC}_6\text{H}_4\text{CO}_2\text{H}$	10.4	226	4 680
2- $\text{IC}_6\text{H}_4\text{CO}_2\text{Na}$	2.0	285	1 120
2- $\text{IOC}_6\text{H}_4\text{CO}_2\text{H}$	10.4	297	660
2- $\text{IOC}_6\text{H}_4\text{CO}_2\text{Na}$	2.0	289	240
2- $\text{IO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$	10.4	289	190
2- $\text{IO}_2\text{C}_6\text{H}_4\text{CO}_2\text{Na}$	2.0	290	200
3- $\text{IC}_6\text{H}_4\text{CO}_2\text{H}$	10.4	227	11 250
3- $\text{IC}_6\text{H}_4\text{CO}_2\text{Na}$	2.0	282	1 080
3- $\text{IOC}_6\text{H}_4\text{CO}_2\text{H}$	10.4	270	1 000
3- $\text{IOC}_6\text{H}_4\text{CO}_2\text{Na}$	2.0	283	630
3- $\text{IO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$	10.4	270	2 100
3- $\text{IO}_2\text{C}_6\text{H}_4\text{CO}_2\text{Na}$	2.0	270	1 700
4- $\text{IC}_6\text{H}_4\text{CO}_2\text{H}$	10.4	249	14 150
4- $\text{IC}_6\text{H}_4\text{CO}_2\text{Na}$	2.0 <sup>a</sup>	255	15 000
4- $\text{IOC}_6\text{H}_4\text{CO}_2\text{H}$	10.4	244	10 700
4- $\text{IOC}_6\text{H}_4\text{CO}_2\text{Na}$	2.0	251	10 500
4- $\text{IO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$	10.4	insoluble	—
4- $\text{IO}_2\text{C}_6\text{H}_4\text{CO}_2\text{Na}$	2.0	insoluble	—

<sup>a</sup> Methanol added.

the sodium 3- and 4-iodosylbenzoate anions. Structure (10) represents a iodylbenzene derivative in monomeric form, which is expected to be less stable than polymeric structures (11) or (12). The group  $\text{RCO}_2\text{-I(X)-}$  is not stable under basic conditions and is known<sup>16</sup> to hydrolyse to form the (polymerized) iododisyl group. The polymeric iododisyl group ( $-\text{O}-\text{I}-\text{O}-\text{I}-$ ) is known to be stable in alkaline solution.<sup>17</sup> The above reasoning suggests that the sodium 3- and 4-iodosylbenzoates prefer structure (11).

The  $^{13}\text{C}$  NMR spectra of the sodium salts in  $\text{D}_2\text{O}$ , are reported in Table 3, together with the spectra of the corresponding iodo compounds. The spectral data of the analogous 2-isomers are also included for comparison.

From a compilation of the  $^{13}\text{C}$  NMR spectra of polyvalent iodine compounds,<sup>18</sup> (part 3 of this series) changes in the oxidation level from iodine(I) to iodine(III), cause 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, while the chemical shift of the carbon meta to iodine is almost unaffected by the oxidation.

Considering the  $^{13}\text{C}$  NMR spectra of entries 1, 2, 3, entries 7, 8, and entries 12, 13 in Table 3, the following can be concluded: (i) When the iodobenzoic acids are converted to their sodium salts, major changes are observed at the carbon *ipso* to carboxyl group (*ca.* +10 ppm) and at the carbonyl carbon (*ca.* +10 ppm), while the chemical shifts of the other carbons are practically unaffected. (ii) When the iodobenzoic acids are co-ordinated to a trivalent iodine atom, no significant change is observed for the chemical shifts of any carbon atom of the aromatic ring, and only minor changes are observed for the carbonyl carbon atom.

The above considerations suggest that the sodium 3- and 4-iodosylbenzoates have the structure (11): The changes at C-2, C-3, C-4, C-5, and C-6 chemical shifts are those expected by change in the valency at the iodine atom. However, the changes at the chemical shifts of C-1 and C=O can not be explained, unless the carboxyl group has anionic character ( $\text{CO}_2\text{Na}$ ).

**Kinetic Data.**—The use of 2-substituted iododisyl- and iodylbenzoic acids as hydrolysis catalysts is well documented in the literature. To evaluate the questions of structure of the 3- and 4-substituted isomers, compared with the behaviour of the 2-substituted isomer, a microemulsion system for which we have

**Table 3.**  $^{13}\text{C}$ -NMR assignments for 2-, 3-, and 4-iodo-, iodosyl-, and iodyl-benzoic acids and their sodium salts.<sup>a</sup>

Entry	Compound	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C=O
1	2-IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	(CD <sub>3</sub> ) <sub>2</sub> SO	136.9	94.0	140.6	132.5	128.2	130.2	168.1
2	2-IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Na	D <sub>2</sub> O	146.8	91.5	139.9	130.6	127.5	129.1	178.2
3	2-OIC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	(CD <sub>3</sub> ) <sub>2</sub> SO	131.5	120.4	134.5	131.1	126.3	130.4	167.7
4	2-OIC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Na	(CD <sub>3</sub> ) <sub>2</sub> SO/D <sub>2</sub> O	133.3	121.0	134.4	131.8	125.8	130.4	170.8
5	2-O <sub>2</sub> IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	CDCl <sub>3</sub> /DMF	128.4	116.6	135.7	132.1	126.6	130.9	167.1
6	2-O <sub>2</sub> IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Na	D <sub>2</sub> O	131.7	120.1	134.8	131.7	125.1	130.4	172.3
7	3-IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	CDCl <sub>3</sub> /(CD <sub>3</sub> ) <sub>2</sub> SO	131.7	136.9	92.6	139.9	128.9	127.4	165.0
8	3-IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Na	D <sub>2</sub> O	139.1	138.8	95.3	140.7	131.0	129.0	174.2
9	3-OIC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	<i>b</i>	—	—	—	—	—	—	—
10	3-OIC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Na	D <sub>2</sub> O	139.3	133.7	124.6	135.7	131.1	131.6	174.1
11	3-O <sub>2</sub> IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	<i>b</i>	—	—	—	—	—	—	—
12	4-IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	CDCl <sub>3</sub> /(CD <sub>3</sub> ) <sub>2</sub> SO	129.0	129.7	135.9	98.9	135.9	129.7	165.7
13	4-IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Na	D <sub>2</sub> O	136.6	131.4	138.2	98.8	138.2	131.4	175.6
14	4-OIC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	<i>b</i>	—	—	—	—	—	—	—
15	4-OIC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Na	D <sub>2</sub> O	139.0	131.4	133.2	127.4	133.2	131.4	175.5
16	4-O <sub>2</sub> IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	<i>b</i>	—	—	—	—	—	—	—

<sup>a</sup> C-1 is the carbon *ipso* to carboxyl group. <sup>b</sup> Compounds insoluble in, or which react with, usual NMR solvents.

extensive data on the second-order rate constants of numerous nucleophilic species was chosen.<sup>19–27</sup> Thus, 4-nitrophenyldi-phenyl phosphate was subjected to hydrolysis at pH 9.2 in the well-studied 'Mackay' cationic microemulsion<sup>19,22</sup> with the 3-iodosyl- and 4-iodosyl-benzoate and the 3-iodyl- and 4-iodyl-benzoate sodium salts as catalysts. In this system, 2-iodosylbenzoic acid has a second-order rate constant of 1.5 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. By comparison, hydroxide, in the same system, has a second-order rate constant of 0.14 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. Thus, 2-iodosylbenzoic acid in the Mackay microemulsion is one order of magnitude more reactive as a nucleophilic reagent than hydroxide. By contrast, the 3-iodosyl- and 3-iodyl-benzoic acid derivatives have a second-order rate constant of 10<sup>-3</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and the 4-iodosyl- and 4-iodyl-benzoic acid derivatives both have rate constants in the order of 10<sup>-6</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. Thus, the 3-substituted isomers are three orders of magnitude poorer, and the 4-substituted isomers six orders of magnitude poorer as nucleophiles than the 2-substituted isomers. In fact, the hydrolysis rate observed in both the 3- and 4-substituted isomers is more reminiscent of hydrolysis due to that of a substituted benzoic acid (activity at the benzoic acid portion of the molecule) than that of the 2-substituted iodosyl/iodyl group. These kinetic data strongly suggest that the cyclic structure responsible for the activity of the 2-substituted isomers is extremely unlikely in the 3- and 4-substituted isomers and that the small measured rate constants are due to sodium benzoate activity.

One interesting aspect of the IR spectra (Table 1) is the very low carbonyl frequencies seen for 2-iodosylbenzoic acid (1 612 cm<sup>-1</sup>) and 2-iodylbenzoic acid (1 638 cm<sup>-1</sup>). It seems likely that these result from the  $\sigma$ -bond, no-bond resonance discussed in the previous paper.<sup>1</sup>

## Experimental

**Methods.**—Melting points were taken on a Thomas-Hoover melting point apparatus equipped with a microscope and are uncorrected. <sup>1</sup>H NMR spectra were recorded on either a Varian EM-360 (60 MHz), or a Varian VXR-300 (300 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard. <sup>13</sup>C NMR spectra were recorded on a Varian VXR-300 (75 MHz) NMR spectrometer using 5 mm tubes. Solute concentrations were 80–150 mg/cm<sup>3</sup> with either CDCl<sub>3</sub> or (CD<sub>3</sub>)<sub>2</sub>SO as internal lock and TMS as internal reference. IR spectra were recorded on a Perkin-Elmer 283B IR spectrophotometer. Commercially available reagent grade solvents and

reagents were used without further purification. Kinetic measurements were performed using the classic 'Mackay' microemulsion in 0.03 mol dm<sup>-3</sup> borate buffer, pH 9.2. as described.<sup>19,22,25</sup> Kinetic data were analyzed using a program developed by B. L. Knier.<sup>19,22</sup>

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