The Cyclic Structure of 2-Iodosyl- and 2-Iodyl-benzoic Acid Anions: a Basicity and X-Ray Crystallographic Study[1]

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The crystal structures of sodium 2-iodosyl-4-nitrobenzoate and sodium 2-iodyl-4-nitrobenzoate demonstrate a bicyclic structure for each. $\mathrm{p}K_a$ considerations indicate that the anions remain cyclized in solution. The crystal structure of 2-iodyl-5-methylbenzoic acid has also been obtained.

A variety of trivalent and pentavalent iodine compounds have received renewed attention over the past few years as useful synthetic intermediates for various organic transformations. Polyvalent iodine derivatives have been used for halogenation, arylation, α-hydroxylation, and various organic transformations.[2–5]

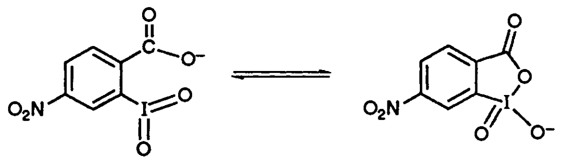
Derivatives of 2-iodosylbenzoic acid and 2-iodylbenzoic acid form an important subclass of these compounds.[6,7] In 1983 Moss and co-workers reported the ability of 2-iodosylbenzoic acid to act as an effective catalyst for the hydrolysis of *p*-nitrophenyl acetate and *p*-nitrophenyl diphenyl phosphonate.[8,9] This process is particularly efficient in pH 8.5 micellar cetyltrimethylammonium chloride.[8] The observed catalytic activity of 2-iodosylbenzoic acid was later extended to include various substituted 2-iodosylbenzoic acids by Moss[10,11] and substituted 2-iodylbenzoic acids by our own group.[12]

2-Iodosylbenzoic acid (**1**) and its derivatives have long been postulated[13] to exist in the cyclic tautomeric form of 1-hydroxy-1,2-benziodoxol-3-one (**2**). A similar structure, denoted 1-hydroxy-1-oxo-1,2-benziodoxol-3-one (**4**), can be drawn for derivatives of 2-iodylbenzoic acid (**3**). This postulate has been confirmed in the solid state by the X-ray crystallographic examination of 2-iodosylbenzoic acid[14,15] and 2-iodylbenzoic acid.[16] However, no such data for the corresponding anions, the active form of the catalysts, have been previously reported. Available data on the structures of iodosyl- and iodylbenzenes not containing carboxyl groups are summarized and discussed in Part III of this series.[17] As mentioned, 2-iodosyl-4-nitro- and 2-iodyl-4-nitrobenzoic acids are highly efficient nucleophilic catalysts for the decomposition of phosphorus esters in cetyltrimethylammonium chloride micellar media.[12] These catalytic hydrolysis reactions are usually carried out at pH 8.5 where the 2-iodosyl- and 2-iodylbenzoic acid derivatives exist as their sodium salts. We have therefore determined, and now report, the crystal structures of these salts [*cf.* (**5**), (**6**) and (**7**), (**8**)] to confirm the expected cyclic structure in the crystalline state and we present arguments to show that this structure persists in aqueous solution. Correlations between their structures and reactivity are discussed.

(**1**) (**2**)

(**3**) (**4**)

(**5**) (**6**)



(**7**) (**8**)

Results and Discussion

$\mathrm{p}K_a$ *Considerations.*—The $\mathrm{p}K_a$ values of 2-iodosylbenzoic acid and 2-iodylbenzoic acid are 7.0[18] and 7.6 ± 0.2,[7,10] respectively, and reflect their unusual structures. The $\mathrm{p}K_a$ of unsubstituted benzoic acid is 4.2. Using $\sigma = 0.88$ ($\sigma_I + \sigma_R = 0.82 + 0.06$)[19] for the iodosyl substituent, monocyclic 2-iodosylbenzoic acid should have a $\mathrm{p}K_a$ of 3.7. The $\mathrm{p}K_a$ of uncyclized 2-iodylbenzoic acid should be approximately the same as that for the *para* isomer, namely, 3.5.[19] This implies that if the tautomeric equilibria for 2-iodosylbenzoic acid and for 2-iodylbenzoic acid in solution favour the cyclic forms in the neutral molecules, then the cyclic forms are more strongly favoured in the corresponding anion equilibria by factors of 2 000 and 13 000, respectively.

X-*Ray Structure Studies.*—Our study represents the first crystal structure determinations of any salts of either a 2-iodosyl- or a 2-iodyl-benzoic acid, and conclusively demonstrates their cyclic character. Perhaps the best evidence for this

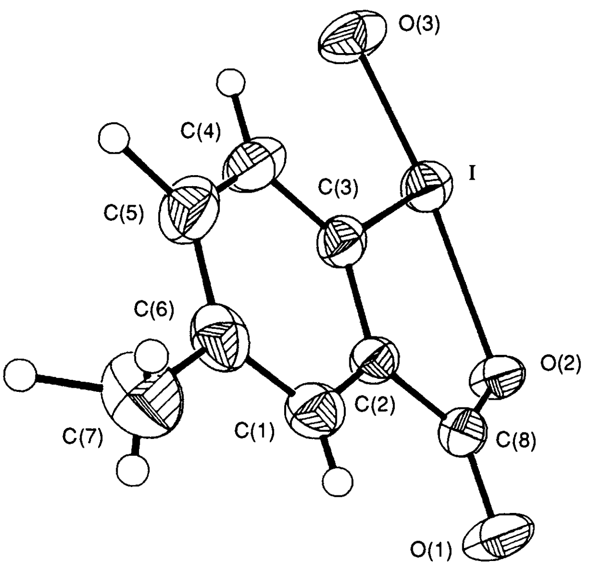


Figure 1. A view of 2-iodosyl-5-methylbenzoic acid showing the atomic numbering and thermal ellipsoids.

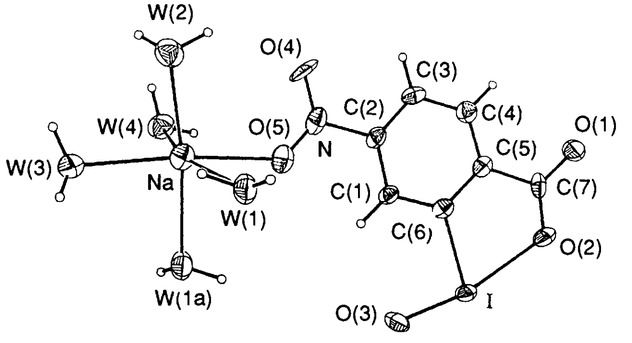


Figure 2. A view of sodium 2-iodosyl-4-nitrobenzoic acid tetrahydrate showing the atomic numbering and thermal ellipsoids. The W(1a) atom around the sodium ion is from a symmetry related molecule.

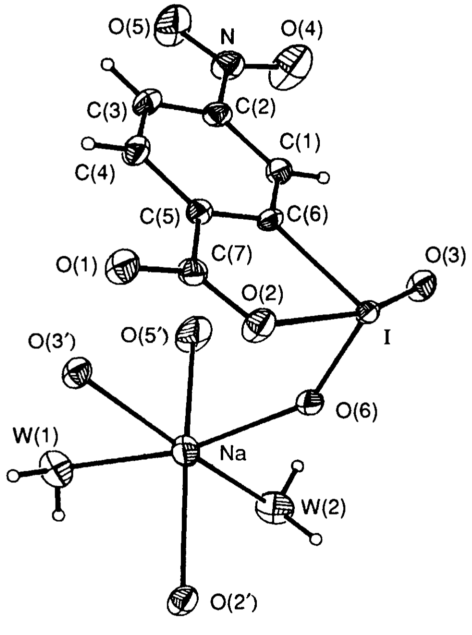


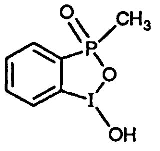
Figure 3. A view of sodium 2-iodyl-4-nitrobenzoic acid dihydrate showing the atomic numbering and thermal ellipsoids. The primed atoms around the sodium ion are from symmetry related molecules.

Table 1. Selected distances/Å and angles/° for 2-iodosyl-5-methylbenzoic acid hydrate ethanolate.

Bond distances/Å			
I–O(2)	2.347(5)	I–O(3)	1.939(6)
I–C(3)	2.085(7)	O(1)–C(8)	1.236(8)
O(2)–C(8)	1.282(8)	C(1)–C(2)	1.371(10)
C(1)–C(6)	1.384(11)	C(2)–C(3)	1.394(9)
C(2)–C(8)	1.483(10)	C(3)–C(4)	1.385(11)
C(4)–C(5)	1.394(11)	C(5)–C(6)	1.404(11)
C(6)–C(7)	1.483(13)		
Bond angles/°			
O(2)–I–O(3)	169.6(2)	O(2)–I–C(3)	74.8(2)
O(3)–I–C(3)	94.8(3)	I–O(2)–C(8)	114.2(4)
C(2)–C(1)–C(6)	122.5(7)	C(1)–C(2)–C(3)	118.7(7)
C(1)–C(2)–C(8)	122.5(6)	C(3)–C(2)–C(8)	118.7(6)
I–C(3)–C(2)	116.9(5)	I–C(3)–C(4)	121.8(5)
C(2)–C(3)–C(4)	121.3(6)	C(3)–C(4)–C(5)	118.4(4)
C(4)–C(5)–C(6)	121.4(8)	C(1)–C(6)–C(5)	117.6(6)
C(1)–C(6)–C(7)	122.7(8)	C(5)–C(6)–C(7)	119.7(7)

is the planar nature of the C–C–C–O–I ring, not only in the acid (Figure 1), but also in both of the anions (Figures 2 and 3). The results of our study show that removal of the proton from the oxygen on the iodine atom causes a decrease in the I–O bond length and an increase in the exocyclic I–O bond linked to the carboxy group. The individual structures are discussed below.

2-Iodosyl-5-methylbenzoic acid. The only presently available studies of a 2-iodosylbenzoic acid were done long ago[14,15] and are, unfortunately, of low accuracy. Therefore, we have determined the crystal structure of 2-iodosyl-5-methylbenzoic acid for comparison with our other results. A view of the molecule is shown in Figure 1, with the pertinent bond lengths given in Table 1. The I–O(3) bond length of 1.933(4) Å is shorter than that reported for the unsubstituted derivative (**2**) (2.005 Å)[15] and slightly shorter than the I–O distance in a closely related phosphole (**9**) (1.952 Å).[20] The I–O(2) distance of 2.346(4) Å is longer than in the unsubstituted derivative (2.298 Å)[15] or the phosphole (2.286 Å).[20] There is probably a correlation between the various I–O bond lengths in the I–oxygen compounds but the lack of precise data precludes further discussion.



(9)

The C(8)–O(1) and C(8)–O(2) distances are unequal with the *exo* C–O being shorter, in keeping with the formulation (**2**). A similar difference was observed in 2-iodylbenzoic acid.[16] However, the previous 2-iodosylbenzoic acid structure determination[15] had the *exo* C–O bond longer than the C–O bond in the iodoxol-3-one ring, which seems unreasonable. There is one long, non-bonded contact of 3.094 Å between I and O(3) of another molecule, a common feature in iodosyl and iodyl compounds (*vide infra*).

Sodium 2-iodosyl-4-nitrobenzoate tetrahydrate. A view of the molecule together with the sodium ion and the co-ordinated water molecules is given in Figure 2, with the pertinent bond lengths in Table 2. The I–O(3) bond of 1.890(8) Å is shorter than in the unsubstituted 2-iodosyl and 2-iodyl carboxylic acids[15,16] or the related phosphole.[20] This decrease is consistent with the loss of the proton from O(3). There is a corresponding increase in the I–O(2) distance. The I atom also forms one short intermolecular contact, 2.952 Å, to the O(2) of another molecule. The C(7)–O(1) bond of 1.251(13) Å is not significantly different from the C(7)–O(2) bond of 1.259(14), consistent with the changes in the I–O bond lengths. These data indicate that in the structure of the anion, canonical form (**7**) contributes somewhat in addition to canonical form (**8**).

An interesting feature of this salt is the interaction of the Na$^+$ ion with the nitro group. The co-ordination around the Na$^+$ ion is very close to octahedral with five water molecules and one oxygen atom from the nitro group. The interaction of the Na$^+$ ion with the nitro group may also be of importance in solution.

Table 2. Selected distances/Å and angles/° for the sodium 2-iodosyl-4-nitrobenzoic acid tetrahydrate

Bond distances/Å			
I–C(6)	2.077(11)	I–O(2)	2.447(8)
I–O(3)	1.890(8)	Na–O(5)	2.472(12)
Na–W(1)	2.529(13)	Na–W(2)	2.404(9)
Na–W(3)	2.442(11)	Na–W(4)	2.459(12)
Na–W(1A)	2.461(9)	C(1)–C(2)	1.386(15)
C(1)–C(6)	1.381(18)	C(2)–C(3)	1.378(15)
C(2)–N	1.502(18)	C(3)–C(4)	1.386(20)
C(4)–C(5)	1.365(17)	C(5)–C(6)	1.416(14)
C(5)–C(7)	1.511(19)	C(7)–O(1)	1.251(13)
C(7)–O(2)	1.259(14)	O(4)–N	1.221(14)
C(5)–N	1.208(13)		
Bond angles/°			
C(6)–I–O(2)	72.9(4)	C(6)–I–O(3)	94.5(4)
O(2)–I–O(3)	167.1(3)	C(2)–C(1)–C(6)	116.4(10)
C(1)–C(2)–C(3)	124.7(12)	C(1)–C(2)–N	116.9(9)
C(3)–C(2)–N	118.4(10)	C(2)–C(3)–C(4)	116.9(11)
C(3)–C(4)–C(5)	121.8(10)	C(4)–C(5)–C(6)	119.1(12)
C(4)–C(5)–C(7)	123.7(10)	C(6)–C(5)–C(7)	117.1(10)
I–C(6)–C(1)	118.9(7)	I–C(6)–C(5)	120.0(9)
C(1)–C(6)–C(5)	121.1(10)	C(5)–C(7)–O(1)	118.7(11)
C(5)–C(7)–O(2)	115.5(9)	O(1)–C(7)–O(2)	125.8(13)
I–O(2)–C(7)	114.1(8)	Na–O(5)–N	131.0(8)
C(2)–N–O(4)	118.2(10)	C(2)–N–O(5)	117.8(10)
O(4)–N–O(5)	124.0(13)		

Sodium 2-*iodyl*-4-*nitrobenzoate dihydrate*. Although the crystal structures of 4-chloroiodylbenzene,[21] iodylbenzene,[22] and 2-iodylbenzoic acid[16] have been determined, no data on salts of iodylbenzoic acid or its derivatives have been reported.

Table 3. Selected distances/Å and angles/° for the sodium 2-iodyl-4-nitrobenzoic acid dihydrate.

Bond distances/Å			
I–O(2)	2.481(3)	I–O(3)	1.798(2)
I–O(6)	1.810(3)	I–C(6)	2.116(3)
Na–O(6)	2.325(3)	Na–W(1)	2.382(3)
Na–W(2)	2.452(3)	Na–O(2A)	2.466(3)
Na–O(3A)	2.495(3)	Na–O(5A)	2.606(3)
O(1)–C(7)	1.239(4)	O(2)–C(7)	1.257(3)
O(4)–N	1.209(5)	O(5)–N	1.214(4)
N–C(2)	1.473(4)	C(1)–C(2)	1.382(4)
C(1)–C(6)	1.378(4)	C(2)–C(3)	1.377(5)
C(3)–C(4)	1.386(5)	C(4)–C(5)	1.384(4)
C(5)–C(6)	1.388(5)	C(5)–C(7)	1.514(4)
Bond angles/°			
O(2)–I–O(3)	166.4(1)	O(2)–I–O(6)	81.7(1)
O(3)–I–O(6)	99.8(1)	O(2)–I–C(6)	72.3(1)
O(3)–I–C(6)	94.1(1)	O(6)–I–C(6)	99.0(1)
I–O(2)–C(7)	113.9(2)	O(4)–N–O(5)	123.6(3)
O(4)–N–C(2)	117.8(3)	O(5)–N–C(2)	118.5(3)
C(2)–C(1)–C(6)	116.6(3)	N–C(2)–C(1)	117.8(3)
N–C(2)–C(3)	119.2(2)	C(1)–C(2)–C(3)	123.1(3)
C(2)–C(3)–C(4)	118.8(3)	C(3)–C(4)–C(5)	120.1(3)
C(4)–C(5)–C(6)	118.9(3)	C(4)–C(5)–C(7)	122.0(3)
C(6)–C(5)–C(7)	119.1(2)	I–C(6)–C(1)	118.1(2)
I–C(6)–C(5)	119.3(2)	C(1)–C(6)–C(5)	122.6(2)
O(1)–C(7)–O(2)	125.6(3)	O(1)–C(7)–C(5)	119.1(2)
O(2)–C(7)–C(5)	115.3(3)		

Table 4. Summary of crystal data and experimental details.

Formula	$C_7H_{11}NO_9NaI$	$C_7H_7NO_8NaI$	$C_{10}H_{15}O_5I$
M	403.06	383.02	342.13
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	6.582(2)	5.771 7(9)	11.380(5)
b/Å	8.818(3)	9.637(2)	3.996 6(8)
c/Å	12.817(6)	10.862(2)	23.470(13)
α/°	72.99(3)	108.72(2)	
β/°	89.40(3)	103.34(4)	95.92(3)
γ/°	69.32(3)	91.01(2)	
$V/Å^3$	660.5(4)	554.1(2)	1 061.8(8)
Z	2	2	4
D_c/ g cm^{-3}	2.026	2.296	2.140
Crystal size/mm	0.16 × 0.08 × 0.20	0.03 × 0.08 × 0.18	0.05 × 0.09 × 0.19
Radiation		Mo-K_α graphite filtered	
μ/cm^{-1}	24.3	29.3	29.8
2θ Range/°	3–45	3–50	3–50
Scan speed/° min^{-1}	4.88–29.30	2.0–29.3	1.0–29.3
Orientation matrix			
No. of observed reflections	16	25	25
Range (2θ/°)	6.8–20.7	7–26	4–23
No. of reflections measured	1 750	2 225	2 338
No. of unique reflections	1 714	2 179	1 889
No. of reflections with $F > 3\sigma F$	1 592	1 931	1 777
R	0.056	0.018	0.038
R_w	0.057	0.018	0.036
No. of parameters	173	175	171
GOF	1.8	0.82	3.1
Max shift/esd	0.006	0.010	0.13
Max/min in difference	3.2/1.2	0.57/0.79	1.5/0.95
g	0.001 03	—	0.000 07

Table 5. Final positional parameters for 2-iodosyl-5-methylbenzoic acid hydrate ethanolate.

Atom	*x*	*y*	*z*
I	1 314(1)	6 927(1)	5 518(1)
O(1)	4 711(4)	11 311(16)	6 059(2)
O(2)	3 244(4)	8 960(13)	5 500(2)
O(3)	−229(5)	5 362(15)	5 681(3)
O(4)	3 885(4)	8 412(15)	4 575(2)
W(1)	−1 933(8)	434(28)	5 785(5)
W(2)	−1 294(9)	313(31)	6 072(5)
C(1)	3 413(6)	10 356(19)	7 025(3)
C(2)	3 004(5)	9 538(17)	6 472(3)
C(3)	1 888(6)	8 094(18)	6 367(3)
C(4)	1 180(6)	7 580(21)	6 805(4)
C(5)	1 624(7)	8 442(23)	7 361(4)
C(6)	2 743(7)	9 910(20)	7 479(3)
C(7)	3 176(12)	10 832(32)	8 076(5)
C(8)	3 728(6)	9 972(18)	5 987(3)
C(9)	3 426(8)	12 299(26)	4 447(4)
C(10)	4 437(9)	14 072(24)	4 766(5)

Table 6. Final positional parameters for the sodium 2-iodosyl-4-nitrobenzoic acid tetrahydrate.

Atom	*x*	*y*	*z*
I	835(1)	3 893(1)	3 714(1)
Na	4 659(8)	−2 125(6)	311(4)
C(1)	2 343(17)	433(14)	3 408(9)
C(2)	3 154(18)	−1 333(14)	3 782(9)
C(3)	3 538(19)	−2 301(15)	4 871(9)
C(4)	3 078(18)	−1 426(15)	5 637(10)
C(5)	2 344(17)	310(14)	5 332(9)
C(6)	1 961(17)	1 248(14)	4 202(9)
C(7)	1 855(18)	1 318(16)	6 136(9)
O(1)	2 292(14)	528(10)	7 140(7)
O(2)	1 027(14)	2 912(10)	5 717(7)
O(3)	1 051(13)	4 129(10)	2 207(6)
O(4)	4 389(19)	−3 793(11)	3 237(8)
O(5)	3 363(17)	−1 375(12)	1 977(8)
N	3 667(17)	−2 237(14)	2 929(9)
W(1)	7 392(14)	−888(11)	707(7)
W(2)	7 231(13)	−5 006(11)	1 008(7)
W(3)	4 914(14)	−2 600(11)	−1 477(7)
W(4)	1 624(14)	−3 176(11)	522(7)

Table 7. Final positional parameters for the sodium 2-iodyl-4-nitrobenzoic acid dihydrate.

Atom	*x*	*y*	*z*
I	4 182(1)	−371(1)	−1 763(1)
Na	−354(3)	−2 315(2)	−450(1)
O(1)	−3 009(4)	−941(3)	−3 152(2)
O(2)	630(4)	1 040(3)	−1 867(2)
O(3)	6 320(4)	−1 698(3)	−2 050(2)
O(4)	3 273(6)	−5 027(4)	−6 393(3)
O(5)	−348(6)	−5 490(3)	−7 567(3)
O(6)	2 851(4)	−972(3)	−641(2)
N	1 207(6)	−4 759(3)	−6 599(3)
C(1)	2 267(6)	−2 742(3)	−4 454(3)
C(2)	575(6)	−3 443(3)	−5 641(3)
C(3)	−1 628(6)	−2 946(4)	−5 974(3)
C(4)	−2 177(6)	−1 677(4)	−5 089(3)
C(5)	−533(6)	−937(3)	−3 890(3)
C(6)	1 654(6)	−1 490(3)	−3 594(3)
C(7)	−1 040(6)	463(4)	−2 900(3)
W(1)	−3 894(5)	−3 826(3)	−760(3)
W(2)	2 755(5)	−3 364(3)	839(3)

The molecule shown in Figure 3 represents the first crystal structure of an iodylbenzoate salt. The pertinent bond distances are given in Table 3. The removal of the proton from O(3) causes the I–O(3) distance to decrease with a corresponding increase in the I–O(2) distance and the C(7)–O distances become more equal relative to the free acid.[16] (*vide supra*). The changes in the I–O and C–O distances observed in the two salts are easily rationalized in terms of maintaining an approximately equal electron density around the I atom in the salts and free acids. In addition, the I–O(6) bond which is approximately normal to the COO–I–benzene plane, is longer than the I–O(3) bond which is the reverse of the situation in the free acid.[16]

In the iodyl derivatives there are intermolecular contacts between the I and oxygen atoms in other molecules that are significantly shorter than van der Waals contacts of 3.4 Å. These are 2.715, 2.955, and 2.857 Å in 4-chloroiodylbenzene,[21] 2.733, 2.578, 2.659 Å in iodylbenzene,[22] and 2.761, 2.705 Å to I(1) and 2.664 and 2.936 Å to I(2) in 2-iodylbenzoic acid.[16] These short contacts have been considered as 'secondary' bonds.[22] A somewhat similar situation exists in the 2-iodyl-4-nitrobenzoic acid salt with two short I–O intermolecular contacts of 2.667 and 2.965 Å which are identical to those observed to I(2) in the free acid. The net result is an approximately octahedral arrangement of bonds around the I atom.[23] A more extensive investigation of these 'secondary' bonds is in progress.

The Na^+ ion is approximately octahedrally co-ordinated by six oxygen atoms. Two of the oxygens are from water molecules, two come from the IO_2 group, one from the carboxylic acid group, and one from the nitro group in another molecule. The interaction with the nitro group is similar to that observed in the iodosyl salt discussed above.

Conclusions

We conclude that 2-iodosyl- and 2-iodyl-benzoic acids, and their corresponding anions, exist predominantly in cyclic structures in both in the solid state and in solution. However, the C–O bond lengths in the carboxy groups of the salts are approximately equal, with the exocyclic C–O bonds being slightly shorter. Hence, structures such as (**6**) and (**8**), where a formal single bond between iodine and one of the carboxy oxygen atoms is drawn, are an oversimplification. Contribution of both canonical structures [(**5**) with (**6**), and (**7**) with (**8**)] is involved in the 2-iodosyl- and 2-iodyl-benzoic acid anions. However, the equilibria between (**1**) and (**2**), and (**3**) and (**4**) lie almost exclusively on the side of tautomers (**2**) and (**4**).

Experimental

Compound Preparation.—2-Iodosyl-5-methylbenzoic acid (m.p. 215–216 °C), 2-iodosyl-4-nitrobenzoic acid (m.p. 204–205 °C), and 2-iodoyl-4-nitro-benzoic acid (m.p. 202–204 °C) were prepared according to standard literature procedures.[24] The single crystals of sodium 2-iodosyl-4-nitrobenzoate were obtained by dissolving 2-iodosyl-4-nitrobenzoic acid in an aqueous solution of one molar equivalent of sodium hydroxide and allowing slow evaporation of the water. The single crystals of sodium 2-iodyl-4-nitrobenzoate were prepared by dissolving 2-iodyl-4-nitrobenzoic acid in aqueous sodium hypochlorite and allowing slow evaporation of the water. 2-Iodosyl-5-methylbenzoic acid was crystallized from water.

X-*Ray Studies.*—The crystal data, experimental conditions and refinement are summarized in Table 4. For all three compounds, crystals were mounted on glass fibres and then on a Nicole P3 diffractometer. Graphite monochromatized molybdenum radiation was used in all three cases. The structures were solved using the heavy atom technique with the location of the I atom determined from the Patterson Function. Observed and difference Fourier syntheses were used to locate the light atoms. Refinement was by blocked-cascade least-squares techniques using isotropic and then anisotropic thermal parameters. The programs used in the data processing, structure solution and refinements were from the DESKTOP SHELXTL system.[25] The scattering factors used were from the usual source[26] and are included in the system. Corrections for anomalous dispersion were included in the calculations. The final positional parameters for 2-iodosyl-5-methylbenzoic acid, sodium 2-iodosyl-4-nitrobenzoate, and sodium 2-iodyl-4-nitrobenzoate are given in Tables 5, 6, and 7, respectively.*

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* Lists of bond lengths, bond angles, hydrogen-atom co-ordinates, and thermal parameters have been deposited at the Cambridge Crystallographic Data centre (see section 5.6.3 in 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1990, Issue 1).

References

1 Studies in the Chemistry of Polyvalent Organoiodine Compounds. Part V. For Part IV see, A. R. Katritzky, B. L. Duell, J. K. Gallos, and H. D. Durst, *Magn. Reson. Chem.*, 1989, **27**, 1007. At the suggestion of the editor the nomenclature has been changed in this part to conform to IUPAC rules. The iodoso group is now named iodosyl and the iodoxy group is iodyl.

2 D. F. Banks, *Chem. Rev.*, 1966, **66**, 243.

3 (*a*) A. Varvoglis, *Chem. Soc. Rev.*, 1981, **10**, 377; (*b*) *Synthesis*, 1984, 709.

4 R. M. Moriarty and K. Hou, *Tetrahedron Lett.*, 1984, **25**, 691.

5 G. F. Koser, 'Hypervalent Halogen Compounds,' in 'The Chemistry of Functional Groups, Supplement. D,' eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1983.

6 H. Siebert and M. Handrich, *Z. Anorg. Allg. Chem.*, 1976, **426**, 173.

7 G. P. Baker, G. Mann, N. Sheppard, and A. J. Tetlow, *J. Chem. Soc.*, 1965, 3721.

8 R. A. Moss, K. W. Alwis, and G. O. Bizzigotti, *J. Am. Chem. Soc.*, 1983, **105**, 681.

9 R. A. Moss, K. W. Alwis, and J. Shin, *J. Am. Chem. Soc.*, 1984, **106**, 2651.

10 R. A. Moss, K. W. Kim, and S. Swarup, *J. Am. Chem. Soc.*, 1986, **108**, 788.

11 R. A. Moss, S. Chatterjee, and B. Wilk, *J. Org. Chem.*, 1986, **51**, 4303.

12 A. R. Katritzky, B. L. Duell, H. D. Durst, and B. Knier, *Tetrahedron Lett.*, 1987, **28**, 3899.

13 V. Meyer and W. Wachter, *Chem. Ber.*, 1892, **25**, 2632.

14 E. Shefter and W. Wolf, *Nature (London)*, 1964, **203**, 512.

15 E. Shefter and W. Wolf, *J. Pharm. Sci.*, 1965, **54**, 104.

16 J. Z. Gougoutas, *Cryst. Struct. Commun.*, 1981, **10**, 489.

17 A. R. Katritzky, J. K. Gallos, and H. D. Durst, *Mag. Reson. Chem.*, 1989, **27**, 815.

18 B. L. Duell, Ph.D. Thesis, 1977, University of Florida.

19 V. V. Lyalin, G. P. Syrona, V. V. Orda, L. A. Alekseeva, and L. M. Yagulpol'skii, *Zh. Org. Khim.* (*Engl. Transl.*), 1970, **6**, 1433.

20 T. M. Balthozor, J. A. Miles, and B. R. Stults, *J. Org. Chem.*, 1978, **43**, 4538.

21 A. A. Bothner-By and A. I. Medalia, *J. Am. Chem. Soc.*, 1952, **74**, 4402.

22 E. M. Archer, *Acta Crystallogr.*, 1948, **1**, 64.

23 N. W. Alcock and J. F. Sawyer, *J. Chem. Soc., Dalton Trans.*, 1980, 115.

24 A. R. Katritzky, G. P. Savage, J. K. Gallos, and H. D. Durst, Org. Prep. Proc. Int. 1989, 21(2), 157.

25 G. M. Sheldrick, DESKTOP SHELXTL, Nicolet XRD Corporation, Wisconsin, USA, 1986.

26 International Tables for X-Ray Crystallography, Vol. IV, The Kynoch Press, Birmingham, England, 1974.

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