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Solution structure of bis(acetoxy)iodoarenes as observed by ^{17}O NMR spectroscopy

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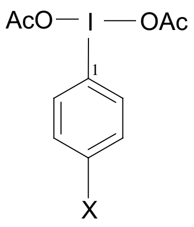
Abstract—A group of *para*-substituted bis(acetoxy)iodoarenes has been studied by ^{17}O and ^{13}C NMR. Only one signal for all the oxygens of the acetoxy groups has been observed. Both ^{17}O and ^{13}C chemical shifts of this group show a strong invariance with *para* substitution. The absence of covalent I–O bonds and an ion pair structure is proposed for the title compounds.

Organic polyvalent iodine compounds have experienced unprecedented development during the last decade due to their very useful oxidizing properties.[1a,b,c] Moreover, their biological properties have been recognized,[1c] particularly for diaryliodonium salts; for example, the oxygen donor ability of several iodosylbenzene derivatives in biological systems has been investigated.[2] On the other hand, notwithstanding the obvious importance of ^{17}O NMR spectroscopy for studying oxygen bonds,[3] there is, to the best of our knowledge, only one paper,[4] where some exploratory results on organic polyvalent iodine derivatives, including **1a**, have been reported. Agreement between their ($\delta = 302$ ppm) and our chemical shift ($\delta = 301$ ppm) values for **1a** is quite good. However, some features of these ^{17}O NMR spectra are unexpected, and the authors[4] themselves declare that they cannot offer a good explanation of these results. We have thus started a systematic study of organic polyvalent iodine derivatives in the hope that more data could be of some help to an understanding of these puzzling observations and preliminary results on some bis(acetoxy)iodoarenes **1** are presented.[†]

For I(III) derivatives a 'T-shaped' structure (Fig. 1) is commonly assumed,[1b] albeit in the solid state[5] the presence of weak inter- and intramolecular coordination bonds of remarkably constant orientation around the iodine atom is recognized. The lengths of these *interactions* are less than the sum of the van der Waals radii for the atoms concerned. The reported[6] solution (DMSO-d_6) ^{13}C NMR shift ($\delta = 175.25$ ppm) of the carboxylic carbons of **1a** is, however, within the usual range of such carbons. Our measurements (Table 1) on **1a**–**h** ($CDCl_3$ solution) are in quite good agreement with this report and show no appreciable variation, for the carbons of the acetoxy groups, with *para* substitution ($\delta_{C=O} = 176.45 \pm 0.16$ ppm, $\delta_{Me} = 20.32 \pm 0.05$ ppm). A quite satisfactory agreement is also found for the ring carbons of derivatives **1a**–**d** with data reported by Katritzky et al.[7] Unfortunately, the acetoxy group shifts were not given. Previous IR studies,[8] both in the solid state and in solution, in seeming agreement with an 'ester' structure, showed the presence of different absorptions for the two oxygens of the ester group, albeit the measured values for the 'carbonyl' stretching were displaced to values



a X= H
b X= Me
c X=OMe
d X=Cl
e $X=NO_2$
f $X=CO_2Me$
g X=F
h X=CN

Figure 1. Bis(acetoxy)iodoarenes **1**.

Keywords: ^{17}O NMR; ^{13}C NMR; Polyvalent iodine; Solution structure.

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[†] ^{17}O NMR spectra were recorded at 40.662 MHz and natural isotopic abundance on a Varian VXR-300 spectrometer, using saturated $CDCl_3$ solutions at 298 K. Signals were referenced to tap water, by the substitution method. Oxygenated X groups shifts are in their 'usual' range while their half-height line widths are comparable with those of the acetoxy groups.

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Table 1. ^{17}O and ^{13}C NMR data[a] ($CDCl_3$ solution) of compounds **1**

Compounds **1**	δ (ppm)	$\nu_{1/2}$ (Hz)	$\delta_{C=O}$ (ppm)	δ_{Me} (ppm)	δ_{C1} (ppm)
1a	301	1050	176.34	20.31	121.58
1b	298	950	176.29	20.37	118.36
1c[b]	298	1300	176.31	20.36	111.64
1d	298	950	176.40	20.30	118.81
1e[c]	300	1000	176.61	20.27	126.72
1f[d]	296	1100	176.52	20.31	125.65
1g	298	1150	176.40	20.28	115.72
1h	300	1400	176.59	20.28	125.21

[a] ^{17}O δ, ppm from tap water; ^{13}C δ, ppm from $CDCl_3$ central line (77.0 ppm).

[b] $\delta_{OMe}(^{17}O) = 55$ ppm.

[c] $\delta_{NO_2}(^{17}O) = 568$ ppm.

[d] $\delta_{C=O}(^{17}O) = 345$ ppm, $\delta_{OMe}(^{17}O) = 133$ ppm.

ca. 100 cm^{-1} less than those expected for the corresponding carbon compounds. As a tentative rationalization of this observation, the authors proposed a chelation of the ester carbonyl group, in analogy with certain acyloxy derivatives of B(III) either a partial zwitterionic structure with weakening of the carbonyl bond and strengthening of the carbon–oxygen single bond. ^{17}O NMR spectra (1) yielded only a single resonance for the two oxygens of the ester groups, a result not consistent with the usual ester structure.

Hydrolysis of compounds **1** to iodoarenes and acetic acid, partly observed in one experiment with **1g**, yields a single signal in the ^{17}O NMR spectrum, but sharper ($\nu_{1/2} = 220$ Hz) and at a rather different chemical shift ($\delta = 257.3$ ppm). The large values of $\nu_{1/2}$, observed throughout the series, rule out the presence of free carboxylate anions. This observation is also in agreement with results[9] based on conductivity and freezing point measurements. Moreover, a remarkable invariance of the ^{17}O chemical shifts with *para* substitution is apparent, only partly expected for single I–O bonds and from the above reported invariance of the ^{13}C acetoxy shifts. In fact, even in the absence of conjugation, the sensitivity of ^{17}O NMR should have allowed, at least for the I–O bonds, the observation of a chemical shift variation in a series of *p*-substituted derivatives. A $\Delta\delta$ value of up to 14 ppm has in fact been measured[10], for example, for *p*-substituted benzyl alcohols. Indeed, *ipso* carbons (C_1) show a clear variation with *p*-X substituents (Table 1) and their ^{13}C NMR shifts lie well outside the usual and very characteristic range of C_{Ar}–I carbons, an observation already reported in Ref. 7. It is reasonable to think that some effect, not simply a change of hybridization, and common to all derivatives **1**, counteracts the 'heavy atom effect' operating on iodine derivatives.

The absence of ^{17}O chemical shift variation is even more surprising if compared with ring substituent effects observed on the rates of oxygen atom transfer from iodosobenzenes to metal carbonyls[11] and cytochrome P-450-catalyzed hydroxylation reactions using iodosobenzene derivatives.[2]

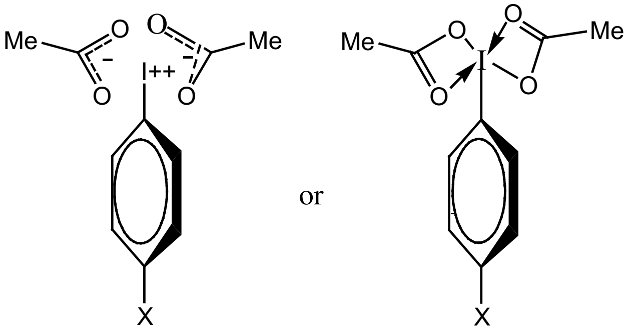

Figure 2. Ion pair (left) and 'dative' (right) structures of **1**.

The observation of a single resonance, coupled with the above discussed shift invariance, is suggestive that derivatives **1** are present in $CDCl_3$ solution as ion pairs (Fig. 2, left). The absence of a covalent bond between iodine and oxygen accounts for the observed invariance of chemical shifts both in ^{13}C as well as in ^{17}O NMR. It is also well known that, in ^{17}O NMR, carboxylic acids[3] and a fortiori their anions[12] give only one signal, as observed for derivatives **1**. We noted above that a free acetate anion could be ruled out because its chemical shift and half-height line widths values were not consistent with our results. In an ion pair there is a strong association between cation and anion and the negative charge localized on the oxygen atoms of the carboxylate is partly relieved, justifying the downfield shift. The same strong association causes a virtual increase of the molecular size and thus large values of half-height line widths are observed. The ion pair assumption is also in agreement with the conductivity results[9] since *free* ions are not present and the two different IR absorptions[8] can be assigned to symmetric and asymmetric stretching vibrations of the carboxylate group.[13] The double cationic character of the iodine atom could very likely be the 'counteracting effect' masking that of the heavy atom. The failed observation[2] of the molecular ion in all the mass spectra of several bis(acetoxy)iodoarenes could be a further indication that they are better described as ion pairs.

The reported[2,11] effects of ring substitution on the reactivity of a variety of polyvalent iodine derivatives, including some bis(acetoxy)iodoarenes, deserve particular attention. It is important to note that, although investigating quite different reaction systems, both groups observed that the greatest effects were caused by *ortho* substitution, particularly when the *ortho* substituent contained oxygen atoms, for example, NO_2

groups. This observation is in agreement, in a very general way, with the special chemical behaviour recognized for, for example, *o*-iodosylbenzoic acid or 2-*t*-Bu-$SO_2C_6H_4IO$, both currently under investigation in our lab. In their paper,[11] Basolo and co-workers show that the reactive species is the *monomeric* substituted iodosobenzene, which is produced by a fast equilibrium between R–$C_6H_4I(OMe)_2$, and R–C_6H_4IO and then rapidly reacts with their substrates. We are actively studying the dialkoxy derivatives but our present results are still not sufficient to indicate whether there is or not a close similarity to derivatives **1**. With stronger reason, we do not extend this similarity to monomeric iodosobenzenes.

Although we think that some of the points discussed above are better understood admitting the proposed ion pair structure, a structure with dative bonds from the carbonyl oxygen lone pairs to the iodine atom (Fig. 2, right), where the iodine atom is bonded via four covalent bonds to the four oxygen atoms of the two carboxylic groups, cannot be ruled out.

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