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Congested C_2 -symmetric aryliodanes based on an *anti*-dimethanoanthracene backbone[†]

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A family of congested aryliodanes based on an *anti*-dimethanoanthracene backbone has been synthesised and two diaryliodonium salts and the iodyl derivative characterised by X-ray analysis. The latter shows a rare water coordination to the iodine(v) centre in the solid state. Applications of these reagents in functional group transfer reactions are reported.

Aryliodanes with their unique and varied reactivity profile have become established reagents for synthesis.¹ Many transformations with these reagents generate chiral products from prochiral substrates. This fact led to the development and application of chiral non-racemic iodanes, either in isolated forms or generated *in situ* from catalytic amounts of chiral iodoarene precursors, which has intensified in recent years.² Examples of chiral aryliodanes which exert significant levels of stereocontrol in their respective applications include the flexible chiral Koser reagent analogue **1**,³ the axially chiral diaryliodoium salt **2**,⁴ and the rigid *C*₂-symmetric μ -oxo-bridged bis-iodane **3**.⁵



Monoiodanes with *backbone* C_2 -*symmetry* are rare, and until recently only the Koser analogue **4** was known.^{3b} However, the recent development of a group of flexible C_2 -symmetric aryliodanes **5**, and the high levels of aysumetric induction they

bring about in several processes showcases the potential of chiral non-racemic aryliodanes in asymmetric synthesis and catalysis. $^{\rm 6}$

Sterically encumbered iodanes are also rare, and only a small number have been described in the literature.⁷ In addition, few systematic studies of the crowding effect on the reactivity of iodanes have been reported to date.⁸ Encouraged by the absence of investigations addressing the aforementioned facts, we embarked on the synthesis of a family of modular, congested aryl- λ^3 - and λ^5 -iodanes based on the C_{2h} -symmetric *anti*-dimethanoanthracene backbone **6** (Scheme 1). This rigid, all carbon framework has a defined chiral space, and is robust towards oxidising and reducing agents. Moreover, we have recently developed a high-yielding synthetic route to this skeleton which allows the synthesis of functionalised and sterically engineered analogues.⁹

Iodoarene 7 was obtained by the iodination of **6** using (diacetoxy)iodobenzene (DIB) and iodine in 74% yield. Initial attempts to oxidise 7 to the (diacetoxy)iodane **8** proved unsuccessful under several reaction conditions. Thus, the oxidation with NaIO₄,¹⁰ CH₃CO₃H,¹¹ K₂S₂O₈¹² and Selectfluor^M in the presence of an acetate source failed.¹³ A procedure utilising sodium perborate in acetic acid proved more promising,¹⁴ however, initial results were inconsistent and reproducibility proved to be difficult. Monitoring this reaction by ¹H NMR spectroscopy, we observed that 7 was initially oxidised to **8** with complete conversion reached after 4 h; however, prolonged reaction times resulted in the reverse reaction and only iodoarene 7 could be detected. We were pleased to isolate **8** in 76% yield after a reaction time of 4 h. These findings confirm previous observations by other researchers that the isolation of congested and electron rich aryliodanes was either difficult or not possible.^{3a,15}

The synthesis of the iodosyl derivative was attempted using standard basic conditions,¹⁶ however, in each case only the starting iodoarene 7 was observed. It is possible that since iodosylbenzene is polymeric in nature,¹⁷ the *anti*-dimethano-anthracene analogue might be too bulky to adopt a zig–zag polymeric structure. This is consistent with observations made by Power in the attempted synthesis of the sterically encumbered TripIO (Trip = 2,4,6-*i*-Pr₃C₆H₂).^{7b}

The synthesis of the iodyl derivative **10** proved more successful. After screening several oxidation conditions, **10** was obtained in a high yield and purity by oxidation with DMDO.¹⁸ This material proved to be insoluble in most organic solvents, except for DMSO,

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Scheme 1 (a) DIB, I₂, EtOAc, rt, 12 h; (b) NaBO₃, AcOH, 60 °C, 4 h; (c) PTSA, CHCl₃, rt, 0.5 h; (d) DMDO, CHCl₃, 0 °C-rt, 12 h; (e) *m*CPBA, BF₃·OEt₂, PhB(OH)₂, CH₂Cl₂, 80 °C to -78 °C, 1 h; (f) PhI(OH)OTs, DCM/TFE (1:1), rt, 4 h; (g) LiX (X = Cl, Br, I, OTf) or AgX (X = BF₄, PF₆), CHCl₃, rt, 0.5 h.

MeOH and DMF. It is a stable solid and unlike most all-carbon iodylarenes reported to date, has a clear melting point as opposed to decomposing violently upon heating (*vide infra*).

The Koser reagent analogue 9 from the reaction of 8 with PTSA in chloroform proved to be unstable and could not be isolated, however, all analytical data were consistent with its *in situ* formation in solution (see ESI† and Scheme 2a).

For the synthesis of diaryliodonium salts in this series, we first attempted the phenylboronic acid/mCPBA procedure developed by Olofsson and were able to isolate the diaryliodonium BF_4 salt **12e** in moderate yield.¹⁹ Fortunately, the preparation of the diaryliodonium tosylate **11** by reacting Koser's reagent with **6** proved high yielding.²⁰

The ease in which **11** was obtained encouraged us to explore an alternative route to other counter ions by anion metathesis.²¹ Thus, by stirring a solution of **11** with lithium triflate in chloroform we were delighted to find that complete anion exchange occurred within 30 min. The precipitated lithium tosylate could be easily removed by filtration to yield the diaryliodonium triflate **12d**, which required no further purification. By varying the metal salt we were able to prepare the diaryliodonium halide salts **12a–c**, the BF₄ salt **12e** and the PF₆ salt **12f** in quantitative yields and in high purity.

Samples of **10** were crystallised from methanol and yielded thin transparent plates which were suitable for X-ray analysis. The X-ray of **10** shows, to the best of our knowledge, the first water coordination to an aryl- λ^5 -iodane (Fig. 1a). This I...OH₂



Scheme 2 (a) 8, PTSA, 3 min, benzoylacetone, MeCN, rt, 3 min, 60%; (b) 8, benzyl 2-methyl-3-oxobutanoate, Et_4NCl , $MeCN/H_2O$ (9:1), rt, 50 min, 80%; (c) 8, benzyl 2-methyl-3-oxobutanoate, Bu_4NN_3 , MeCN/H₂O (9:1), rt, 1 h, 62%; (d) *trans*-stilbene, 8, Phth-NH₂, CH₂Cl₂, rt, 4 h, 95%.



Fig. 1 (a) Crystal structure of **10** drawn with 50% thermal ellipsoids showing water coordination to the iodine(v) centre. (b) A plot of the sheet-like structure of **10** held together by hydrogen bonding and weak intermolecular $I \cdots O$ interactions, drawn with 50% thermal ellipsoids.

interaction is 2.612(5) Å in length and connects the parallel $IO_2 \cdots IO_2$ chains to sheets *via* hydrogen bonding (Fig. 1b). The sheet-like structure is reflected by the morphology of the crystals. The organic residues of the $IO_2 \cdots IO_2$ chains point alternatingly above and below the slightly waved sheet containing the hydrophilic interactions (Fig. 2), with the stacked sheets held together by weak hydrophobic interactions between *anti*-dimethanoanthracene units. It seems plausible that the bulk of these units prevents the formation of a two-dimensional polymer having only $IO_2 \cdots IO_2$ interactions,¹⁷ making it necessary for water to act as a bridging ligand.

Crystals of **11** and **12f**, suitable for X-ray analysis, were obtained from chloroform and revealed that both structures are dimeric in nature due to anion bridging (Fig. 3).²²



Fig. 2 Side-on view of the waved sheet-like structure of 10.



Fig. 3 Thermal ellipsoid plot (50%) of the dimeric structure of (a) 11 and (b) **12f** showing $I \cdots O$ and $I \cdots F$ interactions, respectively.



Scheme 3 Phenylation of diethyl methylmalonate by salts 11 or 12d.



Scheme 4 Oxygenative DA dimerisation mediated by 10.

We have tested our congested iodanes in a series of bench mark reactions and were delighted to find that they largely displayed expected reactivities. First we treated 9, generated in situ from 8 and PTSA, with benzoylacetone and obtained the α -tosylated product in 60% yield (Scheme 2). We then showed that 8 readily participated in DIB mediated halide²³ and azide²⁴ transfer reactions developed within our laboratory, as well as nitrene transfer to trans-stilbene (Scheme 2).²⁵

Interestingly, under otherwise identical reaction conditions, the α -chlorination required 50 min as compared to 3 min with DIB. The decrease in rate by more than one order of magnitude may reflect the increased bulk around the iodine centre; a fact that could prove helpful in future attempts to elucidate the mechanism of such transformations.

Diaryliodonium salts 11 and 12d readily phenylated the sodium enolate derived from diethyl methylmalonate under standard aryl transfer conditions in high yields (Scheme 3).²⁶ Importantly, selective phenyl transfer was observed in an apparent overruling of the 'ortho-effect', and consistent with observations made with diaryliodonium salt 2.4,27 We believe that our reagents represent the most sterically encumbered diaryliodonium salts to mediate aryl transfer reported to date.

Iodane 10 was examined in the oxygenative Diels-Alder (DA) dimerisation of 2,6-dimethylphenol and we were delighted to find that the anti-dimethnaoanthracene derived iodane also mediated this reaction in 54% yield (Scheme 4).¹⁸

Furthermore, we note that in all of the above reactions, the reduced iodoarene 7 could be recovered in high yields.

In conclusion, we have described the synthesis of a series of congested all-carbon aryliodanes based on the C2h-symmetric anti-dimethanoanthracene 6. The diaryliodonium salts of the series were obtained by a novel high-yielding anion metathesis route from tosylate 11. It was shown that despite

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