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CYCLIC TETRAMERS FROM 3,5-DISUBSTITUTED 4-HYDROXYBENZENESULFONYL CHLORIDES THEIR SYNTHESIS AND CHARACTERIZATION

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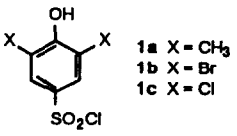
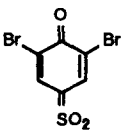
Abstract The reaction of 3,5-dimethyl- (**1a**) and 3,5-dichloro-4-hydroxybenzenesulfonyl chloride (**1c**) with aliphatic tertiary amines in aprotic solvents affords the uncommon cyclic tetramers **3a** and **3b**, respectively

As a part of a wide research project dealing with the incursion of dissociative pathways (elimination-addition mechanisms) in reactions involving reactive derivatives (*i e* esters, chlorides) of carboxylic,[1] sulfonic,[2] and phosphonic[3] acids, we have recently undertaken a mechanistic study on the aminolysis of hydroxyarenesulfonyl chlorides in aprotic solvents [4]

In the course of our work, we have observed that reaction of several aliphatic amines with 3,5-dimethyl-4-hydroxybenzenesulfonyl chloride **1a** affords a high molecular weight product [5] Perusal of the literature revealed that formation of a product different from a sulfonic acid was observed in the alkaline hydrolysis of the 4-phenolsulfonyl chloride **1b** by Zincke and Brune already some eight decades ago [6] These early authors proposed tentatively that this product, which was believed to be a cyclic disulfonate, was formed by dimerization of a quinonoid intermediate of the type **2** which they named 'sulfoquinone'



1a X = CH_3
1b X = Br
1c X = Cl



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Later, Hall investigated the aminolysis of some substituted 4-phenolsulfonyl chlorides in diethyl ether, but no evidence supporting the sulfoquinone intermediate was found by him [7] He reported, however, that starting from **1a**,

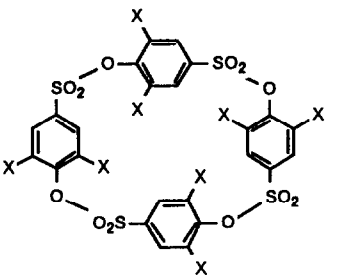
under suitable conditions either high molecular weight linear polymers or a cyclic tetramer could be obtained Experimental details concerning either their formation or their structure have never been published, anyway

Analogous results have been claimed by other authors [8] Field and Lee, however, have recently asserted that reaction of **1c** with pyridine in methylene chloride leads to a linear trimer [9]

Such conflicting results prompt us to disclose our own findings on this matter

RESULTS AND DISCUSSION

When a diluted solution of the chloride **1a** in acetonitrile was treated at room temperature with a slight excess of a tertiary amine such as DABCO, a yellow colour was produced, as noted previously,[6–9] which faded quickly After two hours the reaction was complete, as judged by the disappearance of the sulfonyl chloride monitored by TLC, and after the usual workup of the reaction mixture a white solid was obtained which was repeatedly recrystallized to purity as assessed by TLC analysis The ^{1}H NMR spectrum showed only four singlets, thus suggesting it had a simple, symmetric structure The mass spectrum indicated a molecular ion having *m/z* 736 and the fragmentation pattern clearly showed the repetition of a subunit having *m/z* 184 (corresponding to **1a** *minus* HCl) These results strongly suggested that such product was the tetramer **3a**



3a X = CH_3
3b X = Cl

Inspection of CPK space filling models showed that **3a** has a relatively rigid, highly packed and symmetric structure The aromatic rings are tilted to the plane through the phenolic oxygen atoms, the mutually opposed rings lying above or below this plane This structure agrees indeed with the ^{1}H NMR spectrum of **3a** There are two distinct types of methyl groups, four faced to the interior of the molecule (δ 1 35 ppm, the low chemical shift signal being due to the location of the methyl group in the shielding cone of the adjacent aromatic ring) and four external to the molecule (δ 2.65 ppm, the two equivalent methyl groups of **1a** have δ 2 34 ppm) The aromatic protons give rise to two distinct signals as well, the high field position of the 'inside' hydrogen atoms (δ 6 99 ppm) being due again to the shielding effect of the aromatic rings The chemical shift of the 'outside' aromatic hydrogens (δ 7 99 ppm) is close to that of the two aromatic hydrogens of **1a** (δ 7 69 ppm)

Elemental analysis is also in good agreement with the proposed structure **3a**

The reaction was carried out with other tertiary amines as well under similar conditions As shown in Table 1, tetramer yields ranged from moderate to good, depending on the amine employed

We have found also that the sulfonyl chloride **1c** gave a similar reaction when treated with equimolar amounts of triethylamine or pyridine, either in acetonitrile or methylene chloride, in all cases, the same product was obtained in quite satisfactory yield aside from the solvent and base employed The purity of the recrystallized material was again

checked by TLC ^{1}H NMR and mass spectra again indicated, on grounds similar to those discussed above, it had the cyclic tetrameric structure **3b**

The proposed structure agrees with the preliminary results of X–ray analysis,[10] as shown by the computer–generated perspective drawing depicted in Figure 1

Kinetics and mechanism of the aminolysis of phenolsulfonyl chloride **1a** will be the subject of a forthcoming paper

Table 1 Yields of Tetramer **3a** from the Reaction of Phenolsulfonyl Chloride **1a** (0 2 M) and Tertiary Amines (0 22 M) in Acetonitrile

R_3N	DABCO	Quin[a]	TEA[b]	EDiPA[c]
% Yield[d]	68	77	53	41

a Quinuclidine, b Triethylamine, c Ethyl di–*iso*propylamine, d Assessed by spectrodensitometry on the basis of a calibration curve

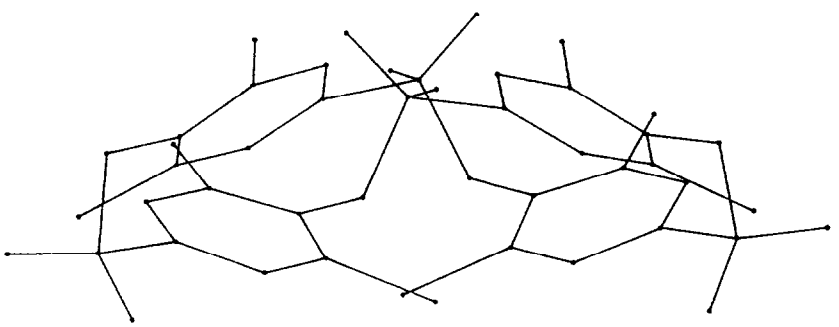


Figure 1 Computer–generated perspective view of tetramer **3b**

EXPERIMENTAL SECTION

The sulfonyl chlorides employed in this work were prepared as reported in the literature [7] The solvents and the amines were analytical grade and were redistilled (or sublimed) prior to use ^{1}H NMR spectra, reported in parts per million (ppm, δ), were recorded with a Varian Gemini 200 spectrometer (200 MHz) with tetramethylsilane as internal standard and $CDCl_3$ as solvent Mass spectra were obtained with a VG 7070EQ – MAT 112 instrument in the EI+ mode Mass spectra of pure **3a** and **3b** showed typical isotopic clusters of the molecular ions fully consistent with the

proposed cyclic tetrameric structures Spectrodensitometry analyses were performed with a Camag TLC–Scanner using a H–P 3390A integrator Samples were deposed on silica gel 60 F_{254} plates (Merck) using an automatic deposer Camag Linomat III and were eluted with methylene chloride

Preparation and Characterization of Tetramer **3a** A solution of DABCO (0 66 g, 6 mmol) in MeCN (12 mL) was added dropwise to a solution of the sulfonyl chloride **1a** (1 2 g, 5 4 mmol) in MeCN (12 mL) at 0°C The resulting solution was stirred at room temperature for 2 h The solvent was removed under reduced pressure and the white solid resulting was repeatedly rinsed with water in order to remove the DABCO hydrochloride product, and dried to afford 0 9 g (90%, calculated as **3a**) of crude product This was finally recrystallized from dioxane and had mp higher than 300 °C ^{1}H NMR δ 7 99 (s, 4H, Ar–*H*), 6 99 (s, 4H, Ar–*H*), 2 65 (s, 12H, CH_3), 1 35 (s, 12H, CH_3), MS *m/z* (relative intensity) 120 (100), 168 (68), 184 (98), 185 (54), 186 (12), 240 (26), 352 (31), 368 (40), 369 (9), 370 (5), 552 (31), 553 (10), 554 (6), 736 (m^+, 73), 737 (m + 1, 29), 738 (m + 2, 20) Anal Calcd for $C_{32}H_{32}O_{12}S_4$ C, 52 16, H, 4 38 Found C, 52 24, H, 4 49

Preparation and Characterization of Tetramer **3b** To a solution of the sulfonyl chloride **1c** (0 5 g, 1 92 mmol) in anhydrous methylene chloride (7 5 mL) a solution of triethylamine (0 27 mL, 1 92 mmol) in anhydrous methylene chloride (2 5 mL) was added dropwise with stirring After 2 h at room temperature a precipitate was filtered, washed with water and with aceton, and dried, affording 0 4 g (93% yield, calculated as **3b**) of a white solid which, after recrystallization from dioxane – chloroform, had mp higher than 300 °C ^{1}H NMR δ 8 31 (d, J = 2 2 Hz, 4H), 7 52 (d, J = 2 2 Hz, 4H), MS *m/z* (relative intensity) 97 (64), 132 (36), 160 (46), 162 (42), 224 (100), 226 (71), 322 (28), 448 (12), 450 (17), 452 (10), 672 (4), 674 (7), 676 (6), 896 (m^+, 6), 898 (m + 2, 16), 900 (m + 4, 21), 902 (m + 6, 15), 904 (m + 8, 8) Anal Calcd for $C_{24}H_8Cl_8O_{12}S_4$ C, 32 02, H, 0 89 Found C, 31 47, H, 1 03

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