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Synthesis and Structure of Tetraaryl Orthocarbonates from Carbonimidic Acid Esters

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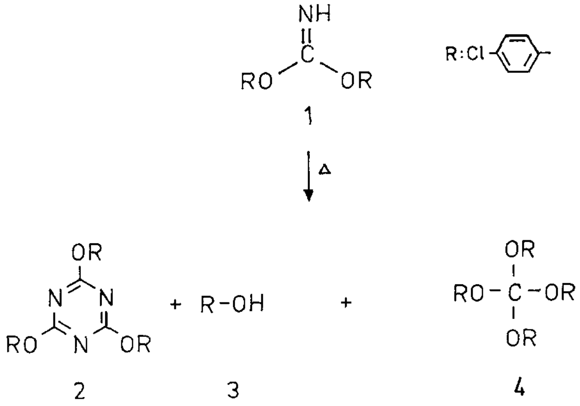
Under the influence of acids arylcyanates trimerize to yield 2,4,6-tris (aryloxy)-1,3,5-triazines [1]. It is also known that the thermal cyclotrimerisation of aromatic cyanic acid esters is catalyzed by small amounts of phenols and water where intermediately a carbonimidic acid ester is formed by addition of the phenol to the cyanate [2].

Martin and coworkers investigated the methanol addition to cyanates. They obtained tetramethoxy methane and substituted triazines via carbonimidic acid dimethylester formed in situ [3]. On the other hand, the corresponding 2,4,6-tris(aryloxy)-1,3,5-triazines and phenols have been isolated exclusively in thermal reactions of carbonimidic acid diarylesters [4].

We found that thermolysis of aromatic carbonimidic acid esters an interesting side reaction takes place. If the carbonimidic acid bis(4-chlorophenyl) ester **1** is heated at 180 °C for 1 hour the appropriate triazine **2**, 4-chlorophenol **3** and tetrakis-(4-chlorophenoxy)methane **4** are obtained as shown in scheme 1.

The crystal structure of **4** was determined by an X-ray structure analysis. Fig. 1 shows a stereoplot of the molecule. Bond lengths and angles are given in Fig. 2. The central C-atom is coordinated by four oxygen atoms forming a nearly regular tetrahedron. The average C-O distance amounts to 1.388 Å. The molecular conformation is defined by the dihedral angles between the four aryl groups. These are listed in table 2. For X-ray data of further tetraaryl orthocarbonates see ref. [5].



Tetraphenoxymethane was obtained at first in 1961 by the reaction of diphenoxy dichloromethane with phenol [6]. Furthermore, the synthesis of other tetraaryl orthocarbonates has been described starting from copper phenoxides which react either with carbon tetrachloride [7, 8] or carbon disulfide [9].

Nothing is known about the formation of tetrakis(aryloxy)methanes from carbonimidic acid esters. Thus the example described herein is the first of this kind.

Experimental

Decomposition of carbonimidic acid ester (**1**)

In a sealed tube 5 g (17.72 mmol) carbonimidic acid bis(4-chlorophenyl)ester **1** [10] are heated at 180 °C for 1 hour. After cooling to room temperature diethylether is added and the 2,4,6-tris(4-chlorophenoxy)-1,3,5-triazine **2** is filtered off.

Yield: 2.05 g	m.p. 215 – 217 °C (acetic acid) (lit. 206 – 208 °C [1])

To remove 4-chlorophenol **3** the etheric solution is washed three times with sodium hydroxide solution (5 %) and with water. After drying with sodium sulfate the solution is concentrated in vacuum. The resulting oily tetrakis(4-chlorophenoxy)methane **4** is crystallized by addition of a small amount of n-hexane.

Yield: 200 mg	m.p. 128 – 129 °C (ethanol) (lit. 129 – 130 °C [8])
^{13}C-NMR($CDCl_3$):	$\delta = 117.82, 121.40, 128.86, 129.77, 150.09$ ppm

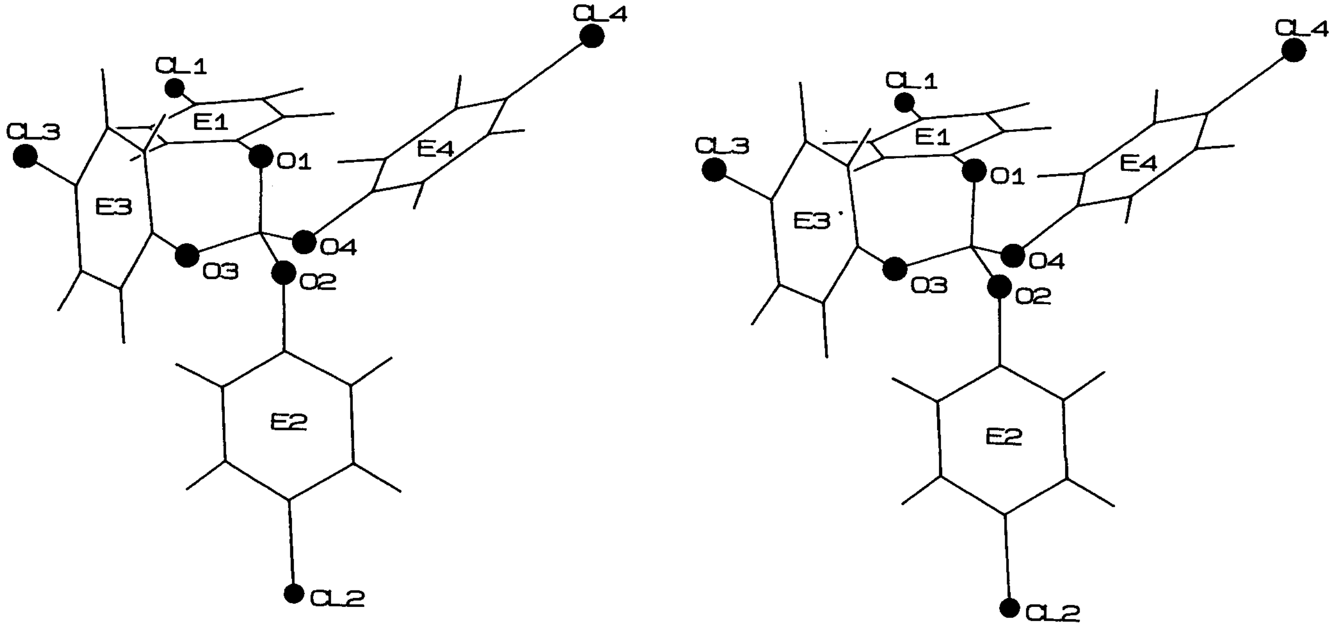


Fig. 1 Molgraf [11] stereoplot of the molecule of 4

X-ray structure determination of 4

Crystal data: $Cl_4C_{25}O_4H_{16}$, triclinic, space group P 1, a = 16.136(1), b = 10.719(4), c = 12.577(2) Å, α = 73.69(2), β = 67.45(2), γ = 73.85(2)°, V = 1188(1) Å³, z = 2, calculated density $D_x = 1.57\ g \cdot cm^{-3}$, linear absorption coefficient $\mu = 5.4\ cm^{-1}$, crystal size: 0.2 × 0.2 × 0.3 mm³.

The intensity data of 3042 independent non-zero reflections (I > σ (I)) were collected up to 2Θ of 46° on an Enraf-nonius Cad4-diffractometer using graphit monochromated

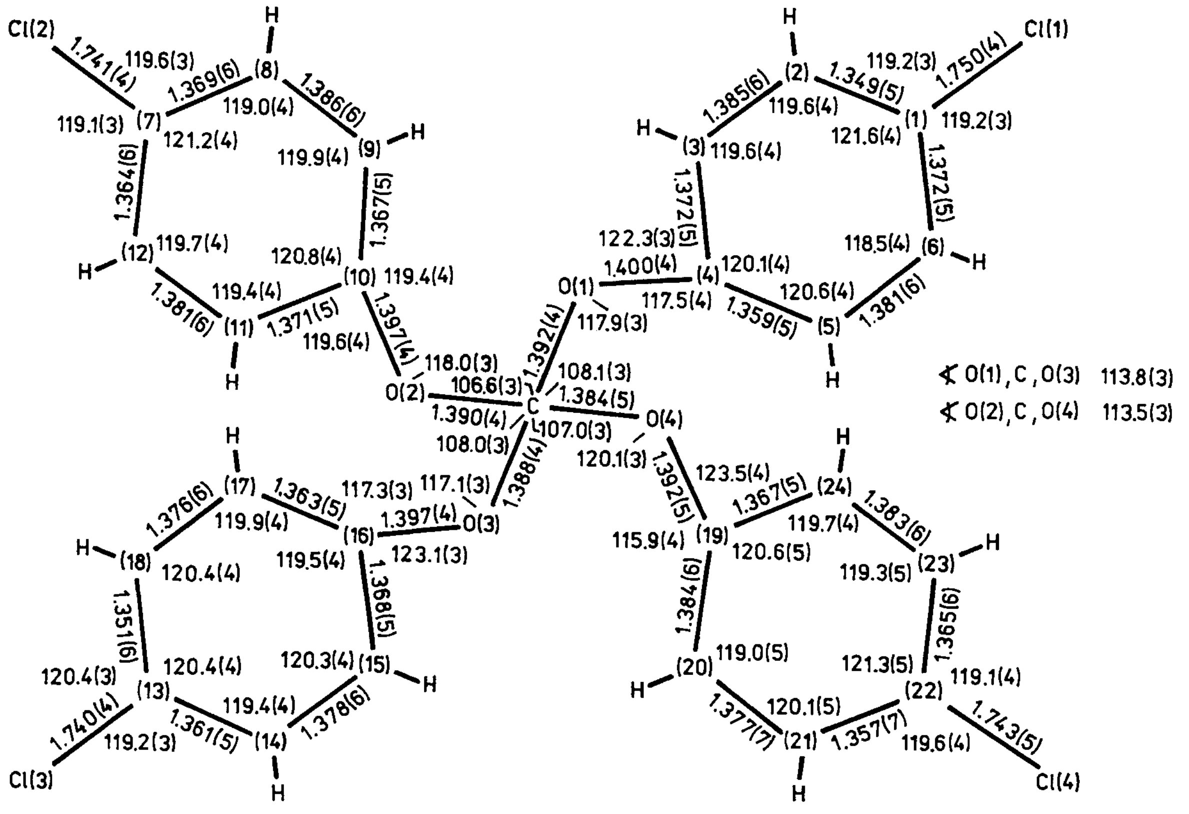


Fig. 2 Bond lengths and angles in the molecule of 4

Table 1 Positional parameters and equivalent isotropic temperature factors of **4** (e.s.d. 's in parentheses)

	x	y	z	B_{eq}/A
Cl(1)	0.5946(1)	0.21312(9)	0.45416(7)	6.33(2)
Cl(2)	1.1817(1)	−0.82421(8)	0.58205(9)	7.31(3)
Cl(3)	0.4150(1)	−0.45437(9)	1.36835(7)	6.44(3)
Cl(4)	1.2755(1)	−0.0413(1)	0.9892(1)	9.72(3)
O(1)	0.8144(2)	−0.1499(2)	0.8217(2)	4.63(5)
O(2)	0.9384(2)	−0.3011(2)	0.7097(2)	5.09(6)
O(3)	0.7420(2)	−0.3514(2)	0.8637(2)	4.90(5)
O(4)	0.9353(2)	−0.3395(2)	0.9013(2)	5.25(6)
C	0.8574(3)	−0.2856(3)	0.8244(3)	4.76(8)
C(1)	0.6602(3)	0.1012(3)	0.5624(2)	4.34(7)
C(2)	0.5811(3)	0.0121(3)	0.6390(3)	5.24(9)
C(3)	0.6316(3)	−0.0752(3)	0.7257(3)	5.24(9)
C(4)	0.7626(3)	−0.0705(2)	0.7313(2)	4.05(2)
C(5)	0.8408(3)	0.0211(3)	0.6538(3)	5.01(8)
C(6)	0.7909(3)	0.1088(3)	0.5673(3)	5.26(9)
C(7)	1.1083(3)	−0.6716(3)	0.6252(3)	4.7(8)
C(8)	1.1948(3)	−0.6077(3)	0.6438(3)	5.11(9)
C(9)	1.1358(3)	−0.4851(3)	0.6758(3)	4.96(8)
C(10)	0.9931(3)	−0.4299(3)	0.6881(2)	4.25(7)
C(11)	0.9073(3)	−0.4945(3)	0.6691(3)	5.01(8)
C(12)	0.9659(3)	−0.6168(3)	0.6376(3)	5.24(8)
C(13)	0.5088(3)	−0.4221(3)	1.2183(3)	4.55(8)
C(14)	0.5232(4)	−0.2955(3)	1.1627(3)	6.8(1)
C(15)	0.6006(4)	−0.2698(3)	1.0445(3)	7.3(1)
C(16)	0.6643(3)	−0.3711(3)	0.9838(2)	4.33(7)
C(17)	0.6461(3)	−0.4970(3)	1.0401(3)	5.17(9)
C(18)	0.5678(4)	−0.5219(3)	1.1580(3)	5.7(1)
C(19)	1.1070(3)	−0.2645(3)	0.9161(2)	4.61(8)
C(20)	1.0016(4)	−0.2677(3)	1.0310(3)	6.0(1)
C(21)	1.0835(4)	−0.2001(4)	1.0520(3)	6.7(1)
C(22)	1.1759(3)	−0.1298(3)	0.9611(3)	5.81(9)
C(23)	1.1919(3)	−0.1261(3)	0.8475(3)	5.71(9)
C(24)	1.1114(3)	−0.1946(3)	0.8248(3)	5.23(9)

MoK_{α}-radiation. The intensities were corrected for Lorentz and polarization effects. An additional correction was necessary because of loss of intensities of 36% after an exposure time of 69 h.

The structure was solved by a straight-forward application of Multan 82 [12]. All hydrogen atoms could be located by difference Fourier syntheses. The final full-matrix least-squares refinement of atomic coordinates, anisotropic thermal parameters of nonhydrogen atoms and isotropic B-values of hydrogens converged with $R = 0.042$ (unit weights). The resulting parameters are listed in table 1.

Table 2 Dihedral angles in the molecule of **4**

	E1	E2	E3
E1: (C(1) to C(6))	–	–	–
E2: (C(7) to C(12))	67.2	–	–
E3: (C13) to C(18))	91.1	77.4	–
E4: (C19) to C(24))	45.1	100.7	128.6

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