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Synthesis and Crystallography of Two Hexachloronaphthalenes. Part II.† 1,2,4,5,6,8-Hexachloronaphthalene and 1,2,4,5,7,8-Hexachloronaphthalene

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1,2,4,5,6,8-Hexachloronaphthalene (**3**) and 1,2,4,5,7,8-hexachloronaphthalene (**6**) have been synthesized by chlorination of 1,5-dinitronaphthalene and 1,8-dinitronaphthalene to 3,4,7,8-tetrachloro-1,5-dinitronaphthalene and 3,4,5,6-tetrachloro-1,8-dinitronaphthalene, respectively. The nitro groups were then replaced by chlorine atoms in one step according to the Ponomarenko reaction. Crystal and molecular structures of the two title isomers were determined by single-crystal X-ray diffraction methods. Two similar, centrosymmetric molecules were found for **3** while two similar molecules not connected by any symmetry element in the space group were found for **6**. Both molecules of **3** were planar, whereas one of the two molecules of **6** was planar and the other one was slightly distorted. The hexachloronaphthalenes **3** and **6** crystallized in the space group $P2_1/c$ and $P2_1/a$, respectively, with the following cell dimensions: **3**, $a = 17.568(5)$, $b = 3.853(2)$, $c = 18.564(6)$ and $\beta = 117.14(2)°$; **6**, $a = 18.553(13)$, $b = 3.882(2)$, $c = 31.55(2)$ and $\beta = 94.74(5)°$. The structures were determined by direct methods and the obtained models, containing a total of 97 parameters for **3** and 189 parameters for **6**, were refined by full-matrix least-squares calculations that gave a final R value of 0.055 for 527 unique reflections with $I \geq 2\sigma(I)$ for **3**, and 0.075 for 1257 unique reflections with $I \geq 2\sigma(I)$ for **6**.

Polychlorinated naphthalenes (PCN) are widespread environmental pollutants. Several of the PCN congeners have been shown to bioaccumulate in biota[1] and have also been detected in human adipose tissue,[2,3] blood[4] and in mother's milk.[5] PCN have been industrially produced because of their high chemical and thermal stability and used mainly in the electrical industry.[6] The production has declined, at least in part, owing to the unfavourable environmental and toxic properties these compounds possess.[1,6,7] In particular, the penta- and hexa-chlorinated naphthalenes (pentaCNs/hexaCNs) have been shown to cause skin problems (chloracne) and liver damage.[6,8]

Apart from the distribution of products and items containing PCN, PCN are also released into the environment through processes in which chlorine and organic matter are present, e.g., chlorine production[9] and municipal waste incineration.[10] Commercial products of polychlorinated biphenyls (PCB) also contribute to the release since trace amounts of PCN are present also in these products.[11]

The major hexaCN component in one of the commercial PCN products (Halowax 1014) has tentatively been identified as either 1,2,4,5,6,8-hexaCN (**3**), 1,2,4,5,7,8-hexaCN (**6**) or a mixture of the two,[12] cf., Scheme 1. The two hexaCNs were synthesized by treating 1,5-diaminonaphthalene and 1,8-diaminonaphthalene with 3-methylbutyl nitrite in the presence of copper(II) chloride.[12,13] The crude products generated were, however, complex mixtures of CNs and the yields of **3** and **6** were poor.

In addition to the pathway described above, **3** has also been prepared via two other pathways. 1,5-Ditosylamino-2,4,6,8-tetraCN was prepared by chlorination of 1,5-ditosylaminonaphthalene. This product was then hydrolysed to 1,5-diamino-2,4,6,8-tetraCN, which was subsequently transformed into **3** by substitution of the amino groups according to the Sandmeyer reaction.[13,14] The hexaCN **3** has also been synthesized via the chlorination

† Part I, Jakobsson, E., Eriksson, L. and Bergman, Å. *Acta Chem. Scand. 46* (1992) 527.

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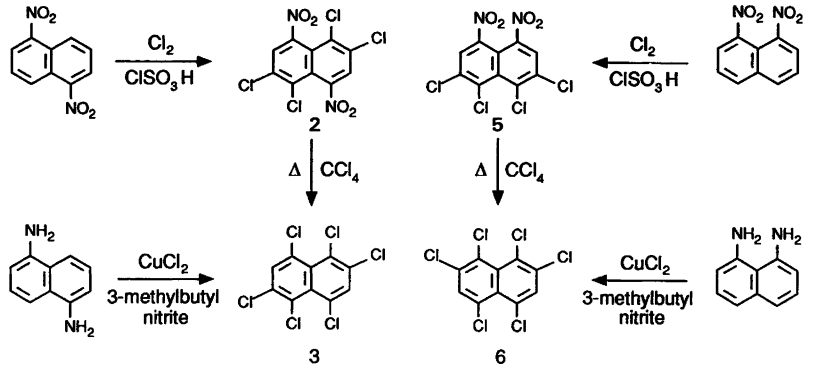

Scheme 1.

of 1,5-dinitronaphthalene with subsequent replacement of the nitro groups by chlorine atoms,[12] cf., Scheme 1. In the present study, the conditions in the latter synthesis were improved and also used for the preparation of **6**. The aim of the study was to synthesize **3** and **6**, in order to verify the previously tentatively determined structures, to describe their crystal structures and to make them available for biological and toxicological studies.

Four other hexaCNs, of the theoretical 10 isomers, have been synthesized and described elsewhere. Thus, 1,2,3,5,6,7- and 1,2,3,4,6,7-hexaCN have been prepared via dechlorination of octaCN with lithium aluminium hydride[15] or zinc.[13] 1,2,3,4,5,6-HexaCN have been synthesized by chlorination of 2-nitronaphthalene to 2-nitro-3,4,5,6,7,8-hexaCN. This compound was then reduced to the corresponding 2-aminohexaCN and the amino groups were reductively removed by diazotisation.[13,16] Treatment of octaCN with either selenium or sulfur, afforded 3,4,5,6,7,8-hexachloronaphtho[1,8-*cd*][1,2]-diselenole and 3,4,5,6,7,8-hexachloronaphtho[1,8-*cd*][1,2]-dithiole, respectively. These compounds were subsequently reduced to 1,2,3,5,6,7-hexaCN with Raney nickel.[13,17,18]

Experimental

Chemicals. 1,5-Dinitronaphthalene and 1,8-dinitronaphthalene were purchased from Aldrich, chlorosulfonic acid from Merck and iodine from Mallinckrodt. The chlorine (>99.8%) was from AGA Gas AB and all solvents used were of analytical grade. Thin-layer chromatography was performed on silica gel plates (Merck, DC Fertigplatten, Kieselgel 60 F254) with hexane–chloroform (1:1) as the mobile phase. Open silica gel chromatography was per-

Table 1. Crystal data and structural parameters.

	3	**6**
Empirical formula	$C_{10}H_2Cl_6$	$C_{10}H_2Cl_6$
Formula weight/u	334.84	334.84
Space group	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)
Wavelength/Å	1.5418 (Cu Kα)	0.7107 (Mo Kα)
a/Å	17.568(5)	18.553(13)
b/Å	3.853(2)	3.882(2)
c/Å	18.564(6)	31.55(2)
β/°	117.14(2)	94.74(5)
V/Å^3	1118.3(6)	2264(3)
Z	4	8
F(000)	656	1312
μ/mm^{-1}	13.714	1.478
Crystal dimensions/mm^3	0.010×0.038×0.53	0.588×0.114×0.042
Scan-mode	θ/2θ	θ/2θ
2θ-range/°	5.35–89.96	3.26–39.99
Transmission factor range, T_{min} and T_{max}	–	0.842 and 0.941
Measured reflections	1107	3464
Unique observed reflections [$I \geq 2\sigma(I)$]	527	1257
Number of refined parameters	97	189
Goodness-of-fit on F^2	1.095	1.435
Final *r* indices [$I > 2\sigma(I)$][a]	$R1 = 0.0547$	$R1 = 0.0751$
R indices (all data)[a]	$R1 = 0.1318$, $wR2 = 0.1205$	$R1 = 0.1273$, $wR2 = 0.2426$
Largest diff. peak and hole/e Å^{-3}	0.356 and −0.309	0.44 and −0.51
Cell weight/u	1339.26	2678.52

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR2 = \{\Sigma[W(F_o^2 - F_c^2)^2]\}/\Sigma[w(F_o^2)^2]$.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Estimated standard deviations are given in parentheses.

	x	*y*	*z*	U_{eq}
3 (1,2,4,5,6,8-hexachloronaphthalene)				
Molecule 1				
Cl(1)	0.6298(2)	0.1619(11)	0.4239(2)	0.061(1)
Cl(2)	0.7516(2)	0.0856(10)	0.6022(2)	0.054(1)
Cl(3)	0.5395(2)	0.5995(11)	0.6983(2)	0.057(1)
C(1)	0.5110(6)	0.4519(33)	0.4681(6)	0.026(3)
C(2)	0.5954(7)	0.2976(31)	0.4925(6)	0.025(3)
C(3)	0.6488(7)	0.2645(33)	0.5705(7)	0.033(3)
C(4)	0.6298(7)	0.3491(34)	0.6323(7)	0.035(3)
C(5)	0.5508(6)	0.5019(31)	0.6125(6)	0.029(3)
Molecule 2				
Cl(4)	0.8746(2)	0.4606(11)	0.7943(2)	0.063(1)
Cl(5)	0.7463(2)	0.7970(10)	0.8394(2)	0.055(1)
Cl(6)	0.9504(2)	0.6944(11)	0.6485(2)	0.060(1)
C(6)	0.9906(7)	0.4589(34)	0.9589(6)	0.035(3)
C(7)	0.9425(7)	0.6940(34)	1.0553(6)	0.031(3)
C(8)	0.8667(7)	0.7661(33)	0.9922(7)	0.037(4)
C(9)	0.8479(7)	0.6894(34)	0.9141(6)	0.034(3)
C(10)	0.9066(7)	0.5350(34)	0.8942(6)	0.033(3)
6 (1,2,4,5,7,8-hexachloronaphthalene)				
Molecule 1				
Cl(1)	1.1093(3)	1.3146(20)	0.1532(2)	0.062(2)
Cl(2)	0.9009(3)	1.2915(17)	0.2539(2)	0.056(2)
Cl(3)	0.7943(3)	0.9401(20)	0.1896(2)	0.065(2)
Cl(4)	0.7601(3)	0.7941(24)	0.0988(2)	0.088(3)
Cl(5)	0.8244(3)	0.5550(19)	0.0189(2)	0.063(2)
Cl(6)	1.0813(3)	1.0287(20)	0.0660(2)	0.066(2)
C(1)	1.0189(10)	1.2073(59)	0.1568(6)	0.042(6)
C(2)	0.9948(10)	1.2804(58)	0.1946(6)	0.038(6)
C(3)	0.9240(10)	1.1982(59)	0.2024(6)	0.042(6)
C(4)	0.8761(10)	1.0582(62)	0.1740(6)	0.045(6)
C(5)	0.8993(10)	0.9792(58)	0.1321(6)	0.038(6)
C(6)	0.8516(10)	0.8374(58)	0.0968(6)	0.038(6)
C(7)	0.8793(10)	0.7370(60)	0.0602(6)	0.038(6)
C(8)	0.9498(10)	0.7952(58)	0.0533(6)	0.038(6)
C(9)	0.9963(10)	0.9467(62)	0.0826(6)	0.042(6)
C(10)	0.9740(10)	1.0447(58)	0.1239(6)	0.040(6)
Molecule 2				
Cl(7)	1.3276(3)	0.1701(19)	0.4410(2)	0.059(2)
Cl(8)	1.0598(3)	0.2474(18)	0.4767(2)	0.060(2)
Cl(9)	1.0077(3)	0.5915(19)	0.3940(2)	0.064(2)
Cl(10)	1.0450(3)	0.8382(21)	0.3106(2)	0.071(2)
Cl(11)	1.1627(3)	0.9328(18)	0.2514(2)	0.056(2)
Cl(12)	1.3649(3)	0.4126(20)	0.3565(2)	0.059(2)
C(11)	1.2424(10)	0.2987(61)	0.4217(6)	0.038(6)
C(12)	1.1921(10)	0.2428(62)	0.4491(6)	0.043(6)
C(13)	1.1208(10)	0.3304(56)	0.4392(6)	0.032(5)
C(14)	1.0975(10)	0.4931(59)	0.4016(6)	0.037(5)
C(15)	1.1491(9)	0.5503(53)	0.3698(5)	0.027(5)
C(16)	1.1316(10)	0.7048(62)	0.3286(6)	0.042(6)
C(17)	1.1815(10)	0.7586(60)	0.3012(6)	0.038(5)
C(18)	1.2537(9)	0.6691(52)	0.3121(5)	0.029(5)
C(19)	1.2746(10)	0.5254(59)	0.3497(6)	0.039(6)
C(20)	1.2242(10)	0.4558(58)	0.3816(6)	0.034(6)

formed on Kieselgel 60 (<0.063 mm particles), from Merck.

Instruments. Gas chromatography–mass spectrometry (GC–MS) was performed on two instruments; one quadrupole and one ion-trap instrument. The quadrupole was a Finnigan 4021 instrument upgraded with a 4500 ion source and an Incos data system. The gas chromatograph was a Varian 3400 equipped with a DB-5 fused silica capillary column, 30 m × 0.25 mm, 0.025 mm film thickness (J&W Scientific) and the temperature program was 80 °C (2 min); 10 °C min^{-1}; 280 °C. Helium was used as the carrier gas and the temperature of the injector was 260 °C. Electron ionization (EI) was used as the ionization method at an ion source temperature of 140 °C and an electron energy of 70 eV. The ion-trap mass spectrometer was a Finnigan ITS40 instrument also equipped with a Varian 3400 gas chromatograph. The GC parameters were identical with those described above. Both mass spectrometers were programmed to scan from 100 to 450 u.

Table 3. Bond lengths (Å). Estimated standard deviations in the last digit are given in parentheses. The following symmetry transformations were used to generate equivalent atoms: #1: $-x+1,-y+1,-z+1$; #2: $x,-y+3/2,z-1/2$; #3: $x+2,-y+1,-z+2$; #4: $x,-y+3/2,z+1/2$.

3 (1,2,4,5,6,8-hexachloronaphthalene)		Cl(4)–C(6)	1.72(2)
		Cl(5)–C(7)	1.74(2)
		Cl(6)–C(9)	1.73(2)
Cl(1)–C(2)	1.720(11)	Cl(7)–C(11)	1.72(2)
Cl(2)–C(3)	1.765(12)	Cl(8)–C(13)	1.73(2)
Cl(3)–C(5)	1.734(11)	Cl(9)–C(14)	1.71(2)
C(1)–C(5)#1	1.402(13)	Cl(10)–C(16)	1.74(2)
C(1)–C(1)#1	1.45(2)	Cl(11)–C(17)	1.72(2)
C(1)–C(2)	1.464(14)	Cl(12)–C(19)	1.73(2)
C(2)–C(3)	1.325(14)	C(1)–C(2)	1.34(2)
C(3)–C(4)	1.373(14)	C(1)–C(10)	1.42(3)
C(4)–C(5)	1.394(14)	C(2)–C(3)	1.40(2)
C(5)–C(1)#1	1.402(13)	C(3)–C(4)	1.33(3)
Cl(4)–C(10)	1.698(11)	C(4)–C(5)	1.46(3)
Cl(5)–C(9)	1.739(11)	C(5)–C(6)	1.47(3)
Cl(6)–C(7)#2	1.726(11)	C(5)–C(10)	1.45(3)
C(6)–C(6)#3	1.44(2)	C(6)–C(7)	1.36(2)
C(6)–C(10)	1.446(14)	C(7)–C(8)	1.36(2)
C(6)–C(7)#3	1.44(2)	C(8)–C(9)	1.35(3)
C(7)–C(8)	1.342(14)	C(9)–C(10)	1.45(3)
C(7)–C(6)#3	1.44(2)	C(11)–C(12)	1.34(2)
C(7)–Cl(6)#4	1.726(11)	C(11)–C(20)	1.42(3)
C(8)–C(9)	1.366(14)	C(12)–C(13)	1.38(2)
C(9)–C(10)	1.379(14)	C(13)–C(14)	1.38(3)
		C(14)–C(15)	1.46(2)
6 (1,2,4,5,7,8-hexachloronaphthalene)		C(15)–C(16)	1.44(3)
		C(15)–C(20)	1.46(3)
		C(16)–C(17)	1.34(2)
Cl(1)–C(1)	1.74(2)	C(17)–C(18)	1.40(2)
Cl(2)–C(3)	1.75(2)	C(18)–C(19)	1.34(3)
Cl(3)–C(4)	1.70(2)	C(19)–C(20)	1.45(3)

^1H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions with a JEOL EX270 instrument at 270 MHz and room temperature.

The crystallographic investigations were performed on a Siemens STOE/AED2 diffractometer equipped with a graphite monochromator. The programs SHELXTL-PC[19] and SHAKAL-92[20] were used to draw Figs. 2 and 3, respectively.

*3,4,7,8-Tetrachloro-1,5-dinitronaphthalene (**2**).* 1,5-Dinitronaphthalene (2.5 g, 11.5 mmol, **1**) was dissolved in chlorosulfonic acid (20 ml) in a two-necked reaction flask and iodine (0.34 g, 1.4 mmol) was added. Chlorine was introduced and condensed using a condenser cooled with dry ice in acetone. After 1 h a total volume of about 20 ml chlorine had been condensed. The introduction of chlorine was stopped and no more dry ice was added to the condenser. The reaction mixture was allowed slowly to reach room temperature during which time the chlorine evaporated off. The solution was carefully poured onto ice (about 500 ml) and after being stirred for 30 min the mixture was extracted with dichloromethane. The solvent was evaporated off and the product was recrystallized from acetone–ethanol. Yield 3.3 g (9.3 mmol, 81%) of white needles. M.p. 254.5–256.0°C. MS: *m/z* (rel. ab., %): 319 [100, $(M-Cl)^+$], 321 (95), 323 (31), 284 [22, $(M-2Cl)^+$], 262 [15, $(M-2NO_2)^+$], 243 (11), 215 [18, $(M-NO_2-NO-CO-Cl)$], 192 (23). ^1H NMR (270 MHz, $CDCl_3$): δ 8.0. ^{13}C NMR (270 MHz, $CDCl_3$): δ 146.08, 134.90, 130.86, 126.90 (intense) and 123.47. UV [dichloromethane (log ε)]: 248 nm (5.0).

*1,2,4,5,6,8-Hexachloronaphthalene (**3**).* 3,4,7,8-Tetrachloro-1,5-dinitronaphthalene (100 mg, 0.28 mmol, **2**) and tetrachloromethane (1.0 ml) was heated in a Pyrex ampoule for 20 min in an oven set at 300°C according to

Table 4. Selected bond angles (°) with estimated standard deviations in the last digit given in parentheses. The following symmetry transformations were used to generate equivalent atoms: #1: $-x+1,-y+1,-z+1$; #2: $x,-y+3/2,z-1/2$; #3: $x+2,-y+1,-z+2$; #4: $x,-y+3/2,z+1/2$.

3 (1,2,4,5,6,8-hexachloronaphthalene)		C(6)–C(5)–C(4)	124(2)
		C(10)–C(5)–C(4)	119(2)
C(5)#1–C(1)–C(1)#1	118.3(11)	C(7)–C(6)–C(5)	120(2)
C(5)#1–C(1)–C(2)	124.3(9)	C(7)–C(6)–Cl(4)	117(2)
C(1)#1–C(1)–C(2)	117.4(11)	C(5)–C(6)–Cl(4)	123(2)
C(3)–C(2)–C(1)	119.3(10)	C(8)–C(7)–C(6)	122(2)
C(3)–C(2)–Cl(1)	117.8(9)	C(8)–C(7)–Cl(5)	117(2)
C(1)–C(2)–Cl(1)	122.9(7)	C(6)–C(7)–Cl(5)	121(2)
C(2)–C(3)–C(4)	124.7(11)	C(7)–C(8)–C(9)	122(2)
C(2)–C(3)–Cl(2)	120.6(9)	C(8)–C(9)–C(10)	121(2)
C(4)–C(3)–Cl(2)	114.6(9)	C(8)–C(9)–Cl(6)	115(2)
C(3)–C(4)–C(5)	118.2(11)	C(10)–C(9)–Cl(6)	124(2)
C(4)–C(5)–C(1)#1	121.9(10)	C(9)–C(10)–C(5)	117(2)
C(4)–C(5)–Cl(3)	111.5(8)	C(9)–C(10)–C(1)	125(2)
C(1)#1–C(5)–Cl(3)	126.5(8)	C(5)–C(10)–C(1)	117(2)
C(6)#3–C(6)–C(10)	119.3(12)	C(12)–C(11)–C(20)	121(2)
C(6)#3–C(6)–C(7)#3	118.2(12)	C(12)–C(11)–Cl(7)	113(2)
C(10)–C(6)–C(7)#3	122.6(9)	C(20)–C(11)–Cl(7)	126(2)
C(8)–C(7)–C(6)#3	119.4(11)	C(11)–C(12)–C(13)	121(2)
C(8)–C(7)–Cl(6)#4	114.7(9)	C(14)–C(13)–C(12)	122(2)
C(6)#3–C(7)–Cl(6)#4	125.9(8)	C(14)–C(13)–Cl(8)	120(2)
C(7)–C(8)–C(9)	123.1(11)	C(12)–C(13)–Cl(8)	118(2)
C(8)–C(9)–C(10)	122.0(11)	C(13)–C(14)–C(15)	119(2)
C(8)–C(9)–Cl(5)	117.3(9)	C(13)–C(14)–Cl(9)	117(2)
C(10)–C(9)–Cl(5)	120.7(9)	C(15)–C(14)–Cl(9)	124(2)
C(9)–C(10)–C(6)	118.0(10)	C(16)–C(15)–C(14)	125(2)
C(9)–C(10)–Cl(4)	116.7(8)	C(16)–C(15)–C(20)	118(2)
C(6)–C(10)–Cl(4)	125.3(8)	C(14)–C(15)–C(20)	117(2)
		C(17)–C(16)–C(15)	122(2)
6 (1,2,4,5,7,8-hexachloronaphthalene)		C(17)–C(16)–Cl(10)	114(2)
		C(15)–C(16)–Cl(10)	123(2)
C(2)–C(1)–C(10)	122(2)	C(16)–C(17)–C(18)	120(2)
C(2)–C(1)–Cl(1)	114(2)	C(16)–C(17)–Cl(11)	124(2)
C(10)–C(1)–Cl(1)	125(2)	C(18)–C(17)–Cl(11)	116(2)
C(1)–C(2)–C(3)	120(2)	C(19)–C(18)–C(17)	121(2)
C(4)–C(3)–C(2)	124(2)	C(18)–C(19)–C(20)	122(2)
C(4)–C(3)–Cl(2)	121(2)	C(18)–C(19)–Cl(12)	115(2)
C(2)–C(3)–Cl(2)	115(2)	C(20)–C(19)–Cl(12)	123(2)
C(3)–C(4)–C(5)	118(2)	C(11)–C(20)–C(19)	125(2)
C(3)–C(4)–Cl(3)	119(2)	C(11)–C(20)–C(15)	119(2)
C(5)–C(4)–Cl(3)	123(2)	C(19)–C(20)–C(15)	116(2)
C(6)–C(5)–C(10)	117(2)		

Sundström.[21] Thirty min after the ampoule had been taken out from the oven it was chilled for an additional 30 min in the refrigerator during which time the product crystallized. The ampoule was opened, the solvent evaporated off and the product was recrystallized from hexane. It should be noted that a slight increase in the pressure was generated in the ampoule during the reaction. Yield 75 mg (0.22 mmol, 80%) of white needles. M.p. 175.5–176.0°C. MS: *m/z* (rel. ab., %): 332 (50, M^+), 334 (100), 336 (72), 338 (37), 297 [37, $(M-Cl)^+$], 262 [20, $(M-2Cl)^+$], 192 [14, $(M-4Cl)^+$]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.81. ^{13}C NMR (270 MHz, $CDCl_3$): δ 134.57, 132.98 (intense), 130.73, 130.33, 128.44. UV [hexane (log ε)]: 252 nm (5.1).

*3,4,5,6-Tetrachloro-1,8-dinitronaphthalene (**5**).* 1,8-Dinitronaphthalene (1.05 g, 4.8 mmol, **4**) was dissolved in chlorosulfonic acid (20 ml) in a two-necked reaction flask and iodine (0.15 g, 0.6 mmol) was added. The reaction was performed as described above for the synthesis of **2**. The reaction mixture was poured onto ice (about 500 ml) and after being stirred for 30 min the mixture was extracted with dichloromethane. The solvent was evaporated off and the product was purified on an open silica gel column using chloroform–hexane (1:1) as the mobile phase and then recrystallized from acetone–ethanol. Yield 0.681 g (1.9 mmol, 40%) of white needles. M.p. 198.5–200.0°C. MS: *m/z* (rel. ab., %): 308 [78%, $(M-NO_2)^+$], 310 (100), 312 (49), 314 (10), 278 [34, $(M-NO_2-NO)^+$], 250 [44, $(M-NO_2-NO-CO)^+$], 229 (28), 215 [86, $(M-NO_2-NO-CO-Cl)^+$], 192 [11, $(M-2NO_2-2Cl)^+$]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.40. ^{13}C NMR (270 MHz, $CDCl_3$): δ 144.41, 136.44, 135.33, 131.62, 127.71 (intense), 117.46. UV [hexane (log ε)]: 252 nm (4.9).

*1,2,4,5,7,8-Hexachloronaphthalene (**6**).* 3,4,5,6-Tetrachloro-1,8-dinitronaphthalene (100 mg, 0.28 mmol, **5**) and tetrachloromethane (1.0 ml) was heated in a Pyrex ampoule for 20 min in an oven set at 300°C according to Sundström.[21] The product was finally recrystallized from hexane. Yield 67 mg (0.20 mmol, 71%) of white needles. M.p. 139.0–139.5°C. MS: *m/z* (rel. ab., %): 332 (50, M^+), 334 (100), 336 (81), 338 (37), 297 [8, $(M-Cl)^+$], 262 [19, $(M-2Cl)^+$], 192 [12, $(M-4Cl)^+$]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.76. ^{13}C NMR (270 MHz, $CDCl_3$): δ 135.49, 133.20, 131.92 (intense), 128.04, 128.00. UV [hexane (log ε)]: 253 nm (5.2).

Crystallography. Needle-shaped crystals of **3** and **6** were formed by recrystallization from methanol. The space groups were found to be $P2_1/c$ (No. 14) for **3** and $P2_1/a$ (No. 14) for **6**, indicated by the reflection conditions $0k0{:}k = 2n$, $h0l{:}l = 2n$ and $0k0{:}k = 2n$, $h0l{:}h = 2n$, respectively. Lattice parameters were refined by least-squares calculations based on setting angles of 22 reflections in **3** and 50 selected reflections in **6**. The intensities were collected at room temperature with the graphite monochromator set to reflect Cu $K\alpha$ for the crystal of **3** and Mo $K\alpha$ for the crystal of **6**. The intensity data were corrected for Lorentz and polarisation effects. Correction for absorption effects was unsuccessful for the crystal of **3** probably due to the crystal being very thin. In the case of **6**, the intensity data were corrected for absorption effects by Gaussian numerical integration with the program SHELX-76.[22] Crystal data for both compounds are found in Table 1. The crystal structures were determined by direct methods using the program SHELXS-86[23] and the models obtained were refined by full-matrix least-squares calculations with the program SHELXL-93.[24] All

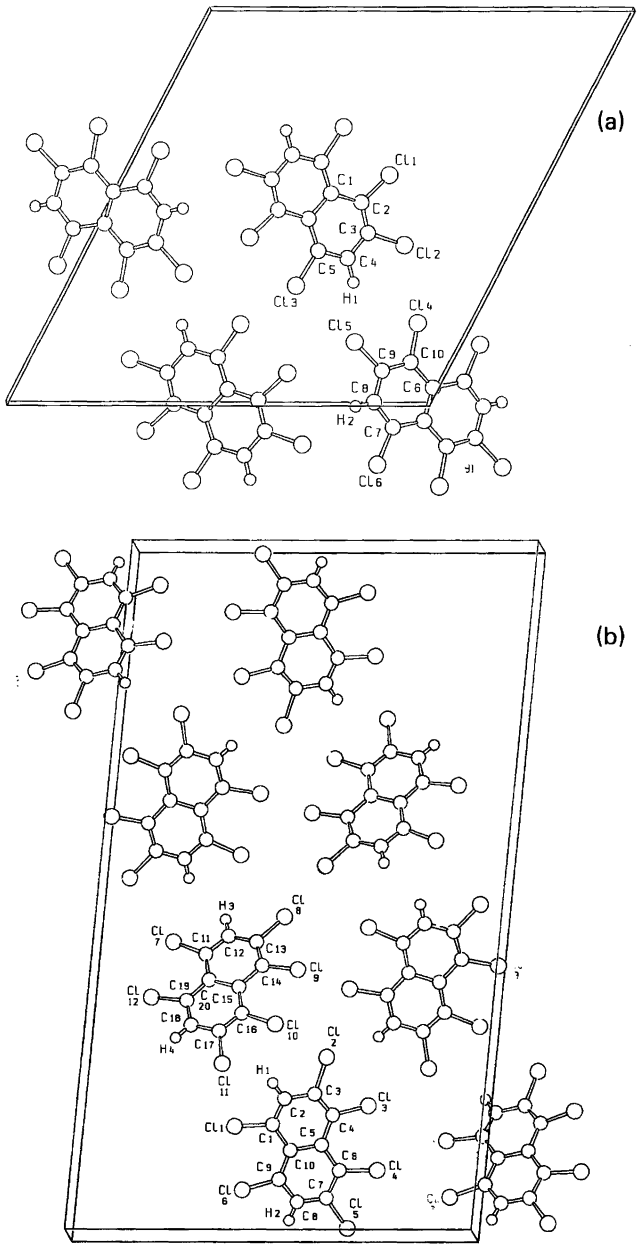

Fig. 1. Numbering scheme and the unit cell content of (a) the two molecules of 1,2,4,5,6,8-hexachloronaphthalene (**3**) and (b) the two molecules of 1,2,4,5,7,8-hexachloronaphthalene (**6**).

non-hydrogen atoms could be located in the first electron density map. The hydrogen positions were calculated and the distances between the hydrogens and the corresponding carbons were constrained in the least-squares calculations to be 1.08 Å. The hydrogen atoms were given the same isotropic displacement factors as the carbon atoms to which they were connected. All chlorine atoms were refined anisotropically and the rest of the atoms isotropically.

The weighting scheme employed, $w = 1/[\sigma^2(F^2) + (0.0435\ P)^2]$, $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$ for compound **3** and $w = 1/[\sigma^2(F^2) + (0.0438\ P)^2 + 39.63\ P]$, $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$ for compound **6**, with $\sigma(F^2)$ determined from counting statistics. There were no changes larger than 0.002σ in any of the parameters varied in the last least-squares cycle. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2, bond lengths in Table 3 and some selected bond angles in Table 4. The numbering scheme of the molecules is shown in Fig. 1. A list of the anisotropic displacement factors for non-hydrogen atoms, the observed and the calculated structure factor amplitudes can be obtained on request from one of the authors (L. Eriksson).

Results and discussion

1,2,4,5,6,8-HexaCN (**3**) and 1,2,4,5,7,8-hexaCN (**6**) were synthesized via chlorination of 1,5-dinitronaphthalene and 1,8-dinitronaphthalene, respectively, followed by replacement of the nitro groups with chlorine atoms according to the Ponomarenko reaction,[21,25–28] cf., Scheme 1. The synthesis of **3** via this pathway has previously been reported,[12] but the reaction conditions were not optimized and the structures of the products (**2** and **3**) were only tentatively determined. The chlorination in the previous study was performed with refluxing chlorine at 50 °C according to Kadunce *et al.*[29] In the present study, it was found that if a large volume (about 20 ml) of chlorine is condensed into the reaction flask the yield of 3,4,7,8-tetrachloro-1,5-dinitronaphthalene was much higher (81%). This is probably due to the higher chlorine

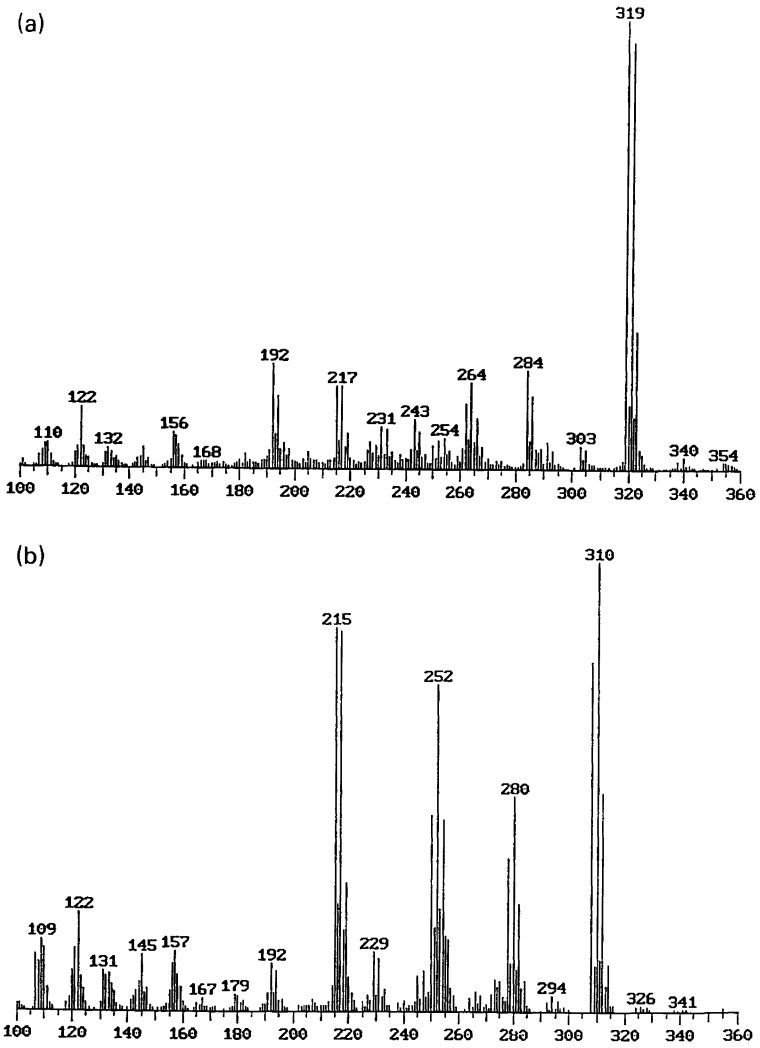

Fig. 2. Mass spectra of (a) 3,4,7,8-tetrachloro-1,5-dinitronaphthalene and (b) 3,4,5,6-tetrachloro-1,8-dinitronaphthalene.

concentration and lower reaction temperature. 1,8-Dinitronaphthalene was chlorinated under similar conditions and, again, in this synthesis one major product, 3,4,5,6-tetrachloro-1,8-dinitronaphthalene, was formed. The yield of **5** was lower (40%), but the by-products were much more polar than **5**, and could thus easily be removed on an open silica gel column. It is notable that although there are two more hydrogen atoms to be available for replacement in **2** and **5**, the chlorination does not proceed any further.

The nitro groups in **2** and **5** were replaced by chlorine atoms via a method first described by Ponomarenko[25–28] and later used for the syntheses of, e.g., di- and tri-CNs as well as 1,2,3,4,5,6,7-heptaCN.[21] The tetrachlorodinitronaphthalene and tetrachloromethane are heated in a glass ampoule. The reaction-time and temperature must be carefully controlled to avoid side reactions. At higher temperatures further chlorination, in addition to the replacement of the nitro groups, occurred as also reported by Sundström.[21] At lower temperatures by-products due to polymerisation reactions were formed. With the appropriate reaction-time and temperature no other CNs but the hexaCN were formed. It is striking that, according to GC–MS, not even small amounts of other nitroCNs or CNs were present in the products from the two reactions. Most syntheses of hexaCNs available in the literature generate products contaminated with considerable amounts lower chlorinated CNs.[13] Auger *et al.*[13] improved the conditions but still 10–20% of mainly pentaCNs were formed which, only to some extent, could be removed by recrystallization and, to obtain the pure products, reversed-phase high-performance liquid chromatography (HPLC) was used.

The mass spectra of the two dinitrotetraCNs (**2** and **5**) were remarkably dissimilar as shown in Fig. 2. The spectrum of **2** had only one major ion corresponding to a loss of a chlorine atom, $(M-Cl)^+$, while the spectrum of **5** showed several intense ions due to the loss of NO_2, NO and CO. These fragmentation patterns are similar to those of 1,5-dinitronaphthalene (**1**) and 1,8-dinitronaphthalene (**4**), respectively.[30,31] Brittain *et al.*[31] proposed a mechanism for the loss of CO involving attack of one of the oxygens in the 1-nitro-group after the loss of the 8-nitro-group with the formation of an intermediate five-membered ring. It is notable that the loss of CO is less abundant when the 8-position is substituted by a chlorine atom as in **2**. It is also noteworthy that when the mass spectra were recorded on an ion-trap mass spectrometer, the molecular ions could not be detected from either of the two tetrachlorodinitronaphthalenes (**2** and **5**), whereas when a quadrupole mass spectrometer was used, low intensity molecular ions were detected from both compounds. In other details, the spectra were similar and the fragmentation of the two hexaCNs (**3** and **6**) were identical on both instruments.

Two similar, crystallographically unrelated molecules, both located on symmetry centres in the space group, were found for **3** while two similar molecules not connected by any symmetry element in the space group were found for **6**. Both molecules of **3** were planar with a mean deviation of 0.012 Å and 0.014 Å, respectively. One of the two molecules of **6** was planar with a mean deviation of 0.022 Å, whereas the other one was slightly distorted with Cl(3) and Cl(4) pointing to each side of the ring plane, cf., Fig. 3. It is not obvious whether the lower-energy conformation is the planar or the distorted one. In the planar conformation the overlap of the π-orbitals is probably greater whereas in the distorted conformation, the interaction between the chlorine atoms in the 1,8-positions is less pronounced. Crystal data of octachloronaphthalene has shown that this compound is remarkably distorted from the planar structure with the chlorine atoms pointing out from the plane and with a remarkable distortion of the aromatic ring from the planar structure.[32]

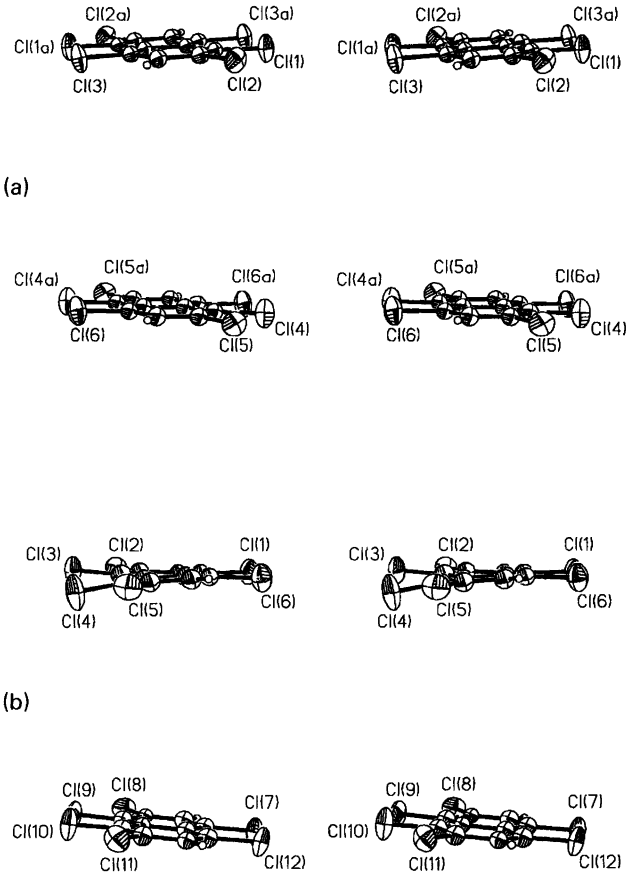

Fig. 3. Perspective view perpendicular to the central C–C bond in (a) the two molecules of 1,2,4,5,6,8-hexachloronaphthalene (**3**) and (b) the two molecules of 1,2,4,5,7,8-hexachloronaphthalene (**6**). Non-hydrogen atoms are shown as 50% probability ellipsoids.

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