Single Crystal ^{35}Cl NQR of 2,3,4,4-Tetrachloro-1-oxo-1,4-dihydronaphthaline and of 2,2,3,4-Tetrachloro-1-oxo-1,2-dihydronaphthaline*

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2,3,4,4-Tetrachloro-1-oxo-1,4-dihydronaphthaline, β-TKN, crystallizes in the orthorhombic space group D_{2h}^{16}-Pnma with $Z=4$, and the ^{35}Cl NQR spectrum consists of three lines with an intensity ratio of 2:1:1. The crystal structure of 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline, α-TKN, is described in literature as belonging to the polar space group C_2^2–$P2_1$ with $Z=2$. In contradiction to the reported space group and Z, we observed a three line ^{35}Cl NQR spectrum with an intensity ratio of 2:1:1. Therefore, the crystal structure of α-TKN was redetermined at $T=296$ K: space group C_{2h}^2-$P2_1/m$, $Z=2$, $a=888.4$ (2) pm, $b=692.3$ (2) pm, $c=869.6$ (2) pm, $\beta=91.483$ (5)°. The ^{35}Cl nuclear quadrupole coupling tensors have been investigated using a 4π Zeeman NQR goniometer and FT NQR for tracing the zero splitting cones.

According to the crystal structure of β-TKN, two symmetry related zero splitting cones have been found for $Cl^{(2)}$, two for $Cl^{(3)}$, and four for $Cl^{(4)}$ ($T=297$ K). From the single crystal Zeeman split NQR measurements of α-TKN one zero splitting cone has been found for $Cl^{(3)}$, one for $Cl^{(4)}$, and two for $Cl^{(2)}$ ($T=290$ K).

The asymmetry parameters η and the direction cosines of the principal axes Φ_{xx}, Φ_{yy}, and Φ_{zz} of the nuclear quadrupole coupling tensors have been determined. The results are: $Cl^{(j)}$, $\nu(^{35}Cl^{(j)})$, $e^2Qqh^{-1}(^{35}Cl^{(j)})$, $\eta(^{35}Cl^{(j)})$ for β-TKN (at $T=297$ K): $Cl^{(2)}$, 37.442 MHz, 74.469 MHz, 0.184; $Cl^{(3)}$, 36.854 MHz, 73.083 MHz, 0.160; $Cl^{(4)}$, $Cl^{(4')}$, 38.685 MHz, 77.307 MHz, 0.070 and for α-TKN (at $T=290$ K): $Cl^{(2)}$, $Cl^{(2')}$, 38.297 MHz, 76.501 MHz, 0.086; $Cl^{(3)}$, 36.943 MHz, 73.700 MHz, 0.123; $Cl^{(4)}$, 36.311 MHz, 72.314 MHz, 0.160. By comparing the crystal structures and the ^{35}Cl NQR results, the C–Cl bonds in the title compounds are discussed.

Introduction

Some derivatives of naphthaline in the crystalline state show photochromy. Crystals of 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthaline, called β-TKN, and 2,4,4-trichloro-1,4-dihydronaphth[1,8-cd]isothiazole-1,1-dioxide, called TCNS, become coloured under the influence of light [1, 2]. An isomeric compound of β-TKN, the 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline, called α-TKN, is, in contrast, not of comparable sensitivity to light. Recently crystal structure studies and ^{35}Cl nuclear quadrupole resonance (NQR) experiments on polycrystalline β-TKN, α-TKN, and TCNS have been reported [3].

β-TKN crystallizes in the orthorhombic space group D_{2h}^{16}-Pnma with $Z=4$ [4] and the ^{35}Cl NQR spectrum consists of three lines with an intensity ratio of 2:1:1. The crystal structure of α-TKN is described in literature as belonging to the polar space group C_2^2-$P2_1$ with $Z=2$ [5]. In contradiction, we observed three ^{35}Cl NQR lines with an intensity ratio of 2:1:1.

In the following we report on single crystal ^{35}Cl NQR experiments on β-TKN and α-TKN.

The study of NQR spectra in single crystals with application of an additional magnetic field (Zeeman split NQR) allows the determination of the three principal axes of the nuclear quadrupole coupling tensor, $eQ\Phi_{ii}h^{-1}$ ($i=x, y, z$), in direction and magnitude with respect to the crystal axes. Thereby the electric field gradient tensor (EFGT), including its deviation from rotation symmetry, is determined. The three principal axes and the asymmetry parameter of the EFGT, $\eta=$

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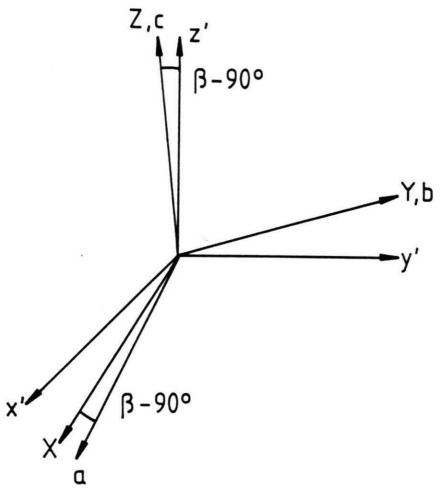


Fig. 1. Coordinate systems used throughout the paper. x', y', z' is the laboratory system which coincides with the axes of the three mutually perpendicular Helmholtz coils of the 4π Zeeman goniometer. ***a***, ***b***, ***c*** is the crystal system, X, Y, Z is the orthogonal axes system, which is chosen in such a way that $\boldsymbol{b} \parallel Y$, $\boldsymbol{c} \parallel Z$, from which choice $\sphericalangle(X, \boldsymbol{a}) = \beta - 90°$ follows.

$|\Phi_{xx} - \Phi_{yy}|/|\Phi_{zz}|$, which describes the deviation of the EFGT from rotational symmetry, can be compared with bond directions and with the charge distribution at the site of the nucleus considered.

By the application of a magnetic field which may be oriented at any angle with respect to the crystal axes (4π Zeeman goniometer), high accuracy in the determination of the direction cosines of the EFGT can be attained [6]. This allows a quantitative comparison of the bond directions, bond angles and electron density distribution found from X-ray and/or neutron diffraction with the EFGT.

Experimental

Large single crystals of β-TKN were obtained by cooling a saturated solution of the compound in benzene from $T \approx 310$ K down to room temperature [7]. Crystals of α-TKN were grown from a saturated solution in benzene, too.

The ^{35}Cl NQR spectra were studied on single crystals with the 4π Zeeman goniometer [6] at 297 K for β-TKN and at 290 K for α-TKN. A Fourier transform (FT) NQR spectrometer was used, and the zero splitting cone method [8] was applied.

An orthorhombic β-TKN crystal was adjusted optically on a goniometer head in such a way that the ***b***-axis of the crystal was parallel to the z'-axis of the Zeeman goniometer. The orientation of the crystal (***a***, ***b***, ***c***) with respect to the Zeeman coil system (laboratory coordinate system x', y', z') and the orthogonal axes system (X, Y, Z) is shown in Figure 1. The monoclinic α-TKN crystal used for the Zeeman spectroscopy was orientated in such a way that the normal of the (001) plane was parallel to the z'-axis of the Zeeman goniometer.

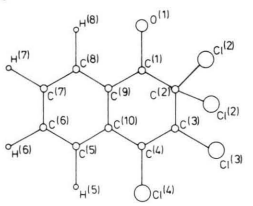
The half-width of the ^{35}Cl NQR lines of polycrystalline α-TKN was measured as a function of temperature by use of FT NQR.

The structure of α-TKN was redetermined by X-ray single crystal technique (Mo Kα-radiation) at room temperature. In Table 1 the experimental details and crystallographic data (lattice constants, space group, etc.) are given.

Table 1. Experimental conditions of the crystal structure determination and crystallographic data of 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronapthaline (α-TKN).

Formula	$C_{10}H_4OCl_4$	
Molar mass, g/mol	281.95	
Crystal habitus	parallelepiped	
Size, mm^3	$0.35 \times 0.4 \times 0.6$	
Colour	yellow	
Diffractometer	Stoe-Siemens AED-2	
Wavelength, λ/pm	71.069 (Mo Kα)	
$(\sin\vartheta/\lambda)_{max}$/pm^{-1}	0.006497	
Monochromator	graphite (002)	
Temperature, T/K	296	
Lattice constants	a/pm	888.4(2)
	b/pm	692.3(2)
	c/pm	869.6(2)
	β/°	91.483(5)
Volume of the unit cell	$V \cdot 10^{-6}$/pm^3	534.66
Space group	C_{2h}^2-P2_1/m	
Number of formula units per unit cell	$Z = 2$	
ϱ_{calc}/(Mg m^{-3})	1.751	
ϱ_{pykn}/(Mg m^{-3})	1.75	
Linear absorption coefficient, μ/m^{-1}	983	
Absorption correction	numeric	
Scan	$\omega/2\theta$	
Number of measured reflections	2687	
Symmetry independent reflections	1325	
Reflection considered	1304	
Number of free parameters	101	
$F(000)$	280	
$R(F)$	0.0410	
$R_w(F)$	0.0512	

Numbering of atoms in the molecule



Point positions: $Cl^{(2)}$ in 4f: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \bar{z}$; $x, \frac{1}{2}-y, z$;
all other atoms in 2e:
$x, \frac{1}{4}, z$; $\bar{x}, \frac{3}{4}, \bar{z}$

Table 2. Positional and thermal parameters (with standard deviation) of 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN). The temperature factors are of the form:

$T = \exp[-2\pi^2(U_{11} \cdot h^2 \cdot a^{*2} + U_{22} \cdot k^2 \cdot b^{*2} + U_{33} \cdot l^2 \cdot c^{*2} + 2U_{12} \cdot h \cdot k \cdot a^* \cdot b^* + 2U_{13} \cdot h \cdot l \cdot a^* \cdot c^* + 2U_{23} \cdot k \cdot l \cdot b^* \cdot c^*)]$.

U and U_{ij} are given in $(pm)^2$.

Atom	x/a	y/b	z/c	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$C^{(1)}$	0.0992(3)	0.2500(0)	0.2457(3)	610(17)	448(14)	379(14)	0(0)	−98(13)	0(0)
$C^{(2)}$	0.2629(4)	0.2500(0)	0.1838(3)	769(20)	435(14)	318(13)	0(0)	12(13)	0(0)
$C^{(3)}$	0.3877(3)	0.2500(0)	0.3017(3)	531(16)	515(15)	432(15)	0(0)	63(13)	0(0)
$C^{(4)}$	0.3604(3)	0.2500(0)	0.4517(3)	456(15)	431(13)	402(14)	0(0)	−60(11)	0(0)
$C^{(5)}$	0.1848(3)	0.2500(0)	0.6717(3)	478(16)	594(16)	329(13)	0(0)	−44(12)	0(0)
$H^{(5)}$	0.2556(39)	0.2500(0)	0.7370(45)	609(97)					
$C^{(6)}$	0.0409(4)	0.2500(0)	0.7274(4)	620(18)	592(17)	397(15)	0(0)	42(13)	0(0)
$H^{(6)}$	0.0116(38)	0.2500(0)	0.8470(44)	617(92)					
$C^{(7)}$	−0.0828(4)	0.2500(0)	0.6270(4)	493(16)	557(17)	572(18)	0(0)	31(14)	0(0)
$H^{(7)}$	−0.1926(40)	0.2500(0)	0.6723(46)	722(106)					
$C^{(8)}$	−0.0609(3)	0.2500(0)	0.4705(4)	487(16)	490(15)	528(17)	0(0)	−89(14)	0(0)
$H^{(8)}$	−0.1362(38)	0.2500(0)	0.4059(43)	553(91)					
$C^{(9)}$	0.0824(3)	0.2500(0)	0.4131(3)	492(14)	361(12)	347(13)	0(0)	−59(11)	0(0)
$C^{(10)}$	0.2082(3)	0.2500(0)	0.5147(3)	448(14)	356(12)	341(12)	0(0)	−33(10)	0(0)
$Cl^{(2)}$	0.2769(1)	0.0398(1)	0.0660(1)	1102(6)	614(4)	510(4)	−179(3)	56(4)	36(3)
$Cl^{(3)}$	0.5672(1)	0.2500(0)	0.2326(1)	630(6)	1038(7)	648(6)	0(0)	218(4)	0(0)
$Cl^{(4)}$	0.5096(1)	0.2500(0)	0.5823(1)	464(4)	824(6)	551(5)	0(0)	−111(3)	0(0)
$O^{(1)}$	−0.0057(3)	0.2500(0)	0.1552(3)	784(16)	994(18)	432(12)	0(0)	−220(12)	0(0)

Results

Crystal Structure of 2,2,3,4-Tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN)

The systematic absence of certain reflexions in the X-ray diffraction pattern is consistent with two space groups, either C_{2h}^2-$P2_1/m$ or C_2^2-$P2_1$. ^{35}Cl NQR shows three lines with an intensity ratio of 2:1:1. Therefrom one concludes that there are three positions occupied by the chlorine atoms, one by two Cl atoms and two each by a single atom. From the metric of the unit cell and the mass density, $Z = 2$ follows. Then the ^{35}Cl NQR is compatible with the centrosymmetric space group C_{2h}^2-$P2_1/m$ (for the discussion about the two space groups see [3, 5]). By using the SHELX-86 program, the crystal structure was solved in approximation. Thereform the positional parameters of the Cl, C, and O atoms followed. The refinement of the atomic positions was done with SHELX-76. Difference Fourier maps were calculated and anisotropic temperature factors were refined for all atoms except the hydrogen atoms. The hydrogen positional parameters could be taken from the difference Fourier maps, and thermal parameters of H were refined isotropically.

The data of the unit cell of α-TKN are given in Table 1. Positional and thermal parameters of the atoms in the unit cell of α-TKN are summarized in Table 2. The intramolecular distances are shown in Fig. 2 and the intramolecular angles in Figure 3. Table 3 lists the intermolecular contacts in the lattice of α-TKN.

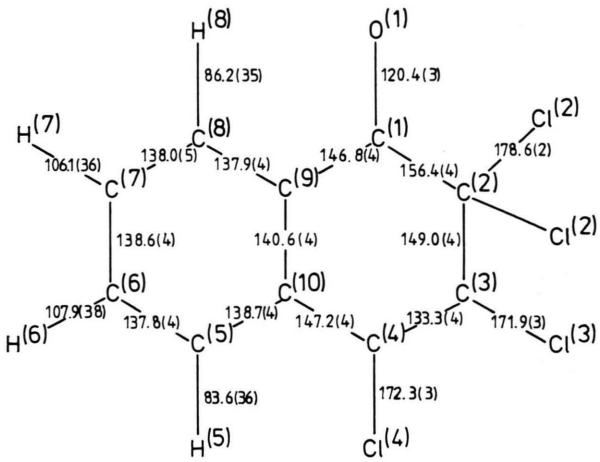


Fig. 2. Intramolecular bond distances (in pm) in a 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN) molecule.

Single Crystal ^{35}Cl NQR on 2,3,4,4-Tetrachloro-1-oxo-1,4-dihydronaphthaline (β-TKN)

In Fig. 4, we first show the numbering of the atoms in β-TKN.

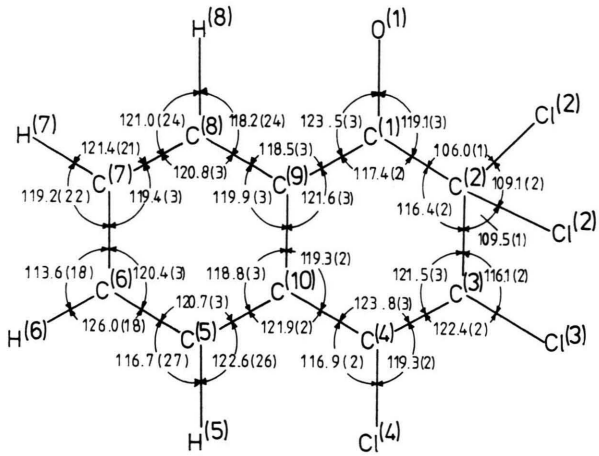


Fig. 3. Intramolecular bond angles (in angular degrees) in a 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN) molecule.

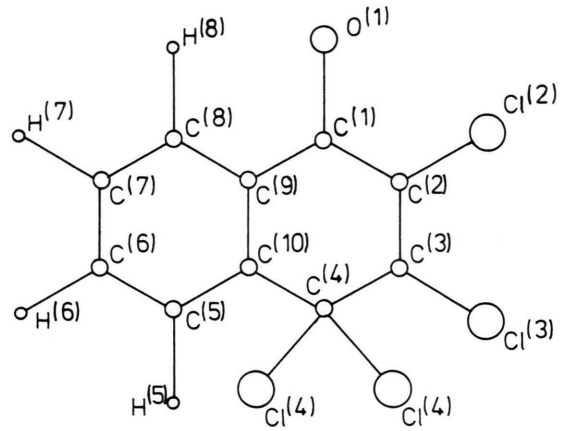


Fig. 4. Numbering of the atoms in a 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthaline (β-TKN) molecule.

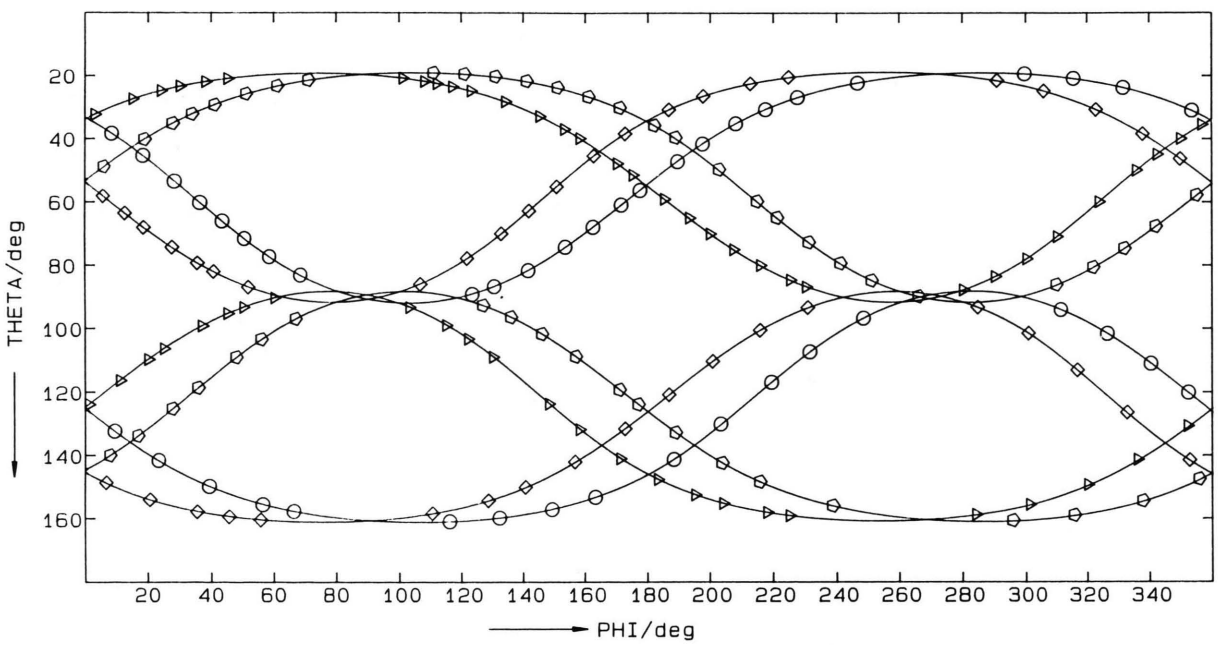


Fig. 5. Zero splitting cones of the ^{35}Cl NQR Zeeman spectrum in 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthaline (β-TKN) for $Cl^{(4)}$ at 297 K. The angles ϑ and φ are given with respect to the laboratory system (x', y', z') (see Figure 1). Symbols ◇, ○, △, ⬠: four symmetry correlated cones for $Cl^{(4)}$.

The zero splitting cones of β-TKN are drawn in Fig. 5 for the higher-frequency line $\nu_1 = \nu(^{35}Cl^{(4)})$ and in Fig. 6 for the two lower-frequency lines $\nu_2 = \nu(^{35}Cl^{(2)})$ and $\nu_3 = \nu(^{35}Cl^{(3)})$. The angles ϑ and φ describe the azimuthal and equatorial angles and correspond to the cartesian system built up by the three Helmholtz coil pairs of the 4π goniometer (x', y', z'); φ is the angle in the (x', y')-plane.

The transformation of the EFGT's into the coordinate system ***a***, ***b***, ***c*** (crystal system ≡ orthogonal axes system X, Y, Z; see Fig. 1) has been carried out using the symmetry elements of the unit cell (three mirror

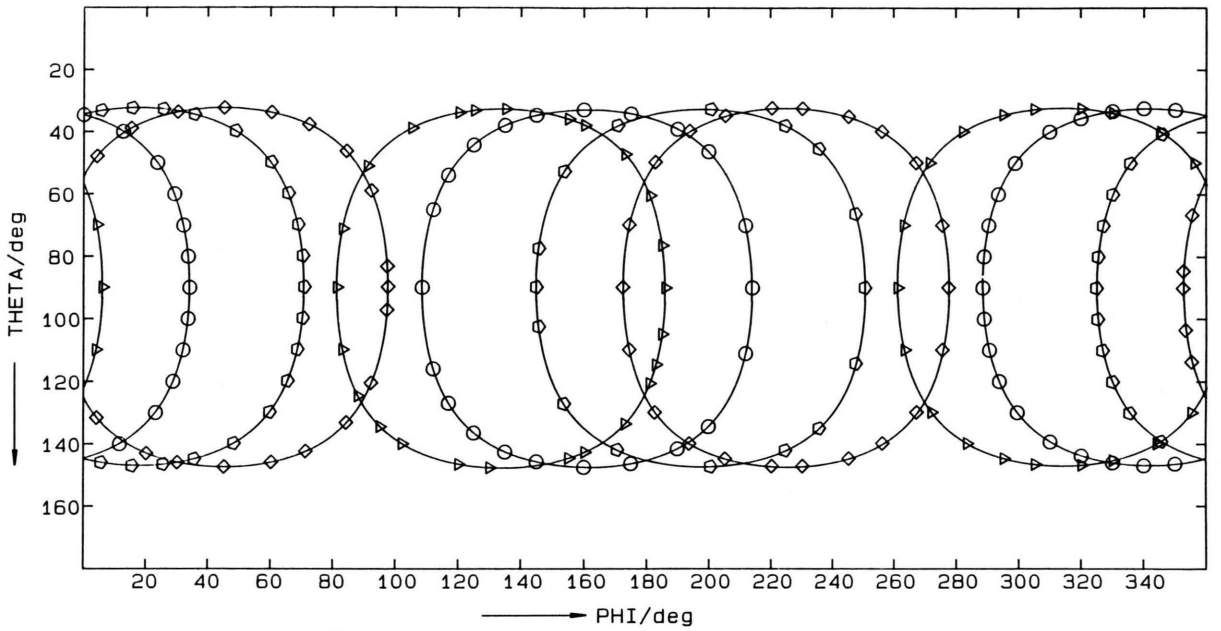


Fig. 6. Zero splitting cones of the ^{35}Cl NQR Zeeman spectrum in 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthaline (β-TKN) for $Cl^{(2)}$ and $Cl^{(3)}$ at 297 K. △, ◇: $Cl^{(2)}$, ○, ⬠: $Cl^{(3)}$.

planes) which are also obeyed by the EFGT's. Four cones are seen for $Cl^{(4)}$ (Fig. 5) and two cones for each of the sp^2 carbon bound chlorine atoms, $Cl^{(2)}$ and $Cl^{(3)}$ (Figure 6). Owning to the 4π geometry of the Zeeman goniometer the symmetry-related cone, created by the operation $\bar{1}$, is determined for each cone, too. These cones also occur in NQR spectroscopy in the absence of a centre of symmetry, introduced through the property of the EFGT to be a second rank tensor.

From the zero splitting cones the principal axes of the EFGT, their direction cosines and the asymmetry parameters η are calculated. With the values of η and the resonance frequencies in zero magnetic field, the nuclear quadrupole coupling constants (NQCC's) e^2Qqh^{-1} (^{35}Cl) are found from the relation for $I=3/2$

$$\nu(m=\pm 1/2 \rightleftarrows m=\pm 3/2) = \tfrac{1}{2}e^2Qqh^{-1}(1+\eta^2/3)^{1/2}. \quad (1)$$

The results are given in Table 4. The set of the direction cosines (λ, μ, ν) in Table 5 is given with respect to the crystal system (the symmetry-related cones and C–Cl bond directions created by $\bar{1}$ are not listed). The corresponding bond directions $C^{(j)}$–$Cl^{(j)}$ are included.

Table 3. Intermolecular contacts d/pm < 400 in 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN) ($\parallel$ = distances between atoms in the same plane and $\perp$ = distances between atom in different planes. The planes are located at $y=0.25$ and $y=0.75$). For the intramolecular distances and angles see Figs. 2 and 3.

$Cl^{(2)}\cdots Cl^{(3)}$	358.7	$\perp$	$Cl^{(3)}\cdots Cl^{(4)}$	388.5	$\perp$
$Cl^{(2)}\cdots O^{(1)}$	364.5	$\perp$	$Cl^{(4)}\cdots C^{(7)}$	363.2	$\parallel$
$Cl^{(2)}\cdots C^{(7)}$	379.0	$\perp$	$Cl^{(4)}\cdots C^{(4)}$	366.2	$\perp$
$Cl^{(2)}\cdots C^{(5)}$	379.4	$\parallel$	$Cl^{(4)}\cdots C^{(3)}$	371.3	$\perp$
$Cl^{(2)}\cdots C^{(6)}$	385.5	$\parallel$	$Cl^{(4)}\cdots Cl^{(4)}$	374.8	$\perp$
$Cl^{(2)}\cdots C^{(6)}$	393.5	$\perp$	$Cl^{(4)}\cdots C^{(8)}$	396.2	$\parallel$
$Cl^{(3)}\cdots C^{(8)}$	385.3	$\parallel$	$O^{(1)}\cdots C^{(6)}$	362.5	$\perp$
$Cl^{(3)}\cdots O^{(1)}$	387.0	$\parallel$	$O^{(1)}\cdots C^{(6)}$	375.3	$\parallel$

Table 4. ^{35}Cl NQR frequencies, nuclear quadrupole coupling constants e^2Qqh^{-1} (^{35}Cl), and asymmetry parameters η(^{35}Cl) for 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthaline (β-TKN) at $T=297$ K. The deviations are given in parenthesis.

Atom	NQR line	ν(^{35}Cl) / MHz	e^2Qqh^{-1}(^{35}Cl) / MHz	η(^{35}Cl)
$Cl^{(2)}$	ν_2	37.442(3)	74.469(6)	0.1835(24)
$Cl^{(3)}$	ν_3	36.854(3)	73.083(6)	0.1601(19)
$Cl^{(4)}$, $Cl^{(4')}$	ν_1	38.685(3)	77.307(6)	0.0695(20)

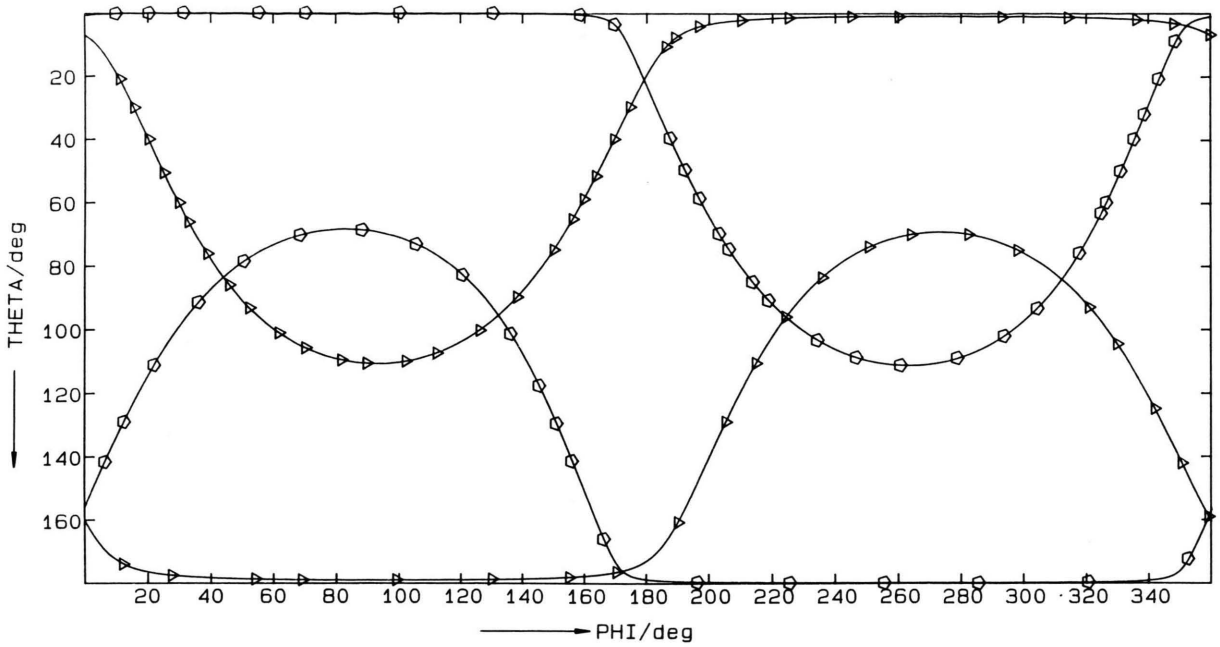


Fig. 7. Zero splitting cones of the ^{35}Cl NQR Zeeman spectrum in 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronapthaline (α-TKN) for $Cl^{(2)}$ at 290 K. Symbols △, ⬠: two symmetry correlated cones for $Cl^{(2)}$.

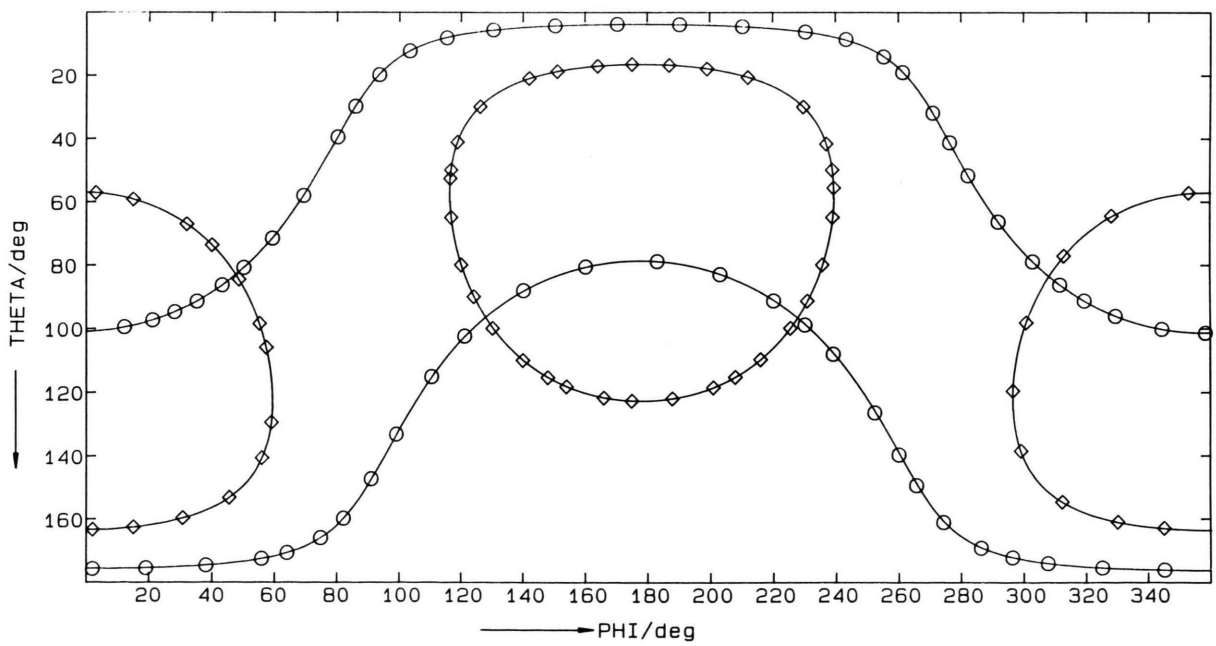


Fig. 8. Zero splitting cones of the ^{35}Cl NQR Zeeman spectrum in 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN) for $Cl^{(3)}$ and $Cl^{(4)}$ at 290 K. ◇: $Cl^{(3)}$, ○: $Cl^{(4)}$.

Table 5. Direction cosines of the principal axes Φ_{ii}^{j} ($i = x, y, z$ and j = number of the chlorine atom = 2, 3, 4) and the bond directions $C^{(j)}-Cl^{(j)}$ ($j = 2, 3, 4$), resp. C–O, with respect to the crystal axes ([100] ≙ X, [010] ≙ Y, [001] ≙ Z) in 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthaline (β-TKN) at 297 K.

Atom	Φ_{ii}	λ	μ	ν
$Cl^{(4)}$	Φ_{xx}^{4}	−0.09194	0.56897	−0.81682
	Φ_{yy}^{4}	−0.98583	−0.16644	0.01923
	Φ_{zz}^{4}	−0.13889	0.80519	0.57653
$Cl^{(2)}$	Φ_{xx}^{2}	0.00062	1.00000	−0.00077
	Φ_{yy}^{2}	0.71415	−0.00098	−0.69998
	Φ_{zz}^{2}	−0.69998	−0.00012	−0.71416
$Cl^{(3)}$	Φ_{xx}^{3}	−0.00066	1.00000	−0.00170
	Φ_{yy}^{3}	−0.30747	−0.00172	−0.95156
	Φ_{zz}^{3}	−0.95156	0.00023	0.30747
Bond				
$C^{(j)}-X^{(j)}$ (X = Cl, O)				
$C^{(2)}-Cl^{(2)}$		−0.68441	0.00000	−0.72911
$C^{(3)}-Cl^{(3)}$		−0.95604	0.00000	0.29326
$C^{(4)}-Cl^{(4)}$		−0.16333	0.80671	0.56791
$C^{(1)}-O^{(1)}$		0.22786	0.00000	−0.97370

Table 7. Direction cosines of the principal axes Φ_{ii}^{j} ($i = x, y, z$ and j = number of the chlorine atom = 2, 3, 4) and the bond directions $C^{(j)}-Cl^{(j)}$ ($j = 2, 3, 4$), resp. C–O, with respect to the orthogonal axes system (X, Y, Z) in 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN) at 290 K.

Atom	Φ_{ii}	λ	μ	ν
$Cl^{(2)}$	Φ_{xx}^{2}	−0.10260	0.57673	0.81044
	Φ_{yy}^{2}	0.99184	0.00367	0.12744
	Φ_{zz}^{2}	0.07566	0.81692	−0.57177
$Cl^{(3)}$	Φ_{xx}^{3}	−0.00058	−0.99999	−0.00126
	Φ_{yy}^{3}	−0.36921	0.00140	−0.92933
	Φ_{zz}^{3}	0.92934	−0.00009	−0.36922
$Cl^{(4)}$	Φ_{xx}^{4}	−0.00268	−1.00000	0.00205
	Φ_{yy}^{4}	0.64224	−0.00331	−0.76649
	Φ_{zz}^{4}	0.76649	−0.00074	0.64224
Bond				
$C^{(j)}-X^{(j)}$ (X = Cl, O)				
$C^{(2)}-Cl^{(2)}$		0.06962	0.81488	−0.57544
$C^{(3)}-Cl^{(3)}$		0.92756	0.00000	−0.37366
$C^{(4)}-Cl^{(4)}$		0.76902	0.00000	0.63922
$C^{(1)}-O^{(1)}$		−0.77370	0.00000	−0.63356

Table 6. ^{35}Cl NQR frequencies, nuclear quadrupole coupling constants $e^2Qqh^{-1}(^{35}Cl)$, and asymmetry parameters $\eta(^{35}Cl)$ for 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN) at $T = 290$ K. The deviations are given in parenthesis.

Atom	NQR line	$\nu(^{35}Cl)$ / MHz	$e^2Qqh^{-1}(^{35}Cl)$ / MHz	$\eta(^{35}Cl)$
$Cl^{(2)}$, $Cl^{(2')}$	ν_1	38.297(3)	76.501(6)	0.0855(1)
$Cl^{(3)}$	ν_2	36.943(3)	73.700(6)	0.1231
$Cl^{(4)}$	ν_3	36.311(3)	72.314(6)	0.1600

Single Crystal ^{35}Cl NQR on 2,2,3,4-Tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN)

Figure 7 shows the zero splitting cones of the ^{35}Cl NQR Zeeman spectrum for the higher-frequency line $\nu_1 = \nu(^{35}Cl^{(2)})$, and in Fig. 8 the cones are plotted for the two lower-frequency lines $\nu_2 = \nu(^{35}Cl^{(3)})$ and $\nu_3 = \nu(^{35}Cl^{(4)})$ (in projection with respect to the laboratory system x', y', z'). They are related pairwise by the axis 2_1 of the space group C_{2h}^{2}-$P2_1/m$ and by the centre of symmetry. The mirror plane m is perceived, too.

The laboratory system is transformed into an orthogonal coordinate system be using the symmetry elements of the crystal. The orientation of the laboratory system with respect to the crystal system and the orthogonal axes system is chosen in such a way that $\boldsymbol{b} \parallel Y$, $\boldsymbol{c} \parallel Z$ and $\sphericalangle(X, \boldsymbol{a}) = \beta - 90°$ (see Figure 1).

Table 6 shows the ^{35}Cl NQR frequencies, the NQCC's, and the η values of α-TKN at 290 K.

The direction cosines of the EFGT principal axes and of the corresponding bond $C^{(j)}-Cl^{(j)}$ are given with respect to the orthogonal system X, Y, Z (see Fig. 1) in Table 7.

Discussion

^{35}Cl NQR on 2,3,4,4-Tetrachloro-1-oxo-1,4-dihydronaphthaline (β-TKN)

As known from the study of ^{35}Cl EFGT's of chlorine atoms bound to carbon atoms in CCl_3 groups and aromatic systems, the direction of the main principal EFGT axis $\Phi_{zz}^{(j)}$ is dominated by the bond direction $C^{(j)}-Cl^{(j)}$. Often one finds a slight deviation between the C–Cl bond direction found from X-ray diffraction and the direction of the corresponding Φ_{zz}. A small difference between the angle $\sphericalangle(C^{(j)}-Cl^{(j)}, C^{(k)}-Cl^{(k)})$ observed by X-ray diffraction and the angle $\sphericalangle(\Phi_{zz}^{(j)}, \Phi_{zz}^{(k)})$ observed by single crystal NQR is seen, too.

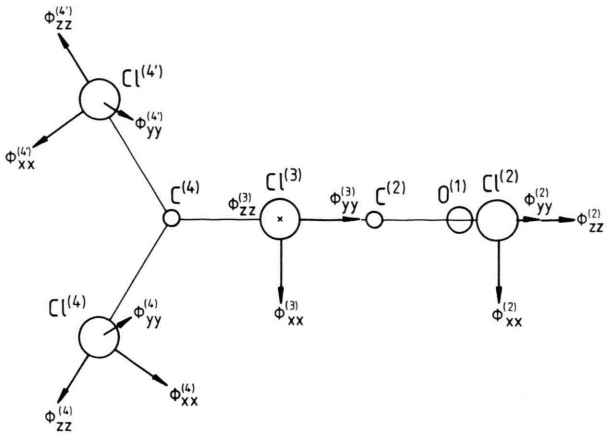


Fig. 9. Projection of a 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthaline (β-TKN) molecule along the bond $Cl^{(3)}$–$C^{(3)}$ onto the paper plane (only the ring $C^{(i)}$, $i = 1, 2, 3, 4, 9, 10$, is given). The orientations of $\Phi_{xx}^{(j)}$, $\Phi_{yy}^{(j)}$, and $\Phi_{zz}^{(j)}$ ($j = 2, 3, 4$) are shown.

Table 8. Angles between the principal axes of the EFGT's and the structure elements (bonds, normal of the ring plane $= \boldsymbol{n} \equiv \boldsymbol{b}$) in 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthaline (β-TKN).

$\sphericalangle(C^{(2)}-Cl^{(2)}, \Phi_{zz}^2)$	1.24°
$\sphericalangle(C^{(2)}-Cl^{(2)}, \Phi_{yy}^2)$	88.76°
$\sphericalangle(C^{(2)}-Cl^{(2)}, \Phi_{xx}^2)$	89.99°
$\sphericalangle(C^{(3)}-Cl^{(3)}, \Phi_{zz}^3)$	0.84°
$\sphericalangle(C^{(3)}-Cl^{(3)}, \Phi_{yy}^3)$	89.14°
$\sphericalangle(C^{(3)}-Cl^{(3)}, \Phi_{xx}^3)$	89.99°
$\sphericalangle(C^{(4)}-Cl^{(4)}, \Phi_{zz}^4)$	1.47°
$\sphericalangle(C^{(4)}-Cl^{(4)}, \Phi_{yy}^4)$	87.84°
$\sphericalangle(C^{(4)}-Cl^{(4)}, \Phi_{xx}^4)$	89.41°
$\sphericalangle(C^{(2)}-Cl^{(2)}, (C^{(3)}-Cl^{(3)})$	63.86°
$\sphericalangle(\Phi_{zz}^2, \Phi_{zz}^3)$	63.48°
$\sphericalangle(Cl^{(4)}-C^{(4)}-Cl^{(4)})$	107.55°
$\sphericalangle(\Phi_{zz}^4, \Phi_{zz}^{4'})$	107.25°
$\sphericalangle(C^{(1)}-O^{(1)}, C^{(2)}-Cl^{(2)})$	56.36°
$\sphericalangle(C^{(1)}-O^{(1)}, \Phi_{zz}^2)$	57.59
$\sphericalangle(\Phi_{zz}^2, \boldsymbol{b})$	−90.00°
$\sphericalangle(\Phi_{yy}^2, \boldsymbol{b})$	−89.95°
$\sphericalangle(\Phi_{xx}^2, \boldsymbol{b})$	0.00°
$\sphericalangle(C^{(2)}-Cl^{(2)}, \boldsymbol{b})$	90.00°
$\sphericalangle(\Phi_{zz}^3, \boldsymbol{b})$	89.98°
$\sphericalangle(\Phi_{yy}^3, \boldsymbol{b})$	−89.91°
$\sphericalangle(\Phi_{xx}^3, \boldsymbol{b})$	0.00°
$\sphericalangle(C^{(3)}-Cl^{(3)}, \boldsymbol{b})$	90.00°
$\sphericalangle(\Phi_{zz}^4, \boldsymbol{b})$	36.37°/143.63°
$\sphericalangle(\Phi_{yy}^4, \boldsymbol{b})$	−80.42°
$\sphericalangle(\Phi_{xx}^4, \boldsymbol{b})$	55.32°
$\sphericalangle(C^{(4)}-Cl^{(4)}, \boldsymbol{b})$	36.22°/143.77°

In the discussion and in the figures we handle the principal axes Φ_{ii} ($i = x, y, z$) as if they were vectors even though they have second rank tensor properties. This is done to avoid the $\pm$ signs and to correlate them directly to the direction cosines given in Tables 5 and 7, where the signs are chosen in such a way that $\Phi_{zz} \parallel C-Cl$.

Table 8 lists the angles between the directions $C^{(j)}$–$Cl^{(j)}$ and the respective EFGT axes Φ_{ii} ($i = x, y, z$). The numbering of the atoms in β-TKN was given in Figure 4.

In Fig. 9 β-TKN is viewed along the bond $Cl^{(3)}$–$C^{(3)}$, that is along $-\Phi_{zz}^{(3)}$ (only the ring $C^{(i)}$, $i = 1, 2, 3, 4, 9, 10$, is given). From the crystal symmetry (space group) and the atomic positions, planarity of the naphthalene ring system follows. In the projection shown, $C^{(3)}$ and $C^{(9)}$ are positioned behind $Cl^{(3)}$, $C^{(1)}$ behind $C^{(2)}$ and $C^{(10)}$ behind $C^{(4)}$.

From Table 8 it is seen that $\Phi_{zz}^{(j)}$ is parallel to the $C^{(j)}$–$Cl^{(j)}$ in good approximation. The deviations are in the range $0.8 \leqq \Delta/° \leqq 1.6$. Considering the principal axes Φ_{ii} ($i = x, y, z$) for $Cl^{(2)}$ and $Cl^{(3)}$ we find that Φ_{zz} and Φ_{yy} are located in the plane of the naphthalene ring (within $\leqq 0.2°$) and Φ_{xx} is perpendicular to the ring plane (within $\leqq 0.15°$). The deviations are in the range of the accuracy of the measurements. For $Cl^{(4)}$ the angles between the Φ_{zz} and the normal of the naphthalene ring ($\equiv \boldsymbol{b}$) are 36.4° respectively 143.6°. The respective bond angles (normal $\boldsymbol{n}$ of the plane, $C^{(4)}$–$Cl^{(4)}$) and (normal $\boldsymbol{n}$ of the plane, $C^{(4)}$–$Cl^{(4')}$) are 36.22° and 143.77°, respectively.

These results of the single crystal ^{35}Cl NQR on β-TKN are consistent with the mirror plane of the space group D_{2h}^{16}-Pnma.

The η-values of $Cl^{(2)}$ and $Cl^{(3)}$ (see Table 5) are in the range usually found for chlorine atoms bound to sp^2 carbon atoms [9–12] ($0.117 \leqq \eta \leqq 0.216$). The η-value of $Cl^{(4)}$, bound to a sp^3 carbon atom, is 0.0695 (other CCl_2 groups [9–12]: $0.008 \leqq \eta \leqq 0.056$).

^{35}Cl NQR and Crystal Structure of 2,2,3,4-Tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN)

Table 9 shows the angles between the bond directions $C^{(j)}$–$Cl^{(j)}$ and the corresponding EFGT axes Φ_{ii} ($i = x, y, z$).

In Fig. 10, α-TKN is projected along the bond $Cl^{(3)}$–$C^{(3)}$, that is along the $-\Phi_{zz}^{(3)}$ axis (only the ring $C^{(i)}$, $i = 1, 2, 3, 4, 9, 10$, is shown). As in Fig. 9, $C^{(3)}$ and $C^{(9)}$ are located behind $Cl^{(3)}$ and $C^{(1)}$ behind $C^{(2)}$.

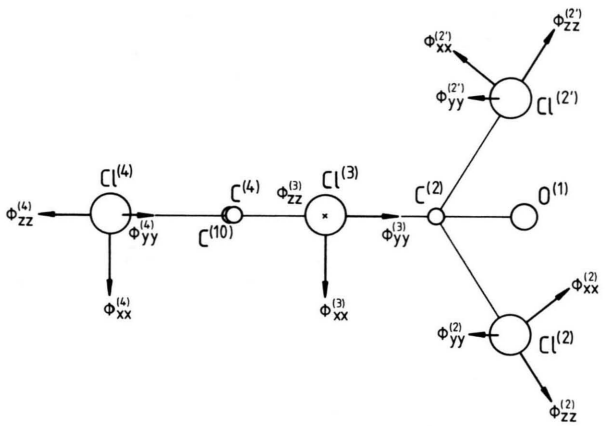


Fig. 10. Projection of a 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN) molecule along the bond $Cl^{(3)}-C^{(3)}$ onto the paper plane (only the ring $C^{(i)}$, $i = 1, 2, 3, 4, 9, 10$, is given). The orientations of $\Phi_{xx}^{(j)}$, $\Phi_{yy}^{(j)}$, and $\Phi_{zz}^{(j)}$ ($j = 2, 3, 4$) are shown.

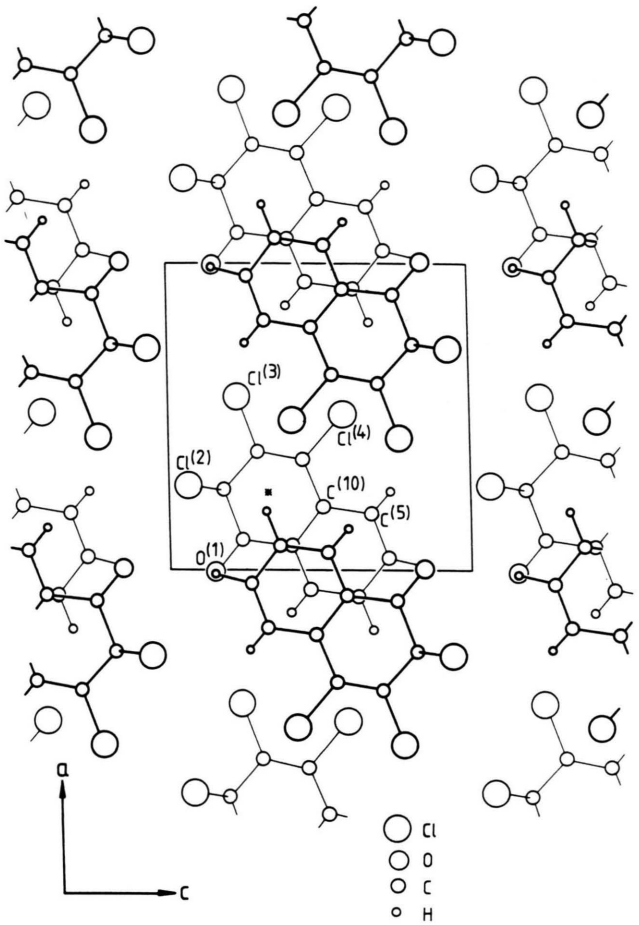


Fig. 11. Projection of the crystal structure of 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN) along the ***b***-axis onto the plane (***ac***). A few atoms of the molecule for which the coordinates are given in Table 2 are named (the molecule is marked by *).

Again, the EFGT principal axes (Φ_{zz}) are within $\leqq 0.4°$ parallel to the respective C–Cl bond. The Φ_{zz} and Φ_{yy} of the chlorines, $Cl^{(3)}$ and $Cl^{(4)}$ are located in the plane of the naphthalene ring (deviations $\leqq 0.2°$) and Φ_{xx} is perpendicular to this plane ($\sphericalangle(\Phi_{xx}^{(j)}, \boldsymbol{b}) \leqq 0.2°$). The angle between the Φ_{zz} of $Cl^{(2)}$ and the normal $\boldsymbol{n}$ of the naphthalene ring ($\equiv \boldsymbol{b}$) is 35.2° respectively 144.8° (bond angles $\sphericalangle(\boldsymbol{b}, C-Cl^{(2)}) = 35.42°$ and $\sphericalangle(\boldsymbol{b}, C-Cl^{(2')}) = 144.57°$). The principal axes Φ_{ii} ($i = x, z$) of $Cl^{(2)}$ are located in the plane through the atoms of the CCl_2 group (deviations $-0.6° \ldots -0.1°$), and Φ_{yy} is perpendicular to this plane ($\sphericalangle(\Phi_{yy}, \boldsymbol{b}) = 89.3° \ldots 89.6°$). These results of the ^{35}Cl Zeeman split NQR are compatible with a mirror plane (which is shown in the space group $P2_1/m$).

The η-values of $Cl^{(3)}$ and $Cl^{(4)}$ (see Table 6) are in the range usually found for chlorine atoms bound to sp^2 carbon atoms, respectively $\eta(Cl^{(2)})$ is comparable to the values of Cl atoms bound to sp^3 C atoms [9–12].

The ^{35}Cl NQR frequencies of the polycrystalline α-TKN were measured in 77 K–362 K and the linewidths of ν_i ($i = 1, 2, 3$) were determined: $\Delta\nu_{1/2}(\nu_1 \leftrightarrow Cl^{(2)}) = 6.2 \ldots 7.9$ kHz, $\Delta\nu_{1/2}(\nu_2 \leftrightarrow Cl^{(3)}) = 3.5 \ldots 4.4$ kHz and $\Delta\nu_{1/2}(\nu_3 \leftrightarrow Cl^{(4)}) = 4.6 \ldots 6.6$ kHz. There is no sign that the higher-frequency line $\nu_1 = \nu(^{35}Cl^{(2)})$ has a doublet structure.

The crystal structure of α-TKN is reported in [5]. The authors described the structure within the polar space group C_2^2-$P2_1$, with $Z = 2$. The least squares refinement leads to a reliability factor $R = 3.9\%$ ($R_w = 5.3\%$) for the arrangement in $P2_1$. This and the nonlinear optical effect of the second harmonic generation (SHG) of laser light with an efficiency factor of 5 higher than in α-quartz observed by Zweegers et al. [5] were the reasons that the space groaup C_{2h}^2-$P2_1/m$ has been rejected by the authors.

We have repeated the crystal structure determination and found $R = 4.1\%$ ($R_w = 5.1\%$) in $P2_1/m$ and $R = 3.95\%$ ($R_w = 4.79\%$) in $P2_1$. The intramolecular geometry (bond distancies and bond angles, respectively) we determined (space group $P2_1/m$) is shown in Figs. 2 and 3. There are several intermolecular contacts observed within the van der Waals distances (see Table 3).

Table 9. Angles between the principal axes of the EFGT's and the structure elements (bonds, normal of the ring plane $= \boldsymbol{n} \equiv \boldsymbol{b}$) in 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN).

$\sphericalangle (C^{(2)}-Cl^{(2)}, \Phi^2_{zz})$	0.40°
$\sphericalangle (C^{(2)}-Cl^{(2)}, \Phi^2_{yy})$	−89.93°
$\sphericalangle (C^{(2)}-Cl^{(2)}, \Phi^2_{xx})$	−89.80°
$\sphericalangle (C^{(3)}-Cl^{(3)}, \Phi^3_{zz})$	0.29°
$\sphericalangle (C^{(3)}-Cl^{(3)}, \Phi^3_{yy})$	−89.73°
$\sphericalangle (C^{(3)}-Cl^{(3)}, \Phi^3_{xx})$	89.99°
$\sphericalangle (C^{(4)}-Cl^{(4)}, \Phi^4_{zz})$	0.19°
$\sphericalangle (C^{(4)}-Cl^{(4)}, \Phi^4_{yy})$	89.77°
$\sphericalangle (C^{(4)}-Cl^{(4)}, \Phi^4_{xx})$	−89.96°
$\sphericalangle (Cl^{(2)}-C^{(2)}-Cl^{(2)})$	109.15°
$\sphericalangle (\Phi^2_{zz}, \Phi^{2'}_{zz})$	109.55°
$\sphericalangle (C^{(3)}-Cl^{(3)}, C^{(4)}-Cl^{(4)})$	61.67°
$\sphericalangle (\Phi^3_{zz}, \Phi^4_{zz})$	61.62°
$\sphericalangle (C^{(1)}-O^{(1)}, C^{(2)}-Cl^{(2)})$	71.89°
$\sphericalangle (C^{(1)}-O^{(1)}, \Phi^2_{zz})$	72.31°
$\sphericalangle (C^{(2)}-Cl^{(2)}, \boldsymbol{b})$	35.42°/144.57°
$\sphericalangle (\Phi^2_{zz}, \boldsymbol{b})$	35.22°/144.78°
$\sphericalangle (\Phi^2_{yy}, \boldsymbol{b})$	89.78°
$\sphericalangle (\Phi^2_{xx}, \boldsymbol{b})$	54.77°
$\sphericalangle (C^{(3)}-Cl^{(3)}, \boldsymbol{b})$	90.00°
$\sphericalangle (\Phi^3_{zz}, \boldsymbol{b})$	−90.00°
$\sphericalangle (\Phi^3_{yy}, \boldsymbol{b})$	−89.93°
$\sphericalangle (\Phi^3_{xx}, \boldsymbol{b})$	0.08°
$\sphericalangle (C^{(4)}-Cl^{(4)}, \boldsymbol{b})$	90.00°
$\sphericalangle (\Phi^4_{zz}, \boldsymbol{b})$	−89.96°
$\sphericalangle (\Phi^4_{yy}, \boldsymbol{b})$	−89.82°
$\sphericalangle (\Phi^4_{xx}, \boldsymbol{b})$	− 0.20°

In Fig. 11 the arrangement of the two molecules within the unit cell is shown in projection along the ***b***-axis onto the plane (***ac***).

Based on the results of the ^{35}Cl NQR experiments we favour the centrosymmetric space group $P2_1/m$. The mirror plane in the crystal symmetry is proved within the accuracy of the Zeeman NQR spectroscopy by the orientations found for $\Phi^{(2,2')}_{ii}$. Also the fact that the linewidths $\Delta\nu_{1/2}$ of $\nu(^{35}Cl^{(2,2')})$ is comparable with $\Delta\nu_{1/2}$ of $\nu(^{35}Cl^{(3)})$ and of $\nu(^{35}Cl^{(4)})$ supports the assumption of crystallographic equivalence of $Cl^{(2)}$ and $Cl^{(2')}$.

It cannot be excluded that the intensive laser light together with a weak photochromy of α-TKN may introduce local polarity leading to the nonlinear optical effect observed by Zweegers et al. [5].

The question whether a centre of symmetry is present or absent, is in many cases not a simple one. From X-ray diffraction it is hard to decide, praticularly if the deviation from a centrosymmetric arrangement in the unit cell is very small. This is the case for α-TKN as one finds in looking on the positional parameters of the crystal structure description in C_2^2-$P2_1$ [5]. For instance, the y positional parameters y of $C^{(1)} \cdots C^{(10)}$, $O^{(1)}$, $Cl^{(3)}$, $C^{(4)}$ are 0.781 ± 0.005 for $P2_1$ the standard deviation is given to 0.002) [5] and 0.7500(0) for $P2_1/m$. The decision by the minimum of the reliability factor R may be misleading; the introduction of new degrees of freedom by cancelling the element $\bar{1}$ easily lowers R. The contradiction: centre of symmetry in α-TKN or not, is given by the oppposite answer of ^{35}Cl single crystal NQR and the nonlinear optical effects. An experiment in which the strength of the ***E***-field of the light is varied and thereby the nonlinearity of the crystal is measured, may give an answer about an induced local acentricity in photochromic crystals.

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