^{35}Cl NQR, Crystal Structure, and C–Cl Bond Length of Cyclohexadienones

Stefanie Brummer*, Helmut Paulus, and Alarich Weiss
Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt, Darmstadt, West Germany

Z. Naturforsch. **43a,** 873–884 (1988); received July 20, 1988

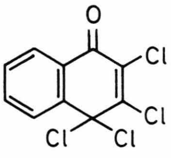
The ^{35}Cl NQR spectra of 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 and 2,4,4,6-tetrachloro-cyclohexadiene-2,5-one-1 were studied from 77 K up to the decomposition temperature, their crystal structure having been determined by single crystal X-ray diffraction. The first compound crystallizes in the monoclinic space group $C_{2h}^2-P2_1/m$ with two molecules in the unit cell. The lattice constants are $a = 887.2\,(3)$ pm, $b = 704.8\,(3)$ pm, $c = 824.0\,(3)$ pm, $\beta = 96.10(1)^\circ$. The second compound crystallizes orthorhombic, space group D_{2h}^{18}–Cmca, with 8 molecules in the unit cell which has the dimensions $a = 711.2(2)$ pm, $b = 1388.4(3)$ pm, $c = 1729.8(4)$ pm. The structures determined belong to the stable phases of the title compounds as seen from the NQR spectra as a function of temperature which show no sign for a phase transition between the melting point and 77 K.

In both title compounds the molecules are planar. Their symmetry is compared with other chloro-cyclohexadiene-2,5-ones-1 and chloro-cyclohexadiene-2,5-diones-1,4.

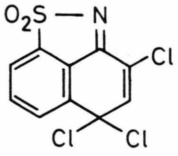
The intramolecular distances $d_{(C-Cl)}$ of the sp^2 carbon atoms and the ^{35}Cl NQR frequencies assigned to the corresponding Cl atoms correlate quite well according to the theory: $\nu(^{35}\mathrm{Cl}) \sim (d_{(C-Cl)})^{-3}$. The relation is $\nu(^{35}\mathrm{Cl})/\mathrm{MHz} = 2 + 174 \cdot 10^6 \cdot (d/\mathrm{pm})^{-3}$.

Introduction

Some derivatives of naphthaline show in the crystalline state photochromy and recently crystal structure studies and ^{35}Cl nuclear quadrupole resonance, NQR, experiments on 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthaline (*β*-TKN) and 2,4,4-trichloro-1,4-dihydronaphth[1,8-cd]isothiazole-1,1-dioxide (TCNS) have been reported [1]. The photochromy of these compounds, the structures of which are shown below, is connected with the dienone part of the molecules.

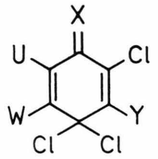


β-TKN



TCNS

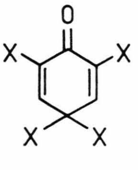
It was of interest, to study the crystal structure and the ^{35}Cl NQR spectra of solids, which have chemically similar structure, e.g.



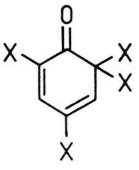
X = O, N–
Y = H, Cl, CH_3
U = Cl, –CH=CH–
W = H, Cl, CH_3, –CH=CH–

In the following, we report structural and NQR spectroscopical studies on 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ① and 2,4,4,6-tetrachloro-cyclohexadiene-2,5-one-1 ②.

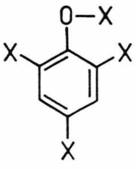
The structure of compound ② and of several related substances is discussed in literature at length. The tetrachloro-cyclohexadiene-2,5-one-1, called in early days trichlorophenol-chlorine, was first prepared by Benedikt [2]. Three different structure formulas were proposed:



I



II



III

---

* Part of the Dissertation (D 17) of Stefanie Brummer.

Reprint requests to Prof. Dr. Al. Weiss, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, D-6100 Darmstadt.

0932-0784 / 88 / 1000-0873 $ 01.30/0. – Please order a reprint rather than making your own copy.

Fort [3] proved by UV-, Raman-, and IR-spectroscopical studies of a large number of compounds, related to the one studied by Benedikt, that only the semiquinoid structures (I and II) are realized. Sørensen and Jerslev [4] reported the crystal structures of 2,4,4,6-tetrahalogeno-cyclohexadiene-2,5-ones-1 (I with X = Cl, Br). They described nine different para-semiquinoid cylcohexadienones in the polar space group C_{2v}^{17} – Aba2, with 8 molecules in the unit cell. A different finding is preported here for one of the compounds studied in [4]. It will be shown, that the ^{35}Cl NQR frequencies, C–Cl bond lengths, and molecular symmetry in the solid state are connected within the group of cyclohexadienones.

Experimental

Synthesis

2,4,4,6-Tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ① was synthesized from 2,4-dichloro-3,5-dimethyl-1-phenol, $2,4\text{-}Cl_2\text{-}3,5\text{-}(CH_3)_2\text{-}C_6HOH$, following the prescription of Morita and Dietrich [5]. A solution of the phenol in glacic acetic acid was saturated with Cl_2 at 50–60 °C. ① was recrystallized from methanol and CCl_4; colourless, monoclinic, prismatic crystals were formed with a melting point of 105–106 °C (105–106 °C [5]); yield: 63%. The pyknometric density is 1.68 Mg m^{-3}.

2,4,4,6-Tetrachloro-cyclohexadiene-2,5-one-1 ② was prepared, following the work of Švec et al. [6]. 2,3,4-Trichloro-1-phenol, $2,3,4\text{-}Cl_3\text{-}C_6H_2OH$, was dissolved in 75% acetic acid and chlorinated at 80 °C. By cooling to 0 °C, ② precipitated. Recrystallization from CCl_4 and n-hexane gives colourless prisms, melting point (123 ± 1) °C (123.2 °C [6]); yield: 50% (50.7% [6]). The pyknometrically measured density is 1.80 Mg m^{-3} (1.85 Mg m^{-3} [4]).

^{35}Cl NQR

The ^{35}Cl nuclear quadrupole resonance spectra for the compounds ① and ② were recorded on polycrystalline samples with a superregenerative NQR spectrometer as a function of temperature. The experimental conditions were: Zeeman modulation, variable quench frequency, time constant 10 s. Different methods were used to generated the various temperatures at the sample site (temperature range and estimated error in T, method): $300 \leqq (T \pm 0.5)/\mathrm{K} \leqq 400$, oil thermostate; $200 \leqq (T \pm 0.3)/\mathrm{K} \leqq 300$, methanol thermostate; $120 \leqq (T \pm 0.8)/\mathrm{K} \leqq 200$, thermostatized nitrogen gas stream; (77 ± 0.3) K, liquid nitrogen bath. The temperature at the sample site was measured via a copper-constantan thermocouple. The frequencies determined are accurate to ± 0.005 MHz; this limitation is due to the NQR line width.

Crystal Structure Analysis

The structure of the compounds ① and ② were determined by single crystal technique at room temperature using MoKα-radiation. In Table 1 the experimental details and crystallographic data (lattice constants, space group, etc.) are given.

Results

Crystal Structure of 2,4,4,6-Tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ① and of 2,4,4,6-Tetrachlorocyclohexadiene-2,5-one-1 ②

By using appropriate computer programs, SHELX-86, the crystal structures were solved in approximation. Therefrom the positions of 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 hydrogens. The hydrogen positions could be taken from the difference Fourier maps and isotropic temperature factors were refined for them. In Table 1 the data for the unit cell of ① and ② are given. Table 2 lists the positional and thermal parameters of the atoms in the unit cell of ①, whereas in Table 3 these parameters are given for compound ②.

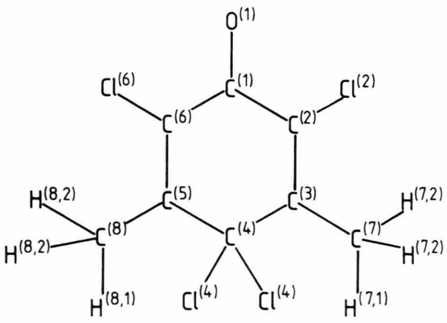
^{35}Cl NQR

Compound ① gives a three line ^{35}Cl NQR spectrum thoughout the whole temperature range covered ($77 \leqq T/\mathrm{K} \leqq 372$). In Fig. 1, the frequencies observed, ν_1, ν_2, and ν_3, are plotted as a function of temperature. The curves are smooth within the whole range and the intensity ratio is constant $I(\nu_1):I(\nu_2):I(\nu_3) = 2:1:1$. In Fig. 1 also the ^{35}Cl NQR frequencies of ② are plotted as function of temperature. Again a three line spectrum is found, ν_1, ν_2, and ν_3, and again the intensity range is, throughout the temperature region covered, $I(\nu_1):I(\nu_2):I(\nu_3) = 2:1:1$; again there is no discontinuity in the $\nu = f(T)$ curves.

Table 1. Experimental conditions of the crystal structure determination and crystallographic data of 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ① and 2,4,4,6-tetrachloro-cyclohexadiene-2,5-one-1 ②.

Compound	①	②
Formula	$Cl_4(CH_3)_2C_6O$	$Cl_4H_2C_6O$
Molar mass, g/mol	259.95	231.89
Crystal habitus	prism	prism
Size, mm^3	$0.28 \times 0.44 \times 0.46$	$0.3 \times 0.3 \times 0.9$
Colour	colourless	colourless
Diffractometer	Stoe-Stadi-4	Stoe-Stadi-4
Wavelength, λ/pm	71.069 (MoKα)	71.069 (MoKα)
Monochromator	graphite	graphite
Temperature, T/K	296	295
Linear absorption coefficient, μ/m^{-1}	1021	1220
Absorption correction	empirical	numeric
Scan	$\omega/2\theta$	$\omega/2\theta$
Number of measured reflections	3530	3854
Symmetry independent reflections	1273	1064
Number of free parameters	87	65
$F(000)$	260	912
$R(F)$	0.0403	0.0345
$R_W(F)$	0.0374	0.0366
Point positions $Cl^{(4)}$, $H^{(7,2)}$, and $H^{(8,2)}$ in 4f:		$Cl^{(4)}$ in 16g:
	$x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{x}, \frac{1}{2}+y, \bar{z};$ $x, \frac{1}{2}-y, z$	$x, y, z; \bar{x}, \bar{y}, \bar{z}; x, \bar{y}, \bar{z}; \bar{x}, y, z; x, \frac{1}{2}-y, \frac{1}{2}+z;$ $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z; x, \frac{1}{2}+y, \frac{1}{2}-z; \bar{x}, \frac{1}{2}-y, \frac{1}{2}+z;$ $\frac{1}{2}+x, \frac{1}{2}+y, z; \frac{1}{2}-x, \frac{1}{2}-y, \bar{z}; x+\frac{1}{2}, \frac{1}{2}-y, \bar{z};$ $\frac{1}{2}-x, \frac{1}{2}+y, z; \frac{1}{2}+x, \bar{y}, \frac{1}{2}+z; \frac{1}{2}-x, y, \frac{1}{2}-z;$ $\frac{1}{2}+x, y, \frac{1}{2}-z; \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$
	All other atoms in 2e:	All other atoms in 8f:
	$x, \frac{1}{4}, z; \bar{x}, \frac{3}{4}, \bar{z}$	$0, y, z; 0, \bar{y}, \bar{z}; \frac{1}{2}, y, \frac{1}{2}-z; \frac{1}{2}, \bar{y}, \frac{1}{2}+z; \frac{1}{2}, \frac{1}{2}+y, z;$ $\frac{1}{2}, \frac{1}{2}-y, \bar{z}; 0, \frac{1}{2}+y, \frac{1}{2}-z; 0, \frac{1}{2}-y, \frac{1}{2}+z$
Lattice constants a/pm	887.2(2)	711.2(2)
b/pm	704.8(3)	1388.4(3)
c/pm	824.0(3)	1729.8(4)
$\beta/°$	96.10(1)	
Volume of the unit cell, $V \cdot 10^{-6}/pm^3$	512.33	1708.06
Space group	$C_{2h}^2-P2_1/m$	$D_{2h}^{18}-Cmca$
Formula units/unit cell	$Z=2$	$Z=8$
$\varrho_{calc}/(Mg\ m^{-3})$	1.685	1.804
$\varrho_{pykn}/(Mg\ m^{-3})$	1.68	1.80

Numbering of atoms in the molecule



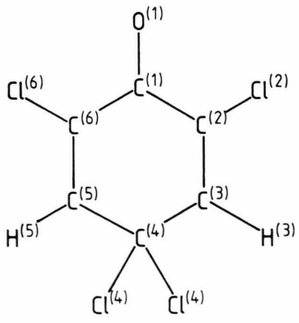


Table 2. Positional and thermal parameters (with standard deviations) of 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ①. The temperature factors are of the form

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

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}
$C^{(1)}$	0.3326(4)	0.2500(0)	0.0596(4)	635(19)	441(16)	392(18)	0(0)	15(16)	0(0)
$C^{(2)}$	0.1726(3)	0.2500(0)	−0.0129(4)	508(16)	417(15)	449(19)	0(0)	158(15)	0(0)
$C^{(3)}$	0.1281(3)	0.2500(0)	−0.1709(4)	447(15)	394(14)	479(19)	0(0)	61(14)	0(0)
$C^{(4)}$	0.2462(3)	0.2500(0)	−0.2882(4)	490(15)	484(16)	336(16)	0(0)	4(13)	0(0)
$C^{(5)}$	0.4111(3)	0.2500(0)	−0.2220(4)	427(14)	433(15)	443(19)	0(0)	50(14)	0(0)
$C^{(6)}$	0.4448(3)	0.2500(0)	−0.0618(4)	430(15)	385(14)	491(19)	0(0)	−34(14)	0(0)
$C^{(7)}$	−0.0344(4)	0.2500(0)	−0.2427(5)	446(17)	709(22)	660(26)	0(0)	−15(18)	0(0)
$H^{(7,1)}$	−0.0424(32)	0.2500(0)	−0.3727(13)	600(0)					
$H^{(7,2)}$	−0.0948(18)	0.3617(20)	−0.2009(23)	600(0)					
$C^{(8)}$	0.5264(4)	0.2500(0)	−0.3411(5)	521(19)	894(27)	597(25)	0(0)	191(19)	0(0)
$H^{(8,1)}$	0.4802(31)	0.2500(0)	−0.4661(16)	700(0)					
$H^{(8,2)}$	0.5943(19)	0.3702(20)	−0.3244(26)	700(0)					
$Cl^{(2)}$	0.0418(1)	0.2500(0)	0.1287(1)	786(6)	810(6)	659(7)	0(0)	364(5)	0(0)
$Cl^{(4)}$	0.2154(1)	0.0424(1)	−0.4143(1)	731(4)	869(5)	628(5)	−347(4)	33(4)	−67(3)
$Cl^{(6)}$	0.6314(1)	0.2500(0)	0.0244(1)	495(4)	650(5)	776(7)	0(0)	−162(5)	0(0)
$O^{(1)}$	0.3687(3)	0.2500(0)	0.2051(3)	905(19)	1124(21)	358(14)	0(0)	−22(14)	0(0)

Table 3. Positional and thermal parameters (with standard deviations) of 2,4,4,6-tetrachloro-cyclohexadiene-2,5-one-1 ②. The temperature factors are of the form

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

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}
$C^{(1)}$	0.0000(0)	0.2740(2)	0.3278(1)	343(11)	394(12)	417(13)	15(9)	0(0)	0(0)
$C^{(2)}$	0.0000(0)	0.2392(2)	0.4092(1)	434(12)	423(12)	356(12)	−32(9)	0(0)	0(0)
$C^{(3)}$	0.0000(0)	0.1468(2)	0.4284(1)	494(13)	430(13)	352(12)	20(9)	0(0)	0(0)
$H^{(3)}$	0.0000(0)	0.1269(2)	0.4887(1)	450(0)					
$C^{(4)}$	0.0000(0)	0.0702(2)	0.3687(1)	484(13)	368(12)	470(13)	33(10)	0(0)	0(0)
$C^{(5)}$	0.0000(0)	0.1029(2)	0.2865(1)	474(13)	446(13)	371(12)	−41(10)	0(0)	0(0)
$H^{(5)}$	0.0000(0)	0.0501(2)	0.2407(1)	450(0)					
$C^{(6)}$	0.0000(0)	0.1957(2)	0.2691(1)	364(10)	462(12)	327(11)	28(9)	0(0)	0(0)
$Cl^{(2)}$	0.0000(0)	0.3279(1)	0.4786(0)	964(6)	518(4)	448(4)	−125(3)	0(0)	0(0)
$Cl^{(4)}$	0.2041(1)	−0.0035(0)	0.3831(0)	648(4)	510(3)	725(4)	80(2)	−21(2)	169(2)
$Cl^{(6)}$	0.0000(0)	0.2334(1)	0.1744(0)	655(5)	708(5)	346(4)	97(3)	0(0)	0(0)
$O^{(1)}$	0.0000(0)	0.3580(1)	0.3109(1)	687(12)	405(10)	568(11)	58(8)	0(0)	0(0)

Table 4. 2,4,4,6-Tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ① and 2,4,4,6-tetrachlorohexadiene-2,5-one-1 ②. $\nu(^{35}Cl)=f(T)=\sum a_i\,T^i$; Z = number of measurements; σ = standard deviation; $T=T_2\ldots T_1$ is the temperature range of measurement.

^{35}Cl NQR line	Z	$\frac{\sigma}{kHz}$	$\frac{a_{-1}}{MHz\cdot K}$	$\frac{a_0}{MHz}$	$\frac{a_1\cdot 10^3}{MHz\cdot K^{-1}}$	$\frac{a_2\cdot 10^6}{MHz\cdot K^{-2}}$	$\frac{T}{K}$
Compound ①							
ν_1	26	3.50	0.2575	38.3787	−1.5673	−5.5716	77 ... 372
ν_2	26	3.88	2.9202	36.2862	0.14722	−6.8821	77 ... 372
ν_3	26	4.16	8.0620	36.0594	0.48674	−6.4842	77 ... 372
Compound ②							
ν_1	28	3.91	−11.8899	38.7166	−2.8099	−0.98744	77 ... 383
ν_2	28	2.94	− 8.6919	36.9867	−1.6630	−1.6367	77 ... 383
ν_3	28	3.51	−11.1238	36.8901	−2.4016	−11.1238	77 ... 383

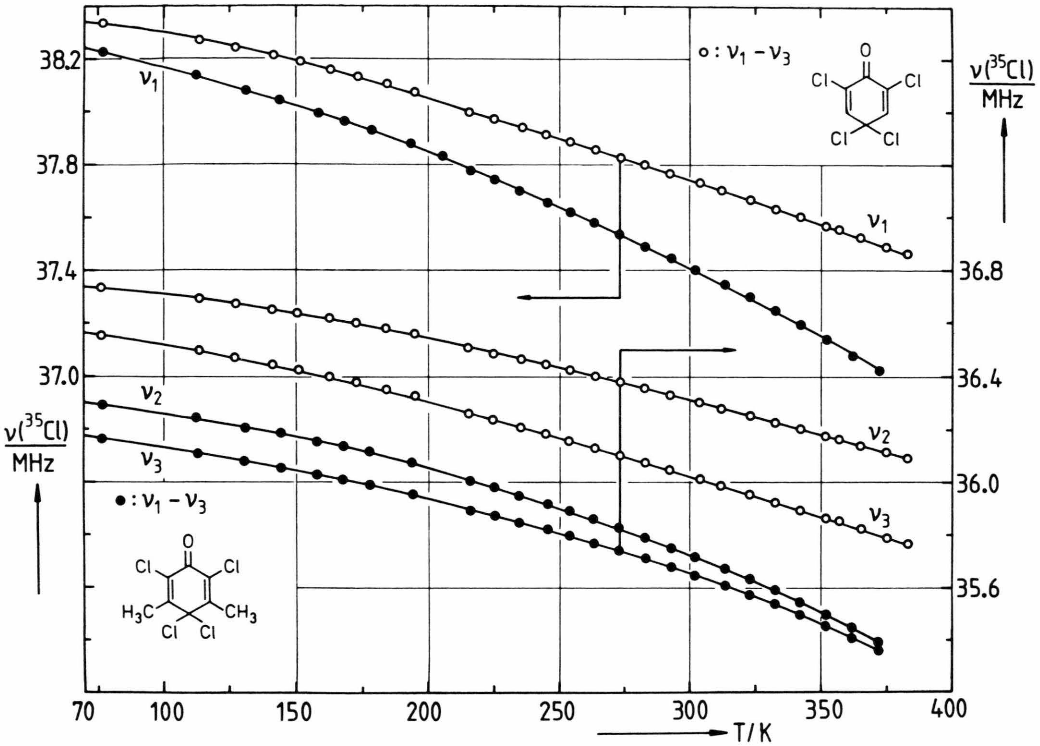


Fig. 1. ^{35}Cl NQR frequencies of 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ① and of 2,4,4,6-tetrachloro-cyclohexadiene-2,5-one-1 ② as functions of temperature. The intensity of ν_1 is twice that the intensity of ν_2 and ν_3 for both compounds.

Table 5. ^{35}Cl NQR frequencies of 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ① and 2,4,4,6-tetrachloro-cyclohexadiene-2,5-one-1 ② at 77 K and at room temperature. The frequencies are given to ±0.005 MHz. The signal to noise ratio (S/N) was determined with lock in technique, time constant = 10 s.

^{35}Cl NQR line	$\frac{T}{K}$	$\frac{\nu(^{35}Cl)}{MHz}$	$\frac{S}{N}$	$\frac{T}{K}$	$\frac{\nu(^{35}Cl)}{MHz}$	$\frac{S}{N}$
Compound ①						
ν_1	77	38.228	44	293.0	37.444	27
ν_2	77	36.293	18	292.9	35.751	10
ν_3	77	36.161	14	292.9	35.675	10
Compound ②						
ν_1	77	38.342	37	292.6	37.770	69
ν_2	77	36.738	18	292.6	36.330	35
ν_3	77	36.556	23	292.6	36.044	33

The temperature dependence of the ^{35}Cl NQR frequencies is in qualitative agreement with the theory of Bayer [7]. Following this, $\nu(^{35}Cl) = f(T)$ can be approximated by a power series:

$$\nu(^{35}Cl) = f(T) = \sum a_i \cdot T^i, \quad (-1 \leqq i \leqq +2). \qquad (1)$$

The coefficients of the power series (1) are listed in Table 4. In Table 5, frequencies at selected temperatures are given for the compounds ① and ②. The signal to noise ratio is given, too. The corresponding ^{37}Cl NQR frequencies were observed at room temperature for both compounds. The frequency ratio is

$\nu(^{35}\mathrm{Cl})/\nu(^{37}\mathrm{Cl}) = 1.269$; it was not followed up as a function of temperature.

Discussion

In the following, we shall discuss first the crystal structure and ^{35}Cl NQR spectra of 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ① and of 2,4,4,6-tetrachloro-cyclohexadiene-2,5-one-1 ②.

The crystal structure of compound ② is reported in literature [4]. The authors described the structure of several 2,4,4,6-tetrahalogeno-cyclohexadiene-2,5-ones within the polar space group C_{2v}^{17}–Aba2, with $Z = 8$. For compound ② their least squares refinement led to a reliability factor $R = 0.13$. The unit cell they propose, contains four crystallographically different Cl-atoms; the two Cl-atoms bonded to $C^{(4)}$ are inequivalent. Consequently, the ^{35}Cl NQR spectrum should show four lines with equal intensity. In contrast, we observe a three line ^{35}Cl NQR spectrum with the intensity ratio $I(\nu_1):I(\nu_2):I(\nu_3) = 2:1:1$. This intensity ratio is not observed accidentally at one temperature but throughout the temperature range $77 \leqq T/\mathrm{K} \leqq 383$. It follows: There are three different kinds of Cl-atoms in the unit cell. Since it is known that a Cl-atom bonded to an sp^2 carbon is quite different and low in its ^{35}Cl NQR frequency compared with a Cl-atom bonded to a sp^3 carbon, the two Cl-atoms in 4-position belong to the higher frequency and the intensity ratio shows their crystallographical equivalence (they are, of course, chemically equivalent in the free molecule). The ^{35}Cl NQR equivalence of the two chlorine atoms in 4-position demands a mirror plane, bisecting the angle $\mathrm{Cl}^{(4)}-\mathrm{C}^{(4)}-\mathrm{Cl}^{(4)}$, and it demands the location of $C^{(4)}$ at this plane. The ^{35}Cl NQR equivalence of the two atoms $\mathrm{Cl}^{(4)}$ cannot be produced by a twofold axis since $\mathrm{Cl}^{(6)}$ and $\mathrm{Cl}^{(2)}$ are spectroscopically inequivalent.

We have repeated the crystal structure determination of Sørensen and Jerslev [4], found the centrosymmetric space group D_{2h}^{18}-Cmca and a reliability factor $R = 3.45\%$. The size of the unit cell we determined is in agreement with the reported lattice constants [4] (our value; [4] in pm): $a = 711.2(2)$; 705, $b = 1388.4(3)$; 1385, $c = 1729.8(4)$; 1729. In the crystal structure of ② proposed in [4] the bond lengths $\mathrm{C}^{(4)}-\mathrm{Cl}^{(4)}$ are quite different within one molecule: $\mathrm{C}^{(4)}-\mathrm{Cl}^{(4)} = 175.7(22)$ pm, $\mathrm{C}^{(4)}-\mathrm{Cl}^{(4')} = 182.3(23)$ pm. This large difference is very unlikely as are the short intermolecular distances $\mathrm{O}^{(1)} \ldots \mathrm{Cl}^{(4')} = 307.8(20)$ pm and $\mathrm{O}^{(1)} \ldots \mathrm{Cl}^{(4)} = 309.9(20)$ pm. We conclude that the description of the crystal structure of 2,4,4,6-tetrachlorohexadiene-2,5-one-1 ②, as given in this paper, is correct, but we cannot exclude that there exists another phase of this compound which was studied by [4].

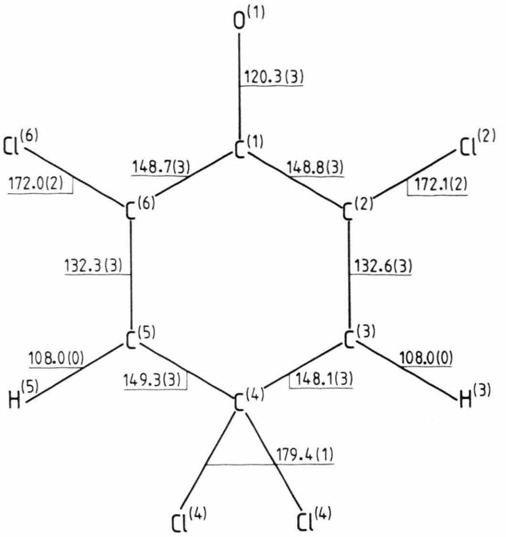


Fig. 2. Intramolecular bond distances (in pm) in the molecule 2,4,4,6-tetrachloro-cyclohexadiene-2,5-one-1 ②.

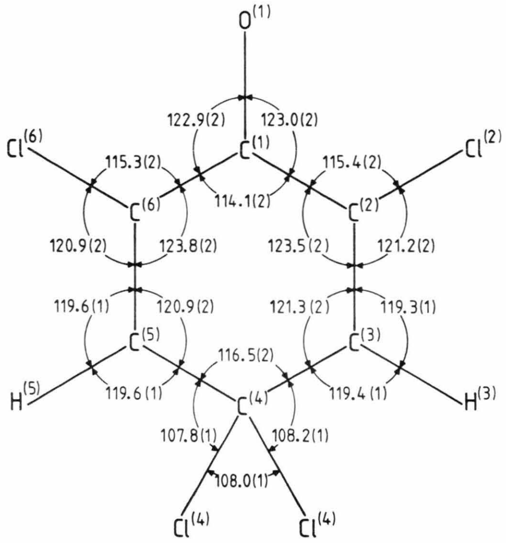


Fig. 3. Intramolecular bond angles (in angular degrees) in the molecule 2,4,4,6-tetrachloro-cyclohexadiene-2,5-one-1 ②.

Figures 2 and 3 show the intramolecular geometry (bond distances and bond angles, respectively) we determined.

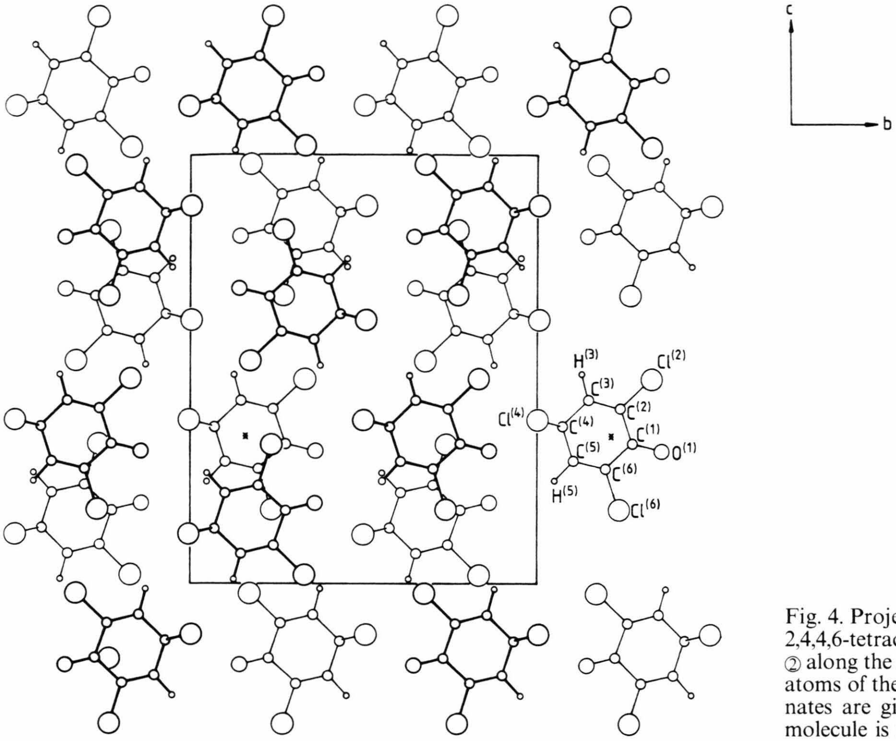


Fig. 4. Projection of the crystal structure of 2,4,4,6-tetrachloro-cyclohexadiene-2,5-one-1 ② along the *a*-axis onto the plane (bc). A few atoms of the molecule for which the coordinates are given in Table 3 are named (the molecule is marked by *).

There are several intermolecular contacts within the van der Waals distances observed. They are listed in Table 6. In Fig. 4 the arrangement of the eight molecules within the unit cell is shown in projection along the *a*-axis onto the plane (bc). Strings of molecules are seen, oriented parallel to the *c*-axis, and the strings are connected by van der Waals interactions within one layer of molecules in the planes $x = 0$ and $x = 1/2$. There is weak interaction between the layers, since $a/2 = 355.6$ pm. The most interesting point of the structure of compound ② is the strict planarity of the molecules within the lattice, reflected by the symmetry of the unit cell, proven by the crystal structure, and supported by the ^{35}Cl NQR spectrum.

Compound ① crystallizes monoclinic, space group $C^2_{2h}-P2_1/m$, $Z = 2$, see Table 1. In Figs. 5 and 6 the intramolecular bond distances and bond angles, respectively, are given. Some intermolecular contacts <450 pm are listed in Table 6. The symmetry of the space group reflects the strict planarity of the molecule ① in the solid phase and the ^{35}Cl NQR spectrum supports the finding of the X-ray diffraction experiment. In Fig. 7 the crystal structure of compound ① is shown in projection of the unit cell along [010]. Strings of molecules are running along the direction [100] and van der Waals contacts connect them. Again there is weak interaction between the molecules lying in the planes $y = 1/4$ and $y = 3/4$ ($b/2 = 352.4$ pm).

The results of the NQR experiments were given in Tables 4 and 5 and the temperature dependence of the ^{35}Cl NQR frequencies is shown in Figure 1. The most interesting feature of the ^{35}Cl NQR is the three line spectrum for both compounds studied. By the intensity ratio $I(\nu_1):I(\nu_2):I(\nu_3) = 2:1:1$, found for both compounds, the crystallographic (and therefore the chemical) equivalence of the two $C^{(4)}$ bonded to the sp^3 carbon is proved.

From the temperature dependence of the ^{35}Cl NQR frequencies, see Fig. 1, one finds, that the lattice of compound ① is somewhat "softer" than that of compound ②; $\nu_i(^{35}\mathrm{Cl})$ of ② depends less on T. One notes that the temperature factors of the atoms (see Tables 2 and 3), for tetrachloro-cyclohexadienone ② are lower than for tetrachloro-dimethyl-cyclohexadienone ①. Calculating an overall temperature factor

$$\langle U\rangle = \sum \langle U_i\rangle / \sum n_i = (1/\sum n_i)\cdot\sum [(1/3)\cdot(U_{11}+U_{22}+U_{33})_i], \qquad (2)$$

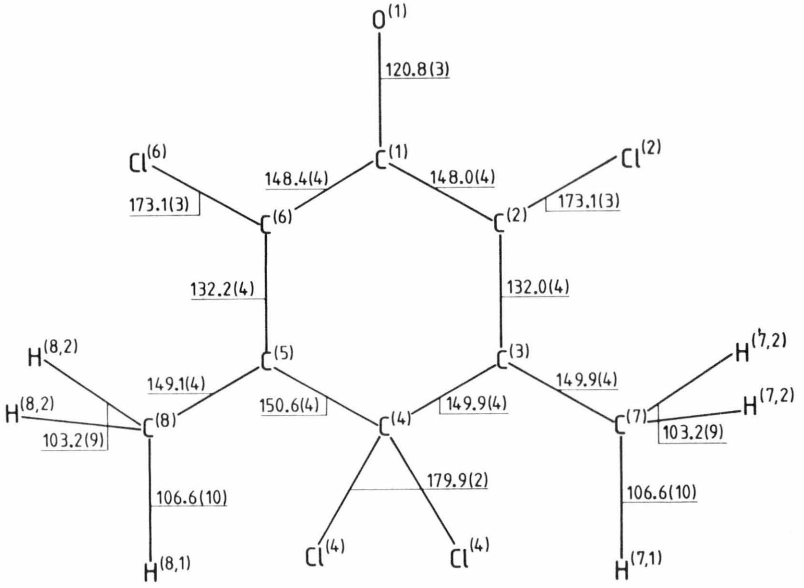


Fig. 5. Intramolecular bond distances (in pm) in the molecule 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ①.

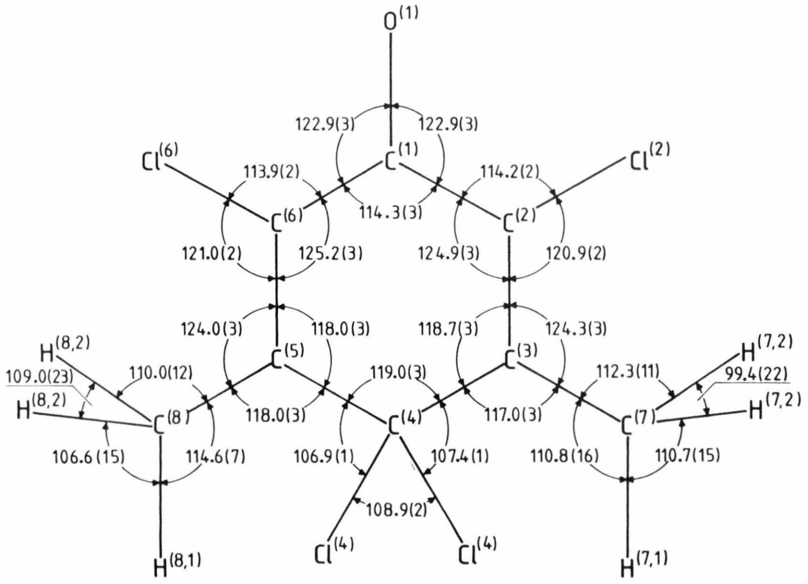


Fig. 6. Intramolecular bond angles (in angular degrees) in the molecule 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ①.

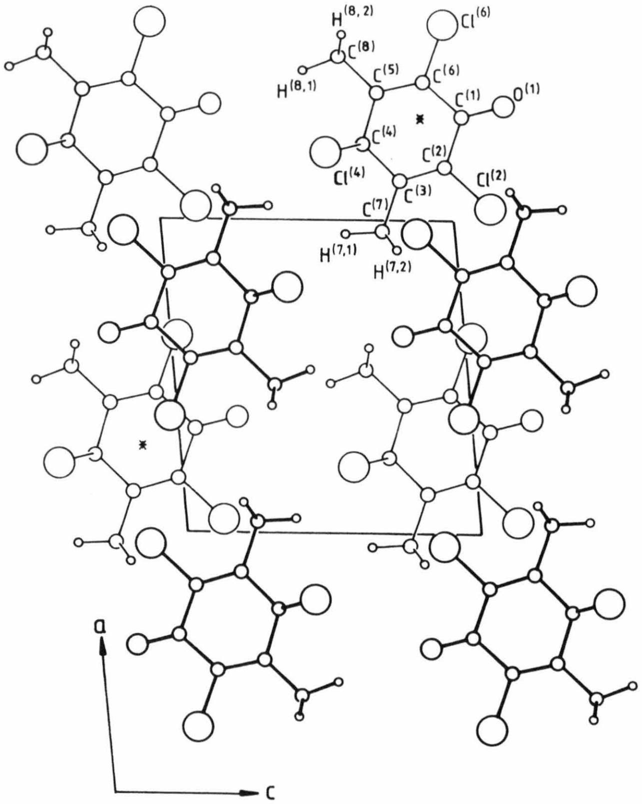


Fig. 7. Projection of the crystal structure of 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ① along the *b*-axis onto the plane (ac). A few atoms of the molecule for which the coordinates are given in Table 2 are named (the molecule is marked by *).

one gets $\langle U \rangle = 594\ (\mathrm{pm})^2$ for ① and $\langle U \rangle = 480\ (\mathrm{pm})^2$ for ②. Restricting the averaging procedure to the chlorine atoms, the values are $712\ (\mathrm{pm})^2$ and $614\ (\mathrm{pm})^2$ for ① and ②, respectively. Agreement of X-ray diffraction and ^{35}Cl NQR is qualitatively satisfactory; it is not useful to stress this aspect more on the basis of the present experimental evidence.

It seems to be worth-while to compare the crystal structures reported here with the information on structure and symmetry of the photochromic crystalline systems 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthaline (β-TKN) ③ and 2,2,4-trichloro-1,4-dihydronaphth[1,8-cd]isothiazole-1,1-dioxide (TCNS) ④ [1, 8]; for the structure of these molecules, see the introduction. The ^{35}Cl NQR of β-TKN ③ and of TCNS ④ is given in [1], too. For one more compound with the structure of interest to our discussion both, the crystal structure and ^{35}Cl NQR are known; this is 2,3,4,4,5,6-hexachloro-cyclohexadiene-2,5-one-1 ⑥, in short HCP. The crystal structure of this cyclohexadiene-2,5-one-1 was determined by Gali et al. [9]. It shows that HCP ⑥ is not strictly planar in its carbon ring system in agreement with ^{35}Cl NQR [1].

Table 6. Intermolecular contacts $d/\mathrm{pm} < 450$ in 2,4,4,6-tetrachloro-3,5-dimethyl-cyclohexadiene-2,5-one-1 ① and 2,4,4,6-tetrachloro-cylohexadiene-2,5-one-1 ②. – $\parallel$ = distances between atoms in the same plane and $\perp$ = distances between atoms in different planes. The planes are located at $y = \frac{1}{4}$ and $y = \frac{3}{4}$ for ① and at $x = 0$ and $x = \frac{1}{2}$ for ②.

Compound ①			Compound ②		
$Cl^{(2)} \ldots Cl^{(6)}$	365.1	$\parallel$	$Cl^{(2)} \ldots Cl^{(6)}$	349.1	$\parallel$
$Cl^{(2)} \ldots Cl^{(4)}$	401.7	$\perp$	$Cl^{(2)} \ldots Cl^{(4)}$	355.5	$\perp$
$Cl^{(2)} \ldots Cl^{(2)}$	413.9	$\perp$	$Cl^{(2)} \ldots Cl^{(4)}$	401.2	$\perp$
$Cl^{(2)} \ldots Cl^{(4)}$	417.8	$\parallel$	$Cl^{(2)} \ldots Cl^{(2)}$	422.7	$\perp$
$Cl^{(4)} \ldots O^{(1)}$	383.8	$\parallel$	$Cl^{(4)} \ldots O^{(1)}$	311.2	$\perp$
$Cl^{(4)} \ldots Cl^{(6)}$	393.5	$\perp$	$Cl^{(4)} \ldots Cl^{(6)}$	403.0	$\perp$
$Cl^{(4)} \ldots Cl^{(4)}$	397.7	$\perp$	$Cl^{(4)} \ldots Cl^{(4)}$	404.4	$\parallel$
$Cl^{(4)} \ldots O^{(1)}$	441.4	$\perp$	$Cl^{(4)} \ldots Cl^{(6)}$	405.4	$\parallel$
$Cl^{(6)} \ldots O^{(1)}$	399.9	$\perp$	$Cl^{(6)} \ldots O^{(1)}$	396.3	$\perp$
$Cl^{(6)} \ldots Cl^{(6)}$	422.1	$\perp$	$Cl^{(6)} \ldots Cl^{(6)}$	441.5	$\perp$
$C^{(7)} \ldots Cl^{(2)}$	365.0	$\perp$			
$C^{(7)} \ldots Cl^{(4)}$	372.1	$\perp$			
$C^{(7)} \ldots Cl^{(6)}$	387.6	$\parallel$			
$C^{(7)} \ldots Cl^{(8)}$	389.5	$\parallel$			
$C^{(8)} \ldots O^{(1)}$	378.4	$\perp$			
$C^{(8)} \ldots Cl^{(4)}$	381.3	$\perp$			
$C^{(8)} \ldots O^{(1)}$	385.0	$\parallel$			

Searching the literature it is a surprising fact that non of the molecules of chlorinated cyclohexadiene-2,5-diones-1,4 is planar. In Table 7 we have compiled the molecular symmetry of chloro-cyclohexadiene-2,5-ones-1 and chloro-cyclohexadiene-2,5-diones-1,4. All the chloro-cyclohexadiene-2,5-diones-1,4 show either the molecular symmetry 1 or $\bar{1}$. In Table 8 we compare the intramolecular distances $C^{(2)} = C^{(3)}$, $C^{(5)} = C^{(6)}$, $C^{(1)} = O^{(1)}$, and $C^{(4)} = O^{(4)}$. The shortest bond length C = O is 119.9 pm, the longest one 122.7 pm. In general, the bond length seems to be dependant on Hammett's sigma parameters, decreasing with high electronegative substitution of the ring system. The lengths $C^{(2)} = C^{(3)}$ are found in the range $135 \geqq d/\mathrm{pm} \geqq 132$ and the variation is in the same range for $d(C^{(5)} = C^{(6)})$ except β-TKN and TCNS, for which two molecules a strong influence of the attached ring systems appears (137 pm and 140 pm, respectively).

Table 7. Molecular symmetry of the chloro-cyclohexadiene-2,5-ones-1 and of the chloro-cyclohexadiene-2,5-diones-1,4.

Compound	Space group	*Z*	Symmetry of the molecule	Deviation from planarity of the ring d/pm	Ref.
$Cl_4(CH_3)_2C_6O$ ①	$C_{2h}^{2}-P2_1/m$	2	m	none	this work
$Cl_4C_6H_2O$ ②	$D_{2h}^{18}-Cmca$	8	m	none	this work
β-TKN ③	$D_{2h}^{16}-Pnma$	4	m	none	[8]
TCNS ④	$C_{2h}^{2}-P2_1/m$	2	m	none	[1]
HCP, Cl_6C_6O ⑥	$C_{4h}^{6}-I4_1/a$	16	1	$-4.3 \ldots +0.7$	[9]
2,3-Cl_2-5,6-$(CN)_2$-C_6O_2 ⑦	$D_{2h}^{15}-Pbca$	8	1	$-2.4 \ldots +1.9$	[10]
2,3,5,6-Cl_4-C_6O_2 ⑧	$C_{2h}^{5}-P2_1/a$	2	$\bar{1}$	$-1.4 \ldots +1.4$	[11–14]
2,5-Cl_2-3,6-$(OH)_2$-C_6O_2 ⑩	$C_{2h}^{5}-P2_1/a$	2	$\bar{1}$	$0.0 \ldots +1.4$	[15]
2,5-Cl_2-$C_6H_2O_2$ ⑪	$C_{2h}^{5}-P2_1/c$	2	$\bar{1}$	$-0.05 \ldots +0.05$	[16]
2,6-Cl_2-$C_6H_2O_2$ ⑫	$C_{2h}^{5}-P2_1/c$	4	1	$-0.7 \ldots +1.2$	[17]
2,3-Cl_2-$C_6H_2O_2$	$D_{4}^{4}-P4_12_12$	4	2	$-1.4 \ldots +0.8$	[16]
2-Cl-$C_6H_3O_2$	$D_{2}^{4}-P2_12_12_1$	4	1	$-0.9 \ldots +1.0$	[18]
$C_6H_4O_2$	$C_{2h}^{5}-P2_1/a$	2	$\bar{1}$	$-6.4 \ldots +4.4$	[19, 20]

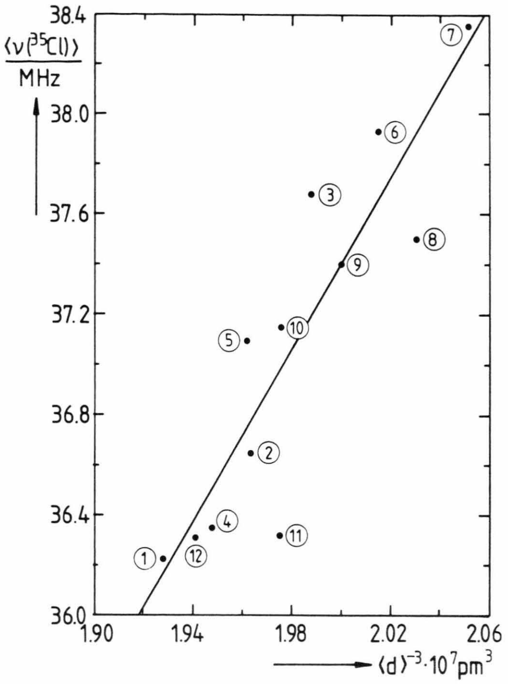


Fig. 8. Mean values of the frequencies of the ^{35}Cl NQR signals $\langle \nu \rangle$ versus $\langle d(\mathrm{C-Cl}) \rangle^{-3}$. $\langle d(\mathrm{C-Cl}) \rangle$ = mean values of the C–Cl bond lengths for Cl bonded to sp^2 carbon. For the numbers of the compounds see Table 9.

Table 8. Intramolecular distances (im picometer) in chloro-cyclohexadiene-2,5-ones-1 and in chloro-cyclohexadiene-2,5-diones-1,4.

Compound	$C^{(2)}=C^{(3)}$	$C^{(5)}=C^{(6)}$	$C^{(1)}=O^{(1)}$ or $C^{(4)}=O^{(4)}$	Ref.
$Cl_4(CH_3)_2C_6O$ ①	132.0	132.2	120.8	this work
$Cl_4C_6H_2O$ ②	132.6	132.3	120.3	this work
β-TKN ③	134.1	139.6	122.1	[8]
TCNS ④	132.9	136.9	–	[1]
HCP, Cl_6C_6O ⑥	132.6	132.7	120.1	[9]
2,3-Cl_2-5,6-$(CN)_2$-C_6O_2 ⑦	133.9	134.3	129.6, 119,9	[10]
2,3,5,6-Cl_4-C_6O_2 ⑧	134,4	≡134.4	121.1	[11–14]
2,5-Cl_2-3,6-$(OH)_2$-C_6O_2 ⑩	134.6	≡134.6	122.2	[15]
2,5-Cl_2-$C_6H_2O_2$ ⑪	134.0	≡134.0	122.2	[16]
2,6-Cl_2-$C_6H_2O_2$ ⑫	132.7	133.7	121.3, 121.7	[17]
2,3-Cl_2-$C_6H_2O_2$	135.0	133.5	122.2	[16]
2-Cl-$C_6H_3O_2$	134.6	134.0	122.6, 122.7	[18]
$C_6H_4O_2$	132.2	≡132.2	122.2	[19, 20]

A point we wish to stress in the discussion of crystal structure and NQR is the comparison of the NQR resonance frequencies with the bond lengths $d_{(\mathrm{C-Cl})}$. Strictly speaking, the nuclear quadrupole coupling constant (NQCC) $= e^2 \Phi_{zz} Q h^{-1}$ should be compared with $d_{(\mathrm{C-Cl})}$. However, since the secular equation for a spin $I = 3/2$ system is degenerate, since we have only measurements on polycrystalline samples of ① and ②, and since most of the ^{35}Cl NQR studies done on chlorodienones relay on polycrystalline material, we use the resonance frequencies $\nu_i(^{35}\mathrm{Cl})$ instead of the nuclear quadrupole constant $= e^2 \Phi_{zz} Q h^{-1}(^{35}\mathrm{Cl})$. The error introduced by this procedure is rather small. The asymmetry parameter, $\eta = |\Phi_{xx} - \Phi_{yy}| / |\Phi_{zz}|$, does not exceed 20% [11] in chlorocyclohexadiene-2,5-diones-1,4. From

$$\nu(^{35}\mathrm{Cl}) = \tfrac{1}{2} e^2 \Phi_{zz} Q h^{-1}(^{35}\mathrm{Cl}) \{1 + \eta^2/3\}^{1/2} \tag{3}$$

the error thereby introduced is less than 2%. The electric field gradient, EFG, at the chlorine nucleus site is proportional to the inverse third power of the distance of the charge creating the EFG from the nucleus.

$$e \Phi_{zz} = \mathrm{EFG} = n e \cdot r^{-3}. \tag{4}$$

In Table 9 we have listed for a number of chloro-cyclohexadiene-2,5-ones-1 and chloro-cyclohexadiene-2,5-diones-1,4 ^{35}Cl NQR frequencies (at $T = 77$ K) as a function of the intramolecular bond distance $d_{(\mathrm{C-Cl})}$. In Fig. 8 the data are plotted according to (4). The correlation is quite satisfactory. We find:

$$\nu(^{35}\mathrm{Cl})/\mathrm{MHz} = a + b(d_{(\mathrm{C-Cl})})^{-3}$$

$$= (2 \pm 12) + (174 \pm 59) \cdot 10^6, \tag{5}$$

where ν is given in MHz, a in MHz and b in MHz · pm^3. The slope of the curve, b is $(174 \pm 59) \cdot 10^6$ MHz · pm^3, determined by least squares adjustment. The error in a is large, due to the third power law, (5).

The correlation shows the sensitivity of NQR frequencies for bond distances. It shows furthermore, that the overwhelming part of the EFG at the chlorine site is produced by the Cl–C bond; intramolecular EFG's play a minor part. We have not correlated $d_{(\mathrm{C-Cl})}$ with ν (^{35}Cl) for sp^3 carbon since we do not have enough data available. A trial, done some time ago, was not successful [31].

Acknowledgement

We are grateful to the Stiftung Volkswagenwerk for support of this work.

Table 9. ^{35}Cl NQR frequencies at 77 K and intramolecular distances for chloro-cyclohexadiene-2,5-ones-1 and chloro-cyclohexadiene-2,5-diones-1,4. $\nu(^{35}Cl)$ is given in MHz at $T = 77$ K. $d = d(C-Cl)$ = distance C–Cl for Cl bonded to sp^2-C (in pm); $\delta = \delta(C-Cl)$ = distance C–Cl for Cl bonded to sp^3-C (in pm); $\langle\nu\rangle$, $\langle d\rangle$, $\langle\delta\rangle$ = mean values.

Compound	$\nu(^{35}Cl)$	$\langle\nu\rangle$	d	$\langle d\rangle$	δ	$\langle\delta\rangle$	Ref.
$Cl_4(CH_3)_2C_6$ ①	36.161	36.227	173.1	173.1			this work
	36.293		173.1				
	38.228	38.228			179.9	179.9	
$Cl_4C_6H_2O$ ②	36.556	36.647	172.0	172.05			this work
	36.738		172.1				
	38.342	38.342			179.4	179.4	
β-TKN, 2,3,4,4-Cl_4-$C_{10}H_4O$ ③	37.318	37.681	171.4	171.35			[1, 8]
	38.044		171.3				
	39.131	39.131			180.0	180.0	
TCNS, 2,4,4-Cl_3-$C_{10}H_3NSO_2$ ④	36.351	36.351	172.5	172.5			[1]
	38.276	38.276			179.6	179.6	
α-TKN, 2,2,3,4-Cl_4-$C_{10}H_4O$ ⑤	36.752	37.095	171.9	172.1			[1, 21]
	37.438		172.3				
	39.019	39.019			178.6	178.6	
HCP, Cl_6C_6O ⑥	37.553	37.933	170.7	170.58			[1, 9, 22]
	37.865		170.4				
	38.157		170.0				
	38.157		171.2				
	39.997	40.049			178.8	178.65	
	40.100				178.5		
2,3-Cl_2-5,6-$(CN)_2$-C_6O_2 ⑦	38.34	38.355	169.5	169.65			[10, 23]
	38.37		169.8				
Chloranil, 2,3,5,6-Cl_4-C_6O_2 ⑧	37.4417	37.503	169.99	170.14			[11–14, 24–26]
	37.4698		170.31				
	37.5148		169.97				
	37.5851		170.30				
Chloranil · perylene, 2,3,5,6-Cl_4-$C_6O_2 \cdot C_{20}H_{12}$ ⑨	37.3448	37.398	171.0	171.0			[27, 28]
	37.3595		171.0				
	37.4102						
	37.4775						
2,5-Cl_2-3,6-$(OH)_2$-C_6O_2 ⑩	37.148	37.148	171.7	171.7			[15, 29, 30]
2,5-Cl_2-$C_6H_2O_2$ ⑪	36.321	36.321	171.7	171.7			[16, 29]
2,6-Cl_2-$C_6H_2O_2$ ⑫	36.266	36.314	172.7	172.7			[17, 29]
	36.361		172.7				

[1] S. Brummer and Al. Weiss, Ber. Bunsenges. Phys. Chem. **91**, 873 (1987).

[2] R. Benedikt, Monatsh. **4**, 233 (1883).

[3] R. Fort, Ann. Chim. Paris (13) **4**, 203 (1959).

[4] A. M. Sørensen and B. Jerslev, Acta Chem. Scand. **22**, 319 (1968).

[5] E. Morita and A. W. Dietrich, J. Chem. Eng. Data **17**(2), 260 (1972). – E. Morita and A. W. Dietrich, Can. J. Chem. **47**, 1943 (1969).

[6] P. Švec, A. M. Sørensen, and M. Zbirovsky, Org. Prep. Proced. Int. **5**, 209 (1973). – P. Švec and M. Zbirovsky, Scientific Papers, Prague Institute of Chemical Technology **C 21**, 23 (1974).

[7] H. Bayer, Z. Phys. **130**, 227 (1951).

[8] H. Veenvliet and T. Migchelsen, Z. Kristallogr. **134**, 291 (1971).

[9] S. Gali, C. Miravittles, and M. Font-Altaba, Acta Cryst. B **31**, 2510 (1975).

[10] G. Zanotti, R. Bardi, and A. Del Pra, Acta Cryst. B **36**, 168 (1980).

[11] S. S. Chu, G. A. Jeffrey, and T. Sakurai, Acta Cryst. **15**, 661 (1962).

[12] I. Ueda, J. Phys. Soc. Japan **16**, 1185 (1961).

[13] H. J. van Weperen and G. J. Visser, Acta Cryst. B **28**, 338 (1972).

[14] J. L. Baudour, Y. Delugeard, H. Cailleau, M. Sanquer, and C. M. E. Zeyen, Acta Cryst. B **37**, 1553 (1981).

[15] E. K. Andersen, Acta Cryst. **22**, 188 (1967).

[16] B. Rees, Acta Cryst. B **26**, 1304 (1970).

[17] B. Rees, Acta Cryst. B **26**, 1298 (1970).

[18] B. Rees, Acta Cryst. B **26**, 1292 (1970).

[19] J. Trotter, Acta Cryst. **13**, 86 (1960). – J. Trotter, Acta Cryst. **14**, 553 (1961).

[20] F. van Bolhuis and C. T. Kiers, Acta Cryst. B **34,** 1015 (1978).
[21] F. P. A. Zweegers, C. A. G. O. Varma, and R. A. G. de Graaff, Acta Cryst. B **35,** 100 (1979).
[22] P. Bray and P. Ring, J. Chem. Phys. **21,** 2226 (1953).
[23] D. Gegiou and F. Milia, Chim. Chron. New Series **10,** 59 (1981).
[24] D. C. Douglass, J. Chem. Phys. **32,** 1882 (1960).
[25] H. Chihara and N. Nakamura, J. Phys. Soc. Japan **44,** 1567 (1978).
[26] H. Chihara and N. Nakamura, J. Chem. Phys. **59,** 539 (1973).
[27] K. Kozawa and T. Uchida, Acta Cryst. C **39,** 1233 (1983).
[28] H. Chihara and N. Nakamura, Bull. Chem. Soc. Japan **44,** 2676 (1971).
[29] P. Bray, S. Moskowitz, H. Hooper, R. Barnes, and S. Segel, J. Chem. Phys. **28,** 99 (1958).
[30] M. Hashimoto and K. Mano, Bull. Chem. Soc. Japan **45,** 706 (1972).
[31] M. Hashimoto, V. Nagarajan, N. Weiden, and Al. Weiss, J. Chem. Phys. **78,** 618 (1983).