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Structural Elucidation of an Octachloro Component of Technical Chlordane (Compound K) by Spectroscopic and X-Ray Methods

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The technical chlordane constituent designated compound K is a formal isomer of chlordane ($C_{10}H_6Cl_8$) which is formed by chlorination of α-chlordene (1) ($C_{10}H_6Cl_6$) via a Wagner–Meerwein rearrangement. Structural elucidation of K involves dechlorination reactions, especially spectroscopic studies (MS, ^1H NMR, and ^{13}C NMR) of various photodechlorination products (3–7). From these data a structure for compound K is proposed. Confirmation of this structure is obtained by single-crystal x-ray diffraction. According to the results, compound K corresponds to 2,4,4,5,6,6,7,8-octachlorooctahydro-1,5-etheno-pentalene (2).

The pesticide technical chlordane is a multicomponent mixture of chlorinated hydrocarbons which is formed by chlorination of the Diels–Alder adduct of hexachloro-cyclopentadiene and cyclopentadiene. Only a few components of this mixture are well characterized. These are chlordene, heptachlor, cis- and trans-chlordane, cis- and trans-nonachlor (Velsicol Chemical Corp., 1971), four isomeric chlordenes designated α-, β-, and γ-chlordene (Gäb et al., 1975, 1976; Cochrane et al., 1975; Wilson and Sovocool, 1977), and chlordene-C (Gäb et al., 1977). α-Chlordene can add chlorine to give a formal isomer of chlordane ($C_{10}H_6Cl_8$), which appears as peak K (referred to as compound K) in the gas chromatogram of technical chlordane (Polen, 1966).

Recently, Wilson and Sovocool (1977) reported on the structure of compound K. Four possible alternatives (I, II, III, IV) were discussed (Figure 1). Although structure IV seemed to be most consistent with the spectroscopic data no unequivocal verification of this structure could be obtained. It was suggested that compound K is 2,4,5,5,6,7,8,8-octachloro-2,3,3a,4,5,7a-hexahydro-1,4-methano-1H-idene. The present study was undertaken to examine the proposed structures by means of spectroscopic analysis of compound K and its photodechlorination products as well as by x-ray diffraction.

EXPERIMENTAL SECTION

Chromatography. A Packard 417 gas chromatograph was employed for both qualitative and quantitative purposes. A glass column (diameter, 3 mm; length, 2 m) packed with 5% QF-1 on Chromosorb W-AW-DMCS (80–100 mesh) was used. Temperatures were: inlet, 250 °C; detector, 300 °C; column, 180 °C. The nitrogen flow rate was 30 mL/min. Column chromatography was carried out with silica gel from Merck, Darmstadt (grain size 0.2–0.06 mm) as adsorbent, and n-hexane as eluent. For thin-layer chromatography silica gel 60 TLC plates with a layer thickness of 0.25 mm (Merck, Darmstadt) were used, with n-hexane as developing solvent. After developing plates were sprayed with 1% diphenylamine solution and irradiated with UV light for about 5 min (λ 254 nm) to detect substances.

Table I gives the respective TLC and GLC characteristics of compounds (1–7).

Chlorination of α-Chlordene (1). α-Chlordene (1) (3.0 g) was suspended in 100 mL of CCl_4 and treated with Cl_2 at 60 °C for 1 h. After cooling, excess chlorine was driven off with N_2 and the solvent in the remaining clear solution was removed under reduced pressure. The oily residue was subjected to column chromatography on 150 g of silica gel and eluted with n-hexane. Crystallizations from the eluates yielded 2.75 g of compound K (2).

Reduction of Compound K (2) with $CrCl_2$. Compound K (2) (0.45 g) was dissolved in 80 mL of acetone. Aqueous $CrCl_2$ (30 mL) (Fisher Scientific) was added under nitrogen, and the mixture was refluxed for 3 h. The reaction mixture was cooled, diluted with 500 mL of distilled water, and extracted with benzene. The combined extracts were dried and evaporated. The crystalline residue (0.33 g) consisted of α-chlordene and mono-dechloro-α-chlordene [from dechlorination at the allylic position in (1)] in the ratio 1.8:1.

UV Dechlorination of Compound K (2). In a typical UV irradiation procedure, 0.5 g of compound K (2) was dissolved in 80 mL of n-hexane. A quartz water-jacketed cooling finger containing a Hg high-pressure lamp (HPK 125 W Philips, with wavelengths above 230 nm) was immersed in the solution. After an irradiation time of 35 (105) min, dechlorination products were determined by GC analysis in the following quantities: 14.8% (6.5%) of 3, 51.0% (34.8%) of 4, 21.4% (36.3%) of 5, 2.2% (8.3%) of 6, and <1% (3.5%) of 7. Repeated irradiations were performed when additional quantities of minor photoproducts were required. Separation of the products was carried out on a 100-g silica gel column which was eluted with n-hexane.

Spectroscopy. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Model 577 grating spectrometer.

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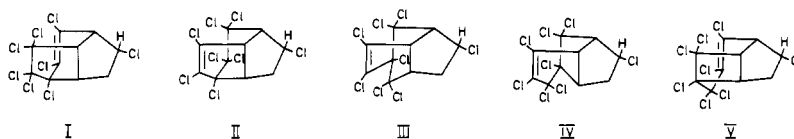
Figure 1. Alternative structures (I–V) of compound K.

Table I. Chromatographic and Spectroscopic Characteristics of the Compounds (1–7)

Compd	R_f	Rel retention time[a]	Mp, °C[b]	MS data, m/e (rel intensity, %)[c]	^{13}C data, chemical shifts, δ
1	0.39	1	193–195	336 (19) M⁺, 301 (79) (M-Cl)⁺, 265 (37) (M-Cl-HCl)⁺, 230 (100) (M-2Cl-HCl)⁺	33.88 (C-6); 53.62 (3a); 55.76 (C-4); 59.82 (C-6a); 63.44 (C-5); 81.22 (C-1); 126.58, 127.67, 134.07, 138.08 (C-2, C-3, C-7, C-8)
2	0.32	3.23	119–121	406 (7) M⁺, 371 (2.5) (M-Cl)⁺, 335 (15) (M-Cl-HCl)⁺, 299 (22) (M-Cl-2HCl)⁺, 261 (37) $C_7H_2Cl_5^+$, 214 (100) $C_6H_2Cl_4^+$	40.66 (C-3); 56.44, 58.24, 60.05, 60.39 (C-1, C-2, C-3a, C-6a); 87.62 (C-5); 89.82, 98.02 (C-4, C-6); 131.38, 133.68 (C-7, C-8)
3	0.42	1.64	nd[d]	372 (17) M⁺, 337 (22) (M-Cl)⁺, 301 (43) (M-Cl-HCl)⁺, 265 (63) (M-Cl-2HCl)⁺, 227 (41) $C_7H_3Cl_4^+$, 180 (100) $C_6H_3Cl_3^+$	40.89 (C-3); 58.94, 60.21, 61.23, 61.48 (C-1, C-2, C-3a, C-6a); 72.66 (C-5); 84.96, 93.71 (C-4, C-6); 129.61, 130.70 (C-7, C-8)
4	0.35	1.95	130–132	372 (13) M⁺, 337 (8) (M-Cl)⁺, 301 (35) (M-Cl-HCl)⁺, 265 (36) (M-Cl-2HCl)⁺, 227 (53) $C_7H_3Cl_4^+$, 180 (100) $C_6H_3Cl_3^+$	41.02 (C-3); 55.63, 59.17, 60.02, 60.02 (C-1, C-2, C-3a, C-6a); 81.89 (C-5); 89.64, 98.64 (C-4, C-6); 132.57, 134.47 (C-7, C-8)
5	0.38	1.32	nd	338 (12) M⁺, 303 (45) (M-Cl)⁺, 267 (27) (M-Cl-HCl)⁺, 231 (66) (M-Cl-2HCl)⁺, 193 (63) $C_7H_4Cl_3^+$, 146 (100) $C_6H_4Cl_2^+$	41.27 (C-3); 58.54, 60.31, 61.49, 61.95 (C-1, C-2, C-3a, C-6a); 64.79 (C-5); 86.48, 95.60 (C-4, C-6); 129.85, 133.16 (C-7, C-8)
6	0.16	2.41	151–153	338 (5) M⁺, 303 (21) (M-Cl)⁺, 267 (15) (M-Cl-HCl)⁺, 231 (52) (M-Cl-2HCl)⁺, 193 (100) $C_7H_4Cl_3^+$, 146 (41) $C_6H_4Cl_2^+$	
7	0.24	1.27	nd	304 (8) M⁺, 269 (57) (M-Cl)⁺, 233 (35) (M-Cl-HCl)⁺, 197 (100) (M-Cl-2HCl)⁺, 159 (65) $C_7H_5Cl_2^+$, 112 (35) $C_6H_5Cl^+$	

[a] Relative to α-chlordene (1) (t_R = 2.20 min, 5% QF-1, 180 °C). [b] Uncorrected. [c] The relative intensity of the molecular and fragment ions refers to the first peak in each Cl cluster; of the given peaks the highest was considered as 100%. [d] nd = not determined.

^{1}H and ^{13}C NMR spectra were recorded on a Varian CFT 20 (80 resp. 20 MHz) spectrometer. CDCl$_3$ was used as solvent, (CH$_3$)$_4$Si as internal reference.

Mass spectra were measured with a LKB 9000 S GC–MS combination operating at 70 eV.

Determination of the Crystal Data. For the x-ray crystallographic study crystals were grown from a petroleum ether solution. The cell constants were determined by least-squares methods from 54 Cu Kα$_1$ resp. K α$_2$ reflections on two different zero-layer Weissenberg films.

Collection of the X-Ray Intensities. Dimensions of the crystal used for intensity measurements were 0.37 × 0.26 × 0.50 mm. Intensities were collected on a Stoe semiautomatic two-circle diffractometer (equiinclination setting), using Mo Kα radiation from a graphite crystal monochromator (μ = 15 cm^{-1}). The ω-scan technique was used to record the intensities for all reflections up to $2\theta_o$ = 41.6° (sin θ_o/λ = 0.5 Å^{-1}) and counter angles Y > 5.0°. The observation of individual backgrounds was omitted. Background corrections were calculated from an empirical curve of background vs. counter and crystal angles, measured 0.8° above and below the inclination angle. Ten

reflections of the 0th layer were monitored several times during the collection of the intensities of the higher layers. There was no significant variation and because of this a special layer scaling was not necessary. The data were corrected for Lorentz and polarization effects. No absorption correction was performed. In total, 1407 nonzero (I_N > 0) intensities (out of 1489) were collected and used in the refinement of the structure parameters.

Solution and Refinement of the X-Ray Structure. The position of the chlorine atoms was determined by MULTAN (Germain et al., 1971) (180 reflexions, six ambiguities, 64 solutions). The E map based on the solution with the highest combined "figure of merit" revealed eight very high peaks. All carbon atoms were located by one difference Fourier synthesis. Block-diagonal refinement of the atomic coordinates with isotropic and anisotropic temperature factors resulted in a discrepancy index R_1, defined as $\sum||F_o| - |F_c||/\sum|F_o|$, of 0.044. No weighting scheme was used. Thereafter the positions of the six hydrogen atoms were calculated geometrically. Additional refinement with anisotropic (hydrogen atoms, isotropic) temperature factors reduced the discrepancy

Table II. ^{1}H NMR Characteristics of Compound K (2) and Its Photodechlorination Products (3-7)

Compd	δ, ppm									Coupling constants, J, Hz
	H-1	H-2	H-3	H-3'	H-3a	H-5	H-6a	H-7	H-8	
2	3.41	4.65	3.04	2.61	3.84		4.05			1,6a = 5; 2,3 = 6.5; 3,3' = 16.5; 3,3a = 4; 3',3a = 10; 3a,6a = 8
3	3.37	4.59	3.20	2.55	3.70	3.95	3.86			2,3 = 6.5; 3,3' = 16.5; 3',3a = 10
4	3.31	4.62	3.04	2.59	3.77		4.01	5.95		1,6a = 4.5; 1,7 = 1; 2,3 = 6; 3,3' = 16.5; 3,3a = 4; 3',3a = 10; 3a,6a = 8
5	3.34	4.61	3.17	2.53	3.68	3.73	3.90	5.95		1,7 = 1; 5,7 = 7.5; 2,3 = 6.5; 3,3' = 16.5; 3',3a = 10; 3,3a = 3.5
6	3.34	4.32	3.03	2.54	3.76		3.99	5.87	5.53	1,7 = 1.5; 1,8 = 3.5; 2,3 = 6; 3,3' = 16.5; 3,3a = 4; 3',3a = 10; 3a,6a = 8; 6a,8 = 1.5; 7,8 = 9.5
7	3.34	4.31	3.14	2.52		3.55-3.95		5.91	5.62	2,3 = 6.5; 3,3' = 16.5; 3',3a = 10; 5,7 = 7.5; 7,8 = 9.5

index to its final value of 0.029.

RESULTS AND DISCUSSION

The results of the spectroscopic studies are given in Tables I and II. The ^{1}H NMR parameters of compound K are characteristic of a five-membered ring having a methylene group, δ_{H-3} 3.04, $\delta_{H-3'}$ 2.61; a chloromethylene group, δ_{H-2} 4.65, and three methine protons at bridgeheads, δ_{H-1} 3.41, δ_{H-3a} 3.84, δ_{H-6a} 4.05. The assignment of the protons is based on decoupling experiments. By comparison of the ^{1}H data with those of α-chlordene, a precursor of K, only slight differences become apparent. The respective chemical shifts and coupling constants are similar to a large extent. The greatest changes in the ^{1}H shielding from α-chlordene to K are observed at the methylene protons and amount to about 0.45 ppm. Obviously, essential structural elements of the molecule such as the vicinal arrangement of the >CHCl and >CH$_2$ groups remain unchanged in the reaction α-chlordene → K.

The ^{13}C NMR data show that K has one chlorine-substituted double bond, since there are two singlets in the sp^2 carbon range at δ_C 133.68 and δ_C 131.38. The resonances at δ_C 98.02, δ_C 89.82, and δ_C 87.62 can be attributed to two dichloromethylene and a chloromethine carbon. According to the ^{13}C shifts of the respective carbon atoms in the spectra of the dechlorination products 3, 4, and 5, the resonance at δ_C 87.62 was assigned to the chloromethine carbon, in contrast to Wilson and Sovocool (1977). The assignments of the protonated carbons at δ 60.39 (C-2), 60.05 (C-1), 58.24 (C-6a), 56.44 (C-3a), and 40.66 (C-3) are based on selective proton decoupling experiments (Wilson and Sovocool, 1977).

The structural elements proved by the NMR data of K can be combined in a chemically reasonable way in different structures, which, however, cannot be unequivocally distinguished by means of the available spectroscopic results. The fact that K is formed by chlorine addition to α-chlordene reduces the possibilities of combining these elements to each other. Supposing that both a simple chlorine addition to the C-2/C-3 double bond (structure I) or to the C-7/C-8 double bond (structure II) in α-chlordene, respectively, and a chlorine addition to C-2/C-3 or C-7/C-8, respectively, at a simultaneous 1,2 shift (structures 2 and V or III and IV, respectively) may occur, only six structures for K can be considered (see Figures 1 and 2).
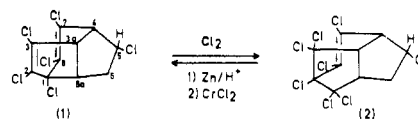

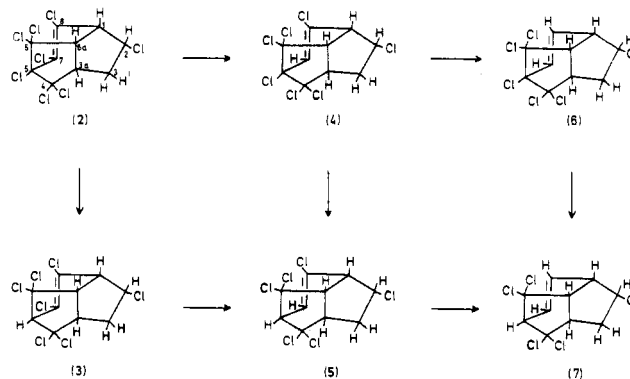Figure 2. Formation of α-chlordene (1) and compound K (2).

Figure 3. Photodechlorination products of compound K (2).

Oxidation reactions of α-chlordene with CrO$_3$ show a different reactivity of the two chlorinated double bonds. The epoxide ($\nu_{C=C}$ = 1590 cm^{-1}) obtained, as well as the dicarboxylic acid ($\nu_{C=C}$ = 1610 cm^{-1}) illustrate that the oxidative attack occurs exclusively at the C-2/C-3 double bond in α-chlordene (Gäb, 1975). This result is the first hint that this double bond might also be favored by the chlorine addition.

In order to confirm this supposition, an attempt was made to replace the chlorine atoms of the double bond or the allylic chlorine in K, respectively, by hydrogen, so as to obtain information about the exact position of the double bond by means of coupling relations of these protons with those of the five-membered ring.

For this purpose photodechlorination reactions of K were carried out in protonated solvents, which lead to the substitution of vinylic (Vollner et al., 1971; Gäb et al., 1975) and allylic chlorine atoms (Gäb et al., 1975). The obtained photodechlorination products 3-7 (Figure 3) were submitted to NMR spectroscopic analysis after separation by column chromatography.

The ^{1}H NMR spectrum of 4 compared to that of K displays an additional signal in the region of olefinic resonances (δ_{H-7} = 5.95) that is split into a doublet by a

long-range coupling with H-1 ($^4J_{1,7}$ = 1 Hz). The two olefinic protons of the didechlorinated compound 6 appear in the spectrum at δ_{H-7} = 5.87 and δ_{H-8} = 5.53. Whereas H-7 is split into a double doublet by vicinal coupling with H-8 ($^3J_{7,8}$ = 9.5 Hz) and by long-range coupling with H-1 ($^4J_{1,7}$ = 1.5 Hz), the couplings $^3J_{7,8}$ = 9.5 Hz, $^3J_{1,8}$ = 3.5 Hz, and $^4J_{6a,8}$ = 1.5 Hz lead to a splitting of H-8 into an octet. The dechlorination of the allylic position in 3 is indicated by a signal at δ_{H-5} = 3.95. Due to obstructive overlapping of resonance lines in this region of the spectrum, it is not easy to determine the coupling constants of H-5 beyond reasonable doubt. The NMR data of the didechlorinated compound 5 demonstrate that the dechlorination positions are located at C-5 and C-7, which is confirmed by the shift values of δ_{H-5} = 3.73 and δ_{H-7} = 5.95 as well as by the vicinal coupling $^3J_{5,7}$ = 7.5 Hz. Finally the tridechlorinated compound 7 should be mentioned among the photodechlorination products of K, which is formed by substitution of hydrogen by chlorine at the three possible positions (C-5, C-7, and C-8). The chemical shifts and coupling constants of the protons H-5, H-7, and H-8 are quite similar to those in 5 and 6.

On account of the data obtained from the spectra of 4 and 6 the structures II, III, and IV can be excluded for compound K, since neither the vicinal coupling nor the long-range coupling of the respective olefinic protons (H-7 in 4 and H-7, H-8 in 6) with the methine proton adjacent to the >CHCl group (H-1 in 4 and 6) should occur with respect to these structures. The elimination of the alternative structure V is based on the supposition that the dechlorination of the allylic chlorine in V should result in a chloromethylene group, whose resonance should be about 0.5-1.0 ppm at lower field than the values measured for the allylic protons in 3, 5, and 7 (δ_{H-5} = 3.7-3.95). If, on the other hand, the dechlorination took place at the chloromethine carbon in V, a long-range coupling with an olefinic proton would have to be expected, whose prospective value is not in accordance with the experimental value of 7.5 Hz ($J_{5,7}$ in 5 and 7).

Comparing the chemical shifts of the respective protons in 2-7, the greatest differences can be determined for proton H-2 in 6 and 7. In both cases the diamagnetic shift of H-2 ($\Delta\delta \simeq$ 0.3 Hz) must be considered to be a result of the dechlorination at C-8, which points to a close steric positioning of protons H-2 and H-8. Since the respective protons in II, III, and V are rather distant from one another, this result provides an additional argument against these alternative structures.

Although the data which have been discussed so far exclude the structures II-V, no clear distinction can be made between the structures I and 2. Evidence for the real structure of K is given by the ^{13}C data of the compounds 2-5. The large difference in the chemical shifts of the two dichloromethylene groups in K, δ_C = 98.02 and δ_C = 89.82, suggests that they are not α to one another, as in I and II, but rather are separated and in quite different environments (Wilson and Sovocool, 1977). This argument is supported by the fact that dechlorination of the allylic position in K leads to a diamagnetic shift of the dichloromethylene carbons of 4.3 and 4.8 ppm (cf. the data of K with those of 3), which only appears to be reasonable in connection with structure 2, but not with I.

The structure of K was definitively proved by an x-ray structural analysis.

The space group of the colorless prismatic crystals of compound K grown from a petroleum ether solution is $P2_1/b$. The crystal data are: a = 14.470 (1) Å, b = 13.787 (1) Å, c = 7.8719 (5) Å, α = 112.77 (1)°, V = 1447.9 (2) Å^3,
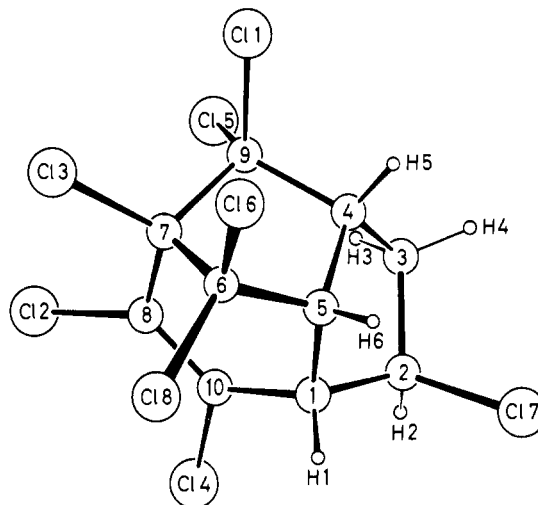
Figure 4. A view of the molecule with the atomic numbering scheme. The symbol C has been omitted.

Table III. Fractional Atomic Parameters and Their Estimated Standard Deviations (in parentheses)

Atom	x	y	z
Cl-1	0.3074 (1)	0.5119 (1)	0.5406 (1)
Cl-2	0.3163 (1)	0.3815 (1)	−0.1558 (2)
Cl-3	0.1879 (1)	0.4491 (1)	0.1790 (1)
Cl-4	0.4351 (1)	0.1771 (1)	−0.2612 (1)
Cl-5	0.4311 (1)	0.4979 (1)	0.2544 (2)
Cl-6	0.1791 (1)	0.3082 (1)	0.4262 (1)
Cl-7	0.5142 (1)	0.0882 (1)	0.2422 (1)
Cl-8	0.1813 (1)	0.1795 (1)	0.0434 (1)
C-1	0.3931 (3)	0.1744 (3)	0.0737 (5)
C-2	0.4934 (3)	0.1838 (3)	0.1406 (5)
C-3	0.5007 (3)	0.2944 (3)	0.2851 (5)
C-4	0.4019 (2)	0.3260 (3)	0.3622 (5)
C-5	0.3402 (2)	0.2293 (3)	0.2532 (5)
C-6	0.2483 (3)	0.2714 (3)	0.2254 (5)
C-7	0.2800 (3)	0.3660 (3)	0.1792 (5)
C-8	0.3290 (3)	0.3188 (3)	−0.0075 (5)
C-9	0.3547 (3)	0.4201 (3)	0.3293 (5)
C-10	0.3805 (3)	0.2324 (3)	−0.0505 (5)
H-1	0.377 (2)	0.108 (2)	0.014 (4)
H-2	0.539 (2)	0.166 (3)	0.041 (5)
H-3	0.522 (3)	0.345 (3)	0.222 (5)
H-4	0.542 (3)	0.298 (3)	0.385 (5)
H-5	0.398 (2)	0.343 (2)	0.496 (4)
H-6	0.335 (2)	0.185 (2)	0.317 (4)

Z = 4. The calculated density of 1.879 g/cm^3 agrees rather well with the experimental density of 1.83 g/cm^3 obtained from the dimensions and weight of a big crystal. Determination of the structure 2 is based on 1407 nonzero reflections which led to a final discrepancy index R_1 of 0.029 by application of direct methods and block-diagonal refinement. A view of the molecule with the atomic numbering scheme used in the x-ray diffraction part of this paper is shown in Figure 4. The atomic parameters are given in Table III. The thermal parameters of the heavy atoms are listed in Table IV. The hydrogen isotropic thermal parameters vary within -1.2 Å$^2 < B < 2.2$ Å^2 and are not given in a table. A view of the molecule with thermal ellipsoids is shown in Figure 5.

From the bond distances (Table V) it is clearly evident that the C–C double bond is located between C-8 and C-10. Its value of 1.333 Å even lies slightly below the value of 1.34 Å which has been stated for a genuine double bond (Allmann, 1975). The remaining C–C distances unequivocally show single bond character. However, the values are widely spread from 1.494 Å (C-1–C-10) to 1.575

Table IV. Thermal Parameters (multiplied by 10^4) of the Heavy Atoms and Their Estimated Standard Deviations[a]

At-om	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl-1	48 (1)	37 (1)	128 (2)	13 (1)	1 (2)	−16 (2)
Cl-2	99 (1)	70 (1)	145 (3)	33 (2)	12 (3)	138 (2)
Cl-3	42 (1)	38 (1)	199 (3)	22 (1)	−41 (2)	59 (2)
Cl-4	73 (1)	81 (1)	112 (2)	38 (1)	72 (2)	51 (2)
Cl-5	50 (1)	40 (1)	205 (3)	−29 (1)	−10 (2)	83 (2)
Cl-6	32 (1)	62 (1)	162 (2)	3 (1)	46 (2)	75 (2)
Cl-7	41 (1)	42 (1)	185 (3)	13 (1)	−44 (2)	60 (2)
Cl-8	33 (1)	40 (1)	184 (2)	−18 (1)	−53 (2)	37 (2)
C-1	30 (2)	21 (2)	117 (8)	4 (4)	−7 (7)	18 (7)
C-2	30 (2)	37 (3)	142 (9)	5 (4)	12 (7)	42 (8)
C-3	25 (2)	41 (3)	191 (10)	−2 (4)	−11 (7)	43 (9)
C-4	28 (2)	32 (3)	95 (8)	−3 (4)	−14 (7)	40 (7)
C-5	26 (2)	30 (2)	98 (8)	−5 (4)	−3 (7)	51 (7)
C-6	23 (2)	36 (3)	106 (8)	−5 (4)	−10 (7)	37 (7)
C-7	30 (2)	25 (2)	118 (8)	13 (4)	−17 (7)	38 (7)
C-8	47 (2)	33 (3)	91 (8)	−5 (4)	−17 (7)	43 (7)
C-9	34 (2)	28 (2)	92 (8)	0 (4)	3 (7)	25 (7)
C-10	34 (2)	46 (3)	81 (8)	−7 (4)	11 (7)	23 (8)

[a] The temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table V. Bond Distances (A)[a]

Cl-1-C-9	1.791	C-4-C-5	1.558
Cl-2-C-8	1.710	C-4-C-9	1.575
Cl-3-C-7	1.758	C-5-C-6	1.501
Cl-4-C-10	1.725	C-6-C-7	1.553
Cl-5-C-9	1.792	C-7-C-8	1.532
Cl-6-C-6	1.771	C-7-C-9	1.561
Cl-7-C-2	1.812	C-8-C-10	1.333
Cl-8-C-6	1.787		
		H-1-C-1	0.89
C-1-C-2	1.531	H-2-C-2	0.98
C-1-C-5	1.526	H-3-C-3	1.05
C-1-C-10	1.494	H-4-C-3	0.97
C-2-C-3	1.512	H-5-C-4	0.99
C-3-C-4	1.549	H-6-C-5	0.93

[a] The estimated standard deviations for Cl-C bonds are 0.004 A, for C-C bonds 0.006 A, and for C-H bonds 0.04 A.
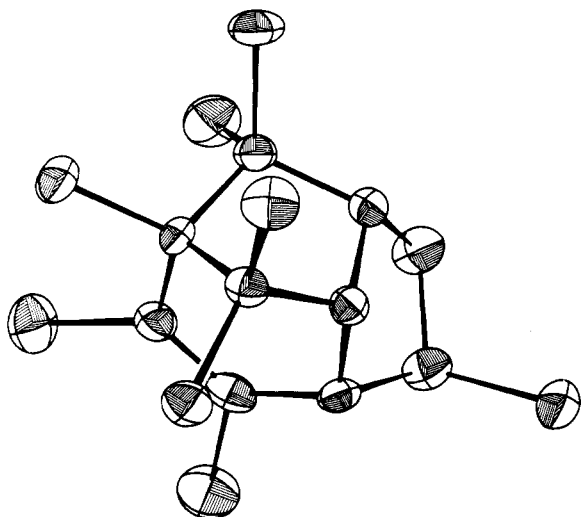

Figure 5. The same view of the molecule like in Figure 4 with thermal ellipsoids shown at the 50% level. Hydrogen atoms are excluded for clarity.

Å (C-4-C-9). A distance of 1.494 Å might result from the influence of the adjacent double bond. The greater distances may be caused by the tension which exists because of the fusion of the rings. The same discrepancy between C-C single bond distances was found for compounds with

Table VI. Bond Angles (deg)[a]

H-1-C-1-C-10	109	C-5-C-6-C-7	100.3
H-1-C-1-C-5	113	C-5-C-6-Cl-6	111.3
H-1-C-1-C-2	111	C-5-C-6-Cl-8	113.8
C-10-C-1-C-5	110.2	C-7-C-6-Cl-6	113.6
C-10-C-1-C-2	110.2	C-7-C-6-Cl-8	111.8
C-5-C-1-C-2	102.2	Cl-6-C-6-Cl-8	106.2
H-2-C-2-C-3	114	C-8-C-7-C-6	106.1
H-2-C-2-C-1	113	C-8-C-7-C-9	107.9
H-2-C-2-Cl-7	104	C-8-C-7-Cl-3	112.6
C-3-C-2-C-1	104.6	C-6-C-7-C-9	103.1
C-3-C-2-Cl-7	110.5	C-6-C-7-Cl-3	112.4
C-1-C-2-Cl-7	109.3	C-9-C-7-Cl-3	113.9
H-4-C-3-H-3	111	C-10-C-8-C-7	120.6
H-4-C-3-C-2	112	C-10-C-8-Cl-2	121.7
H-4-C-3-C-4	109	C-7-C-8-Cl-2	117.8
H-3-C-3-C-2	109		
H-3-C-3-C-4	108	C-7-C-9-C-4	104.0
C-2-C-3-C-4	106.2	C-7-C-9-Cl-1	113.4
		C-7-C-9-Cl-5	110.5
H-5-C-4-C-3	112	C-4-C-9-Cl-1	110.1
H-5-C-4-C-5	110	C-4-C-9-Cl-5	115.0
H-5-C-4-C-9	106	Cl-1-C-9-Cl-5	104.1
C-3-C-4-C-5	105.2		
C-3-C-4-C-9	117.4	C-8-C-10-C-1	123.6
C-5-C-4-C-9	104.1	C-8-C-10-Cl-4	121.2
		C-1-C-10-Cl-4	115.1
H-6-C-5-C-6	112		
H-6-C-5-C-1	110		
H-6-C-5-C-4	110		
C-6-C-5-C-1	113.1		
C-6-C-5-C-4	106.9		
C-1-C-5-C-4	103.5		

[a] The estimated standard deviations for angles involving only nonhydrogen atoms are in the range 0.1–0.3° and for those involving hydrogens in the range 2–4°.

Table VII. Selected Torsion Angles (deg)

Ring C-1-C-2-C-3-C-4-C-5		Ring C-1-C-5-C-6-C-7-C-8-C-10	
C-1-C-2...C-3-C-4	+25.9	C-1-C-5...C-6-C-7	−72.3
C-2-C-3...C-4-C-5	0.0	C-5-C-6...C-7-C-8	+67.3
C-3-C-4...C-5-C-1	−24.8	C-6-C-7...C-8-C-10	−36.5
C-4-C-5...C-1-C-2	+40.5	C-7-C-8...C-10-C-1	1.4
C-5-C-1...C-2-C-3	−41.5	C-8-C-10...C-1-C-5	0.0
		C-10-C-1...C-5-C-6	38.7

Ring C-4-C-5-C-6-C-7-C-9		Ring C-1-C-5-C-4-C-9-C-7-C-8-C-10	
C-4-C-5...C-6-C-7	+41.0	C-1-C-5...C-4-C-9	+99.4
C-5-C-6...C-7-C-9	−46.0	C-5-C-4...C-9-C-7	−8.9
C-6-C-7...C-9-C-4	+33.8	C-4-C-9...C-7-C-8	−78.2
C-7-C-9...C-4-C-5	−8.9	C-9-C-7...C-8-C-10	+73.4
C-9-C-4...C-5-C-6	−20.3	C-7-C-8...C-10-C-1	1.4
		C-8-C-10...C-1-C-5	0.0
		C-10-C-1...C-5-C-4	−76.7

similar characteristics. For instance, Palmer et al. (1975) determined that the C–C distances in 2,2,5-endo,6-exo,-8,9,10-heptachlorobornane, a component of the insecticide toxaphene, varied from 1.50 to 1.56 Å, and in the investigation of the crystal structure of endrin (De Lacy and Kennard, 1972), the C–C distances ranged from 1.48 to 1.57 Å. In the evaluation of the C–Cl distances, the hybridization of the connecting carbon atoms must be considered. Since C-8 and C-10 in K are sp² carbons, their C–Cl bonds are shortened (C-8–Cl-2, 1.710 Å; C-10–Cl-4, 1.725 Å; average, 1.717 Å). This corresponds to the average value of 1.719 ± 0.005 Å reported by Sutton (1965). The other six C–Cl bond lengths are found in the range from 1.758 to 1.812 Å. Their average length of 1.785 Å even lies above the value of 1.767 ± 0.005 Å for paraffinic C–Cl bonds (Sutton, 1965). In the case of the above mentioned chlorinated bornane derivative, the C–Cl distances also

Table VIII. Atom to Plane Distances (Å)[a]

			Plane A		
Atom	C-1*	C-2	C-3	C-4	C-5
Deviation	−0.634	0.003	−0.004	0.004	−0.003

			Plane B				
Atom	Cl-2	Cl-4	C-1	C-5	C-7	C-8	C-10
Deviation	−0.001	−0.008	0.004	−0.007	0.001	−0.002	0.013

			Plane C		
Atom	C-4	C-5	C-6*	C-7	C-9
Deviation	−0.054	0.037	0.672	−0.036	0.054

[a] Atoms marked with an asterisk were not included in least-squares plane calculation.

Table IX. Intermolecular Contacts (Å)

Distances involving heavy atoms to 3.6 Å		
Cl-1–Cl-2	$(x, y, z + 1)$	3.505
Cl-3–Cl-7	$(0.5 − x, 0.5 + y, z)$	3.426
Cl-6–Cl-7	$(x − 0.5, 0.5 − y, z + 1)$	3.415

Distances involving hydrogen atoms to 3.1 Å		
Cl-2–H-5	$(x, y, z − 1)$	2.84
Cl-3–H-2	$(x − 0.5, 0.5 − y, − z)$	2.84
Cl-3–H-6	$(x + 0.5, 0.5 − y, z)$	3.02
Cl-3–H-1	$(x + 0.5, 0.5 − y, z)$	3.09
Cl-7–H-1	$(1 − x, − y, − z)$	3.10
Cl-8–H-3	$(x − 0.5, 0.5 − y, − z)$	3.04

vary to a remarkably high degree and range from 1.752 to 1.806 Å (Palmer et al., 1975).

For the atoms of K having sp² bonds, noticeable deviations from the 120° angle are determined (Table VI). Here the angles range from 115.1° (C-1–C-10–Cl-4) to 123.6° (C-8–C-10–C-1) which might be due to the ring tensions and repulsion between the chlorine atoms. The same reasons are responsible for the high degree of variation of the tetrahedron angles from 100.3 (C-5–C-6–C-7) to 117.4° (C-3–C-4–C-9); cf. 2,2,5-endo,6-exo,8,9,10-heptachlorobornane (92.8 to 117.4°; Palmer et al., 1975) and endrin (97.5 to 126.0°; De Lacy and Kennard, 1972).

Considering Table VII with respect to small torsion angles, it is evident that in K all carbon atoms except C-6 are situated in three nearly even planes. Plane A (C-2, C-3, C-4, C-5): This plane consists of four carbon atoms which are part of a five-membered ring. The fifth carbon atom (C1) of this ring system is located at a considerable distance (Δ = −0.634 Å) from the plane (Table VIII). Since the C–C lengths in the plane correspond to normal C–C single bonds the planarity must be due to the overall geometry of the molecule.

Plane B (C-1, C-5, C-7, C-8, C-10 and because of the sp² bond Cl-2, Cl-4): For the most part, the planarity of this group can be explained by bonding theory because of the double bond between C-8 and C-10. The fact that C-5 also lies in the plane cannot be understood with regard to the type of bonding because this atom is not immediately influenced by the sp² bond.

Plane C (C-4, C-5, C-7, C-9): These four atoms comprise an approximately planar ring fragment with a maximum deviation of 0.054 Å from the best plane. C-6, which forms a five-membered ring with the carbons of plane C, deviates 0.672 Å from the plane (Table VIII). In all cases C-6 itself is found to be connected with very great torsion angles.

Dihedral angles formed by the least-squares planes are: plane A–plane B, 83.7°; plane A–plane C, 60.5°; plane B–plane C, 105.7°.

Table IX shows that the contacts to neighboring molecules occur exclusively via chlorine atoms while carbon atoms are definitely not involved. Therefore, the carbon skeleton is sufficiently shielded by chlorine and hydrogen atoms. There are no unusual intermolecular contacts in
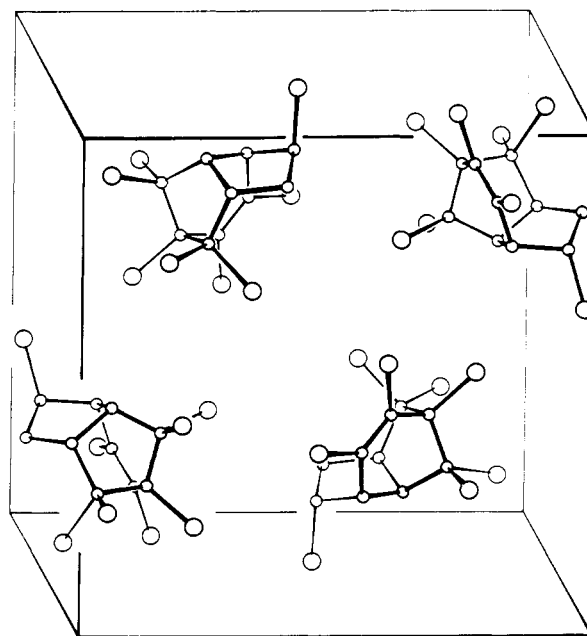

Figure 6. The molecular packing in the unit cell. The y axis is horizontal to the left, the x axis runs from top to bottom, and the z axis comes out of the paper toward the reader. Large circles, chlorine atoms; small circles, carbon atoms. Hydrogen atoms have been omitted.
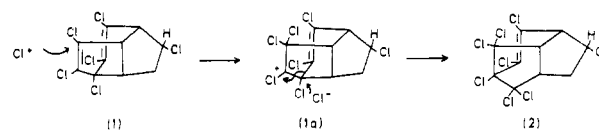

Figure 7. Postulated mechanism of the formation of 2 from 1 by addition of chlorine via a Wagner–Meerwein rearrangement.

the crystal. It may be assumed that the conformation of the molecule is not seriously affected by intermolecular forces. Figure 6 depicts the molecular packing in the unit cell and gives by this way some other views of the molecule.

It is known that compound K is formed in a high yield by chlorination of α-chlordene. The proportion of K in the technical mixture comprises about 4% (Cochrane et al., 1975). The structures of α-chlordene (1) and compound K (2) make clear that the reaction 1 → 2 does not imply a simple chlorine addition, but a chlorine addition which is accompanied by a 1,2 shift (Wagner–Meerwein rearrangement). The postulated reaction mechanism shown in Figure 7 starts with a Cl⁺ attack on the C-2/C-3 double bond in 1 under formation of the intermediate 1a. Stabilization of the cationic intermediate state by Cl⁻ via a 1,2 shift leads to 2.

The reverse reaction, i.e., the formation of α–chlordene from K, proceeds under mild reductive conditions. Both in the reduction of K with zinc and acetic acid (Wilson and Sovocool, 1977) and in the reduction with CrCl₂, α-

chlordene was identified as a main product.

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Photochemistry of Chlorinated Diphenyl Ethers

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The photoreactions of a series of chlorinated diphenyl ethers at wavelengths around 300 nm were investigated as to their photodecomposition rates and products formed. No significant differences in reaction rates were found between chlorodiphenyl ethers with up to four chlorine atoms per molecule which reacted slower than the pentachlorodiphenyl ethers investigated. The major products resulted from photodechlorination reactions but compounds with chlorine substituents in the 2 or 6 positions also gave rise to chlorinated dibenzofurans in about 10% yields. The yields of dibenzofurans were increased in most cases when photolysis was carried out in the presence of acetone. This reaction may also occur under natural conditions in the environment by influence from natural products which have photochemical characteristics similar to that of acetone.

The photoreactions of halogenated aromatic compounds have received considerable attention during recent years, one reason being the increased interest in the environmental chemistry of such compounds. Several groups of chlorinated aromatic compounds are ubiquitous environmental pollutants and a knowledge of the photochemical reactions of these compounds is necessary to gain understanding about the possible routes of activation (e.g., formation of toxic photoproducts) or deactivation (e.g., decomposition and mineralization) in the environment.

In our studies on the photoreactions of compounds of possible environmental significance we recently reported on the photochemistry of alkylated chlorobiphenyls (Ruzo et al., 1976a) and bromobiphenyls (Ruzo et al., 1976b). Both types of compounds are structurally closely related to the well-known pollutants polychlorinated biphenyls (PCB) whose photochemistry have been thoroughly investigated (cf. e.g., Ruzo et al., 1974a,b, 1975). The present paper deals with the photochemistry of polychlorinated diphenyl ethers, PDEs, compounds of obvious structural similarity to all above mentioned compounds. PDEs have

been found present in technical chlorophenol preparations (Firestone et al., 1972; Villanueva et al., 1973; Nilsson and Renberg, 1974; Buser, 1975) and they may therefore reach the environment through the use of these products.

Although the photochemistry of diaryl ether compounds has been extensively studied (cf. Elix and Murphy, 1975, and papers cited therein) only one investigation has been published on the photoreactions of PDEs. Norström et al. (1976) found that 2,2',4-trichloro- and 2,2',4,4'-tetrachlorodiphenyl ether gave dechlorinated diphenyl ether compounds and chlorinated dibenzofurans as major products upon photolysis in hexane solution. The formation of the latter type of products should give rise to concern since chlorinated dibenzofurans have been identified as very toxic by-products in a number of technical products like PCB (Vos et al., 1970; Bowes et al., 1973, 1975a,b; Roach and Pomerantz, 1974; Curley et al., 1975; Nagayama et al., 1976), chlorophenols (Firestone et al., 1972; Plimmer et al., 1973; Jensen and Renberg, 1973; Villanueva et al., 1973; Nilsson and Renberg, 1974; Buser, 1975, 1976; Buser and Bosshardt, 1976) and in hexachlorobenzene (Villanueva et al., 1974).

Ring formation of diaryl ethers to furan-type compounds have also been observed with 2-chlorophenyl 1-naphthyl ether (Henderson and Zweig, 1969) and polychloropyridyl phenyl ethers (Bratt and Suschitzky, 1972). The presence of photolabile chlorine atoms in the ortho position to the ether linkage thus seem to facilitate the ring-formation reactions. A related photochemical cyclodehydrogenation reaction of diaryl ethers and diaryl sulfides to dibenzofurans and dibenzothiophenes, respectively, was recently

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