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Spectroscopic Behavior and X-ray Analysis of the Toxaphene Component 2,2,3-*exo*,8b,8c,9c,10α-Heptachlorocamphene

INTRODUCTION

Although technical toxaphene has been in commercial use for nearly 50 years, today only a few of the ca. 200 constituents of this multicomponent pesticidal mixture are known for certain. These are mainly hexa- to decachlorobornanes (Burhenne et al., 1993), but also considerable amounts of unsaturated C_{10}-chloroterpenes can be detected by GC–MS (Saleh, 1983; Holmstead et al., 1974). On the basis of a comparison of fragmentation pattern with those of already isolated bornenes (Turner et al., 1977), it was postulated that these terpenes had chlorobornene structures (Saleh, 1983). However, no verification of those structures has been reported.

The same C_{10}-chloroterpenes could also be found in most of the aquatic biota samples, especially in fish and fish products obtained from Iceland, Greenland, Norway, and Germany (Lach et al., 1991). They amount to approximately 5–6% of the total toxaphene residues observed by GC–MS/ECNI-SIM and GC–ECD analysis of the sample extract (Lach, 1990).

Recently, we reported on the UV irradiation products ($\lambda = 254$ nm) of technical toxaphene arising from specific dechlorination and dehydrochlorination reactions (Hainzl et al., 1994). Together with 22 chlorobornanes, 5 unsaturated C_{10}-chloroterpenes were isolated. Each of the products exhibited one chlorinated double bond in the 1640–1645 cm^{-1} region of the GC–FTIR spectrum. Also, unlike chlorobornene itself, no typical retro-Diels–Alder fragmentation (RDA) was observed in the mass spectra (Hainzl, 1994).

The present study was undertaken to determine the structure of the commonly occurring unsaturated C_{10}-chloroterpene (Parlar no. **25**) as a model substance and to compare it with the postulated chlorobornene structure.

EXPERIMENTAL PROCEDURES

The isolation of **I** (Figure 1) from the photochemically modified toxaphene has been described elsewhere (Hainzl et al., 1994). The isolated amount of 21 mg had a purity of 99%, determined by GC–ECD. It forms colorless needles with a melting point of 151–153 °C and possesses no characteristic odor. Crystals for X-ray analysis were obtained by evaporation of the solvent (petroleum ether 40–60 °C) during several days.

GC–MS experiments were carried out using an HP 5890/5988A GC–MS system. The temperature of the ion source was 100 °C for ECNI-MS, with CH_4 as reactant gas (emission current ca. 200 μA). EI measurements were performed at 70 eV and 200 °C ion source temperature (mass range *m/z* 45–500).

An HP 5890/5965 GC–FTIR system was used to record the IR spectrum. The temperatures of the transfer lines and of the light pipe were 250 and 280 °C, respectively.

The GC parameters were identical for both GC–MS and GC–FTIR. A 25 m HP-5 column (i.d. 0.2 mm, film thickness 0.33 μm) was used with 1 mL/min helium as carrier gas. The temperature program was as follows: T 140 °C (3 min) to 250 °C (20 min) at 4 °C/min.
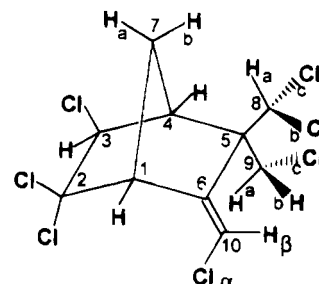
Figure 1. Structure of 2,2,3-*exo*,8b,8c,9c,10α-heptachlorocamphene (Parlar no. **25**) (**I**).

A 400 MHz AC-400 instrument (Bruker) was used for NMR spectroscopy. The solvent was $CDCl_3$ with TMS as an internal standard.

The X-ray measurements were taken with an Enraf-Nonius CAD4 V 5.0 four circle diffractometer with a Mo Kα radiation of $\lambda = 0.71073$ Å (graphite monochromator). A total of 2075 reflections were collected in the 2Θ range of 3–50°.

RESULTS AND DISCUSSION

The EI- and ECNI-MS spectra of **I** are shown in Figure 2A. The fragmentation after chemical ionization shows the M$^-$ ion as base cluster (*m/z* 374, Cl = 35) and a second intensive peak of the [M − Cl]$^-$ ion at *m/z* 339 (Cl = 35). The EI spectrum is dominated by the [M − CHCl$_2$]$^-$ fragment at *m/z* 291 (Cl = 35), while in contrast to the 2,5-*endo*,6-*exo*,8b,8c,10a,10b-octachloroborn-2,3-ene, which is formed by photochemical dehalogenation of 2,2,3-*exo*,5-*endo*,6-*exo*,8b,8c,9c,10a,10b-decachlorobornane (Burhenne, 1993), RDA fragmentation after HCl or Cl$_2$ elimination seems not to occur significantly.

In contrast to the polychlorobornanes (Hainzl et al., 1994), the IR spectrum of **I** (Figure 2B) shows two characteristic bands, one at 3096 cm^{-1} and another at 1645 cm^{-1}, resulting from the olefinic C—H and the C=C valence vibration, respectively. The corresponding C=C valence vibration of polychlorobornenes, however, can be detected at lower frequencies, i.e. 1597 cm^{-1} for the 2,5-*endo*,6-*exo*,8b,8c,10a,10b-octachloroborn-2,3-ene (Burhenne, 1993). All other IR bands of **I** are typical for polychloroterpenes in general but are not characteristic for camphene derivatives.

Figure 3 shows the one-dimensional ^{1}H- and ^{13}C-NMR spectra of **I**; the corresponding data are summarized in Table 1. Remarkable is the occurrence of several couplings with small coupling constants which are responsible for the quasi-quintets in the spectrum. Furthermore, in addition to the signals of sp^3 carbon atoms, two olefinic carbon atoms can be observed in the ^{13}C-NMR spectrum, one tertiary at 122.1 ppm (positive signal in the DEPT-135° experiment) and one quaternary at 140.4 ppm (no signal in the DEPT-135° experiment).

However, with the help of NMR spectra alone it is not possible to elucidate the structure of **I** in all details. Therefore, the solid state structure was determined by X-ray analysis (Figure 4), which shows that **I** possesses a monoclinic elementary cell with a $P2_1$ space group and
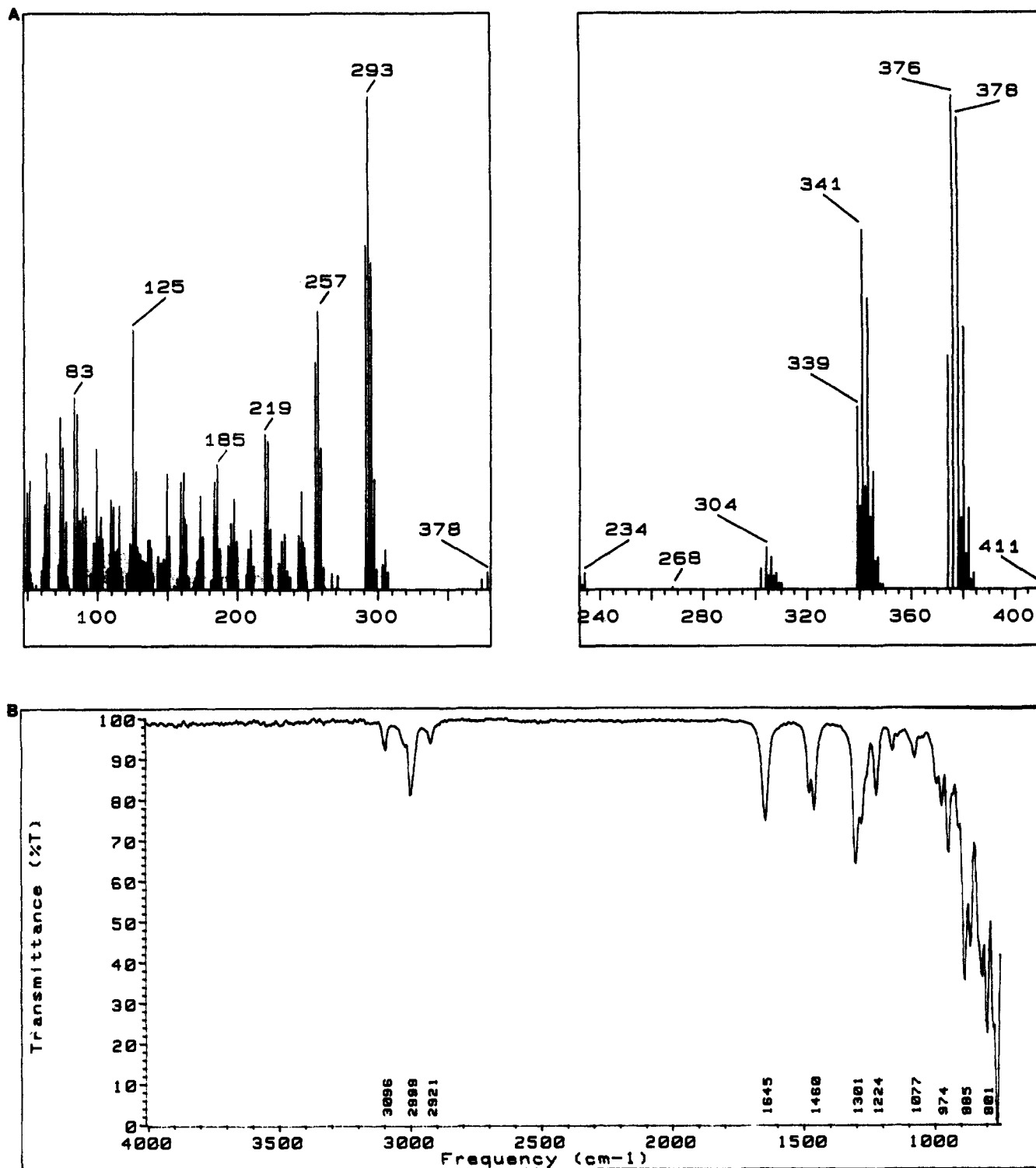
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Figure 2. (A) EI- (left) and ECNI-MS (right) of **I**; (B) IR spectrum of **I**.

$z = 2$. The dimensions of this cell are $a = 7.164$, $b = 12.761$, and $c = 7.956$ Å. The most important bond lengths and angles are summarized in Table 2. The exact positions of all chlorines and protons are identifiable. The bond lengths are somewhat longer than free C–C or C–Cl bondings but are in good agreement with those of polychlorobornanes (Frenzen et al., 1994). Since both bond lengths and angles show no significant deviation from that of unchlorinated camphene, one can suggest that the energy of 2,2,3-*exo*,8b,8c,9c,10α-heptachlorocamphene, due to steric reasons, is not extraordinarily high.

CONCLUSIONS

The class of polychlorocamphenes was unknown until recently. The structure elucidation of compound **25**, 2,2,3-*exo*,8b,8c,9c,10α-heptachlorocamphene (**I**), establishes that highly chlorinated camphene derivatives either are already present in the insecticidal toxaphene mixture or can be formed by photochemical treatment of polychlorobornanes (Hainzl et al., 1994). Since toxaphene has been used intensively in agriculture, high amounts of these substances have been brought into the environment and their ecotoxic potential cannot be estimated. Supposing a weight percentage of 18% of
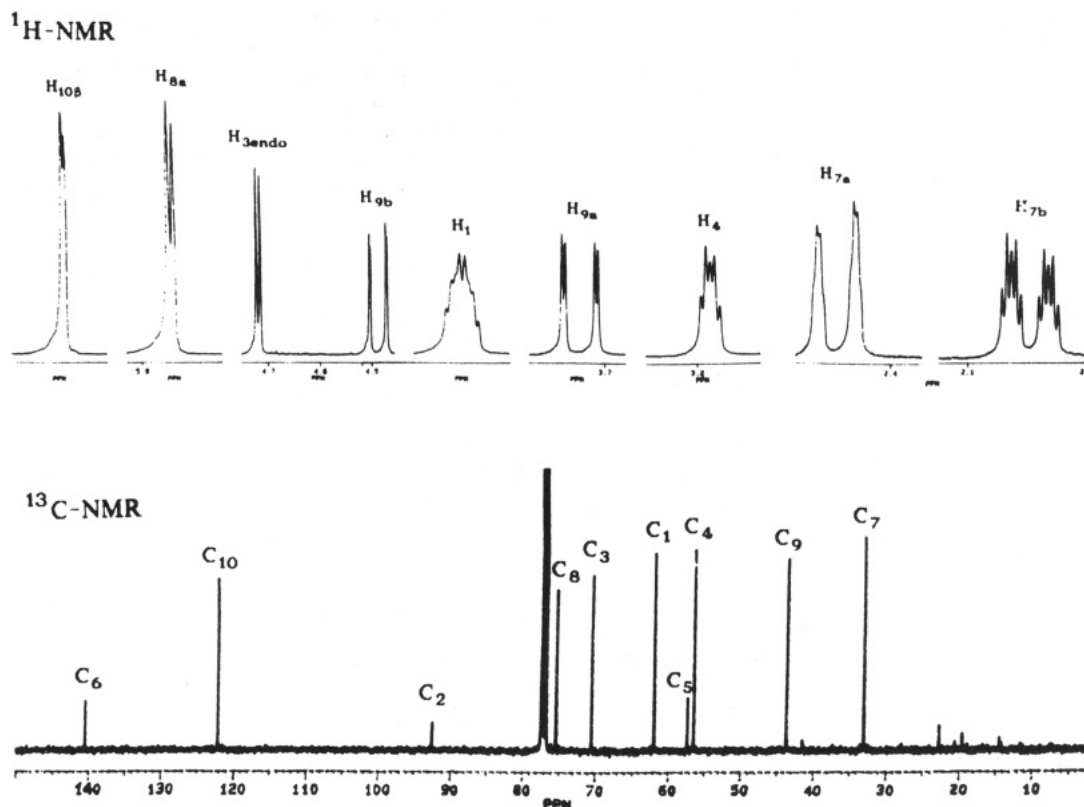
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Figure 3. ^{1}H- and ^{13}C-NMR spectra of **I**.

Table 1. NMR Data of I: (A) Chemical Shift of Protons;^{a} (B) HH Coupling Constants; (C) ^{13}C Chemical Shifts^b

	proton								
	H_1	H_{3endo}	H_4	H_{7a}	H_{7b}	H_{8a}	H_{9a}	H_{9b}	$H_{10\beta}$
(A) shift (ppm)	3.95 m	4.72 d	3.19 qi	2.45 ddd	2.05 dqi	5.88 d	3.72 dd	4.49 d	6.53 d
	$J_{4,1}$	$J_{1,10}$	$J_{7a,7b}$	$J_{7a,1}$	$J_{7a,4}$	$J_{7b,1}$	$J_{7b,4}$	$J_{7b,3endo}$	$J_{8a,9a}$	$J_{9a,9b}$
(B) constant (Hz)	2.7	0.8	12.6	1.3	1.3	1.5	1.5	3.0	1.3	13.0

	carbon									
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
(C) shift (ppm)	61.8 t	92.9 q	70.4 t	56.4 t	57.2 q	140.4 q	32.9 s	75.3 t	43.6 s	122.1 t

^{a} d, doublet; dd, quartet; ddd, octet; m, multiplet; qi, quintet; dqi, double quintet. ^{b} s, secondary; t, tertiary; q, quaternary (determined by DEPT-135° experiment).
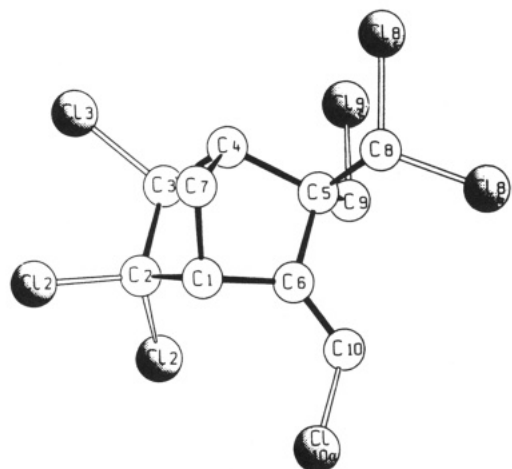

Figure 4. Solid state structure of 2,2,3-*exo*,8b,8c,9c,10α-heptachlorocamphene (**I**) (protons are not shown for clarity).

Table 2. Selected Bond Lengths and Angles of I with Standard Deviation in Parentheses

bond	length (Å)	bond	angle (deg)
C_1-C_2	1.55 (2)	$C_2-C_1-C_6$	109.0 (10)
C_1-C_6	1.52 (2)	$C_2-C_1-C_7$	99.5 (10)
C_1-C_7	1.52 (2)	$C_6-C_1-C_7$	102.0 (10)
C_2-C_3	1.55 (2)	$C_1-C_2-C_3$	103.5 (11)
C_2-Cl_{2exo}	1.783 (13)	$Cl_{2exo}-C_2-Cl_{2endo}$	106.4 (7)
C_2-Cl_{2endo}	1.778 (13)	$C_2-C_3-C_4$	102.3 (10)
C_3-Cl_{3exo}	1.789 (13)	$C_3-C_4-C_5$	108.7 (10)
C_3-C_4	1.58 (2)	$C_3-C_4-C_7$	100.6 (10)
C_4-C_5	1.56 (2)	$C_5-C_4-C_7$	102.2 (9)
C_4-C_7	1.54 (2)	$C_4-C_5-C_6$	100.5 (10)
C_5-C_6	1.53 (2)	$C_8-C_5-C_9$	112.4 (12)
C_5-C_8	1.54 (2)	$C_1-C_6-C_5$	106.7 (10)
C_5-C_9	1.51 (2)	$C_1-C_6-C_{10}$	127.8 (12)
C_6-C_{10}	1.31 (2)	$C_5-C_6-C_{10}$	125.4 (12)
C_8-Cl_{8b}	1.773 (12)	$C_1-C_7-C_4$	94.5 (10)
C_8-Cl_{8c}	1.798 (14)	$Cl_{8b}-C_8-Cl_{8c}$	107.5 (7)
C_9-Cl_{9c}	1.792 (13)	$C_5-C_9-Cl_{9c}$	115.1 (10)
$C_{10}-Cl_{10\alpha}$	1.74 (2)	$C_6-C_{10}-Cl_{10\alpha}$	123.3 (12)

these unsaturated compounds in technical toxaphene (Saleh, 1983) and a total toxaphene usage of 1.3 Mio tons (Voldner and Li, 1993), it can be calculated that in the years between 1950 and 1993 nearly 250 000 tons of polychlorocamphenes have been released into the environment. Investigations of the toxicity and the metabolism of these compounds should therefore be carried out in the near future.

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