

On the Internal Rotation of Toxaphene Congeners.

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Abstract

At ambient temperature proton NMR spectra of the three Toxaphene congeners, 2-exo,3-endo,6-exo,8,9,10,10-Heptachlorobornane, 2,2-3-exo,5-endo,6-exo,8,9,10,10-Nonachlorobornane and 2-exo,3-endo,6,8,8,9,10,10-Octachlorodihydrocamphene show significant broadening of the signals of several protons. At +52°C and -53°C the broadening gets weaker. This is an evidence for internal rotation of a molecule.

One compound, 2-exo,3-endo,6-exo,8,9,10,10-HpCB exists in two stable conformations in ca. 5:1 ratio.

Introduction

Internal rotation is an important element of chemical structure and is often a decisive factor of chemical behavior. It's a requirement of modern organic chemistry, that for correct assessment or prediction of chemical reactivity, all possible conformations should be taken into consideration.

Accordingly, a requirement of environmental chemistry for correct assessment or prediction of degradation or accumulation in the environment, all possible conformations of a pollutant are considered.

Toxaphene congeners offer a wide opportunities for conformational isomerism due to possible rotation of chloromethyl and dichloromethyl groups. There is little information in the literature on this subject.

It was first noticed in 1977 by Turner, Engel and Casida ¹) that several signals in proton NMR spectra of 2,2,5-endo,6-exo,8,9,10,10-Octachlorobornane (10-Cl-B) and 2,2,3-exo,5-endo,6-exo,8,9,10,10-Nonachlorobornane (3-exo,10-Cl₂-B) are broad. However, no clear explanation of this fact was given.

Semi-empirical calculations of the structure of the two most important congeners, 2-endo,3-exo,5-endo,6-exo,8,8,10,10-Octachlorobornane and 2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-Nonachlorobornane suggested the most stable conformations, which are in a good agreement with NMR spectra ²).

Parlar and co-workers assume no rotation occurs and even use different nomenclature for different positions at C-8, C-9 and C-10 atoms (8a, 8b, etc.) ³).

It is necessary to emphasize, that for none of over 50 different Toxaphene congeners more than one conformer was reported.

The purpose of present pilot study was to find an evidence for rotation of chlorosubstituted methyl groups in Toxaphene congeners. We have studied temperature dependence of proton NMR spectra of the three compounds, which spectra at ambient temperature have broadened signals - 2-exo,3-endo,6-exo,8,9,10,10-Heptachlorobornane, 2,2-3-exo,5-endo,6-exo,8,9,10,10-Nonachlorobornane and 2-exo,3-endo,6,8,8,9,10,10-Octachlorodihydrocamphene.

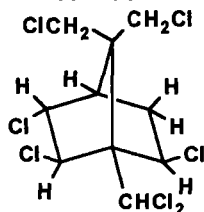
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Experimental Methods

Isolation of Toxaphene congeners was described by us earlier ⁴⁾. NMR-spectra were recorded on Bruker AM-500 spectrometer. Solvent used was CDCl₃, concentrations - about 1%.

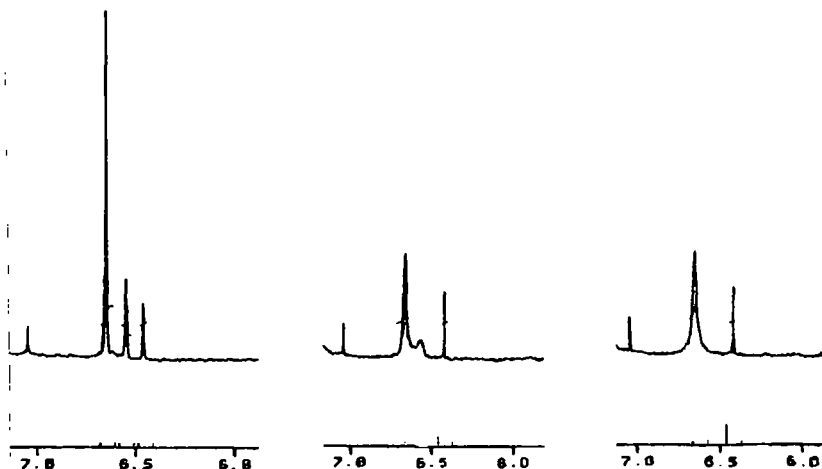
Results and Discussion

1) 2-exo,3-endo,6-exo,8,9,10,10-Heptachlorobornane



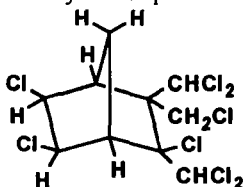
The spectrum at ambient temperature shows two sets of broadened signals without fine structure. At elevated temperature one can observe only one set of signals and weaker broadening. At low temperature broadening disappears, and fine structure of both sets of signals becomes clearly visible.

Fig. 1. Fragments of spectra of 2-exo,3-endo,6-exo,8,9,10,10-Heptachlorobornane (6.0 -7.0ppm). Left - at -58°C, center - at ambient temperature, right - at +52°C.



Therefore, this compound in CDCl₃ solution exists in two conformations in ca 5 : 1 ratio. On NMR time-scale rotation is slow at ambient temperature, fast at +52°C, no rotation takes place at -58°C.

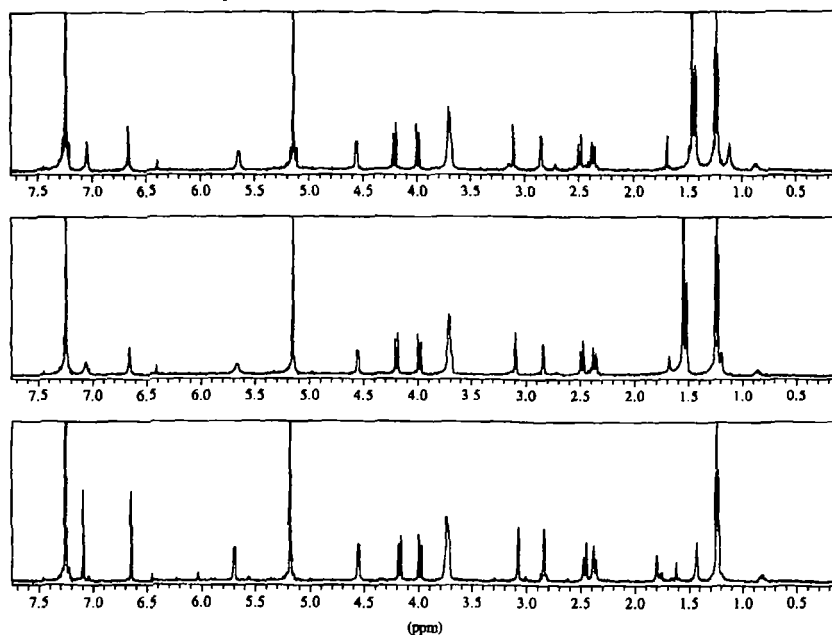
2) 2-exo,3-endo,6,8,8,9,10,10-Octachlorodihydrocamphene



TOXAPHENE

At ambient temperature one can see the most significant broadening of the signals of dichloromethyl protons and of 2-endo proton at 7.1, 6.65 and 5.7ppm. This broadening gets weaker at elevated temperature and disappears at -53°C. However, no sign of another conformation appear.

Fig. 2. Spectra of 2-exo,3-endo,6-exo,8,8,9,10,10-Octachlorodihydrocamphene. Upper - at +52°C; middle - at ambient temperature; lower - at -53°C.



It means, that this compound has rotation behavior like 2-exo,3-endo,6-exo,8,9,10,10-Heptachlorobornane, but the most stable conformation is predominant (> 90%) in equilibration mixture.

3) 2,2-3-exo,5-endo,6-exo,8,9,10,10-Nonachlorobornane



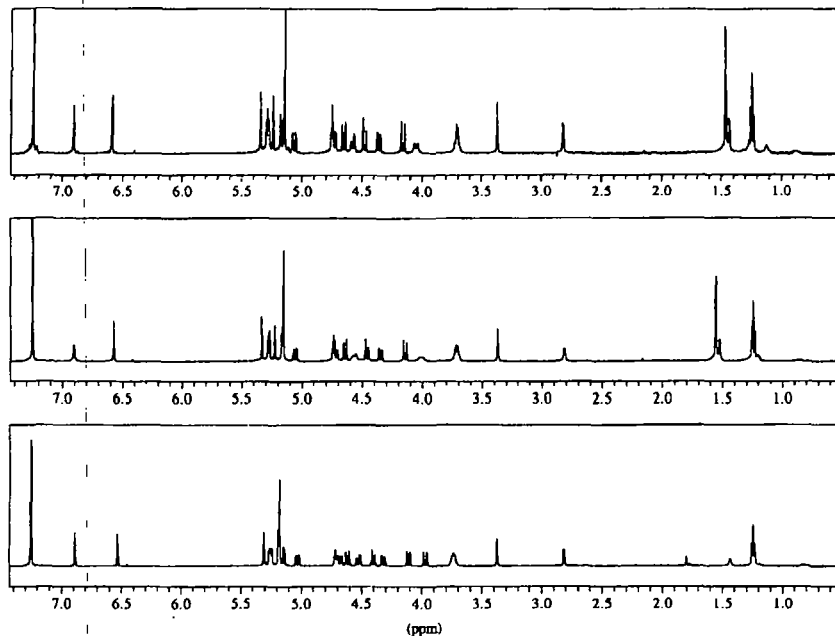
We have obtained this compound as a 1:1 mixture with its close structural analog - 2-exo,3,3,5-exo,6-endo,8,9,10,10-Nonachlorobornane. These two compounds always co-crystallize and all our attempts to separate the pair were unsuccessful.

At ambient temperature three signals of dichloromethyl proton at 6.9ppm, chloromethyl proton at 4.55ppm and chloromethyl proton at 4.0ppm are broad. At elevated temperature the broadening gets weaker. At -53°C broadening disappears, and fine structure becomes clearly visible. Again, there are no signals of the second conformation. It means, that rotation behavior of this compound is similar to

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that of 2-exo,3-endo,6,8,8,9,10,10-Octachlorodihydrocamphene.

Fig.3. Spectra of a mixture of 2,2-3-exo,5-endo,6-exo,8,9,10,10-Nonachlorobornane and 2-exo,3,3,5-exo,6-endo,8,9,10,10-Nonachlorobornane. Upper - at +52°C; middle - at ambient temperature; lower - at -53°C.



At the same time, at -53°C two signals of chloromethyl protons of another component of the mixture, 2-exo,3,3,5-exo,6-endo,8,9,10,10-Nonachlorobornane, at 5.05ppm and 4.35ppm become broader, and their fine structure disappears. This indicates, that the rotation of this compound, fast on NMR time-scale at ambient temperature, at -53°C gets slow enough to be detected.

Conclusions

- 1) Internal rotation of chlorosubstituted methyl groups is possible at least in some Toxaphene congeners.
- 2) Two stable conformations have been detected for 2-exo,3-endo,6-exo,8,9,10,10-Heptachlorobornane.

Literature Cited

- (1) Turner, W.V.; Engel, J.L.; Casida, J.E. *J. Agric. Food Chem.* **1977**, 25(6), 1394-1401.
- (2) Vetter, W.; Scherer, G.; Schlabach, M.; Luckas, B.; Oehme, M. *Fresenius J Anal Chem.* **1994**, 349, 552-558.
- (3) Hainzl, D.; Burhenne, J.; Barlas, H.; Parlar, H. *Fresenius J Anal Chem.* **1995**, 351, 271-285.
- (4) Nikiforov, V.A.; Tribulovich, V.G.; Karavan, V.S. *Organohalogen Compounds* **1995**, 26, 379-382