# Structure-Behaviour Relationships for Toxaphene Congeners. I. Gas Chromatography of Chlorinated Bornanes

Vladimir A. Nikiforov[1], Vyacheslav G. Tribulovich[2], Sergei Bolshakov[2]
[1]St.Petersburg University, Institute of Chemistry, 198904, Universitetsky pr. 2, St.Petersburg, Stary Peterhof, Russia
[2]St.Petersburg University, Department of Chemistry, 199034, Universitetskaya nab., 7/9, St.Petersburg, Russia

## Introduction

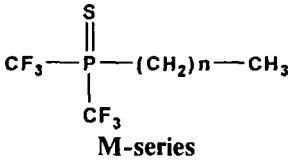
Two general methods have been employed for identification of Toxaphene components:
1)- Isolation of pure compounds from environmental samples and structure elucidation based on MS, MS/MS and $^1$H NMR spectral data[1,2,3]
2)- Isolation of chloroterpenes from technical Toxaphene[4,5,6] or modified formulations, like CB-standard[7], chlorination mixtures of Toxicant B[4], 2-exo,10-Dichlorobornane[4] or 2,10,10-Trichlorobornane[8] or 6,8-Dichlorocamphene[9], followed by structure elucidation and environmental relevance check.

The first method has an advantage of doubtless importance of the isolates, however it is labour-expensive and isolated amounts are usually not sufficient for preparation of analytical standards for the world-wide use. The second often yields compounds in hundreds milligrams, but even more often those compounds have little value, as they are not presented in environmental samples. In other words, this method is almost blind, until there is no information on the structure of target relevant congener.

The first evidence of an environmentally relevant congener is a new peak on a chromatogram, and typical information is retention time plus more or less reliable assessment of a number of chlorine atoms from NICI-MS. The idea of this paper is to find correlations between structure of isomers and their GC retention order and investigate the usefulness of Retention Indices for structure elucidation.

## Results and discussion

Retention times were measured on HP5890 gas chromatograph with ECD.Column - Ultra-2, 25m, 0,32mm i.d., carrier gas - helium, split injection, temperature program 90°C(1min), 10°C/min to 270°C, hold for 10min.
Retention Indices were calculated using cubic spline interpolation and with M-series as reference[10](Code - N). For the compounds, reported in literature[7](Code - P), simple linear approximation was used, with compounds with known indices as reference.

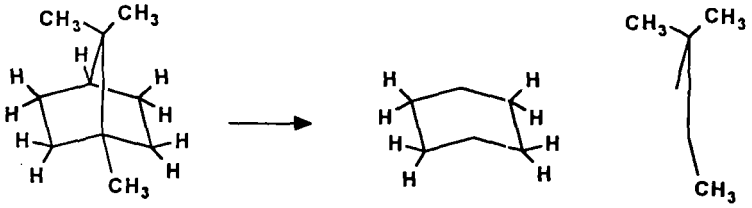



**M-series**

**Table 1. Codes, retention times and retention indices of Polychlorobornanes**

| Code | Compound | RT(min) | RI |
|---|---|---|---|
| **M14** | | 12.86 | 1400 |
| **M16** | | 14.91 | 1600 |
| N01 | 2-exo,3-endo,5-exo,8,9,10,10-HpCB | 16.11 | 1724 |
| N02 | 2-exo,5,5,9,9,10,10-HpCB | 16.32 | 1746 |
| P03 | 2,2,5,5,9,10,10-HpCB | | 1776 |
| **M18** | | 16.81 | 1800 |
| N04 | 2-endo,3-exo,5-endo,6-exo,8,8,10,10-OCB | 17.09 | 1831 |
| N05 | 2-exo,3-endo,5-exo,8,9,10,10-HpCB | 17.40 | 1867 |
| N06 | 2,2,5-endo,6-exo,8,9,10-HpCB | 17.57 | 1886 |
| N07 | 2-exo,3-endo,5-exo,6-exo,8,9,10-HpCB | 17.63 | 1894 |
| N08 | 2-endo,3-exo,6-exo,8,9,10,10-HpCB | 17.64 | 1894 |
| N09 | 2-exo,3-exo,6-endo,8,9,10,10-HpCB | 17.72 | 1903 |
| N10 | 2-exo,3-endo,6-endo,8,9,10,10-HpCB | 17.86 | 1920 |
| N11 | 2,2,5,5,9,9,10,10-OCB | 17.96 | 1931 |
| N12 | 2,2,3-exo,5-endo,6-exo,8,9,10-OCB | 18.16 | 1954 |
| P13 | 2-endo,3-exo,5-endo,6-exo,8,9,10,10-OCB | | 1960 |
| P14 | 2-exo,3-endo,5-exo,8,9,9,10,10-OCB | | 1964 |
| P15 | 2,2,5-endo,6-exo,8,8,9,10-OCB | | 1974 |
| P16 | 2,2,5-endo,6-exo,8,9,9,10-OCB | | 1974 |
| P17 | 2-exo,5,5,8,9,9,10,10-OCB | | 1988 |
| **M20** | | 18.55 | 2000 |
| *P18* | *2,2,5-endo,6-exo,8,9,10,10-OCB* | | *2034* |
| N19 | 2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-NCB | 18.86 | 2035 |
| N20 | 2-exo,3,3,5-exo,6-endo,9,9,10,10-NCB | 18.86 | 2035 |
| P21 | 2,2,5,5,8,9,10,10-OCB | | 2052 |
| N22 | 2,2,3-exo,5,5,9,9,10,10-NCB | 19.04 | 2056 |
| P23 | 2,2,3-exo,5-endo,6-exo,8,9,9,10-NCB | | 2086 |
| N24 | 2,2,3-exo,5-endo,6-exo,8,9,10,10-NCB | 19.32 | 2090 |
| N25 | 2-exo,3,3,5-exo,6-endo,8,9,10,10-NCB | 19.32 | 2090 |
| P26 | 2,2,5-endo,6-exo,8,8,9,10,10-NCB | | 2096 |
| N27 | 2,2,3-exo,5,5,8,9,10,10-NCB | 19.52 | 2112 |
| P28 | 2,2,5-endo,6-exo,8,9,9,10,10-NCB | | 2116 |
| N29 | 2,2,5,5,8,9,9,10,10-NCB | 19.97 | 2127 |
| P30 | 2-exo,3-exo,5-endo,6-exo,8,8,9,10,10-NCB | | 2149 |
| P31 | 2,2,5,5,6-exo,8,9,9,10-NCB | | 2171 |
| N32 | 2,2,3-exo,5-endo,6-exo,8,9,9,10,10-DCB | 20.62 | 2240 |
| N33 | 2-exo,3,3,5-exo,6-endo,8,9,9,10,10-DCB | 21.30 | 2318 |
| N34 | 2,2,5,5,6-exo,8,9,9,10,10-DCB | 21.64 | 2359 |
| N35 | 2,2,3-exo,5,5,8,9,9,10,10-DCB | 21.68 | 2363 |

Bornane molecule can be separated in a "natural way" in two parts :
- a ring of methylene groups, later called "Ring"
- three methyl groups, later called "Metil"



These two fragments, with a different chlorosubstitution pattern will be our "building blocks" for construction of a Toxaphene congener "building". Table 2 reflects a dependence of RI upon the way of construction.

**Table 2. Retention Indices as a function of chlrosubstitution pattern of Ring and Metil**

| Metil<br>Ring | 8,10,10 | 8,9,10 | 8,8,10,10 | 8,9,10,10 | 8,8,9,10 | 8,8,9,10,10 |
|---|---|---|---|---|---|---|
| 2-exo,3-endo,5-exo | | | 1724 | 1867 | | 1964 |
| 2-exo,5,5 | | | 1746 | | | 1988 |
| 2-endo,3-exo,6-exo | | | | 1894 | | |
| 2-exo,3-exo,6-endo | | | | 1903 | | |
| 2-exo,3-endo,6-endo | | | | 1920 | | |
| 2-endo,3-exo,5-endo,6-exo | | | 1831 | 1960 | | 2035 |
| 2,2,5-endo,6-exo | | 1886 | | 2034 | 1974 | 2116 |
| 2,2,5,5 | 1776 | | 1931 | 2056 | | 2127 |
| 2-exo,3-endo,5-exo,6-endo | | 1894 | | | | 2149 |
| 2,2,3-exo,5-endo,6-exo | | 1954 | | 2090 | 2086 | 2240 |
| 2-exo,3,3,5-exo,6-endo | | | 2035 | 2090 | | 2318 |
| 2,2,5,5,6-exo | | | | | 2171 | 2359 |
| 2,2,3-exo,5,5 | | | 2056 | 2112 | | 2363 |

Available M-series(n=14-20) is not completely suitable for Toxaphene congeners, a series with longer retention times is necessary for correct calculation of retention indices. However, based on available information, the following conclusions can be made:

1) RI for the congeners with either the same Metil or the same Ring increase with the extent of chlorination
2) For all types of Metil, the following order of RI for different Rings was found : 2-exo,3-endo,5-exo,6-endo < 2,2,5-endo,6-exo < 2,2,5,5 < 2-exo,3-exo,5-endo,6-exo
3) For all types of Ring, the following order of RI for different Metils was found : 8,8,10,10 < 8,9,10,10 and 8,8,9,10 < 8,9,10,10
4) In general, no quantitative correlation was found between the structure of building blocks and RI. Substitution of one Metil to another at different Rings (and *vice versa*) may lead to different changes in RI
5) An excellent correlation was found, if there is no interaction between the differing parts of Metils and differing parts of Rings. This can be illustrated with examples:

N01, RI=1724 P14, RI=1964
N02, RI=1746 P17, RI=1988

N20, RI=2035 N25, RI=2090
N22, RI=2056 N27, RI=2112

N04, RI=1831 P13, RI=1960 N19, RI=2035
N11, RI=1931 P21, RI=2052 N29, RI=2127

6) Based on the available data and using the rule 5), RI for some unknown congeners can be predicted :

| | |
|---|---|
| 2-endo,3-exo,5-endo,6-exo,8,10,10-HpCB | RI=1678 |
| 2-exo,5,5,8,9,10,10-HpCB | RI=1890 |
| 2-endo,3-exo,5-exo,6-exo,8,8,10,10-OCB | RI=1945 |
| 2-exo,3-endo,6-endo,8,9,9,10,10-OCB | RI=2017 |

7) Calculation of RI for the new peaks on a chromatogram would allow to leave a few structures for consideration, and can be used for structure elucidation as an additional tool along with NMR and MS.

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