

Molecular Structure of BHC and its Related Compounds.

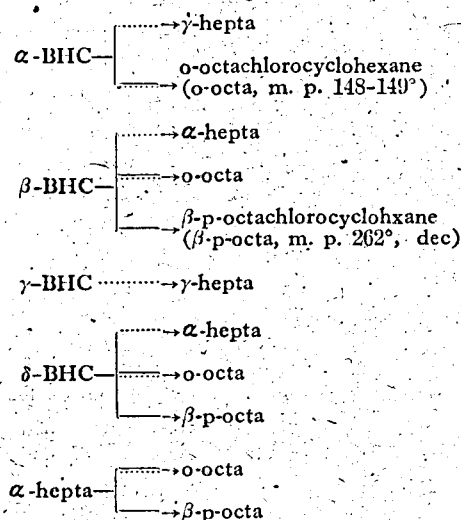
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YAMADA, Masayuki TAMADA, Michiko INOUE and Minoru OHNO (Takei Laboratory, Institute for Chemical Research, Kyoto University), Received Dec. 10, 1949. *Botyu-Kagaku* 14: 42-43 (With English résumé p. 43)

7. BHC (1, 2, 3, 4, 5, 6 Hexachlorocyclohexane) 及其近縁物質の分子構造に就て 大岩俊彦
山田良一, 浜田昌之, 井上道子, 大野稔 (京都大学化学研究所武居研究室) 24. 12. 10 受付

α -BHC, β -BHC, γ -BHC, δ -BHC, α -heptachlorocyclohexane (α -hepta, m. p. 153-154°)⁽³⁾ 及び γ -heptachlorocyclohexane (γ -hepta, m. p. 85-86°)⁽³⁾ を四塩化炭素溶液中で塩素化した処 Fig. 1 の様な反應が行はれることを知つた。圖で實際は有機化学的に物質を分離した事を, 又点線はポーログラフ的觀察^(1-2,3)を示す。

Fig. 1: Results of Chlorination of BHC and its Related Compounds

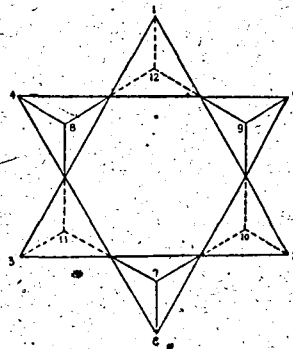


尚 γ -BHC からは o-octa よりアブカリに安定で半波電位約 -0.25 volt (N-甘汞電極標準) の物質も生

成し, 又 γ -hepta からは半波電位約 -0.15 volt (N-甘汞電極標準) の物質は生成するが o-octa の生成は認められない。

α -, β -, γ 及び δ -BHC が何れも椅子型構造であり, β -BHC が II の構造 (Table I) であることは既に決定されてゐる^(4,5,6,7,8,9)。このことと吾々の実験結果から α -hepta, γ -hepta, o-octa 及び β -p-octa も椅子型構造であることが明かとなり, Table I 及び Fig. 2 に示す様な α -BHC, δ -BHC, α -hepta, o-octa 及び β -p-octa の分子構造を決定し, γ -BHC 及び γ -hepta の分子構造を推定した。

Fig. 2: Cyclohexane Ring with Carbon Atom shown as Tetrahedra



以上の吾々の結論は X 線解析に依つて決定された γ -BHC の構造⁽¹³⁾や従来他の手段に依つて推定された

Table I: Configurations of BHC and its Related Compounds

No.	Carbon Number	1		2		3		4		5		6	
	Position of Substitution	12	1	5	9	10	2	6	7	11	3	4	8
I	α -C ₆ H ₆ Cl ₆	Cl	H	Cl	H	H	Cl	Cl	H	H	Cl	H	Cl
II	β -C ₆ H ₆ Cl ₆	H	Cl	Cl	H	H	Cl	Cl	H	H	Cl	Cl	H
III	γ -C ₆ H ₆ Cl ₆	H	Cl	Cl	H	Cl	H	H	Cl	Cl	H	Cl	H
IV	δ -C ₆ H ₆ Cl ₆	Cl	H	Cl	H	H	Cl	Cl	H	H	Cl	Cl	H
V	α -C ₆ H ₅ Cl ₇	Cl	Cl	Cl	H	H	Cl	Cl	H	H	Cl	Cl	H
VI	γ -C ₆ H ₅ Cl ₇	Cl	H	Cl	H	H	Cl	Cl	H	Cl	Cl	H	Cl
VII	o-C ₆ H ₄ Cl ₈	Cl	Cl	Cl	H	H	Cl	Cl	H	H	Cl	Cl	Cl
VIII	β -p-C ₆ H ₄ Cl ₈	Cl	Cl	Cl	H	H	Cl	Cl	Cl	H	Cl	Cl	H

構造^(7,8,9,10,11,12)の多くのものと一致し、又種々の実験結果^(4,5,6,7,8,9,10,11,12)をもよく説明することが出来る。然し乍ら、 δ -BHC の構造に関しては対称の中心を持つと云う Daasch⁽⁹⁾ 及び Kulkarnijatkar 等⁽¹⁴⁾ の推論した構造とは異なるが、谷谷等の有極性であると云う事実⁽¹⁰⁾ 及び中島等が脱塩酸反應速度から推定⁽¹⁶⁾ した構造とは一致する。

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Résumé

From the studies on photochlorination of α -BHC, β -BHC, γ -BHC, δ -BHC, α -heptachlorocyclohexane (α -hepta, m. p. 153—154°)⁽⁹⁾ and γ -heptachlorocyclohexane (γ -hepta, m. p. 85—86°)⁽³⁾ in carbon tetrachloride solution, we found that the reactions shown in Fig. 1 took place. In this figure the solid lines are shown that materials were isolated substantially and the processes of the dotted lines were observed polarographically^(12,3).

Moreover we did not obtain o-octa from either γ -BHC or γ -hepta, but observed polarographically from former a compound which half wave potential was about -0.25 volt (N calomel electrode standard) and from latter another compound being half wave potential about -0.15 volt (N calomel electrode standard).

It has been already determined that α -, β -, γ - and δ -BHC are chair form and the β -BHC is structure II (Table I, Fig. 2).^(4,5,6,7,8,9) From these facts and our experimental results, α -hepta, γ -hepta, o-octa and β -p-octa become necessarily to be chair form, and then we determined the molecular structures of α -BHC, δ -BHC, α -hepta, o-octa and β -p-octa and also assumed the structures of γ -BHC and γ -hepta as shown in Table I.

Our above structures accord with the structure of γ -BHC determined by X-ray analysis⁽¹³⁾ and with that of BHC assumed by various methods^(7,8,9,10,11,12), and also can justify the many previous experimental results^(4,5,6,7,8,9,10,11,12). But the structure of δ -isomer we determined does not agree with the symmetrical form^(9,14), but agrees with the fact that δ -form is polar⁽¹⁵⁾ and with the structure which is assumed by the velocity of dehydrochlorination.⁽¹⁶⁾

防 虫 科 學 第 12 號 正 誤 表

頁	個 所	誤	正
14	右列 7 行目	200. 400. 800. 1600. 3200.	2000. 4000. 8000. 16000. 32000.
21	第 1 図	濃度にされた	濃度にさされた