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ON THE OPTICAL ACTIVITY OF POLYCHLORINATED BIPHENYLS

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ABSTRACT

Commercial mixtures and residue samples of polychlorinated biphenyls comprise approximately one hundred individual chemical compounds. These differ in their physical and chemical nature and physiological effects. The existence of nine of the major, and ten of the minor, constituents of the Aroclors 1242, 1254 and 1260 in optically active forms has now been predicted. These molecules derive optical activity from the resistance to change conformation due to the interference of the chlorine substituents. The activation energy (ΔE), required for the racemisation has been estimated to be greater (ΔE = 25–58 $kcal \cdot mole^{-1}$) than the thermal energy usually available in the ecosystem. The presence of these optical isomers will have a bearing on the toxicity and metabolic interactions of these chemicals.

INTRODUCTION

Environmental contamination by polychlorinated biphenyls (PCBs) has been established over the past few years (Peakall & Lincer, 1970). Regional and international monitoring has proved their presence in many samples of aquatic origin (Risebrough *et al.*, 1968; Anon., 1972; Harvey *et al.*, 1973). A variety of wildlife, as well as domestic animals, accumulated PCBs to sublethal and even acute toxic levels. Due to their resistance to degradation and their accumulation in the food chain, PCBs have also been found in human adipose tissues in Europe and North America (Price & Welch, 1972; Presendorfer *et al.*, 1973).

The ubiquity of PCBs, their toxic and synergistic effects on biota have been studied widely and their chromatographic and biological aspects have been reviewed by Fishbein (1972) and by Quinby (1972). Yet it is surprising that there has not been any investigation into the possibility of optical isomerism of these

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chemicals and the difference with respect to toxicity, synergistic effects and biodegradability which those optical isomers may provide. Thus, West & Todd (1961) state: 'Most of the organic substances involved in the structure and metabolism of living organisms belong to the *D*- or *L*-series. An enzyme will act only upon one form of a substance (*D* or *L*). For example, certain of the *D*-sugars are utilised in the animal body and by microorganisms, whereas the corresponding *L*-sugars are not utilised'.

This paper describes a qualitative and semi-quantitative study of molecular optical isomerism within the group of polychlorinated biphenyls with particular reference to those isomers which will be stable under environmental conditions.

OPTICAL ACTIVITY OF SUBSTITUTED BIPHENYLS

In unsubstituted biphenyl, $C_{12}H_{10}$ (Fig. 1), the intramolecular repulsion o hydrogen atoms in the 2 and 2′ positions and in the 6 and 6′ positions are of mino influence on the conformation of the molecule. For the gaseous state, electro diffraction studies (Bastiansen, 1949) indicate a structure with the planes of th benzene rings tilted against each other.

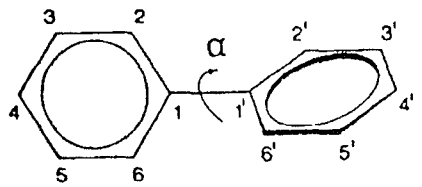


Fig. 1. Biphenyl carbon skeleton, numbers indicating positions of substituents, ∢α indicati relative angle between the phenyl rings.

In the crystalline state, however, the gain in lattice energy is greater than th energy required for surpassing the hydrogen–hydrogen repulsion force for a plan structure. This planar conformation has been confirmed by X-ray structure analys (Dhar, 1949).

Atoms of greater sizes as substituents in the 2 and 2′ positions strongly increa the declination of the two rings from the planar form. This effect has been observe for the molecular structures of dihalogeno biphenyls and for several dihalogen and tetrahalogeno derivatives of dicarboxy biphenyl. Table 1 gives a compilatio of biphenyl compounds, which have been investigated with respect to their confor mation, optical properties resulting therefrom and activation energies for racemisa tion of those optical antipodes.

Further evidence for molecular atropisomerism in biphenyl derivatives has be found in 2,4,2′,4′-tetranitro-6,6′-dicarboxy biphenyl and in 2,4,2′-trinitro-6,

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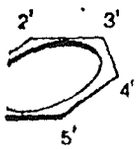
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TABLE I
CONFORMATION, OPTICAL PROPERTIES AND ACTIVATION ENERGIES FOR THE RACEMISATION OF SOME BIPHENYL DERIVATIVES

Compound	*Conformation* $<\alpha$	*Potential optical activity*	*Activation energy for racemisation at (°C) ΔE(kcal · mole^{-1})*	*Reference*
Biphenyl	0° (planar)(a)	No	—	Bastiansen (1950)
Biphenyl	45°(b)	No	<5(c) (20°)	Bastiansen (1949)
2,2′-dichloro bp.(d)	74 ± 5°	Yes	~5(c)	Bastiansen (1950)
2,2′-dibromo bp.	75 ± 5°	Yes	>5(c)	Bastiansen (1950)
2,2′-diiodo bp.	79 ± 5°	Yes	—	Bastiansen (1950)
3,3′-dibromo bp.			20·7	Harris & Cheung (1962)
2,2′-dibromo-4,4-dicarboxy bp.	54 ± 5°	Yes	~5	Bastiansen (1949)
	?	Yes	~19·5	Westheimer (1947)
2,2′-dichloro-6,6′-dicarboxy bp.			19·0	Harris & Cheung (1962)
2,2′-diiodo-5,5′-dicarboxy bp.	?	Isomers isolated	15(c)	Mosenheimer & Höring (1927)
	?	Isomers isolated	21·6	Rieger & Westheimer (1950)
2,3,2′,3′-tetraiodo-5,5′-dicarboxy bp.	?	Isomers isolated	20·7	Harris & Cheung (1962)
2,4,6,2′,4′,6′-hexachloro-3,3′ dicarboxy bp.	?	Isomers isolated	28	Rieger & Westheimer (1950)
	?	Isomers isolated	>30 (100°)	White & Adams (1932)

(*a*) Solid; (*b*) gas; (*c*) estimated; (*d*) bp = biphenyl; (*e*) estimated.

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dicarboxy biphenyl, the latter in solution being slowly racemised with an activation energy of $\Delta E = 22{\cdot}4$ kcal · mole^{-1} at 98·8°C (Kuhn & Albrecht, 1927). As was shown by Rieger & Westheimer (1950), in the case of 2,3,2′,3′-tetraiodo-dicarboxy acids, there is a considerable buttressing effect by large substituents in the 3 and 3′ positions, which increases further the activation energy of the optical isomers, as shown in Table 1.

A similar qualitative repulsion effect can be expected for adjacent chlorine substituents in 2 and 3 positions of the biphenyl structure. Its quantitative effect will be less than for the iodine–iodine pair and can be estimated to be $\Delta E \approx 2$–5 kcal · mole^{-1} for each buttressing chlorine atom.

Supporting evidence for the existence of optical isomerism of PCBs has been observed by White & Adams (1932) in the fact that 2,4,6,2′,4′,6′-hexachloro-3,3′-dicarboxy biphenyl could be resolved into stable optical antipodes. The acid did not racemise under reflux conditions in ethanol or glacial acetic acid nor as sodium salt in boiling water.

OPTICAL ACTIVITY OF POLYCHLORINATED BIPHENYLS

Conformational changes in polychlorinated biphenyls

As can be seen from the experimental and theoretical data presented in Tables 1 and 2, substitution of biphenyl with chlorine will influence the optical properties of these biphenyl compounds. Technical PCB mixtures are produced by catalytic chlorination of biphenyl with Lewis acid catalysts (Beaven *et al.*, 1961). This procedure gives rise to approximately one hundred individual chemical isomers, dependent on the degree of chlorination. They range from unsubstituted biphenyl to polychloro biphenyls with at least eight chlorine atoms per molecule. While most of the commercial PCB mixtures, obtained at certain chlorination levels, have been studied as to their exact composition (Sissons & Welti, 1971; Webb & McCall, 1972), not all of the minor constituents are yet identified and major compounds have been identified only recently after application of combined gas chromatography–mass spectrometry (Sissons & Welti, 1971), gas chromatography–infrared spectroscopy (Webb & McCall, 1972) and proton nuclear magnetic resonance spectroscopy (Sissons & Welti, 1971).

In order to calculate on a semi-quantitative basis the rotational interference of atoms (without corrections for bond-stretching and distortion of bond angles), the bond lengths and structural relations of Fig. 2 were employed.

For the planar conformation, the interatomic distance f between substituents in the 2 and 2′ positions can be calculated as:

$$f = (g^2 + h^2)^{\frac{1}{2}}$$

For:

$$c = a + 2b \cos 60°$$

Fig. 2. Bond lengths, bond
conformation. Bond lengths
$b = 1{\cdot}40$ Å; X = Cl; $e = 1{\cdot}7$

$h =$

$g =$

$f =$

In the case of $x = y$, e

The results for f, calcul
presented in Table 2.

INTERNUCLEAR DISTANCES
THEIR RESPECTIVE SUMS OF

Subst. X	*Subst. Y*	f (Å)
H	H	1·81
H	Cl	1·53
H	Br	1·47
H	I	1·64
Cl	Cl	1·20
Br	Br	1·04
I	I	0·87

(a) Values after Cotton & Wilki
(b) Values after Weast (1969).
(c) ΔE values are calculated as
racemisation of 2,2′-dihalogeno
(d) Values estimated by compar
and Van der Waals radii and sur

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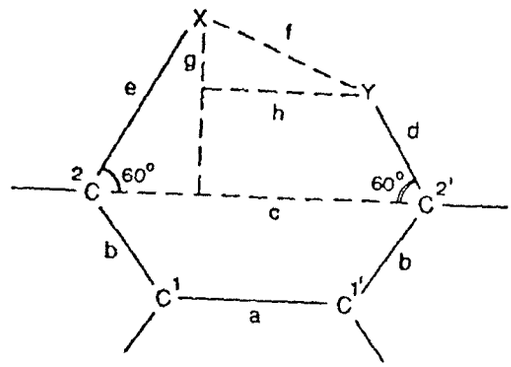


Fig. 2. Bond lengths, bond angles and internuclear distance f in an idealised planar biphenyl conformation. Bond lengths after Fieser & Fieser (1965). Carbon indices as in Fig. 1. $a = 1{\cdot}48$ Å; $b = 1{\cdot}40$ Å; $X = Cl$: $c = 1{\cdot}70$ Å; $X = H$: $c = 1{\cdot}09$ Å; $Y = Br$: $d = 1{\cdot}86$ Å; $Y = I$: $d = 2{\cdot}03$ Å.

$$h = c - e\cos 60° - d\cos 60°$$

$$g = e\sin 60° - d\sin 60°$$

$$f = [(\tfrac{1}{2}e - \tfrac{1}{2}d)^2 + (c - 0{\cdot}5e - 0{\cdot}5d)^2]^{\frac{1}{2}}$$

In the case of $x = y$, $e = d$ and $g = 0$;

$$f = c - e$$

The results for f, calculated for several hydrogen–halogen combinations, are presented in Table 2.

TABLE 2

INTERNUCLEAR DISTANCES f OF BIPHENYL SUBSTITUENTS IN 2 AND 2' POSITIONS WITH THEIR RESPECTIVE SUMS OF COVALENT RADII, VAN DER WAALS RADII AND ACTIVATION ENERGIES FOR THE RACEMISATION

Subst. X	*Subst. Y*	f (Å)	Σ *CR* (Å)	Σ *v.d.WR* (Å)[a]	$\Sigma\, e + d$ (Å)[b]	ΔE[c] *kcal . mole*$^{-1}$
H	H	1·81	0·56	2·40	2·18	<2·5[d]
H	Cl	1·53	1·27	3·00	2·79	~2·5[d]
H	Br	1·47	1·42	3·15	2·95	9
H	I	1·64	1·61	3·35	3·12	10–14
Cl	Cl	1·20	1·98	3·60	3·40	~25[d]
Br	Br	1·04	2·28	3·90	3·72	~40[d]
I	I	0·87	2·66	4·30	4·06	~80[d]

(a) Values after Cotton & Wilkinson (1967).
(b) Values after Weast (1969).
(c) ΔE values are calculated as one half of experimentally observed activation energies for the racemisation of 2,2'-dihalogeno biphenyl derivatives.
(d) Values estimated by comparison of the internuclear distances f with the sums of covalent and Van der Waals radii and sums ($e + d$).

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As the values calculated in Table 2 indicate, distances f of hydrogen–hydrogen and hydrogen–chlorine pairs are greater than their respective sums of covalent radii. For the hydrogen–bromine pair and for the hydrogen–iodine pair both values are of the same magnitude, while for the halogen–halogen pairs the available interatomic space (neglecting molecule distortion) is considerably less than the sums of their covalent radii. This agrees with another empirical calculation, the 'Adams Rule', by which optical isomers of biphenyl derivatives can be obtained at ambient temperatures if the sum of the covalent nuclear distances ($\Sigma\, e + d$) is greater than or equal to 2·90 Å (Westheimer, 1956). Concordant with those parameters are the observed activation energies for the racemisation of optical biphenyl isomers.

It can therefore confidently be predicted that individual polychlorinated biphenyl isomers will exist in optical atrop antipodes, provided that they:

1. fulfil the general requirements for optical activity; *i.e.*, absence of either a plane of symmetry, a symmetry axis or of a centre of inversion or a combination thereof and
2. have chlorine substituents in the 2 and 6 positions of one phenyl ring and have a chlorine substituent in the 2′ position of the second phenyl ring.

As can be estimated by comparison with compounds referred to in Table 1, PCBs meeting these requirements will have activation energies in excess of $\Delta E = 20$ kcal · mole^{-1}; *i.e.*, being sufficiently restrained from change of conformation through the planar form under most environmental conditions, where elevated temperatures are not usually encountered. This fact may be of special importance to the environmental behaviour of those chemicals, particularly to their biological activity towards toxic and synergetic effects and to their biodeterioration in the aquatic ecosystems.

Optically active PCBs in technical and environmental samples

On examination of the substitution possibilities in biphenyl, it will be found that there are 19 PCB isomers satisfying the above-mentioned conditions for optical activity and conformational stability. Including these, there are 78 PCB isomers out of a total of 210 possible structural isomers which meet the basic requirements for optical activity alone. However, most of those have less strained conformational transition states. A tabular summary of all PCB isomers, without any symmetry element in the non-planar conformation, with respect to the number of chlorine atoms in each ring is given in Table 3.

The optical *stability* of the less strained isomers cannot readily be estimated, since there are buttressing and electronic effects of unknown magnitude playing a role for the transition state requirements. However, by comparison with the data of Tables 1 and 2, one can assume their activation energies for racemisation to be $\Delta E \leq 20$ kcal · mole^{-1}. Thus, under ambient conditions, racemisation of any optical isomers will occur.

Most of the mentioned 19 *optically stable* PCB isomers with chlorine substituents

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Number of chlorine atoms in ring B

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$\Delta E \geq 25$ kcal · mole^{-1}. Thei
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Table 4. For the estimation

POLYCHLORINATED BIPH
CONFORMATIONS, THEIR PRESENCE
ACTIVA

Number of chlorines per molecule	*Positions of chlorine substituents*	
4	236	2′
5	236	2′3′
	236	2′4′
	236	2′5′
	2346	2′
6	236	2′3′4′
	236	2′3′5′
	236	2′3′6′
	236	2′4′5′
	2346	2′3′
	2346	2′4′
	2346	2′5′
7	2346	2′3′4′
	2346	2′3′5′
	2345	2′3′6′
	2346	2′3′6′
	2346	2′4′5′
8	2346	2′3′4′6′
	2346	2′3′4′5′

(a) After Sissons & Welti (1971) and
(b) Estimates based on observed and
temperatures.
(c) – indicates a minor constituent.
(d) ··· indicates a major constituen

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respective sums of covalent radii.
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TABLE 3
THEORETICAL POSSIBLE POLYCHLORINATED BIPHENYL ISOMERS WITH OPTICAL ACTIVITY WHEN IN A NON-PLANAR CONFORMATION

		Number of chlorine atoms in ring A					
		0	1	2	3	4	5
Number of chlorine atoms in ring B	0	0	0	0	0	0	0
	1		3	8	8	4	0
	2			10	16	8	0
	3				10	8	0
	4					3	0
	5						0
						Total	78

at least in the 2, 6 and 2′ positions have been observed in one or more of the commercial PCB mixtures (Sissons & Welti, 1971; Webb & McCall, 1972). Each of these isomers is predicted to have an activation energy for the racemisation of $\Delta E \geq 25$ kcal · mole^{-1}. Their exact substitution and estimated activation energies, as well as their presence in three commercial PCB mixtures, are compiled in Table 4. For the estimation of the activation energies, the following parameters

TABLE 4
POLYCHLORINATED BIPHENYLS OF PREDICTED OPTICALLY ACTIVE AND STABLE CONFORMATIONS, THEIR PRESENCE IN SOME COMMERCIAL MIXTURES AND THEIR ESTIMATED ACTIVATION ENERGIES FOR RACEMISATION

Number of chlorines per molecule	*Positions of chlorine substituents*		*Presence in Aroclor*[a] 1242	1254	1260	ΔE(~20°C)[b] *kcal . mole*$^{-1}$
4	236	2′	+[c]	+(?)	+(?)	25
5	236	2′3′	+	++[d]	+	29
	236	2′4′		?	+	25
	236	2′5′	++	++	++	25
	2346	2′	?	?	?	25
6	236	2′3′4′	+(?)	++	++	29
	236	2′3′5′	+(?)	+	?	29
	236	2′3′6′		+	++	58
	236	2′4′5′	+	++	++	25
	2346	2′3′		+	+	29
	2346	2′4′	+		++(?)	25
	2346	2′5′	+	+		25
7	2346	2′3′4′		+	+	29
	2346	2′3′5′		+	++	29
	2345	2′3′6′		+	++	29
	2346	2′3′6′		+	+	58
	2346	2′4′5′		+	++	25
8	2346	2′3′4′6′			+	58
	2346	2′3′4′5′			+	29

(*a*) After Sissons & Welti (1971) and Webb & McCall (1972).
(*b*) Estimates based on observed and estimated values, according to Tables 1 and 2 at ambient temperatures.
(*c*) + indicates a minor constituent.
(*d*) ++ indicates a major constituent.

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serve as a basis. Derived from the internuclear distance f (1·20 Å) related to the sum of the covalent radii (1·98 Å) as in Table 2: the base value for turning a phenyl ring with *chlorine* in 2 or 6 position *past chlorine* in 2′ or 6′ position is estimated as $\Delta E = 25$ kcal · mole^{-1}. For each chlorine substituent in either 3, 5, 3′ or 5′ position, adjacent to chlorine in 2, 6, 2′ or 6′ positions a buttressing effect of $\Delta E = 4$ kcal · mole^{-1} is added. For example, 2,3,6,2′,3′-pentachloro biphenyl would have only one buttressing chlorine; *i.e.*, in 3′ position, since the molecule may change its conformation by turning the ring with chlorines in 2′, 3′ positions past the chlorine in 6 position.

It should be pointed out in this context that European and Japanese products may have similar values for their overall chlorination levels, but do not necessarily represent the same combination of structural isomers in a given mixture. Unfortunately, basic comparative gas chromatographic studies on PCB mixtures from different origins are still missing. By the nature of the preparation, of course, commercial PCB mixtures will most likely contain optical active isomers in form of their racemates. The separation of racemic isomers into their optical antipodes has as yet not been reported.

CONCLUSION

Of the *major* constituents in three commercial mixtures of PCBs; *i.e.*, Aroclors 1242, 1254 and 1260, in total nine different PCB isomers are predicted to exist in environmentally stable optical atropisomers. This fact is regarded to have a major influence on the biochemical activities and biodegradation of those antipodes.

ACKNOWLEDGEMENT

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