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THE ASYMMETRIC NON-CARBON ATOM

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The stereochemistry of compounds with asymmetric carbon was long ago consolidated into a unified system which rests on numerous correlations of the configurations of important classes of compounds and received its principal consummation after the establishment of the absolute configurations. Later, in the fifties, the stereochemistry of compounds exhibiting molecular dissymmetry (without an asymmetric atom) was formulated: substituted biphenyls, allenes, etc. This process is still not completely finished, although there has been great progress in the last decade. It must also be noted that in this period great interest was aroused in the theory of optical activity in general and the method of optical rotatory dispersion was vigorously developed as a tool for the investigation of organic and inorganic compounds.

Until recent years much less attention was paid to molecules containing an asymmetric atom other than carbon. Meanwhile the great diversity of types of such compounds is of great interest for stereochemistry. This region of investigation, which has been exploited particularly intensively during the last 5–6 years, has not been surveyed in the review literature known to us.

1. GENERAL OUTLINE OF THE HISTORY OF THE PROBLEM

In the history of this problem it is possible to distinguish several periods, the start of each being indicated by the origination of a certain idea (naturally, it is impossible to draw sharp boundaries between these periods). The start of the stereochemistry of the non-carbon asymmetric atom can be ascribed to the time when one of the founders of stereochemistry, LeBel[1], obtained an optically active salt (the chloride) of the ethylisobutylisopropylmethylammonium cation by a microbiological method (1891). In the first period the main interest of chemists was in the demonstration of the possibility of the existence of tetra- and tri-substituted non-carbon atoms in an optically active form. This was evidence of the generality of the tetrahedral model and of its applicability also to elements other than carbon. The most important works in the years 1900–1910 were completed by the English stereochemical school (Pope and Peachey): ammonium[2] and sulphonium[3] salts, etc., were separated into antipodes. At the end of the twenties optically active esters of sulphinic acids[4], sulphoxides, and related compounds were obtained. Exhaustion of the possibilities in this direction appeared to be the reason for the considerable reduction in the number of publications (up to the fifties). However, the description work retains significance, for example, a quadruply-substituted sulphur derivative[6] was obtained in the optically active state in 1960, and an amine oxide[7] only in 1963.

The start of the second period can be considered to be the work of Meisenheimer[8,9] (1911–1926). At this time a persistent interest commenced in the nature of optical

activity, which first arose, of course, in the stereochemistry of carbon (beginning with Chugaev). Meisenheimer took up an idea of Werner [10] about the role of the central atom in complexes and introduced it into organic chemistry. He was not only the first who posed the problem of the influence of the nature of the asymmetric central atom on the magnitude of the rotation, but he also carried out experimental work that was a model in its execution. His work retained a demonstrative character (for the semipolar bond in amine oxides and phosphines), but the general statement of the question was elegant. After Meisenheimer, interest in this aspect of the problem was lost for a long time, being maintained only in the laboratory of Mann [11] (Cambridge), where unusual refraction was obtained.

The third period starts at the end of the fifties: compounds with an asymmetric non-carbon atom are used as models for studying reaction mechanisms, in which it is already necessary to take into account differences between carbon and other elements. In recent years the stereochemistry of Si, P, Ge, and As has been practically established and information obtained on the mechanisms of substitution at phosphorus and silicon. The greatest success is the establishment in certain instances of the absolute configuration of non-carbon asymmetric centres, which is one of the main tasks of static stereochemistry. A second task presents much greater difficulty: the determination of the magnitude of the optical rotation as a function of structure. This is still far from solution.

Specific interest in the limits of the problem under review is the problem of the dependence of rotation on the nature of the asymmetric atom. In compiling this review this has received the greatest attention. On the other hand we have not aimed at an exhaustive treatment of the problem of dynamic stereochemistry. Of the older works (which can be found in the well-known handbooks on stereochemistry) we consider in detail only those which are of significant importance in the aspect referred to; the others are simply mentioned. The most recent literature used in the review appeared in Autumn 1963. [The authors have added some more recent references at the end of the bibliography (Ed. of Translation).]

At present, optical activity due to asymmetric atoms of the following elements (other than carbon) has been established: Si, Ge, N, P, As, Sb, S, Se, Te. The material will be considered according to the Groups of the Periodic System, beginning in greater detail with Groups V and VI, whose stereochemistry has a greater history, and then reverting to the more recent work on Group IV. A special Section deals with spirans with a hetero-spiro-atom. The last part of the review contains an attempt to analyse the published material using the semiempirical method of calculating optical rotation developed by Brewster [12-14] for compounds with asymmetric carbon.

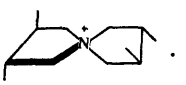
2. GROUP V

Salts of quadruply-substituted ammonium were long ago separated into antipodes [2]; in most instances their optical stability is small on account of the ease of the reverse reaction:

$$R_1R_2R_3R_4\overset{+}{N}\overset{-}{X} \rightleftarrows R_1R_2R_3N + R_4X.$$

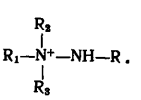
Greater optical stability is exhibited by the spiran systems with a bicyclic nitrogen, first resolved by Mills [15]. Their racemisation is hindered by the necessity for breaking two carbon–nitrogen bonds. [This does not follow (Ed. of Translation).]

There are two interesting points in connection with these systems. Firstly, there are the very rare instances of self-produced resolution observed by Havinga [16,17]: on long standing in a sealed ampoule benzylethylmethylphenylammonium iodide deposited crystals of an (-) enantiomer containing chloroform. Secondly, to this class belongs the only known example of a molecule which is optically inactive, since it is superimposable with its mirror image, although it does not possess a planar centre of symmetry [18]:



Here a rare symmetry element is realised — a fourfold axis of rotation-inversion, the absence of optical activity for such molecules had been suggested earlier [19].

A unique isologue of ammonium has been described in an optically active form — the hydrazonium salt (I) [20]:



(I)

In contrast to ammonium salts, phosphonium and arsonium salts could not be resolved into antipodes for long on account of rapid racemisation. Earlier works [21-23] were unsuccessful but sometimes slight and rapidly disappearing rotation was observed. Enantiomers of phosphonium salts were obtained only in the last decade by a few groups of investigators, especially Vanderwerf and McEwen [24-26]. Certain arsonium salts have also been obtained in an optically active form [27,28]. Of particular interest is the successful use by Kamai and Klabunovskii [29] for the separation of benzylethyl-n-pentylphenylarsonium bromide by selective adsorption of one of the antipodes on dissymmetrical crystals of quartz, for the effectiveness of this rather simple operation was greater than laborious multistage crystallisations.

The optical activity of stibonium salts has still not been observed experimentally, but there can be little doubt about its possibility.

The increase in the valency of the central atom on passing from carbon to the elements of Group V brings about the appearance of new types of asymmetric molecules. Here a new geometrical model is encountered — a distorted tetrahedron with a double bond directed to one of the vertices (Fig. 1). When the three remaining substituents are different, the molecule does not possess a plane of symmetry. This structural type in a pure form is represented in the sulphides of phosphines and arsines, $R_1R_2R_3P{=}S$ and $R_1R_2R_3As{=}S$. Evidently in these molecules a genuine double bond is present. Significantly there is a difference in the properties of the oxides and sulphides: phosphine sulphides, unlike phosphine oxides and amine oxides, do not add on hydrogen halides, which probably indicates the absence of an appreciable negative charge on the sulphur. The essential reason is that sulphides of tertiary amines do not exist [30]; evidently sulphur cannot be the negative end of the dipole of a semipolar bond (in the sense of E^+-S^-), and a double bond is impossible in the case of nitrogen.

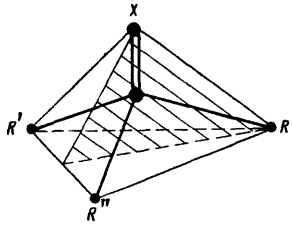
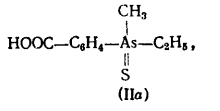
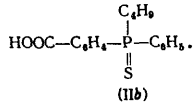


Fig.1.

Sulphides of a tertiary arsine (II*a*) was resolved into antipodes by Mills and Raper[31] in 1925, and its phosphorus analogue (II*b*) by Davies and Mann[32] in 1944. They then posed the question of comparison of the optical rotation of corresponding oxides, sulphides, and selenides, which has still not been investigated experimentally.



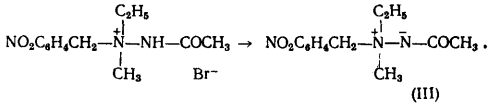
(IIa)



(IIb)

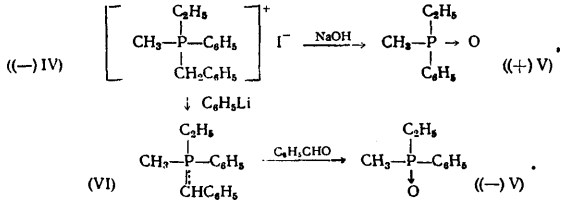
Oxides of ternary phosphines and amines were studied in the classical works of Meisenheimer and coworkers[8,9,33]. As a result of prodigious labour they succeeded in obtaining in an optically active form more than 20 compounds, of which they studied in detail the compounds containing the radicals methyl, phenyl, and ethyl (or benzyl). In many instances the work was restricted to the separation of diastereomers, since the exchange of the optically active anion led to racemisation. The results relating to the influence of the structure and solvent on the molecular rotation will be discussed in the final Section of this review.

Wawzonek[7] obtained a nitrogenous analogue of an amine oxide (III) from the corresponding hydrazonium salt:



(III)

Papers on optically active phosphine oxides appeared again only after 30 years had elapsed. In a series of papers[24,34-37] Vanderwerf and McEwen and their coworkers described various transformations of compounds with asymmetric phosphorus, which enabled them to establish a connection between the relative configurations (IV) and (V):



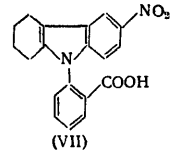
The ready detachment of the benzyl group in an alkaline medium leads to the phosphine oxide with opposite rotation. The transition state has the configuration of a trigonal bipyramid and the stereochemical result is the reversal of the configuration[38]. The action of phenyllithium on the benzylphosphonium salt (IV) gives an optically active Wittig reagent (VI), naturally of the same configuration. With (VI), benzaldehyde gives ((-)IV) as this stage, in accordance with the four-membered cyclic mechanism of the Wittig reaction[39], must involve retention of configuration. This enables the same configuration to be ascribed to the phosphorus atoms in ((-)IV) and ((-)V).

For a long time great interest was aroused in the problem of the possibility of the existence of stable enantiomers of triply-substituted nitrogen, phosphorus, arsenic, and antimony. Meisenheimer[40] did not succeed in resolving phenyltolyl-*o*-carboxyphenylamine into antipodes. At the end of the thirties the frequency of inversion of the pyramids of the hydrides of the Group V elements was evaluated from spectroscopical data[41] (Table 1).

The frequency decreases appreciably as the mass of the substituent is increased, which gave the possibility of stability of the configuration on passing to organic radicals. Mann assumed that the existence of optical antipodes is possible for all elements of the principal subgroup, excluding nitrogen. In 1954 Weston[42] evaluated by quantum chemical methods the configurational stability of the pyramid for $(CH_3)_3E$, by calculating the "racemisation temperature" — the temperature at which the half-period for inversion of the pyramid equals 2 h (Table 2).

According to Weston, the configurations of arsenic and antimony are sufficiently stable at room temperature, but phosphorus at somewhat lower temperature. However, it is not at all clear how T_{rac} changes with change of radicals. For the trialkylsulphonium cation an incorrect result was obtained, since the sulphonium salts are completely stable optically. Evidently care must be taken in using this prediction.

The optical activity of certain aromatic systems with tervalent nitrogen, for example (VII)[43],



(VII)

is probably due to the hindrance of rotation. A stable structure with tervalent nitrogen atoms also occurs in

TABLE 1.

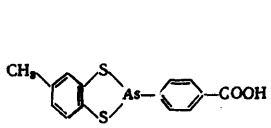
	NH_3	PH_3	AsH_3	PD_3	AsD_3
Frequency of inversion, s^{-1}	$2\cdot10^{10}$	$5\cdot10^{6}$	$16\cdot10^{4}$	$6\cdot10^{3}$	30

TABLE 2.

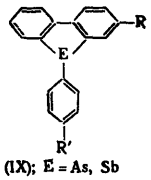
	$(CH_3)_3N$	$(CH_3)_3P$	$(CH_3)_3As$	$(CH_3)_3Sb$	$(CH_3)_3S^+$
T_{rac}, °K	105	280	380	340	210

Troger's base, which was separated into antipodes by Prelog and Wieland[44], who for this made the first use of an asymmetric adsorbent, *d*-lactose.

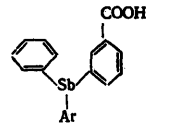
In the fifties Campbell and coworkers[45-49] published a series of papers in which they described optically active derivatives of arsenic, phosphorus, and antimony. The hetero-atom was included in a cyclic system condensed with benzene rings (VIII)–(X).



(VIII)

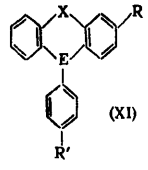


(IX); E = As, Sb



(X); Ar = α-$C_{10}H_7$ or (2-C_6H_5)C_6H_4

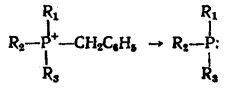
Earlier, structures of similar types were separated into antipodes by Lesslie and Turner[50-52], their distinguishing feature being the presence of two hetero-atoms, uniting aromatic rings (XI).



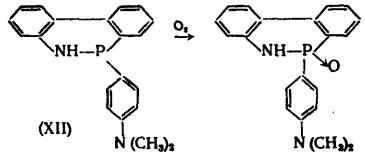
(XI)

Thanks to the specificity of these structures, doubt arose as to whether their optical stability was the result of steric hindrance due to the congestion of the rigidly bound aryl groups or the stability of the folded conformation (along the E–X axis); Mann[53] defended such a point of view. The problem of the asymmetry of the hetero-atom in a ring remained open.

This old problem of stereochemistry was recently solved in Horner's laboratory. Success was achieved in obtaining stable enantiomers of tertiary phosphines[54] and arsines[55] of completely normal structure: with one aryl and two alkyl radicals. An original method was used for this — the detachment of a benzyl† group in the reduction at the mercury cathode of the enantiomorphs of the corresponding phosphonium



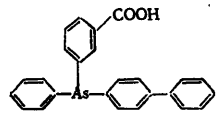
or arsonium salts. These compounds are extremely stable optically, some of them withstanding boiling in solution for many hours without the slightest racemisation! The German investigators found that electrolytic reduction of the onium salts of phosphorus and arsenic and also alkylation, oxidation, and addition of sulphur to $R_1R_2R_3E$ takes place with complete retention of the configuration[56-58]. Campbell[49] also observed retention of the configuration in the oxidation of tervalent phosphorus in the complex (XII)[49]:



(XII)

† It was found subsequently that the allyl group can also be split off electrolytically[57].

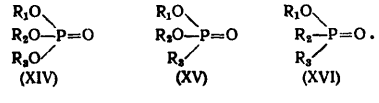
In 1963 Mislow[59] showed that the optical activity of the Lesslie–Turner compounds (XI) is due to the configurational stability of the arsenic atom, whereas these molecules are quite labile conformationally (the energy barrier for the "folding" of the molecule about the E–X axis totals ~ 6 kcal × × mole^{-1}). In this work the triarylarsine (XIII) was also separated into antipodes:



(XIII).

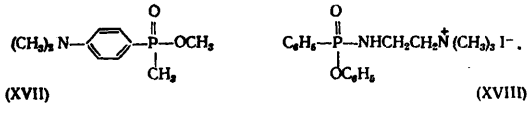
It is free from steric hindrance; optical rotatory dispersion curves without the Cotton effect (up to 310 mμm) are obtained. Hence the question of the possibility of the existence of three-covalent derivatives of the elements of the main subgroup of Group V in an optically active state is confirmed for phosphorus, arsenic, and antimony. The stability of the nitrogen pyramids is evidently too low: for example, the NMR spectra[60] show that for an *N*-alkylethyleneimine the inversion of the nitrogen configuration takes place with a frequency of 60 s^{-1} at room temperature.

In addition to the classes of compounds considered, the elements of Group V form other molecules with a tetrahedral structure: derivatives of acids, for example, (XIV)–(XVI) for phosphorus, and various analogues with sulphur, halogen, or nitrogen instead of oxygen.



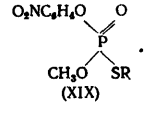
(XIV) (XV) (XVI)

It seems that the first compounds with an asymmetric acidic phosphorus (XVII) and (XVIII) were resolved into antipodes by McEwen and Vanderwerf[61,62], and also by Aaron *et al.*[63]:



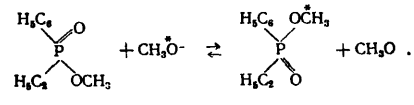
(XVII) (XVIII)

Then Hilgetag and Lehmann[64,65] obtained in an optically active state the ether (XIX), which does not contain a phosphorus–carbon bond.



(XIX)

In addition to the investigators mentioned, Green and Hudson in Switzerland and Michalski in Poland are now working on this problem. Most of the work has been carried out on derivatives of thiophosphoric acid; the main aim is to study the mechanisms of the reactions involving phosphorus[38]. For example, by studying the isotopic exchange:

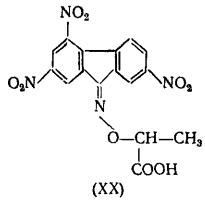


Green and Hudson[66] found that the rate of racemisation is exactly twice the rate of exchange. This is the application to phosphorus of the classical proof of the strict reversal

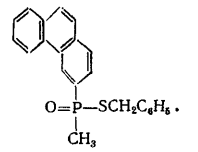
of the configuration for nucleophilic substitution of the S_N2 type, given for carbon (halogen exchange) by Hughes[67].

In Aaron and Miller's laboratory antipodes of esters of phosphonic acids have been used for studying the mechanism of action of cholinesterase[68]; the inhibition constants differ by a factor of ten. This can be of interest to enzymology.

The elegant use[69] of Newman's reagent (XX) for the optical separation of compound (XXI) and the 2-naphthylmethyl ester of methylphosphonic acid is worthy of note:



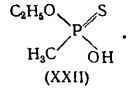
(XX)



(XXI)

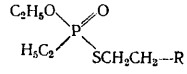
The geometric requirements are evidently very strict, for ester of 2-naphthylphosphonic acid does not give a molecular complex with (XX).

The configurations of the compounds with asymmetric acidic phosphorus are completely unknown; by the example of compound (XXII) it has been established[70] that changing the alkyl radical in the ester part of the molecule does not change the sign of rotation:



(XXII)

One of Michalski's papers[71] shows that the stereochemical course of reactions can depend on fine details of the structure: (XXIII*a*) and (XXIII*b*) with the same configuration



(XXIII) *a*: R = H; *b*: R = Cl,

give with SO_2Cl_2 chlorides with rotations of different sign. It is not possible to discuss in detail all the papers devoted to these systems, and we will merely mention a few[72-76].

The correlation of the configuration of the phosphorus atom in acids with other types of phosphorus compounds is an important and fascinating task. The most convenient method is the replacement of a chlorine atom or alkoxy--group on a hydrocarbon radical by the action of a Grignard reagent, with conversion into the oxide of a tertiary phosphine.

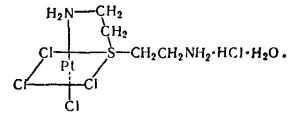
The optical isomerism of analogous derivatives of arsonic acids has not yet been investigated experimentally.

3. GROUP VI

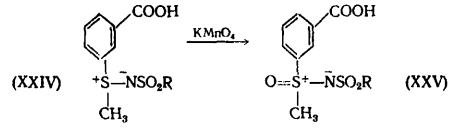
Many types of structure containing an asymmetric sulphur atom are known; the optical activity has usually been observed experimentally. On the other hand, with selenium and tellurium the only type of molecule obtained in an optically active form are onium compounds[77,78]. The case of oxygen is of interest. Meerwein's oxonium compounds[79] hardly merit attention on account of their low stability. There remain Nesmeyanov and Tolstaya's triaryloxonium salts[80,81], for which it is not known precisely whether they have pyramidal or planar structure. According to Syrkin[82] they are compounds of "oxanic" type, as with the salt $[O(HgCl)_3]^+Cl^-$, and therefore should be planar. X-Ray structural analysis of triphenyloxonium salts has still not been completed[83]. Meanwhile a repeat investigation[84] of the salt $[O(HgCl)_3]^+Cl^-$ has recently been made, which showed that the cation has the structure of a pyramid with height ~ 0.5 Å. The problem still remains unsolved; in the case of a pyramidal structure for the triaryloxonium salts, obviously separation of $Ar_1Ar_2Ar_3O^+$ into antipodes could be expected.

Optical activity is observed in compounds where the sulphur is bonded to three or four different groups. First of all, Pope and Peachey[3] in 1900 resolved the methoxycarbonylethylmethylsulphonium cation. Then Philipps and coworkers obtained esters of sulphinic acids[4], sulphoxides[5], and sulphimines[85] in the optically active state. At that time this played a large part in establishing the fact of the existence of the semipolar bond. The optical activity of sulphoxides, distinct from detones, was considered to be the conclusive proof of the tetrahedral configuration of sulphur. Strictly speaking, the tetrahedral structure is still not a proof of the semipolar nature of the sulphur–oxygen bond[86], since a decisive role could be played by the free pair of electrons (absent from the carbonyl carbon of the ketone molecule); geometrically the molecule could resemble an arsine sulphide.

Mann[87] synthesised an interesting structure in 1930: an asymmetric sulphide sulphur atom is produced as a result of coordination with a platinum central atom in a complex. This complex shows quite a large angle of rotation but is rapidly racemised:



Oxidation of coordinationally unsaturated sulphur of sulphoxides leads to symmetrical sulphones, but that of sulphimines to the slightly studied sulphoximines which have four different substituents at sulphur. Only in 1960 did Barash[6], by separating the diastereomers, show that sulphoximines can exist in an optically active form. In 1962 a detailed investigation[88] of the stereochemistry of oxidation of the sulphimine (XXIV) to a sulphoximine was completed:



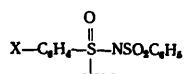
(XXIV) (XXV).

$[\alpha]_D^{20} + 254°$ $[\alpha]_D^{20} + 143.5°$

Each compound was resolved into antipodes and during the oxidation complete preservation of the optical activity and configuration was observed which is confirmed by the proximity of the optical rotatory dispersion curves for enantiomers (XXIV) and (XXV) of the same sign. We note that in sulphones and sulphoximines only one bond is

(formally) semipolar, and sulphur has a decet of electrons and a single positive charge (in accordance with the principle of electrical neutrality [89]).

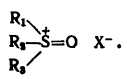
A second example of an optical isomerism of derivatives of quadruply-substituted sulphur was described at the end of 1963, by Levchenko and Kozlov [90]:



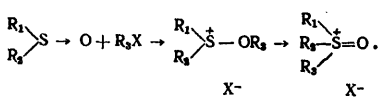
a: X = H, $[\alpha]_D^{24} \pm 16.6°$,
b: X = NO_2, $[\alpha]_D^{24} \pm 5.5°$.

The enantiomers were obtained, probably, in an optically pure state through salts with (-)-1-phenylethylamine.

Optical activity should also be shown by an original class of compound discovered by Kuhn and Trischmann [91] and also by Smith and Winstein [92], namely sulphoxonium salts:



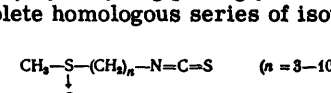
It is remarkable that they contain a true double bond S=O, as is shown by the infrared spectra and also the impossibility of obtaining them by direct oxidation of sulphur in sulphonium salts, although the existence of a positive charge on the sulphur does not hinder the "analogous" formation of sulphones and sulphoximines. The formation of a true double bond in this instance is the only means of fulfilling the principle of electroneutrality. The synthesis of sulphoxonium salts proceeds as follows:



The second stage obviously has a similarity to the regrouping of sulphinic esters and sulphones [93]. Starting with the optically active sulphoxide would probably give an enantiomer of the sulphoxonium salt; this has not yet been described. It is especially interesting that the geometry of the cation is evidently the same as in the sulphides of the Group V elements.

Optically active sulphoxides are encountered in nature, for example, biotin sulphoxide [94], alliin [96], and sulphorafan [95].

Kjaer [97,98], by hydrolysing plant glycosides, isolated almost a complete homologous series of isothiocyanates



exhibiting strong laevo-rotation, as do most natural sulphoxides.

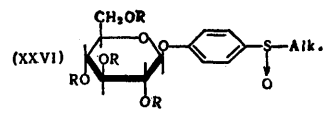
Several interesting specific methods have been used for preparing optically active sulphoxides. Thus a case of stereospecific microbiological oxidation of simple sulphides has been described [99]:



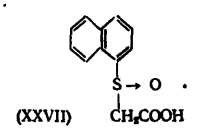
$[\alpha]_D^{21} - 20.2°$.

The authors consider that the substance is not optically pure.

Wagner and Böhme [100] obtained glycosidic derivatives of 4-hydroxyphenylsulphoxides (XXVI), and the diastereomers were then subjected to the action of an enzyme, which cleaved only the β-glycosidic bond:

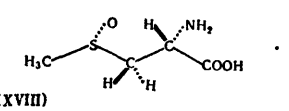


In Poland, Janczewski is working with the oxides of arylcarboxymethyl sulphides [101,102], which are interesting for the large angle of rotation in the visible region, for example, (XXVII) has $[\alpha]_D^{20} = \pm 480°$.



In particular, he described the first case of a pseudoasymmetric non-carbon atom [103].

An asymmetric sulphur atom was the first of the non-carbon atoms whose absolute configuration was established by X-ray analysis [104,105]. The sulphoxide of *S*-methylcysteine contains a carbon atom of known configuration, therefore the configuration of the sulphur was easily determined relative to carbon: ((+)-XXVIII) has sulphur in absolute configuration S:

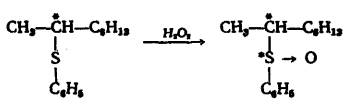


However, this method is not applicable to determining the configuration of sulphur in other compounds. In recent years rather a large number of investigations on asymmetric sulphoxides have been carried out [106-109]. A partial asymmetric synthesis took place by the action of optically active per-acids on sulphides. Using the rule of asymmetric induction this enables the absolute configuration to be described: the S configuration for the (-)-enantiomer:



Let us consider in detail an example from the work of Cram and Pine [110]. In the oxidation of optically active 2-octyl phenyl sulphide with hydrogen peroxide, two diastereomeric sulphoxides were isolated:

I $[\alpha]_D^{25} - 155°$
II $[\alpha]_D^{27} + 140°$



The ratio of the quantities of the diastereomers formed was I : II = 1.6 : 1. Since the absolute configuration of the carbon centre is known, the sulphide can be represented in the Newman projection (Fig. 2).

According to Cram's rule [111], oxygen will be attached preferentially to the least screened electron pair, adjacent to the hydrogen atom in the projection. If conformations

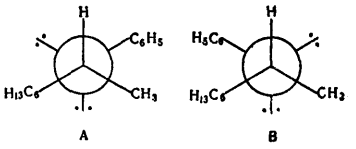


Fig. 2.

A and B were equally probable, then as a result both diastereomers would be formed in equal amounts. However, the effective volume of the n-hexyl group is greater than that of the methyl group, therefore the position adjoining it is less favourable for phenyl. This signifies that conformation A is the more stable, from which one can draw conclusions about the electron pair which can be preferentialy attacked and about the configuration of the asymmetric centre which is produced.

The following reaction enables sulphoxides to be obtained from the esters of sulphinic acids [112]:

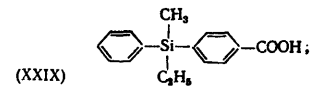
$$R{-}S{-}OR' \;(\underset{O}{\downarrow}) + R''MgX \rightarrow R{-}S{-}R'' \;(\underset{O}{\downarrow}) + Mg(OR')X.$$

It is a convenient method for the synthesis of optically active sulphoxides [113], starting from diastereomeric sulphinic esters, for example, the *l*-methyl ester. It is quite probable that in this reaction there is an inversion of configuration at the sulphur atom; in support of this there are the recently obtained optical rotatory dispersion curves of these classes of compounds [114]. The reversal of the configuration during substitution at the sulphur atom in sulphonic acids has also been established recently [115].

4. GROUP IV

A few compounds of silicon were resolved into antipodes by Kipping [116] at the start of the century. About this time Pope and Peachey [117] resolved ethylhalogenomethylpropyltin. In the thirties their result was confirmed by Manulkin [118], who also described an optically compound of germanium [119], In all three instances a very small angle of rotation was observed, so that the experiments cannot be considered completely reliable.

The first trustworthy example is the resolution of the organosilicon compound (XXIX) recently described by Eaborn and Pitt [120]:



(XXIX)

but the stereochemistry of silicon began in earnest with the work of Sommer's laboratory [121-123], where success was achieved in separating the diastereomers $R_1R_2R_3SiOR^*$, and then isolating optically pure $R_1R_2R_3SiX$, where R_1 = 1-naphthyl, R_2 = phenyl, R_3 = methyl, and X = various substituents, including H, F, Cl, Br, OH, OCH_3, C_2H_5, etc. The American investigators used these enantiomers for a broad study of the stereochemistry and mechanism of substitution at the silicon atom [124-126].

Without dwelling in detail on this work, we will note the cases when the results differ from the corresponding ones for the carbon atom. For example, homolytic replacement of hydrogen by molecular chlorine takes place with retention of the configuration:

$$R_1R_2R_3SiH \xrightarrow{Cl_2} R_1R_2R_3SiCl.$$

Significantly, the configuration is also retained in some, but not all, reactions of nucleophilic substitution reactions of type S_N2:

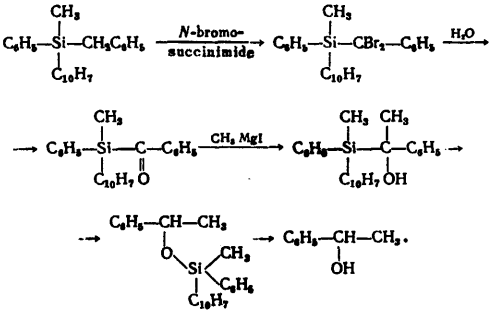
$$R_1R_2R_3SiOCH_3 \xrightarrow{LiAlH_4} R_1R_2R_3SiH,$$
$$R_1R_2R_3SiOCH_3 \xrightarrow{Bu^tMgCl} R_1R_2R_3SiH.$$

This agrees with earlier results about the readiness of the S_N2 reaction at the silicon atom at the head of the bridge [127] which certainly proceeds with retention of the configuration. In comparison with carbon, the anomalous, behaviour of silicon in nucleophilic substitution reactions is explained by the presence in silicon of a vacant *d* orbital, which also serves as an acceptor of the electron pair of the substituting agent at the rate-determining stage of the process.

There is special interest in the asymmetric silicon atom, for this is the first isolated non-carbon atom whose configuration has been determined. Two groups of research workers established simultaneously by different methods the absolute configuration of $R_1R_2R_3SiX$: Pepinsky [128] by means of X-ray analysis of isomorphic crystals of silane and fluorosilane, and Brook and Limburg [129] by chemical means (Fig. 3).

The relative configurations were established earlier by the method of quasiracemates and optical rotatory dispersion [124]: (-)-$R_1R_2R_3SiH$, (-)-$R_1R_2R_3SiF$, and (+)-$R_1R_2R_3SiCl$ have the same configuration.

The following scheme shows the succession of reactions which Brook and Limburg used [129] to establish the configuration:



The regrouping of an α-hydroxysilane into a silicon ether of the corresponding alcohol used here was discovered earlier [130]. Cram's rule, which determines which of the

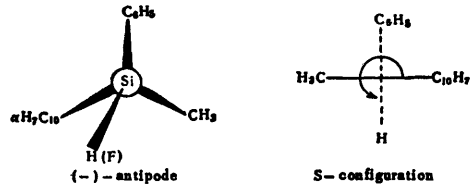
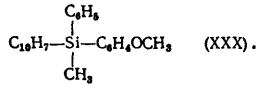


Fig. 3.

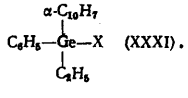
diastereomers is formed in excess, depending on the configuration of the neighbouring asymmetric silicon atom, applies at the stage of addition of the Grignard reagent at the carbonyl group. Finally, from the sign (and configuration) of the 1-phenylethanol the configuration of the silicon atom can be determined unambiguously if it is assumed that regrouping of the α-hydroxysilane (under alkaline conditions) occurs with retention of the configuration.

Eaborn [131] used the optically active compound (XXX) for studying the replacement of an aryl radical by a halogen, with retention of the configuration:



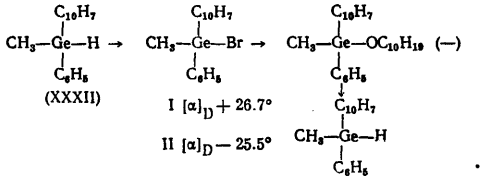
(XXX).

There has been an extremely rapid development of the stereochemistry of the elements of Group IV in the last few years. Following Sommer's method, Bott *et al.* [132] first made a reliable resolution of compound (XXXI) with an asymmetric germanium atom:



(XXXI).

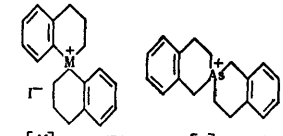
Immediately after this Brook and Peddle [133] published a detailed investigation of the reactions of optically active methyl-1-napthylphenylgermane and its derivatives. The scheme of separation into antipodes, which is similar for silicon and germanium, is:



The second reaction, carried out by Sommer and coworkers for silicon, was found by Brook and Peddle [133] to be completely analogous in steric course for germanium, except for the replacement of hydrogen by bromine, which occurred with racemisation (in the case of silicon there was retention of the configuration). They also established the absolute configuration of the germanium atom, using the structural identity of compound (XXXII) and the analogous silane and employing the method of quasiracemates. As expected, the enantiomers of silane and germane of the same configuration have the same sign of rotation.

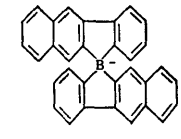
5. SPIRANS WITH A NON-CARBON SPIRO-ATOM

There is a limited group of spiro-compounds containing a hetero-spiro-atom which exhibits optical activity because of the asymmetry of the molecule as a whole. Formally, they are not within the scope of this review, but they are closely connected with the problem of the influence of the nature of the non-carbon atom on the magnitude of the optical rotation. The synthesis and resolution of these compounds was carried out in Mann's laboratory in Cambridge [134-136].



These compounds form a "eutropic series" (unfortunately, of only two members), in which there is an increase in the molecular rotation with the atomic weight (from phosphorus to arsenic).

Torsell [137] described the opposite case (when the spiran system forms an anion, not a cation), the spiro-position being occupied by a boron atom:



(XXXIII).

The molecular rotation of this anion, calculated from the rotation of its salt with an optically active ammonium cation, is -338°. It was first shown that the rotation of the cation (benzylmethylphenylpropylammonium) is independent of the anion and amounts to -258°.

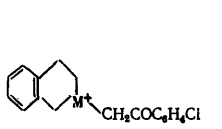
6. INFLUENCE OF THE ASYMMETRIC ATOM ON THE OPTICAL ROTATION

The problem of the optical activity of compounds with an asymmetric non-carbon atom must find a complete solution within the framework of the general problem of the optical activity of both organic and inorganic molecules. However, a general theory has not yet been established. The contemporary theoretical concepts relate mainly to compounds with asymmetric carbon and *a priori* it is not obvious what will be the effect of a change in the nature of the asymmetric centre. The absence of a general theory makes it desirable to seek partial rules applicable to restricted groups of compounds.

An essential obstruction in the path of a quantitative study of the problem is that the limiting value of the angle of rotation is often unknown. The absence of a definite criterion of optical purity was for long a general deficiency in stereochemistry. The main argument was the production of antipodes with rotations identical in magnitude but opposite in sign, but this was not always reliable. It was only in 1959 that Berson and Ben-Efraim [138] proposed an absolute method for the determination of optical purity and maximal rotation, apparently without limitations in principle. However, as yet it has hardly been used, even for carbon compounds (probably on account of the necessity for working with isotopes).

After Meisenheimer, whose work will be further considered below, the dependence of optical rotation on the asymmetric atom became of interest to Mann, who constructed the only example of a "eutropic series" [77] in which

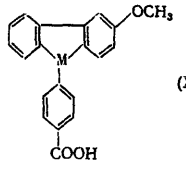
there has been observed a significant increase in molecular rotation in the series: sulphur < selenium < tellurium.



	$[M]_D$ picrate
S	250°
Se	530°
Te	> 750°.

A second example is provided by the spiro-derivatives of phosphorus and arsenic referred to above [136].

The insignificant increase in $[M]_D$ found by Campbell [45-49] for compounds (XXXIV) on replacing As by Sb cannot be considered conclusive, because the rotations of pyridine solutions of the acids were compared.



(XXXIV)

There is no guarantee that the extent of salt formation was the same; it is also completely unknown how the angle is affected by the increase of electron density on the arsenic or antimony atom due to the influence of the substituent through the benzene ring.

Subsequently we will attempt to analyse the published information relating to molecules of comparatively simple structure, on the basis of the system proposed in 1959 by Brewster [12-14]. It was found that this semi-empirical method successfully predicts the sign and magnitude of the rotation of wide circle of compounds with asymmetric carbon atoms (assigned configuration), when steric hindrance and strain do not play a large part [139]; in particular, the method is also applicable with a metal atom as the asymmetric centre [140]. Interesting work on the calculation of the rotation of polymeric hydrocarbons has been published [141].

According to the rule of conformational asymmetry, the contribution to the molecular rotation of the dissymmetrical structural unit represented in Fig. 4 is given by the expression:

$$\Delta [M]_{XY} = + k\,(X{-}H)\,(Y{-}H) = + 160\,(R_X^{1/2} - R_H^{1/2})\,(R_Y^{1/2} - R_H^{1/2}).$$

This is based on the idea of the rotational capacity being proportional to the square root of the atomic refraction, after which the additivity principle applies. The quantities $\Delta[M]_{XY}$ are determined from experimental results and in almost every case they agree well with calculation by the right-hand side of the equation. It can be assumed, as Brewster does in a footnote to one of his papers [14], that the constant k is linked in some manner with the nature of the asymmetric centre and retains a constant numerical value (160–165) only in dealing with carbon. Brewster suggested the possibility of a change in k when the central atom had a polarisability differing greatly from that of carbon. It is completely unknown whether the form of the function is then retained (that is, $k = \beta R_0^{1/2}$, where R_0 is the refraction of the central atom), or whether, within the framework of the stated approximate method, the nature of the asymmetric centre is allowed for in the numerical value of k in another way. It should be noted that in the calculation of $\Delta[M]$ by the conformational asymmetry rule, constant k should be a function of the parameters of two atoms $k = f(1, 2)$, and not $k = f(1)$, where 1 is an asymmetric atom and 2 a neighbour which participates in the formation of an axis of the Newman projection. Since atom 2 is known to be carbon it must be expected that the value of k would only change slightly on changing the asymmetric atom, so that this change would not be experimentally observable at every R_0.

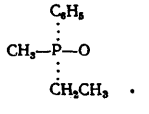
It is significant that when Brook and Limburg established the absolute configuration of silicon in methyl-1-naphthylphenylsilane, in 1963, they noted the agreement of the sign of the rotation for three substances with that predicted by Brewster's method. That showed for the first time the applicability of the atomic asymmetry rule to a non-carbon centre (qualitative aspect).

We calculated [142] the rotation of ethylmethylphenylphosphine by the conformational asymmetry rule using the value of $\Delta[M]_{XY}$ which is used for carbon compounds. Two antipodes are obtained experimentally [9,24], with $[\alpha]_D = \pm 22.8$, $[M]_D = 37.8 \pm 1.7°$. Fig. 5 shows two permissible conformations of this compound. Assuming them to be equally probable [12], we obtain:

$$[M]_D = \frac{-k(C{-}H)(C_{Ar}{-}H) - k(C{-}H)(O{-}H) + k(C{-}H)(O{-}H) + k(C{-}H)^2}{2} = -\frac{140-60}{2} = -40°.$$

For this calculation, it is necessary to know the rotational constant for oxidic oxygen (although it can also be calculated from refractometric data). The only assumption which is made is that the effective volume of oxygen is small in comparison with that of the methyl group.

Bearing in mind the precedent of the absolute configuration of silicon [129], the good agreement suggests that the (+) antipode of the oxide can be ascribed to the R configuration with a high degree of probability:



Since there has been a correlation of the configuration of this compound with a tertiary phosphine and a phosphonium salt [38], their absolute configuration is also determined [142].

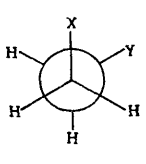


Fig. 4.

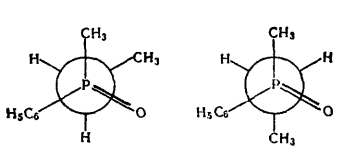


Fig. 5.

A comparison of the rotations of corresponding amine and phosphine oxides in various solvents, from Meisenheimer's data[9], is especially interesting (Table 3). Comparison of the values in Table 3 suggests that the essential role is played not by the nature of the central atom but by the character of its bond with oxygen (possibly, the degree of charge separation). The difference in $[M]_D$, very great in a non-polar solvent, disappears completely on passing to the hydrochloride, when the M–O bonds becomes of the same type as the others. It is significant that this takes place on account of a change in the rotation of the amine oxide, which increases regularly as the polarity of the N–O bond decreases, whereas the rotation of the phosphine oxide (bond not purely semipolar) is almost independent of the solvent. The calculation given above also describes the rotation of the amine oxide hydrochloride. The anomalously low rotation of the amine oxide in benzene may be explained by the formation of associates in the absence of reaction with the medium.

Meisenheimer's results with analogous compounds were not very definite, and are not always understood. Thus benzylmethylphenylphosphine has $[M]_D = +162°$ in HCl and $-17°$ in chloroform! Such a marked difference seems inexplicable. It is true that the experiment in this case, as in some others, is not completely reliable because the value of $[M]_D$ is often estimated from the difference in rotation of the diastereomers.

It is interesting that the molecule of ethylmethylphenyl--phosphine or -arsine is structurally similar to 2-phenylbutane. Calculation by Brewster's method for the two compounds gives a single value: $[M]_D = 40°$, which agrees well with that found experimentally for the hydrocarbon[143]. The results for phosphines and arsines[54–56] do not agree very well with one another but the simplest molecules have $[M]_D = 27.8°$. Here again there is the impression that the replacement of phosphorus by arsenic has no effect. The following discussion shows that this can be explained by distortion of the tetrahedron of the hetero-atom in the absence of a fourth substituent (compare Fig. 6).

The presence of a free electron pair instead of a fourth substituent necessitates the approach of the phosphorus atom to the plane of formation. If the Newman projection is constructed along the R_2–P bond, then the change in the angles of the pyramid also leads to a change in the angles between the substituents in the projections, the direction of which is easily understood. Evidently, in the limit the atom of phosphorus tends to take up a position in the plane $R_1R_2R_3$, and in the projection R_1 and R_3 would be situated on a single straight line. Actually at this moment the molecule acquires planar symmetry and loses its optical activity but as a matter of fact this state is not reached.

Further, $\Delta[M]_D$ is evidently, as Brewster once proposed, a sinusoidal[12] function of the angle formed by the bonds in the Newman projection; the tabulated values of $\Delta[M]_D$ are specially standardised by the direct multiplier $1/\sin 60° = 2/\sqrt{3}$ for the normal angle of 60°. Therefore if we wish to calculate the influence of a variable angle the multiplier should be $(2/\sqrt{3})\sin\varphi$. For the limiting point $\varphi = 30°$,

$$[M]'_D = \frac{2}{\sqrt{3}} \sin 30° [M]_D = \frac{1}{\sqrt{3}} \times 40° \simeq 23°.$$

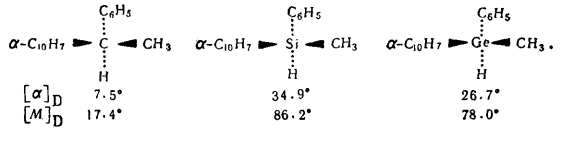
Consequently, in this way the lower limit for the angle of rotation can be roughly evaluated; as a result:

$$23° < [M]_D < 40°.$$

It is evident that the experimental value does not contradict this inequality.

Unfortunately there is no information on the rotation of phosphine salts; it seems that $[M]_D$ of the cation must be close to 40°.

The most valuable material for comparison relates to Group IV, for which Brook[144] constructed the first "isoconfigurational series" of enantiomers $R_1R_2R_3R_4M$ with identical structure and configuration, which differ only in the nature of the asymmetric atom M:



First of all it appeared that all (+) enantiomers have the absolute configuration R: the nature of the central atom does not affect the sign of the rotation. The optical rotatory dispersion curves are essentially similar and have a positive Cotton effect (Fig. 7).

The carbon analogue exhibits a much smaller angle of rotation: Brook finds that the rotation is a linear function of the electronegativity of the central atom.

It appears possible that the increase in $[M]_D$ on passing from carbon to silicon and germanium is due to the appearance of free *d* orbitals. It is known that there is an electronic displacement in the direction from aryl to silicon or

TABLE 3. $[M]_D$ of a phosphine oxide and amine oxide in various solvents.

	$(CH_3)(C_2H_5)(C_6H_5)P \rightarrow O$	$(CH_3)(C_6H_5)(C_2H_5)N \rightarrow O$
Benzene (absolute)	+47°	+8–9°
Water	+38°	+24°
HCl	+40°	+40°

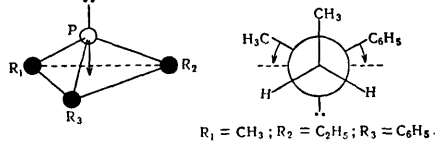


Fig. 6.

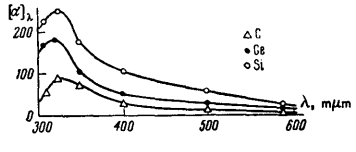
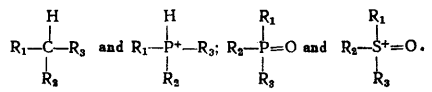


Fig. 7.

germanium [145]. There are several consequences, one of which may also affect the optical rotation: (1) increased electron density on the asymmetric atom; (2) shortening of the metalloid–aryl bonds on account of partial doubling of the bonds; (3) hindrance to free rotation about these bonds for the same reason.

Whereas in a carbon compound the rotation about C–aryl bonds, generally speaking, is free, then on account of the partial double bond character, some orientation of the ring can be preferred. In this sense it is interesting that passing from silicon to germanium has little effect on $[M]_D$. If the reason actually consists in the presence of the *d* orbital then a subsequent change, to an asymmetric tin atom, should slightly affect the rotation.

The relation of concentration of electron density at the asymmetric atom to the optical rotation is also of interest. This can most conveniently be traced by introducing various substituents in the aromatic ring adjacent to the asymmetric atom. In one instance [90] the replacement of hydrogen by a nitro-group significantly reduced the angle. Unfortunately investigations of this type have not been carried out in carbon stereochemistry, with a few exceptions [146-148]. Valuable information can be obtained by comparison of structurally analogous molecules containing asymmetric atoms which belong to different groups of the Periodic System (influence of charge), for example:



Such data are still absent. Naturally the study of each of these problems requires considerable experimental work.

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ABILITY OF ELEMENTS TO FORM POLYMERS WITH INORGANIC CHAIN MOLECULES

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The chemistry of organoelemental compounds is being intensively developed as an independent branch of chemistry in the direction of studying the general regularities of the formation and transformation reactions of the organoelemental compounds, the investigation of the reactivitv of various compounds, and also in the field of the synthesis and study of the properties of high-molecular-weight compounds.

The development of the chemistry of high-molecular--weight organoelemental compounds is linked not only with the study of the transformation reactions of the monomeric compounds into polymers, but also with the investigation of the possible uses of various elements and their compounds for the synthesis of polymers. The synthesis of organoelemental polymers is complicated by the variety, not only of monomeric compounds, but also of elements whose monomeric compounds can be used for this purpose. Therefore we consider some aspects of the theory which characterise the ability of various elements to form homo- and hetero--chain polymers. Polymers which do not contain carbon atoms in the chain are known as polymers with inorganic main-chain molecules, framed‡ by various organic, inorganic, and organoelemental groups.

At present the general principles which determine the formation of inorganic chains of molecules of various elements have been insufficiently worked out, and the known reactions for the synthesis of polymers, for example, polyorganosiloxanes, are always accompanied by the formation of cyclic compounds, which serve as "monomers" for the synthesis of high-molecular-weight compounds.

The use of inorganic cyclic compounds framed by organic groups for the production of polymers is also linked with the fact that unsaturated compounds of the general formulae $R_nE{=}O$ and $R_nE{=}ER_n$, capable of polymerising through the double bonds, as in the synthesis of organic homo- and hetero-chain polymers[1-3], have not yet been obtained.

An attempt will be made here to establish the most important factors which determine the ability of elements to form inorganic rings and chain molecules, framed by organic and organoelemental groups. It is evident that the routes to the formation of inorganic rings and chain molecules are extremely varied, not only on account of the large number of elements which can be used to construct these chains, but also on account of the diverse types of chemical bonds which may be used in the formation of cyclic and chain polymeric compounds.

Two types of chemical bonds play an important part in the formation of polymers with inorganic chain molecules: covalent and coordination. They can be the basis for the formation of large molecules of various structures. Aggregates, consisting of a large number of ionic particles bound to one another by ionic bonds, for example, ionic crystals, cannot be considered as proper molecules, and such structures are not true polymers, although they consist of a large number of structural units. It is true that covalent bonds between elements with different electronegativities have polar character, or, in other words, are partly ionic, preventing the strict demarcation of polymers with inorganic chain molecules from ionic aggregates (crystals). Usually ionic aggregates have a three-dimensional structure, whereas for polymers there is greater interest in chains of linear, branched, or network type of molecular structure. The present review considers mainly polymers with chain molecules of such structure, for otherwise we would have to consider a large number of inorganic compounds going beyond the bounds of polymer

‡ Not considered in the text of the review.

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‡ The term "framed" presumably means having side-groups of the type mentioned (Ed. of Translation).