Molecular structure and rubber-like elasticity

II. The stereochemistry of chain polymers

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A survey of the known structures of molecules containing two or more singly linked carbon atoms has shown that the staggered bond configuration is favoured. It is suggested that these molecules may be examples of a general rule—the 'principle of staggered bonds'—which specifies the bond positions for successions of singly linked carbon atoms, just as the 'tetrahedral principle' specifies the bond positions on any one carbon atom.

If this is true, it is possible to predict molecular configurations. The number of alternative configurations, all obeying the principle of staggered bonds, increases rapidly with the number of carbon atoms, but the most probable configuration of a particular molecule can sometimes be predicted on geometrical grounds.

The simpler types of carbon chain are described. The chain-type in a crystalline long-chain polymer may sometimes be deduced from a knowledge of the identity period of the molecules, which is readily found from X-ray or electron diffraction patterns.

The principle of staggered bonds is also obeyed in molecules containing singly linked nitrogen, oxygen and sulphur atoms. The configurations of hetero-atomic chains containing these atoms are therefore of the same types as carbon chains.

In molecules containing double bonds, the principle of staggered bonds may still be operative, a double bond being regarded in the familiar simple geometrical way as two distorted single bonds. The non-planar chain forms of gutta-percha, rubber and polychloroprene are attributed to the co-operation of two influences: the principle of staggered bonds, and the repulsion between methyl or chlorine side substituents and particular CH_2 groups in the chains.

In Part I of this work (Bunn 1941) the determination of the crystal structures of three long-chain polymers by interpretation of X-ray diffraction photographs was described. In all three crystals—β gutta-percha, rubber and polychloroprene—the molecules have non-planar zigzag chain forms and are asymmetric. It is now necessary to consider the bearing of the new knowledge of molecular geometry on the possibility of understanding rubber-like properties in terms of molecular physics. It is widely believed that the flexibility, softness and other characteristic properties of rubber-like substances are in some way due to the flexibility of the molecules themselves.

Long-chain molecules owe their potential flexibility to the swivelling of the chain units round the single bonds as axes, and it is therefore necessary to consider which bond positions are the most stable and what hindrances there are to rotation away from these positions. The present paper deals chiefly with the question of the most stable bond positions. The enquiry has interest, not only in relation to the problem of the origin of rubber-like properties, but also because it opens the way to a systematic consideration of chain types. There is already evidence that in many crystalline long-chain polymers, such as rubber hydrochloride (Gehman, Field & Dinsmore 1938), polyisobutylene (Fuller, Frosch & Pape 1940) and some of the polyesters (Fuller 1940), the chains have, not the fully extended plane zigzag form of polyethylene (Bunn 1939) but somewhat shortened (necessarily non-planar) forms. It should be possible to discover what these forms are by interpretation of X-ray diffraction photographs, but the difficulties are in some cases formidable; some assistance in the form of guiding principles for the construction of possible chain types is desirable. It is the purpose of this paper to show that there already exists sufficient evidence to suggest a general principle regulating bond positions in aliphatic molecules containing sequences of singly linked atoms. It will be called the principle of staggered bonds.

In the three molecules whose structures were determined in Part I, every fourth chain bond is a double bond; the question of bond positions is less simple for such molecules than it is for those in which all the bonds are single. The latter will therefore be considered first.

<center>BOND POSITIONS IN SATURATED MOLECULES</center>

A survey of all the well-established structures of simple, saturated organic molecules, whether in the gaseous state or in crystals, has been made, and has shown that the favoured positions of the bonds of two singly linked carbon atoms are as shown in figure 1. The tetrahedral angles between the bonds of any one carbon atom are preserved (within a few degrees), and the two trios of bonds abc and $a'b'c'$ of two singly linked carbon atoms are staggered with respect to each other. Thus, for ethane, both the electron diffraction pattern (Pauling & Brockway 1937) and the infra-red absorption spectrum (Bartholomé & Karweil 1938) suggests that the two trios of hydrogen atoms spend most of their time in the staggered position; they undoubtedly rotate round the C—C bond as axis, but the rotation is not a revolution at constant speed, or a random rotation, but a rapid switching from one to another of the three equivalent positions.

In 1, 2-dichlorethane, $CH_2Cl . CH_2Cl$, both X-ray diffraction patterns (Ehrhardt 1932) and electron diffraction patterns (Beach & Palmer 1938) indicate that the halogen atoms spend most of their time at the maximum possible distance from each other, that is, with the C—Cl bonds at positions a, a' of figure 1. The same is true for the corresponding di-bromo-ethane, $CH_2Br . CH_2Br$, and for the chlorobromo compound, $CH_2Cl . CH_2Br$ (Beach & Turkevitch 1939). There is some indication that there may be alternative positions with the C—C—X planes at 80° to each other, in addition to the most frequent position with these planes at 180°. An angle of 80° means 20° deviation from alternative staggered positions ab' or ac' of figure 1; the deviation may be due to mutual repulsion of the halogen atoms. (The electric dipole moment of C—Cl is high.) That there are alternative positions in $CH_2Cl . CH_2Cl$ is also shown by the appearance in the Raman spectrum of a doublet for the C—Cl vibration; the two components of the doublet have different intensities at room temperature, showing that one position (the 180° position according to X-ray and electron diffraction patterns) is favoured, but the intensities become more nearly equal with rise of temperature, showing that the second position is visited relatively more frequently at higher temperatures (Kohlrausch 1932).
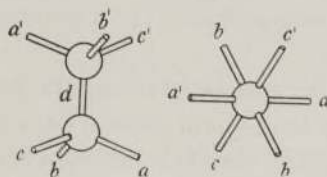

FIGURE 1. Bond positions in saturated molecules.

In 1, 1, 2-trichlorethane, $CHCl_2 . CH_2Cl$, the angle between the planes Cl—C^1—C^2 and C^1—C^2—Cl is 70°—within 10° of the precise staggered position (Turkevitch & Beach 1939); and in $Br(CH_3)CH$—$CH(CH_3)Br$ the staggered position is again the most stable, the bromine atoms being in positions aa' of figure 1 (Stevenson & Schomaker 1939). In cyclohexane there are only two structures which allow tetrahedral angles between the carbon bonds; the 'chair' ⌐⌐ and 'boat' ⌣⌣ forms of Sachse. It is interesting to find that in gaseous cyclohexane the molecules have the 'chair' form, in which all the bonds are staggered (figure 2c); the 'boat' form, in which the bonds are opposed, does not occur (Pauling & Brockway 1937). In trimethyl methane (Beach & Stevenson 1938) and in tetramethyl methane (Pauling & Brockway 1937), there is some indication

that the hydrogen atoms of the methyl groups may be most frequently at positions 30° from the staggered position, that is halfway between the staggered and opposed configurations. The evidence for all these molecules is provided by the electron diffraction patterns of the gases.
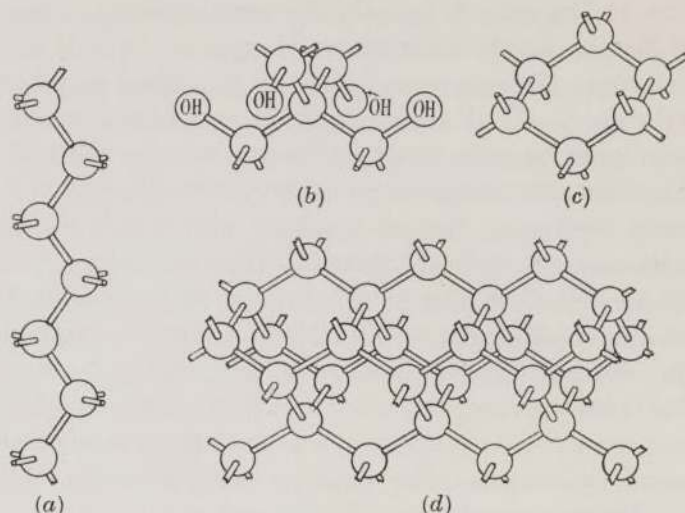

FIGURE 2. Structures of some singly-linked molecules. (*a*) Normal paraffin hydrocarbons. (*b*) Penta-erythritol. (*c*) Cyclo-hexane. (*d*) Diamond.

In crystals, likewise, the staggered configuration is favoured. The plane zigzag of carbon atoms in long-chain normal paraffin hydrocarbons such as poly-ethylene (Bunn 1939) is simply a repetition of the plane zigzag *ada'* (or *bdb'* or *cdc'*) of figure 1, and assuming that the hydrogen atoms are in the tetrahedral positions, all the bond orientations in the molecule (see figure 2*a*) conform to the model of figure 1. In penta-erythritol, $C(CH_2OH)_4$ (Llewellyn, Cox & Goodwin 1937), and its tetra-acetate (Goodwin & Hardy 1938) we find the same scheme of bond orientation (figure 2*b*), while in diamond (Bragg 1913) the scheme attains its most extended expression, a perfect diamond crystal (figure 2*d*) being simply a gigantic molecule composed of carbon atoms all linked together in precisely the manner shown in figure 1. The carbon atoms of succinic acid, $HOOC.CH_2.CH_2.COOH$, form a plane zigzag as in the normal paraffin hydrocarbons (Verweel & MacGillavry 1938). The same is true for the tartrate ion in Rochelle salt (Beevers & Hughes 1941).

In 1, 2-di-iodo-ethane, $CH_2I.CH_2I$, the distance between the iodine atoms (Klug 1935) leaves little doubt that they are at the maximum possible distance from each other, that is, the C—I bonds are at positions *aa'*

of figure 1. Similarly, the positions of the halogen atoms in the crystalline hexachloro and hexabromo derivatives of cyclohexane (Dickinson & Bilicke 1928) indicate strongly that the carbon ring (like that of gaseous cyclohexane) has the 'chair' form, in which the bonds of linked carbon atoms are staggered (figure 2c).*

Reason for the staggered configuration

The number of instances in which the staggered configuration is the most stable is sufficient to suggest that it may be a quite general rule which regulates the bond positions on successions of singly linked carbon atoms, just as Van 't Hoff's tetrahedral model specifies the bond positions on any one carbon atom. In this connexion it is relevant to enquire into the reason for the staggered configuration. The tetrahedral disposition of the bonds of any one carbon atom is primarily due, not to mutual repulsion of the atoms or groups held by the bonds, but to a strong orienting tendency of the bonds
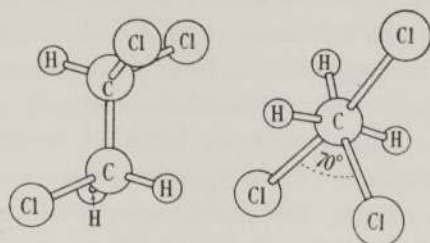

FIGURE 3. Molecular structure of 1, 1, 2 trichlorethane $CHCl_2.CH_2Cl$.

themselves (the shared electron links being most stable when tetrahedrally disposed), and it may be that the staggered configuration of the bonds of linked carbon atoms is due to a similar orienting tendency of the bonds themselves. Although there is no clear evidence on this point, one influence —the effect of electric dipole moments—may be discounted; in the molecule of 1, 1, 2-trichlorethane, $CHCl_2.CH_2Cl$, all the electric dipole moments H^+—C^- and C^+—Cl^- favour the opposed configuration; that is to say, if the configuration were determined mainly by the dipole moments, the angle between the planes Cl—C^1—C^2 and C^1—C^2—Cl would be $120°$, giving the maximum distances between the chlorine atoms. Actually (figure 3) the angle is $70°$, within $10°$ of the staggered bond position; there are two $70°$

* Since this paper was first written, Schomaker & Stevenson (*J. Chem. Phys.* 1940, **8**, 637) have also pointed out that the staggered configuration is favoured, citing some of the evidence given here.

positions, between which oscillation occurs. Evidently the electric dipole effect is small; the staggered bond configuration is therefore due either to an orienting tendency of the bonds themselves or to atomic interactions not attributable to electric dipole effects, or to both these factors. Kistiakowsky, Lacher & Ransom (1938) have suggested that, quite apart from the question as to which configuration is the most stable, the potential barrier to rotation is due to interaction between the electron pairs constituting the bonds. It should perhaps be mentioned that quantum-mechanical calculations of the forces in the ethane molecule have recently been made by several investigators. Some of these appear to point to the opposed configuration as the more stable; but the problem is a complex one, and different authors do not agree about the contributions of various factors (see Gorin, Walter & Eyring 1939; Eucken & Schäffer 1939). The theoretical treatment must therefore be regarded as tentative. Meanwhile, the experimental evidence must be accepted, which is strongly in favour of the general stability of the staggered configuration. The barrier to rotation is 3000 cal. in ethane (Pitzer 1937) and at least 5000 cal. in 1, 1-dichlorethane and similar molecules (Beach & Palmer 1938; Beach & Turkevitch 1939).

Deviations from the staggered positions must be expected when the bonds hold atoms or groups of very different sizes, or still more when the atoms take part in certain ring structures. Thus, in cyclopentane, the carbon atoms form a plane ring, in which the bonds are opposed, not staggered (Pauling & Brockway 1937). The reason is, no doubt, that the preservation of the tetrahedral angles between the bonds on any one carbon atom is a more urgent necessity than the maintenance of the staggered bond scheme for successive carbon atoms.

PREDICTION OF STRUCTURES OF SATURATED MOLECULES

If the principle of staggered bonds is of general validity (with the reservations mentioned in the last paragraph), it can be used for predicting the possible configurations of saturated molecules. It will not, in general, indicate only one possible structure for any particular molecule, because alternative bond positions will (except in the simplest molecules) give rise to different configurations; but it will usually indicate a limited number of possible structures, each of which can be tried out in turn. A useful way of regarding the possible single-bonded structures comes from the realization that all single-bonded carbon structures which conform to figure 1 are portions of the diamond structure (figure 2d). It is not to be expected that the precise geometry of any particular structure can be predicted,

because the interaction of different groups will give rise to distortions of the 'ideal' model; but an approximate prediction is better than no prediction at all.

In attempting to predict the structure of any particular molecule, it will be necessary to consider first the possible alternative bond-sequences, to select if possible the most probable of these, and then to consider what distortions of the ideal model are likely to occur.

For large molecules there may be many possible bond sequences, but it will often happen that consideration of atomic radii and the clearances between different parts of the molecule will show that one bond sequence is more probable than all others. As an example, consider how the simple plane zigzag chain of the normal paraffin hydrocarbons arises. Any two chain bonds such as a' and d in figure 1 are at the tetrahedral angle to each other. For the next chain bond there are three possible positions, a, b and c. If it took up position b, the carbon atoms on a' and b would be only $2 \cdot 9$ A apart; since the radius of a CH_2 group is $1 \cdot 8$–$2 \cdot 05$ A, it is evident that there would be considerable repulsion between the groups in these positions. The same is true for bond position c, which is exactly equivalent to b in this respect. In position a, however, the carbon atoms on a' and a are at the maximum possible distance from each other ($3 \cdot 9$ A); this position is therefore more probable than the other two. The same applies to all the chain bonds, hence the most probable chain configuration is the plane zigzag (figure $2a$). This is the structure which chains of CH_2 groups are likely to have at low temperatures, and thus it is not surprising that this is the structure we find in crystalline normal paraffin hydrocarbons.

NOMENCLATURE OF CHAIN TYPES

When side substituents are present on a carbon chain, the plane zigzag may not be the most probable form of chain. It will be useful to have a simple way of referring to different chain types. For any three chain bonds, we have seen that there are three different configurations, $a'da$, $a'db$ and $a'dc$; these will be called A, B and C respectively. Repetition of A gives the plane zigzag (figure $2a$) which has an identity period of $2 \cdot 53$ A; this chain is best symbolized AA or A_2, since this indicates the two-atom identity period as well as the bond sequence. Other chain types are illustrated in Fig. 4. Repetition of B gives rise to a right-handed spiral chain $BBBB$ or B_4 with a four-atom period of $3 \cdot 6$ A; in the end-view of this chain, the atoms fall at the corners of a square. Repetition of C gives the corresponding left-handed spiral C_4.

Alternation of A and B gives rise to a left-handed spiral chain $(AB)_3$ with a six-atom period of $6 \cdot 2$ A; in the end-view, the chain atoms fall at the corners of an equilateral triangle. Alternation of A and C gives the corresponding right-handed spiral $(AC)_3$. Alternation of B and C gives the cyclohexane ring $(BC)_3$, already illustrated in figure $2c$. Other simple chain types which are not spirals, but merely non-planar zigzags, are also shown in figure 4.
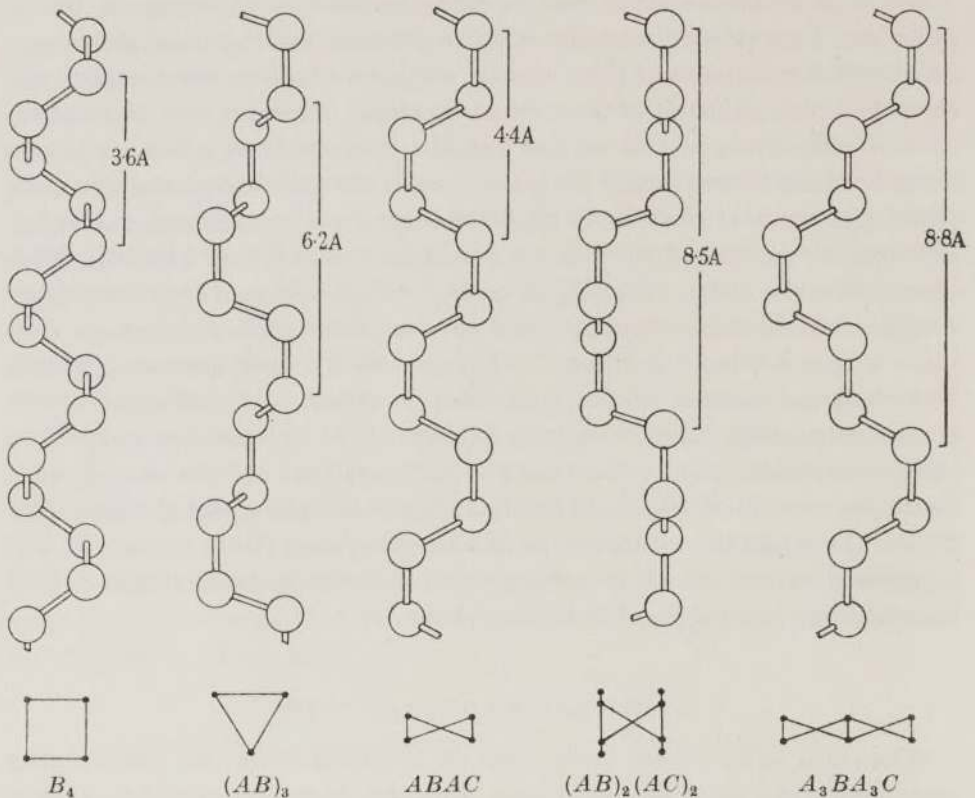

FIGURE 4. Some of the simpler single-bonded chain-types.

DETERMINATION OF CHAIN TYPE IN CRYSTALLINE POLYMERS

These chain types arising from regular repetitions of particular bond sequences are those likely to be found in crystalline chain polymers. Each chain type has its own characteristic identity period, and the identity periods of the simpler types are quite different from each other (see figure 4). Evidently it should be possible to find the type of chain in a polymer molecule by mere determination of the identity period of the molecule; this is

quite easily found from the X-ray (or electron) diffraction patterns of crystalline chain polymers, since in a stretched or rolled out specimen the identity period of the crystals in the direction of stretching or rolling (calculated directly from the distance between the layer lines on the diffraction pattern) is the identity period of the molecules themselves. The figures given are 'ideal' identity periods, based on the precise staggered bond model of figure 1. Some departure from these figures may be expected, though not enough to lead to uncertainty for the simpler chain types.

When a chain polymer is found to have a long identity period, more than one chain type may appear eligible; for with increase in the number of atoms per period the number of different bond sequences (some with similar identity periods) increases rapidly. In such cases, knowledge of the chemical structure of the chain molecules may help towards the selection of the correct chain type; each chemical unit in the chain would be expected to have a similar configuration, and thus the chemical structure of the chain would be reflected in the bond sequence. (For this purpose, enantiomorphic configurations such as AB and AC are equivalent.) As an example, rubber hydrochloride, which is believed to be chemically

$$(-CH_2-CH_2-CH_2-C(CH_3)Cl-)_n,$$
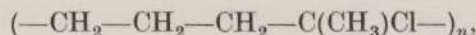
is a crystalline substance with a molecular identity period of 9·1 A (Gehman, Field & Dinsmore 1938). The chain structure A_3BA_3C (figure 4) is suggested for this molecule, since 9·1 A is sufficiently near the 'ideal' period of 8·8 A, and the bond sequence is compatible with the chemical structure of the molecule.*

STRUCTURES CONTAINING POLYVALENT ATOMS OTHER THAN CARBON

The amount of evidence on molecules containing nitrogen, oxygen and sulphur atoms bonded with carbon is less than that relating to carbon-carbon links, but what evidence there is suggests that in these molecules also the principle of staggered bonds is obeyed. This would perhaps be expected, because these atoms are stereochemically similar to carbon, having their bonds fixed at the tetrahedral angle to each other, and therefore the interactions of the bonds of successions of any of these atoms might be expected to be similar to those of carbon sequences.

The only evidence on nitrogen compounds is that the identity periods of

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* Since this was written, the crystal structure of rubber hydrochloride has been determined by interpretation of X-ray diffraction patterns. The predicted molecular structure has proved to be correct.

poly-hexamethylene adipamide $(-NH(CH_2)_6 . NH . CO . (CH_2)_4 . CO-)_n$ (Fuller 1940), and natural silk $(-CHR . CO . NH-)_n$ (Kratky & Kuriyama 1931) are such that the chains must be plane or nearly plane zigzags similar to the carbon chain in normal paraffin hydrocarbons; and the bond structure of hexamethylene tetramine, $(CH_2)_6N_4$, is the same as that of a portion of the diamond structure (Dickinson & Raymond 1923; Wyckoff & Corey 1934).

The oxygen and sulphur compounds which have been examined are penta-erythritol tetra-acetate, $C(CH_2O . CO . CH_3)_4$, in which the singly linked oxygen atoms participate in plane zigzag chains (Goodwin & Hardy 1938); trimethylene oxide $(CH_2O)_3$ and the corresponding sulphur compound $(CH_2S)_3$ which have ring structures with chair forms like cyclohexane (Moerman 1937; Moerman & Wiebenga 1937); paraldehyde $(CH_3 . CHO)_3$, which probably has the same ring structure (Carpenter & Brockway 1936). In all these, the bonds are staggered. In metaldehyde $(CH_3CHO)_4$ the molecules are non-planar eight-atom rings in which there is some deviation from the staggered bond positions. The identity periods of some of the polyesters $(-CO-(CH_2)_x-CO-O-(CH_2)_y-O-)_n$ indicate that the chains are nearly fully extended zigzags like $(CH_2)_n$ (Fuller 1940); there cannot be much deviation from the staggered positions here.

Assuming that the staggered positions are favoured in such molecules, configurations for molecules containing these atoms can be predicted. The chain forms illustrated in figure 4 are valid for chains containing these atoms, though the identity periods will necessarily be different. It has been remarked (Fuller & Erickson 1937) that the identity periods of certain long-chain polyesters indicate that the chains cannot be plane zigzags; for instance, polyethylene-succinate,

$$(-CO-CH_2-CH_2-CO-O-CH_2-CH_2-O)_n,$$
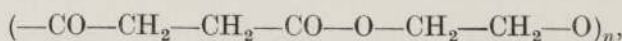
has an identity period of $8 \cdot 3$ A, whereas a plane zigzag chain would have a period of $9 \cdot 8$ A. The non-planar zigzag chain form which has been suggested for this molecule by Fuller & Erickson is actually $ABAC$ illustrated in figure 4. (The period for the molecule is necessarily twice $ABAC$ on account of the chemical constitution of the molecule.) These authors consider that this chain configuration results simply from attractions of atoms or dipoles placed at intervals along the chain. The present point of view is that the possible chain forms are determined by the principle of staggered bonds, though the choice by any particular molecule of one chain form rather than another no doubt depends on attractions or repulsions of certain atoms or groups not only in the same molecule but also in neighbouring molecules in

the crystal. $ABAC$ is not the only chain form possible for this molecule; $(AB)_2(AC)_2$ (figure 4) seems also eligible.

The complex chain forms of poly-oxy-methylene, $(—CH_2—O—)_n$, and poly-oxy-ethylene, $(—CH_2—CH_2—O—)_n$, probably also result from the operation of the principle of staggered bonds, combined with the effects of the interactions of particular atoms or dipoles. The identity periods—17·35 and 19·5 A respectively, each containing nine chemical units (Sauter 1932, 1933)—seem remarkably long for molecules of such essentially simple chemical structure; but it must be remembered that comparatively simple bond sequences may lead to long identity periods. Repetition of $ABABAC$ leads to an 18-atom period $(ABABAC)_3$ of about 17·5 A; this seems a possible chain form for poly-oxy-methylene.

BOND POSITIONS IN UNSATURATED MOLECULES

This enquiry started as an attempt to understand the non-planar chain forms of three unsaturated polymer molecules; it was undertaken as a necessary step in the approach to the question of molecular flexibility. Now return to these unsaturated chains, and consider them against the background of the principle of staggered bonds. The interest centres on the positions of the single bonds $(CH_2—CH_2)$ which join isoprene or chloroprene units $(—CH_2—CR=CH—CH_2—)$. But first of all the configuration of the isoprene and chloroprene units themselves needs some comment.

Each such unit is roughly planar (see figures 2, 4 and 7 of Part I). This is in accordance with expectation, since in ethylene (Thompson 1939) and its chloro substitution products (Brockway, Beach & Pauling 1935), all the atoms lie in a plane—a configuration consistent with the simple geometrical c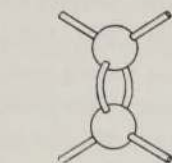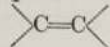onception of the double bond shown in figure 5. There are, however, some large distortions, the greatest being those of the bonds holding methyl groups or chlorine atoms. Thus, in β gutta-percha the bond holding the methyl group lies over 20° out of the plane $CH_2—C=CH$ (see figure 6). In rubber, the distortions are different in the two isoprene units which make up the molecular identity period; the greatest is as much as 35°. In polychloroprene, whose molecular structure is analogous to that of β gutta-percha, the corresponding distortion of the C—Cl bond is even higher—40°. These distortions appear to be due chiefly to repulsion between the methyl or chlorine side-substituent and one of the chain CH_2 groups (5 and 4b in figure 6). But in rubber, since the configurations of the two isoprene units

FIGURE 5. Bond positions in group $\rangle C=C\langle$

in its period are different, the distortions must be due partly to the effect of packing together the awkwardly shaped molecules; each molecule is distorted by the other molecules surrounding it; the Van der Waals' forces of attraction responsible for holding the molecules together in a precise crystalline formation are strong enough to give rise to very appreciable distortions of bond positions.

These distortions are surprisingly large. It is well established (by the great stability of *cis* and *trans* isomers) that rotation round a double bond requires a high energy—a state of affairs well illustrated by the traditional simple geometrical picture of the double bond shown in figure 5—and therefore it might have been expected that the single bond positions would be severely restricted. This is not so; evidently distortions up to 40° are fairly easily brought about.
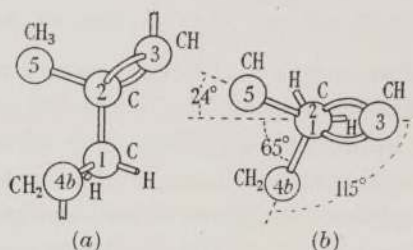

(a)   (b)

FIGURE 6. Bond positions in β gutta-percha.

Now return to the main question—the reasons for the positions of the single CH_2—CH_2 bonds which join isoprene or chloroprene units together. These bonds make large angles with the CH_2=C—CH planes, and give the chains their pronouncedly non-planar character. In β gutta-percha, plane CH_2—CH_2—C makes an angle of 115° with plane CH_2—C=CH and 89° with plane CH_2—C—CH_3 (see figure 6b). In polychloroprene the angles are not very different. In rubber, the two isoprene units in the period have different configurations; in one of them, the angles specified are 109 and 86°; in the other they are $169\frac{1}{2}$ and $45\frac{1}{2}$°. These bond positions are, no doubt, partly due to the presence of the substituent methyl group or chlorine atom; owing to its presence, the CH_2 chain group cannot be in the plane of the isoprene unit, but is pushed to one side. Thus the same repulsion which is responsible for pushing the methyl group away from the CH_2—C=CH plane (the repulsion between CH_3 group 5 and CH_2 group 4b in figure 6) is also responsible, at any rate partly, for the pronouncedly non-planar character of the chain. But in view of the preference for the staggered bond configuration in singly linked molecules—a preference which, it is suggested,

is due largely to an orienting tendency of the bonds themselves rather than to interactions between the atoms held by the bonds—the question arises whether there is a similar influence in the unsaturated molecules under discussion. From this point of view, it is interesting to note that in β gutta-percha, if the double bond is represented in the simple geometrical way shown in figure 6, then the three bonds of atom 2 are staggered with respect to those of atom 1; this is shown most clearly in figure 6b. There is some distortion, but, nevertheless, an approximation to the staggered configuration, if it is justifiable to regard the double bond as two distorted single bonds. In polychloroprene, the bond positions are very similar to those in β gutta-percha. In rubber, the bond orientation for half the isoprene units is again similar, but in the other half the angles (given above) are considerably different from those in β gutta-percha. It is evident that, if we are right in supposing that there is some tendency towards the staggered bond configuration (which, together with the repulsions between atomic groups, is responsible for the non-planar character of the chain) nevertheless this configuration is easily distorted; in rubber crystals, the distortion is brought about by the Van der Waals' forces between adjacent molecules.

Ease of distortion is bound up with the magnitude of the potential barrier to rotation; there is some evidence of this magnitude in simple gas molecules, and it is interesting to find that in those containing the bond sequence —C—C=C, the barrier to rotation is much lower than in saturated molecules. Thus, in propylene, CH_3—$C\!\!\big\langle\genfrac{}{}{0pt}{}{H}{CH_2}$ (Kistiakowsky, Lacher & Ransom 1938), and in acetone, $\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!\!\big\rangle C\!=\!O$ (Schumann & Aston 1938), the barrier of rotation of the methyl group is not more than 1000 cal.—only one-third the figure for ethane and other saturated molecules. It has been suggested (Kistiakowsky *et al.* 1938) that this indicates that the double bond has no orienting influence; the rotation of each methyl group in propylene and acetone is perhaps restricted by only one single bond—the H—C bond in propylene (as compared with three in saturated molecules), and this may be the reason why the restricting potential has only one-third the value found in saturated molecules. However this may be, the smallness of the potential barrier to rotation in such groupings is presumably the reason why the staggered bond configuration is so easily distorted in rubber molecules.

In view of the experimental evidence on rubber and the thermochemical evidence just mentioned, it is to be expected that in general, molecules containing double bonds are likely to exhibit much greater deviations from

the staggered bond positions than are saturated molecules.* This will not always be so, as is evident from the examples of β gutta-percha and poly-chloroprene; presumably in these crystals the Van der Waals' forces arising from the manner of packing of the molecules happen to favour the staggered position, whereas in rubber the packing is such that in some places the Van der Waals' forces oppose the staggered configuration.

The nomenclature already described for saturated chains may also be used for chains containing double bonds, provided that additional informa-tion on the *cis* or *trans* configuration of the double-bonded unit is included. Thus β gutta-percha (figure 2 of Part I) is (*trans*) BAC or (*trans*) CAB, α gutta-percha (figure 5a of Part I) is (*trans*) BAC (*trans*) CAB, and the γ form of *trans* chain (figure 5b of Part I) is (*trans*) BAB (*trans*) CAC. Rubber is (*cis*) BAC (*cis*) BAC. The other form of *cis* chain shown in this diagram is (*cis*) BAC (*cis*) CAB.

The discussion of ease of distortion and the magnitude of the potential barrier to rotation brings us to the question of molecular flexibility, and its connexion with rubber-like properties. This topic will be taken up in Part III of this work, but meanwhile it may be remarked that molecules con-taining double bonds in the chain are likely to be more flexible (other things, such as side-chain hindrances to rotation, being equal) than saturated molecules, simply because the potential barrier to rotation round the single bonds due to the orienting tendency of the bonds themselves is lower when double bonds are present in the chain than in saturated chains; and there-fore, if we accept in a general way the idea that rubber-like properties are likely to be shown only by substances having very flexible molecules, then this constitutes a special reason why polymers having double bonds in their chains are likely to have rubber-like properties. Perhaps this is why so many 1 : 4 polymers of butadiene derivatives, both natural and synthetic, have rubber-like properties—simply because every fourth chain bond is a double bond. To go any further it is necessary to consider both the preferred bond positions (and the potential barriers associated with them) and the effect of side groups in increasing or decreasing the heights of the barriers to rotation. This will be done in Part III.

* This refers only to molecules which, like rubber, contain straightforward double bonds. Resonating systems exhibiting bonds of intermediate character are ex-cluded from consideration.

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