# 135. *The Crystal Structure of Rubber Hydrochloride.*

By C. W. Bunn and (Mrs.) E. V. Garner.

Rubber hydrochloride $[-(CH_2)_3{\cdot}C(CH_3)Cl-]_n$ is of interest in the study of the stereochemistry of long-chain polymers. The form of the chain has previously been predicted on the basis of (*a*) a knowledge of the identity period and (*b*) the assumption that the bonds of linked carbon atoms are everywhere in staggered positions.

The crystal structure has now been determined by *X*-ray methods. The unit cell is monoclinic (pseudo-orthorhombic) with $a = 5{\cdot}83$, $b = 10{\cdot}38$, $c = 8{\cdot}95$ A.; $\beta = 90°$. Two long-chain molecules pass through this unit cell. The symmetry of the arrangement is $P2_1/c$. The predicted chain form (symbolised $A_3BA_3C$), in which the principle of staggered bonds is obeyed, is found to be correct.

The relation between the molecular structure and the physical properties (particularly the melting point) is discussed.

" Rubber hydrochloride," the crystalline substance made by addition of hydrogen chloride to rubber, is of interest for two reasons. First, the periodicity along the fibre axis of drawn specimens (Gehman, Field, and Dinsmore, *Proc. Rubber Tech. Conference*, 1938, p. 961) indicates that the carbon chain has not the simple plane zigzag form found in the paraffin hydrocarbons (Bunn, *Trans. Faraday Soc.*, 1939, **35**, 482), but is somewhat shortened by folding. There is similar evidence that several other chain polymers also have folded chains (Fuller, *Chem. Reviews*, 1940, **26**, 143); the elucidation of the geometry of such molecules would form a useful contribution to our knowledge of the stereochemistry of carbon compounds in general and chain polymers in particular. Rubber hydrochloride appeared to be a suitable substance for crystallographic investigation from this point of view: it gives a well-defined *X*-ray diffraction pattern. Moreover, a prediction of the chain form has been made on the basis of a knowledge of the periodicity and the use of a hypothesis which has been called the principle of staggered bonds (Bunn, *Proc. Roy. Soc.*, 1942, *A*, **180**, 67); the determination of the structure by *X*-ray methods forms the first test of the validity and usefulness of this hypothesis.

Secondly, rubber hydrochloride is interesting on account of its physical properties. Unlike rubber itself, it is crystalline at room temperature, " melting " at about 115°. The present work on its crystal structure forms part of a programme of research being carried out in this laboratory, being a contribution to the attempt to understand the physical properties of chain polymers in terms of molecular structure.

*Chemical Structure.*—The chemical structure of rubber is

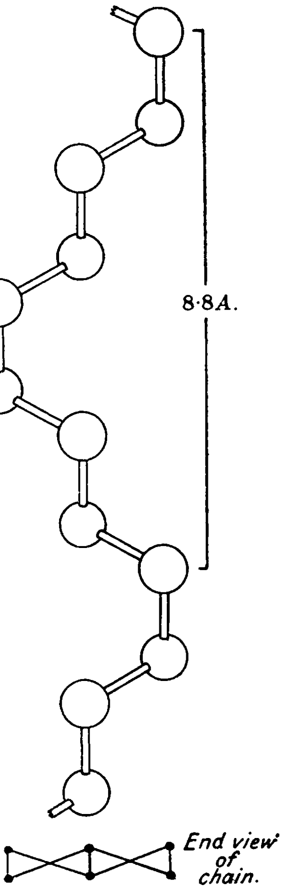
$$[\text{-CMe=CH-(CH}_2)_2\text{-CMe=CH-(CH}_2)_2\text{-}]_n.$$

Hence, on the assumption that hydrogen chloride adds on according to Markownikoff's rule, the chemical structure of rubber hydrochloride is expected to be

$$[\text{-CClMe-CH}_2\text{-(CH}_2)_2\text{-CClMe-CH}_2\text{-(CH}_2)_2\text{-}]_n$$

*Experimental Details.*—The crystal structure was deduced from *X*-ray diffraction photographs taken with copper radiation filtered through nickel foil to remove the *K*-β wave-length. Two types of photograph were used—the usual fibre photograph, with the beam perpendicular to the fibre axis, and also photographs taken while the fibre axis was oscillating with respect to the beam. In both cases the spots were recorded on a cylindrical film, for the sake of obtaining the maximum angular range of reflections. The second type of photograph yielded reflections from planes perpendicular or nearly perpendicular to the fibre axis, some of which do not appear on the first type of photograph.

FIG. 1.
*Chain type* $A_3BA_3C$.



The best orientation of crystals in the specimens was obtained by drawing out a thin strip at 90° and allowing it to cool while still extended. The normal fibre photograph shows 24 reflections, the intensities of which were estimated visually. Attempts to obtain a double orientation by rolling strips of material failed; it was therefore not possible to obtain direct information on the orientation of crystal planes; interpretation rests simply on the positions of the spots on the photographs.

*Unit Cell Dimensions.*—The cell spacing along the fibre axis can be measured directly from the layer-line separation on the normal fibre photograph and is found to be 8·95 A. The cell dimensions in the directions perpendicular to the fibre axis cannot be measured directly, but all the spots on the photograph are found to fit a rectangular cell with $a = 5{\cdot}83$, $b = 10{\cdot}38$, $c$ (fibre axis) $= 8{\cdot}95$ A. From these dimensions, and the reported density of 1·193 g./c.c. (Gehman, Field, and Dinsmore, *loc. cit.*), the number of $\text{-CMeCl-(CH}_2)_3\text{-}$ units in the cell is found to be 3·8. There are evidently four of these units in the cell. On this basis, the true density of a single crystal is calculated to be 1·255. The lower density of the bulk material is presumably due to the presence of a certain amount of amorphous material, which, being inefficiently packed, would be expected to have a lower density than the crystals. Specimens of long-chain polymers usually have somewhat low densities for this reason. In the case of rubber hydrochloride, there is a second reason why the amorphous material is expected to have a low density; hydrochlorination in the specimens examined was not complete, the chlorine content being only 29·3% (Calc. for $C_5H_9Cl$: Cl, 34%), and unreacted molecules or sections of molecules, which would be lighter than the rest, are expected to form part of the amorphous material.

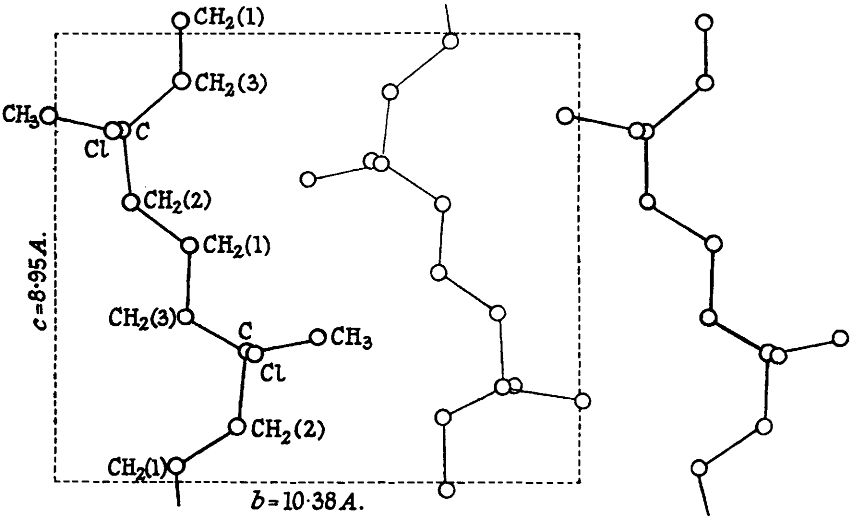
*Space Group and Parameters.*—The space-group symmetry of single crystals can usually be determined unambiguously by observing which types of *X*-ray reflection are systematically absent, and combining this information with that provided by crystal morphology and pyro- or piezo-electric properties. The problem is more difficult in the case of polymers, since these substances cannot be obtained in the form of single crystals; not only can no information be derived about crystal habit and pyroelectric properties, but frequently the information about absent reflections is ambiguous owing to the overlapping of spectra. This means that usually a number of different space groups must be considered. To shorten the search for the correct arrangement, it is desirable to use external evidence, if this appears to limit the possibilities.

For rubber hydrochloride, it is found that, among reflections which can be uniquely indexed, the only systematic absences are the odd orders of $0k0$, and also $h0l$ reflections having $l$ odd; if these absences are not accidental, it appears that there is a screw axis parallel to $b$, perpendicular to which is a glide plane with translation $c/2$. Since the cell is rectangular, the symmetry would be expected to be orthorhombic; but there is no orthorhombic space group giving the particular combination of absences mentioned; in fact, the absences indicate the monoclinic space group $P2_1/c$. There remains, however, the doubt whether some of the " absent " reflections really have small intensities but are too weak to be detected on the photographs; in view of this doubt, it is necessary to consider the stereochemistry of the molecules themselves.

The chain form of rubber hydrochloride molecules has already been predicted (Bunn, *loc. cit.*, 1942, *A*, **180**, 67); it being assumed that the bonds of singly-linked carbon atoms are staggered, the only chain form which has approximately the identity period found in rubber hydrochloride (8·95 A.) is the form $A_3BA_3C$ (Fig. 1). This chain form is also consistent with the probable chemical linking in the molecule (Markownikoff's rule being assumed); the section $^-CH_2{}^-CH_2{}^-CH_2{}^-$ would be likely to have the plane zigzag chain (an $A$ sequence) as in polyethylene; only at the >CMeCl unit is there likely to be a $B$ or $C$ link. The chain $A_3BA_3C$ has a glide plane with translation $c/2$, and the presence of methyl and chlorine substituents (provided they are in equivalent stereo-positions) does not affect this symmetry; the space group $P2_1/c$ is thus consistent with the suggested chain form.

FIG. 2.

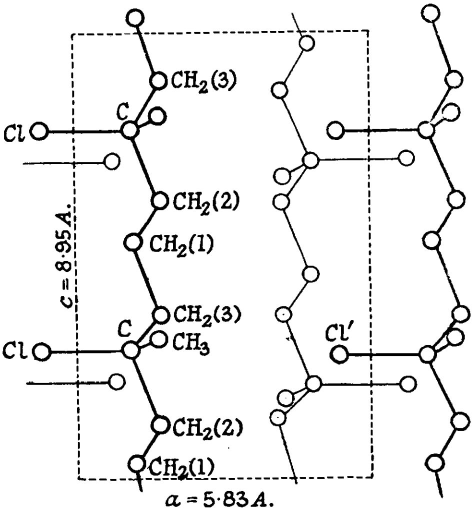
*Crystal structure of rubber hydrochloride seen along the* a *axis.*



On the assumption, then, that this monoclinic space group and the suggested chain form are correct, it remains to determine the atomic parameters by calculation of the intensities of the reflections. Since in the identity period of the molecule there are two [$^-CMeCl^-(CH_2)_3{}^-$] units, and the number of such units in the cell is four, there must be two chain molecules passing through the cell. The orientation of these molecules is fixed: the glide plane is perpendicular to the $b$ axis. There are two alternative positions for the methyl and chlorine substituents; either the chlorine is on bond $p$ (Fig. 4), while the methyl is on bond $q$, or the reverse may be true. The decision that the former is correct, as well as the relation of the chains to the screw axis and the precise atomic parameters, rest on calculations of the intensities of all the reflections. Satisfactory agreement between observed and calculated intensities is attained if it is assumed that the atoms occupy the positions given in Table I. The intensities are given in Table II. The predicted chain structure and the space group $P2_1/c$ are evidently correct.

FIG. 3.

*Crystal structure of rubber hydrochloride seen along the* b *axis.*



If the co-ordinates of any atom are $x$, $y$, $z$, there are corresponding atoms in the same chain at $x$, $\frac{1}{2} - y$, $\frac{1}{2} + y$, and in the second chain at $\bar{x}$, $\bar{y}$, $\bar{z}$ and $x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$.

*Description of Structure.*—Figs. 2, 3, and 4 show projections on planes perpendicular to the three axes of the crystal. Fig. 5 shows one repeating unit of the rubber hydrochloride molecule. The predicted chain form is definitely confirmed. The results of this work thus demonstrate the usefulness of the principle of staggered bonds, on which the prediction was based, and also provide yet another example in which the principle is obeyed.

TABLE I.

*Atomic parameters in fractions of unit cell edges.*

| | *x.* | *y.* | *z.* | | *x.* | *y.* | *z.* |
|---|---|---|---|---|---|---|---|
| $CH_2$ (1) ........... | 0·204 | 0·238 | 0·032 | $CH_3$ .................. | 0·281 | 0·51 | 0·32 |
| $CH_2$ (2) ........... | 0·293 | 0·356 | 0·126 | Cl .................. | −0·11 | 0·39 | 0·283 |
| C .................... | 0·195 | 0·371 | 0·285 | $CH_2$ (3) ........... | 0·293 | 0·252 | 0·37 |

TABLE II.

*Comparison of observed and calculated intensities.*

| | Intensity. | | | Intensity. | | | Intensity. | | | Intensity. | | | Intensity. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Index. | Calc. | Obs. | Index. | Calc. | Obs. | Index. | Calc. | Obs. | Index. | Calc. | Obs. | Index. | Calc. | Obs. |
| 010 | 0 | 0 | 320 | 0 | 0 | 051 | 0 | 0 | 212 | 34 | vw | 203 | 0 | 0 |
| 100 | 74 | m | 060 | 21 | vvw | 151 | 64 | m | 042 | 49 | w | 213 | 31 | vvw |
| 020 | 231 | vs | 250 | | | 301 | | | 222 | | | 043 | | |
| 110 | | | 330 | | | 241 | | | 142 | 91 | w | 223 | | |
| 120 | 0 | 0 | 160 | | | 311 | | | 232 | 18 | 0 | 143 | 2 | 0 |
| 030 | 0 | 0 | 011 | 14 | 0 | 321 | 8 | 0 | 052 | 0 | 0 | 233 | 0 | 0 |
| 130 | 190 | s | 101 | 0 | 0 | 060 | 47 | vvw | 152 | 18 | 0 | 053 | 0 | 0 |
| 200 | | | 021 | 338 | vs | 251 | | | 302 | | | 153 | 42 | vvw |
| 210 | 34 | m | 111 | | | 331 | | | 242 | | | 303 | | |
| 040 | 14 | 0 | 121 | 107 | m | 012 | 20 | 0 | 312 | | | 243 | | |
| 220 | | | 031 | 4 | 0 | 102 | 176 | s | 322 | 2 | 0 | 313 | | |
| 140 | 34 | w | 131 | 10 | 0 | 022 | | | 103 | 0 | 0 | *001 | 0 | 0 |
| 230 | 32 | vw | 201 | | | 112 | | | 023 | 82 | vw | *002 | 157 | s |
| 050 | 0 | 0 | 211 | 48 | w | 122 | 5 | 0 | 113 | | | *003 | 46 | m |
| 150 | 79 | m | 041 | 2 | 0 | 032 | 0 | 0 | 123 | 100 | w | *013 | | |
| 300 | | | 221 | | | 132 | 20 | vw | 033 | 1 | 0 | *004 | 23 | w |
| 240 | | | 141 | 7 | 0 | 202 | | | 133 | 22 | 0 | *104 | | |
| 310 | | | 231 | 10 | 0 | | | | | | | | | |

* The intensities of these planes were estimated independently from a photograph taken with the fibre axis horizontal and oscillated about a vertical axis between 45° and 90° to the *X*-ray beam.

No corrections have been made for thermal vibrations of the atoms. For this reason, the observed intensities should fall away from the calculated intensities with increasing angle of reflection. This does, in fact, occur.

No great accuracy can be claimed for the values of the atomic parameters on account of the small amount of information on which they are based. The possible errors of the parameters also vary with the diffracting power of the atoms concerned. By displacing the atoms by definite amounts and calculating the intensities, we assess the possible errors at about 0·02 A. for chlorine and 0·05 A. for carbon atoms.

FIG. 4.

*Crystal structure of rubber hydrochloride seen along the* c *axis.*

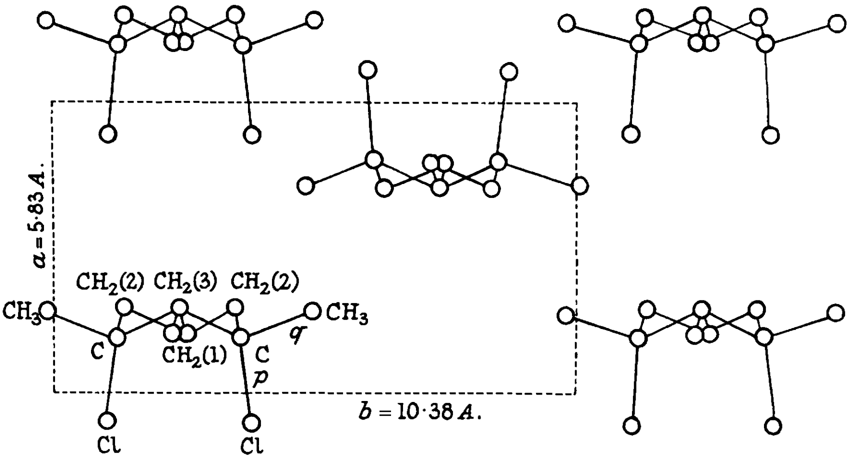
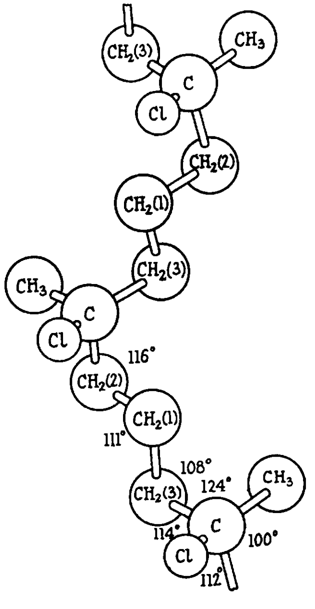


FIG. 5.

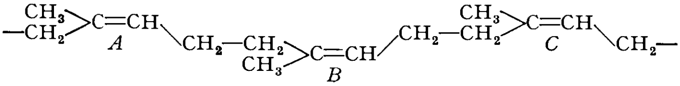
*Geometry of the rubber hydrochloride molecule.*



Within the above limits of experimental error, all C–C distances have the normal value of 1·54 A., and the C–Cl distance is 1·79 A. (compare 1·77 A. in polychloroprene). The nearest distances between carbon atoms in different chains vary from 3·89 A. to 4·11 A., and between carbon atoms and chlorine atoms in different chains from 3·76 to 3·83. None of the bond angles between carbon atoms in the chains differs by more than 4° from the value of 112° found for a paraffin chain (Bunn, *Trans. Faraday Soc.*, 1939, **35**, 482). The angles made by the C–$CH_3$ bond with the two adjacent C–$CH_2$ bonds, however, deviate considerably from the normal value. The angle $CH_2$(3)–C–$CH_3$ (Fig. 6) is 124°, and the angle $CH_2$(2)–C–$CH_3$ is 100°. The apparent reason for these abnormal angles is the repulsion of the $CH_3$ group by $CH_2$(1); this has the effect of enlarging the angle $CH_2$(3)–C–$CH_3$ and at the same time diminishing the angle $CH_2$(2)–C–$CH_3$. An exactly similar distortion of the methyl group from the "ideal" position has been found in rubber (Bunn, *loc. cit.*, 1942), and this too can be attributed to the same cause.

The mode of packing of the molecules shows clearly the reason why the angle β (which in the monoclinic system is not fixed by symmetry) is in this crystal 90°. The chlorine atom of one molecule (Cl′ in Fig. 3) fits into the hollow formed by groups $CH_3$, $CH_2(2)$, and $CH_2(3)$ attached to carbon atom C of the molecule in front, *i.e.*, the next molecule along the *a* axis. This packing ensures that the *z* co-ordinate of Cl′ is about the same as that of C, and since the carbon–chlorine bond is at right angles to the chain axis, the angle β must necessarily be approximately 90°.

*Stereochemistry of the Reaction between Hydrogen Chloride and Rubber.*—In the first place, the structure of rubber hydrochloride now established confirms the original assumption that Markownikoff's rule is obeyed in the addition reaction; the chlorine atom adds on to the carbon bearing the methyl side group, and the hydrogen adds on to the $^{=}CH^{-}$ group. But in addition, it is noteworthy that in the rubber hydrochloride molecule, successive $^{-}(CH_2)_3{}^{-}\dot{C}MeCl^{-}$ groups are alternately left- and right-handed. (The enantiomorphic character of the group does not depend on the geometry of the chain; it is not possible, by rotating round single bonds, to convert a left- into a right-handed unit.) The precise geometry of the addition reaction depends on the form of the rubber molecule in solution, *i.e.*, whether it is extended or coiled up. If it is extended in solution it may be represented thus:



[Actually the molecule is not planar (Bunn, *loc. cit.*), but the above plane projection is sufficient for the present purpose.] The established structure of rubber hydrochloride implies that if a molecule of hydrogen chloride adds on to double bond *A* on this side of the rubber molecule—above the plane of the paper—then addition to *B* and *C* must also occur on this same side of the rubber molecule; and so on for many units, to give a molecule which is regular for at any rate some hundreds of *A*'s (this being the order of size of the crystals of rubber hydrochloride). If the rubber molecules are coiled up in solution, the geometry of the addition reaction is different, but again some geometrically regular repetition must occur; in other words, it appears that when a hydrogen chloride molecule has added on to one double bond, the atomic grouping so formed has a directing influence on the process of addition to the next double bond.

It is interesting in this connection to note that balata hydrochloride is amorphous (Gehman, Field, and Dinsmore, *loc. cit.*). The balata or gutta-percha hydrocarbon is *trans*-polyisoprene, rubber being the *cis*-form; the amorphous character of balata hydrochloride may mean that, owing to the difference in chain structure, addition of hydrogen chloride does not occur in the geometrically regular way noted in the case of rubber, but in such a way that left- and right-handed groupings are formed indiscriminately, yielding chain molecules which, since they are geometrically irregular in structure, cannot form crystalline arrangements.

*Physical Properties of Rubber Hydrochloride.*—The mechanical properties of rubber hydrochloride are similar to those of other crystalline polymers: it can be drawn out to several times its length, the crystals becoming oriented in the process, and it remains extended when released. Near the m. p., the extensibility becomes reversible, the material then being more like rubber (Gehman *et al.*, *loc. cit.*); this behaviour is also typical of crystalline polymers. Interest centres on the m. p., which is about 115°, *i.e.*, very much higher than that of rubber (about 0°) and similar to that of polyethylene (115°).

It has been suggested that ease of rotation round the single bonds of long-chain polymer molecules plays a large part in determining the m. p., and that the ease of rotation round the single bonds in any particular molecule is determined by two factors—the bond-orientation energy and the interaction of the atoms or groups held by the bonds. As regards the second factor, we have to imagine, in the case of the rubber hydrochloride molecule, rotation occurring round bond $C–CH_2(2)$ in Fig. 5, and to consider to what extent the rotation of $CH_2(1)$ is hindered by $CH_2(3)$, $CH_3$, and Cl. [Rotation round bond $C–CH_2(3)$ presents the same geometrical problem.] The hindrance offered by $CH_2(3)$ or by the $CH_3$ group would be expected to be similar to the hindrance in rubber itself, since the configurations of the moving parts are similar in the two molecules. The hindrance offered by the chlorine atom is expected to be less, since the chlorine atom is a little smaller than a $CH_2$ or a $CH_3$ group and also stands further from the carbon atom to which it is attached. Thus, whatever bond rotations occur in the rubber hydrochloride molecule at the m. p., the geometrical hindrance to rotation is not likely to be greater, and may even be less, than in rubber itself. The high m. p. of rubber hydrochloride in comparison with rubber is therefore not to be explained by any steric effects.

Turning to the other factor—the bond-orientation energy—we find that rotation round single bonds is easier when there is an adjacent double bond (as in rubber) than in a saturated molecule (Bunn, *loc. cit.*, 1942). The difference between the m. p.'s of rubber and of its hydrochloride may therefore be due, at any rate partly, to the fact that in rubber every fourth chain bond is a double bond, whereas the hydrochloride molecule is saturated, and the more rigid simply on that account. There are, however, other factors which may also play a part; first, the greater inertia of the moving parts of the rubber hydrochloride molecule owing to the presence of the comparatively heavy chlorine atom, and secondly, the interaction of C–Cl dipoles. Both these factors would tend to increase the m. p. It is not possible at present to assess the relative contributions of these factors.

IMPERIAL CHEMICAL INDUSTRIES LTD., NORTHWICH.

[*Received, April* 30*th*, 1942.]