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THE STRUCTURE OF POLYISOPRENES.
PART II. THE STRUCTURE OF β-GUTTAPERCHA.

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THE STRUCTURE OE β-GUTTAPERCHA.

By G. A. Jeffrey.

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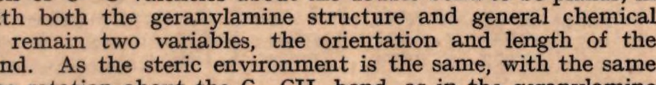
The ultimate goal in studying the crystal structures of the polyisoprenes is the complete picture of the atomic arrangements in the crystal lattices. This can be attained by the synthesis of results from experimental observations on the polyisoprenes themselves and on substances variously related to them. From the detailed X-ray analysis of simple crystalline compounds precise geometrical data about the molecules become available which point to the probable stereochemistry of the polymers. The criterion of the validity of a proposed polymer structure is that it shall be based on well-founded and self-consistent principles and shall account for the X-ray diffraction measurements from the polymer as rigorously as this limited information will allow.

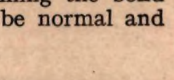
The crystal structure analysis of a simple di-isoprene derivative, geranylamine hydrochloride (I),[1] provides a basis for a model of the trans-linked polyisoprene molecule β-guttapercha. This model differs significantly in the molecular detail from that proposed by Bunn,[2] although it accounts equally well for his observed X-ray intensities on the fibre diagram. The interpretation of these intensties has therefore been re-examined and it has become clear that such data alone cannot determine molecular details of high polymers uniquely, and so should not be relied upon to support structures involving bond distortions for which there is no other evidence.

(I)



$$CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{=}CH\text{—}CH_2\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{=}CH\text{—}CH_2\text{—}NH_3Cl$$

The β-Guttapercha Model.—The β modification of guttapercha is the simplest natural polyisoprene to consider since the fibre-axis length of 4·7 to 4·8 A. reveals a repeating unit along the hydrocarbon chain compatible only with one 'trans' isoprene group. Assuming the bond lengths and angles of the $CH_2\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{=}CH\text{—}CH_2$ group to be normal and the distribution of C—C valencies about the double bond to be planar, in agreement with both the geranylamine structure and general chemical theory, there remain two variables, the orientation and length of the CH_2—CH_2 bond. As the steric environment is the same, with the same barriers to free rotation about the C—CH_2 bond, as in the geranylamine molecule, the same angle of 80° to the isoprene plane can be expected in the crystalline state. Although this may be influenced to some extent by the intermolecular packing in the crystal lattice, the deviation must be small to avoid unbalanced repulsions between the CH_2 and the CH or CH_3 groups. This factor was appreciated by Bunn when, selecting for his model a smaller value of this angle (63°) he also introduced a large bond distortion of the methyl group out of the plane of the double bond valencies (24°) and ascribed it to just such a steric repulsion.[3]



The length of the CH_2—CH_2 bond in the geranylamine hydrochloride

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[1] Jeffrey, *Nature*, 1943, **152**, 446 and Part I of this series, in press.
[2] Bunn, *Proc. Roy. Soc.*, *A*, 1942, **180**, 40.
[3] Bunn, *Trans. Faraday Soc.*, 1942, **38**, 384.

molecule was observed to be shorter than normal. As the electronic process responsible for this bond shortening is as yet imperfectly understood, it cannot be applied directly to the polymer. However, for the purpose of this exploratory approach to the interpretation of the fibre-diagram, two models were considered; one in which the $CH_2—CH_2$ length was 1·45 A. and the $C—CH_2—CH_2$ angle 112° as in geranylamine, and a second with a normal C—C value of 1·54 A. and the tetrahedral angle.

Application to the Crystal Structure.—Accepting, as consistent with the best available experimental evidence, the cell dimensions, space group and general crystal structure proposed by Bunn,[2] the two models described above were adjusted in the unit cell to positions in which the atomic co-ordinates gave a satisfactory agreement between the calculated and observed intensities. The intensities were calculated from the formulæ for the space group $P_{2_1 2_1 2_1}$[4] with appropriate geometrical factors. The carbon atomic scattering factors used were those derived experimentally from the geranylamine structure, and although the two structures are from the point of view of thermal agitation not strictly comparable, these are considered adequate for the purpose of comparison with observations of a qualitative nature. The $\left(f_c, \frac{\sin\theta}{\lambda}\right)$ curve was similar in shape to the theoretical one compiled by James and Brindley[5] with a Debye-Waller temperature factor of $B \times 10^{16} = 2{\cdot}0$.

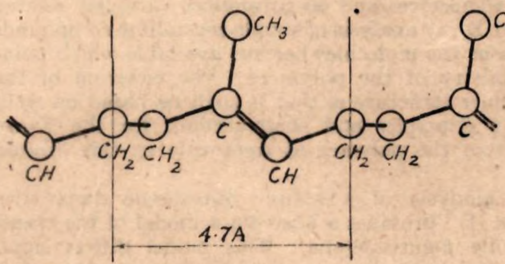

FIG. 1.

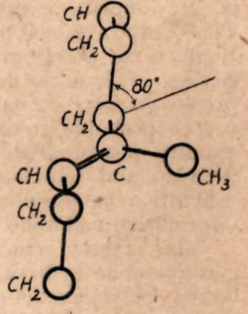

FIG. 2.

TABLE I.—ATOMIC CO-ORDINATES.

	x.	y.	z.	
C_1	0·076	0·109	0·453	CH_2
C_2	0·019	0·071	0·155	CH
C_3	0·978	0·145	0·953	C
C_4	0·921	0·107	0·654	CH_2
C_5	0·987	0·274	0·995	CH_3

bond lengths C—C 1·54 A., C═C 1·33 A.
bond angles C—C═C 122°, C—C—C 109°.

The atomic parameters for the normal model are given in Table I together with the interatomic dimensions. The intensity values calculated from these parameters are shown in Table II for comparison with the observed intensities recorded by Bunn. The corresponding figures for the model containing the shorter $CH_2—CH_2$ bond are very similar and the small differences in the calculated intensities would be of significance only when compared with accurate measurements.

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[4] Lonsdale, *Structure Factor Tables*, 1936.

[5] *International Tables for the Determination of Crystal Structures*, Vol. II, 571.

TABLE II.

*hk*0.	$I_{calc.}$	$I_{obs.}$	*hk*1.	$I_{calc.}$	$I_{obs.}$	*hk*2.	$I_{calc.}$	$I_{obs.}$
110	0	—	011	93	ms	112	1	w
020	1	vw	101	0	—	022	10	
120	538	vs+	111	11	vw	122	3	—
200	295	vs	021	1	—	032	1	w
210	2		121	10	—	202	8	
130	0	—	031	24	w	212	2	
220	3	vw	201	4		132	5	
040	39	m	211	69	ms	222	12	—
230	1	ms	131	10		042	0	—
140	59		221	1	—	232	3	—
310	0	—	041	3	—	142	1	—
320	17	m	231	11	vw			
240	11		141	2				
150	0	—	301	1	w			
330	0	—	311	9				
250	0	—	321	3	—			
060	7	w	051	0	—			
340	4	w	241	4	—			
400	6		151	0	—			
410	1	m	331	6	—			
160	19		251	0	—			
420	1	—	061	1	—			
260	4	vvw	341	0	—			
350	0		401	1	—			
430	1		411	14	w			
170	0	—	161	1	—			
440	0	—	421	1	—			
360	2	vvw						
270	0	—						

Conclusions.—Although the general position of the molecule in the unit cell is necessarily similar, the normal model differs stereochemically from that proposed by Bunn in two important respects; (i) the planar distribution of the C—C bonds about the double bond with no distortion of the methyl group out of the plane, (ii) the orientation of the CH_2—CH_2 bond at 80° as against 63° to the plane of the double bond. Despite these differences the agreement between the observed and calculated diffraction data is at least as good. This result shows that there is no justification for the premise that the X-ray data demand an unusually large distortion in the molecule of β-guttapercha,[3] and also supports the criticisms [6] advanced on more general considerations of Bunn's crystal structure of rubber.[2] Similarly, the bond angle distortions recorded for polychloroprene [2] and rubber hydrochloride [7] cannot be regarded as real in the absence of confirmatory evidence.

The structure for β-guttapercha discussed above although inherently more probable than that proposed by Bunn is not regarded as a final solution. Together with further evidence from indirect sources, it will provide a starting point for a precise X-ray investigation of these polymers when the technical difficulties of extending the diffraction data from fibre-diagrams and expressing them more quantitatively have been overcome.

Summary.

The X-ray diffraction data at present available from β-guttapercha are shown to be insufficient to distinguish fine details of molecular structure.

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[6] Jeffrey, *Trans. Faraday Soc.*, 1942, **38**, 382.

[7] Bunn, *J. Chem. Soc.*, 1942, **654.**

Since a qualitative estimate of the intensities on the fibre-diagram can be adequately satisfied by a model having normal interatomic distances and valency angles, no evidence exists for the improbable distortion of the methyl group out of the plane of the double bond previously ascribed to the molecule.

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