

668. *Molecular Polarisability. The Molar Kerr Constants, Dipole Moments, etc., of Isoprene, Polyisoprenes, and Some Related Hydrocarbons.*

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Comparisons of calculated and observed molar Kerr constants suggest (a) that 2-methylbut-2-ene and isoprene are planar and that in the latter case the *s-trans*-form predominates, (b) that ocimene as a solute is extended with its three C=C bonds nearly parallel to one another, and (c) that squalene and squalane may have helically coiled structures. Gutta-percha appears slightly more anisotropic than rubber.

THE measurements here reported were started in the hope that information on the conformations adopted by various polyisoprenes as solutes in benzene could be obtained from measurements of electric double refraction and dielectric polarisation for such solutions, if considered in conjunction with parallel observations on molecules chosen as models of the presumed repeating units presumed in the polymer chains. None of the compounds now taken has been hitherto examined by a method involving the Kerr effect. The relations of 2-methylbut-2-ene to rubber, and of squalene to the steroids, are points of obvious interest.

EXPERIMENTAL

Solutes.—Isoprene was obtained by dry distillation of natural rubber.¹ The crude condensate, after removal of dipentene by repeated fractionation, was refluxed over a sodium dispersion for 2 hr. under dry nitrogen, and finally twice distilled through a jacketed Dufton column (b. p. 34.1°, n_D^{20} 1.4216, d_4^{20} 0.6805). Ocimene (b. p. 81°/30 mm., d_4^{25} 0.7948, n_D^{25} 1.4835) was a gift from Mr. H. G. McKern, Deputy Director, Museum of Applied Arts and Sciences, Sydney. 2-Methylbut-2-ene was prepared by Norris and Reuter's method² from t-pentyl alcohol; after drying over anhydrous magnesium sulphate, it was fractionally distilled (b. p. 38.5°, d_4^{25} 0.65694, n_D^{25} 1.3846). 2-Methylbutane was a commercial sample fractionated from a sodium dispersion (b. p. 27.9—30.0°, d_4^{25} 0.61455, n_D^{25} 1.3507). Squalene (n_D^{25} 1.4941) and squalane (n_D^{25} 1.4509) were pure products from the Eastman Kodak Co. Specimens of natural rubber (*cis*-polyisoprene) and gutta-percha (*trans*-polyisoprene) were presented by Slazengers (Aust.) Pty. Ltd.; each was extracted with acetone (Soxhlet) for 24 hr. under dry nitrogen,

¹ Bassett and Williams, *J.*, 1932, 2324.

² Norris and Reuter, *J. Amer. Chem. Soc.*, 1927, 49, 2630.

TABLE I.

Incremental values of Δn , Δn^2 , Δd , $\Delta \epsilon$, and ΔB for solutions in benzene * at 25°.

$10^5 w_2$	$10^4 \Delta n$	$10^4 \Delta n^2$	$10^5 \Delta d$	$10^4 \Delta \epsilon$	$10^{10} \Delta B$	$10^5 w_2$	$10^4 \Delta n$	$10^4 \Delta n^2$	$10^5 \Delta d$	$10^4 \Delta \epsilon$	$10^{10} \Delta B$
<i>Solute: Isoprene</i>						<i>Solute: Ocimene</i>					
439	-4	-12	-101	-12	—	2639	-10	-30	-260	47	32
860	-8	-24	-198	-26	1.5	4213	-16	-48	-402	75	53
1532	-14	-41	-349	-44	2.8	6009	-23	-69	-587	106	74
1827	-17	-50	-420	-56	3.0	7381	-27	-81	-700	131	95
2312	-21	-62	-539	-64	4.1						
whence $\Sigma \Delta n / \Sigma w_2 = -0.092$; $\Sigma \Delta n^2 / \Sigma w_2 = -0.271$;						whence $\Sigma \Delta n / \Sigma w_2 = -0.038$; $\Sigma \Delta n^2 / \Sigma w_2 = -0.113$;					
$\Sigma \Delta d / \Sigma w_2 = -0.2306$; $\Sigma \Delta \epsilon / \Sigma w_2 = -0.290$;						$\Sigma \Delta d / \Sigma w_2 = -0.0963$; $\Sigma \Delta \epsilon / \Sigma w_2 = 0.177$;					
$\Sigma \Delta B / \Sigma w_2 = 0.175 \times 10^{-7}$.						$\Sigma \Delta B / \Sigma w_2 = 1.25 \times 10^{-7}$.					
<i>Solute: 2-Methylbut-2-ene</i>						<i>Solute: 2-Methylbutane</i>					
5499	-87	-261	-1584	-132	-8	5906	-110	-330	-2014	-350	-36
7548	-116	-347	-2169	-189	—	8963	-170	-508	-3138	-534	-50
8637	-135	-404	-2556	-225	-14	10,892	-204	-609	-3786	-667	-68
12,771	-199	-594	-3570	-294	-20	13,880	-262	-781	-4788	-797	-92
15,613	-242	-722	-4370	-390	—	16,016	-300	-893	-5484	-958	-106
19,159	-292	-869	-5310	-432	-27	18,594	-342	-1017	-6290	-1112	-132
whence $\Sigma \Delta n / \Sigma w_2 = -0.155$; $\Sigma \Delta n^2 / \Sigma w_2 = -0.462$;						whence $\Sigma \Delta n / \Sigma w_2 = -0.187$; $\Sigma \Delta n^2 / \Sigma w_2 = -0.557$;					
$\Sigma \Delta d / \Sigma w_2 = -0.2825$; $\Sigma \Delta \epsilon / \Sigma w_2 = -0.240$;						$\Sigma \Delta d / \Sigma w_2 = -0.3446$; $\Sigma \Delta \epsilon / \Sigma w_2 = -0.595$;					
$\Sigma \Delta B / \Sigma w_2 = -0.15 \times 10^{-7}$.						$\Sigma \Delta B / \Sigma w_2 = -0.652 \times 10^{-7}$.					
<i>Solute: Squalene</i>						<i>Solute: Squalene</i>					
3029	-6	-18	-116	33	3	5446	-40	-120	-601	-128	-12
5039	-12	-36	-190	53	5	7503	-55	-165	-791	-139	-17
6503	-14	-42	-231	74	6	9985	-70	-210	-1172	-159	-24
7764	-16	-48	-270	91	8	13,995	-108	-324	-1599	-183	-32
8698	-20	-60	-295	101	8	16,236	—	—	—	-272	-38
9745	-20	-60	-324	119	9	18,550	-140	-420	-2050	-346	-44
11,547	-22	-66	-380	138	10	22,011	—	—	—	-376	-50
12,474	-24	-72	-390	147	12						
whence $\Sigma \Delta n / \Sigma w_2 = -0.021$; $\Sigma \Delta n^2 / \Sigma w_2 = -0.063$;						whence $\Sigma \Delta n / \Sigma w_2 = -0.074$; $\Sigma \Delta n^2 / \Sigma w_2 = -0.223$;					
$\Delta d = -0.0408w_2 + 0.073w_2^2$; $\Sigma \Delta \epsilon / \Sigma w_2 = 0.116$;						$\Sigma \Delta d / \Sigma w_2 = -0.1120$; $\Sigma \Delta \epsilon / \Sigma w_2 = -0.171$;					
$\Sigma \Delta B / \Sigma w_2 = 0.094 \times 10^{-7}$.						$\Sigma \Delta B / \Sigma w_2 = -0.232 \times 10^{-7}$.					
<i>Solute: cis-Polyisoprene (rubber)</i>						<i>Solute: trans-Polyisoprene (gutta-percha)</i>					
888	2	6	—	—	-20	505	—	—	—	—	-12
1156	—	—	45	30	-27	865	2	6	25	25	-25
1464	3	9	—	—	—	1374	—	—	—	37	—
1499	—	—	60	39	—	1484	3	9	—	—	-35
1701	4	12	68	44	-39	1908	—	—	52	55	-52
1915	—	—	74	49	—	2394	5	15	67	67	-65
2269	—	—	86	59	-50	2963	6	18	86	83	—
2508	6	18	95	64	—	3243	8	24	91	90	—
2953	7	21	—	—	—						
whence $\Sigma \Delta n / \Sigma w_2 = 0.023$; $\Sigma \Delta n^2 / \Sigma w_2 = 0.069$;						whence $\Sigma \Delta n / \Sigma w_2 = 0.022$; $\Sigma \Delta n^2 / \Sigma w_2 = 0.066$;					
$\Sigma \Delta d / \Sigma w_2 = 0.039$; $\Sigma \Delta \epsilon / \Sigma w_2 = 0.258$;						$\Sigma \Delta d / \Sigma w_2 = 0.0282$; $\Sigma \Delta \epsilon / \Sigma w_2 = 0.280$;					
$\Sigma \Delta B / \Sigma w_2 = -2.26 \times 10^{-7}$.						$\Sigma \Delta B / \Sigma w_2 = -2.64 \times 10^{-7}$.					

Intrinsic viscosities in toluene at 25°.

<i>Rubber</i>					
$10^4 c$	11,253	14,136	17,040	20,433	23,437
$10^5 d_{12}$	86,248	86,256	86,263	86,274	86,281
$10^3 \eta_{sp}$	10,880	16,149	25,530	33,978	48,936
whence $[\eta_{sp}/c]_{c \rightarrow 0} = 4.571$.					
<i>Gutta-percha</i>					
$10^4 c$	9433	13,838	17,478	21,133	24,752
$10^5 d_{12}$	86,283	86,302	86,316	86,338	86,359
$10^3 \eta_{sp}$	1743	2850	3847	4930	6221
whence $[\eta_{sp}/c]_{c \rightarrow 0} = 1.549$.					

* When $w_2 = 0$, $n_0 = 1.4973$, $d_4^{25} = 0.87378$, $\epsilon^{25} = 2.2725$, and $B = 0.410 \times 10^{-7}$.

then dissolved in benzene, precipitated by methanol, and dried *in vacuo*. Their molecular weights were estimated viscosimetrically in toluene (d_4^{25} 0.86220) at 25° in a modified Ostwald-Fenske-type viscometer with an efflux time of 73.4 sec. for the solvent. Intrinsic viscosities $[\eta]$, obtained by plotting $\log [\eta_{sp}/c]$ against c (the concentration of the polymer in g. per 100 ml. of solution) and extrapolation to infinite dilution, then gave molecular weights, *via* the equation³ of Wagner and Flory, $[\eta] = 2.0 \times 10^{-4} M^{0.73}$, as follows:

	$[\eta]$	"Viscosity" M	Degree of polymn.
<i>cis</i> -Polyisoprene	4.571	935,800	13,742
<i>trans</i> - " "	1.459	212,500	3125

Observations and Results Therefrom.—These are listed in Tables 1 and 2. Table 1 shows, for solutions each containing a weight fraction w_2 of solute in benzene, the differences Δn , Δn^2 , Δd , $\Delta \epsilon$, and ΔB between the refractive indexes, the squares of the refractive indexes, the densities, the dielectric constants, and the Kerr effects, respectively, of the solutions and the solvent; all measurements have been made at 25°, the techniques adopted being those described in refs. 4 and 5. (Definitions of symbols and explanations of the calculations used here have also been recently summarised in this *Journal*.⁶) Polarizations, apparent dipole moments, molar Kerr constants, etc., deduced from Table 1 follow as Table 2.

TABLE 2.

Total polarizations and molar Kerr constants at infinite dilution, molecular refractions, and dipole moments calculated from Table 1.

Solute	M_2	$\alpha \epsilon_1$	β	$\gamma' n_1^2$	∞P_2 (c.c.)	R_D (c.c.)	μ (D) *	γ	δ	$10^{12} \infty (mK_2)$
Isoprene	68.1	-0.290	-0.2639	-0.271	25.6	25.3 †	(ca. 0?)	-0.061	0.427	9.75
Ocimene	136.2	0.177	-0.1102	-0.113	56.1	47.7	0.54	-0.025	3.06	42.4
2-Methyl- but-2-ene	70.1	-0.240	-0.3233	-0.462	28.45	24.9	0.34	-0.104	-0.366	6.28
2-Methyl- butane	72.15	-0.595	-0.3944	-0.557	26.2	26.04	0	-0.125	-1.59	1.21
Squalene	410.7	0.116	-0.0467	-0.063	155.5	139.1	0.68	-0.014	0.229	38.4
Squalane	422.8	-0.171	-0.1282	-0.223	149.0	141.8	0	-0.049	-0.566	22.3
<i>cis</i> -Polyiso- prene ...	935,800	0.258	0.0446	0.069	350,200	311,900	33.3	0.015	-5.51	-331,900
<i>trans</i> -Poly- isoprene	212,500	0.280	0.0323	0.066	81,290	71,580	17.2	0.015	-6.44	-90,290

* Calc. by assuming $D_P = 1.05R_D$. † From $n_D^{20} = 1.4216$ and $d_4^{25} = 0.6805$, $R_D = 25.41$ c.c. for the undiluted isoprene.

DISCUSSION

In the following sections the solutes are discussed individually. Where practicable the observed molar Kerr constants will be compared with those calculable from possible molecular models, by using the anisotropic bond polarisabilities listed on p. 3 of ref. 7 together with the resultant dipole moments and other data as now measured.

2-Methylbut-2-ene.—Experiment gives μ_{res} and $\infty (mK_2)$ for this substance as 0.34 D and 6.3×10^{-12} , respectively. Neither property has been previously reported. Computations (by the method described briefly in ref. 4*b*, or fully in ref. 8) for a flat structure (I) with trigonal CCC angles show that the maximum polarisability semi-axes b_1 should be inclined 28° 21' to the double bond in the plane of the molecule. Details are given in

³ Wagner and Flory, *J. Amer. Chem. Soc.*, 1952, **74**, 195.

⁴ Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (b) Chap. XXXVI, in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, London, 3rd edn., Vol. I, p. 2459.

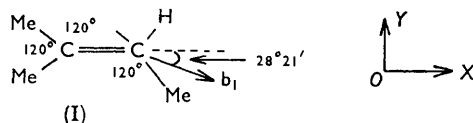
⁵ Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953, Chapter 2; Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

⁶ Le Fèvre and Sundaram, *J.*, 1962, 1494.

⁷ Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

⁸ Eckert and Le Fèvre, *J.*, 1962, 1081.

Table 3. The close approach of ${}_mK$ calc. to ${}_mK$ obs. suggests that the ellipsoid for C=C, although originally deduced from $\text{CH}_2=\text{CCl}_2$, is also satisfactory with non-halogenated



olefins; moreover, it appears that b_1 and the direction of action of μ_{res} are nearly parallel to one another.

TABLE 3.

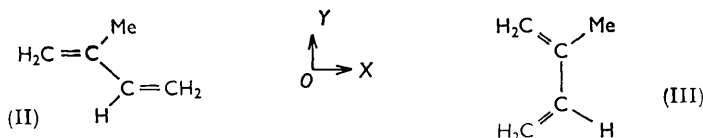
Semi-axes,* moment components, etc., for 2-methylbut-2-ene as (I).

	Direction cosines with †			
	OX	OY	OZ	
$b_1 = 1.098$	0.8800	-0.4749	0	$\mu_1 = 0.34 \text{ D}$
$b_2 = 0.911$	0.4749	0.8800	0	$\mu_2 = 0$
$b_3 = 0.799$	0	0	1	$\mu_3 = 0$

whence $10^{35}\theta_1 = 0.81$, $10^{35}\theta_2 = 0.74$, and $10^{12}{}_mK = 6.5$.

* Molecular and bond polarisabilities quoted throughout Tables and text as 10^{-23} c.c. units.
 † OX and OY are in the molecular plane with OX parallel to C=C; OZ is perpendicular to OX and OY.

Isoprene.—With hexane, heptane, or pentene as solvents,⁹ and from observations on the pure liquid,¹⁰ moments between 0 and 0.3 D have been reported for isoprene; in the vapour state, over the temperature range 358—477°K, Hannay and Smyth¹¹ found $\mu = 0.38 \text{ D}$. The present appear to be the first measurements for solutions in benzene. They indicate a polarity well below μ_{vapour} . when R_D is used as the distortion polarisation, $\mu = 0.12 \text{ D}$; if ${}_D P$ is taken as 1.05 R_D , then $\mu = 0$. Farmer and Warren,¹² from the polarisation-temperature relationship for liquid isoprene, deduced μ as 0.15 D; they noted that the total polarisation increased with rise of temperature. From Raman



spectra an equilibrium between an *s-cis*- (III) and an *s-trans*-form (II) has been inferred,¹³ with 10% and 15% of (II) in the mixture at -60° and $+50^\circ$, respectively.

Calculations of polarisabilities for these two planar models are in Table 4. The resultant moment observed is assumed to act in the XO direction in both cases, but because of the uncertainty of such near-zero values the ${}_mK$'s expected if μ_{isoprene} were 0 or 0.3 D are also given. The ${}_mK$ found is $9.7_5 \times 10^{-12}$ but the predicted ${}_mK$'s for forms (II) and (III) are too close to one another and too small to justify a firm choice of the more appropriate; it seems, however, that even if μ is 0.3 D the solute cannot contain less than about 50% of form (II). When μ is taken as 0.2 D, the ${}_mK$'s calc. and found are equal for the *s-trans*-form; with a still lower moment (e.g., 0.12 D, as in Table 4) the ${}_mK$

⁹ Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

¹⁰ Altschuller, *J. Phys. Chem.*, 1953, **57**, 538.

¹¹ Hannay and Smyth, *J. Amer. Chem. Soc.*, 1943, **65**, 1931.

¹² Farmer and Warren, *J.*, 1933, 1297.

¹³ Volkenstein, Nikitin, and Yakovleva, *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, 1950, **14**, 471; Nikitin and Yakovleva, *Zhur. fiz. Khim.*, 1954, **28**, 692.

found exceeds the ${}_mK$ calc. for both (II) and (III), and thus strongly suggests a 100% content of form (II).

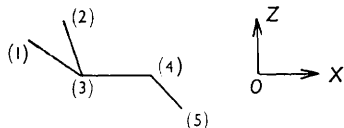
TABLE 4.

Semi-axes, molar Kerr constants, etc., for isoprene as (II) or (III).

		Direction cosines with			
		<i>OX</i>	<i>OY</i>	<i>OZ</i>	
Model II:	$b_1 = 1.162$	1	0	0	$\mu_1 = 0.12 \text{ D}^*$
	$b_2 = 0.820$	0	1	0	$\mu_2 = 0$
	$b_3 = 0.721$	0	0	1	$\mu_3 = 0$
whence $10^{35}\theta_1 = 1.91$, $10^{35}\theta_2 = 0.15$, and $10^{12}{}_mK = 8.6_6$.					
Model III:	$b_1 = 1.068$	0.9744	0.2250	0	$\mu_1 = 0.12 \text{ D}^*$
	$b_2 = 0.914$	-0.2250	0.9744	0	$\mu_2 = 0$
	$b_3 = 0.721$	0	0	1	$\mu_3 = 0$
whence $10^{35}\theta_1 = 1.08$, $10^{35}\theta_2 = 0.09_5$, and $10^{12}{}_mK = 4.9_4$.					

* If $\mu_1 = 0$, the ${}_mK$'s calc. become $8.0_3 \times 10^{-12}$ and 4.53×10^{-12} , respectively, or, with $\mu = 0.3 \text{ D}$, 11.9×10^{-12} and $7.0_2 \times 10^{-12}$.

2-Methylbutane.—This molecule may assume an infinite number of conformations between the four extremes (IV)—(VII). In (IV) the bisector of angle $C_{(1)}-C_{(3)}-C_{(2)}$ is *trans* to the $C_{(4)}-C_{(5)}$ bond and lies in the plane of $C_{(3)}-C_{(4)}$ and $C_{(4)}-C_{(5)}$; (V) is as (IV) but with the said bisector *cis* to $C_{(4)}-C_{(5)}$; in (IV) and (V) the imaginary line $C_{(1)} \cdots C_{(2)}$ is perpendicular to the plane containing the $C_{(3)}-C_{(4)}-C_{(5)}$ bonds. In (VI) or (VII) the link $C_{(2)}-C_{(3)}$ is *trans* or *cis*, respectively, to $C_{(4)}-C_{(5)}$ and coplanar with $C_{(3)}-C_{(4)}$ and $C_{(4)}-C_{(5)}$. Arbitrary axes are placed so that *OX* is parallel to $C_{(3)}-C_{(4)}$ and *OZ* at 90° to *OX* in the $C_{(3)}-C_{(4)}-C_{(5)}$ plane. The calculated polarisabilities and their locations are given in Table 5.



(IV; V-VII not shown)

TABLE 5.

Polarisability semi-axes, molar Kerr constants, etc., for four conformations of 2-methylbutane.

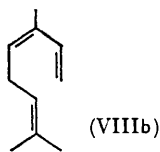
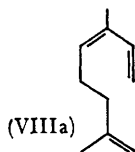
		Direction cosines with					Direction cosines with				
		<i>OX</i>	<i>OY</i>	<i>OZ</i>			<i>OX</i>	<i>OY</i>	<i>OZ</i>		
Model (IV)	Principal polarisabilities	$b_1 = 0.932$	0.7912	0	0.6115	Model (VI)	Principal polarisabilities	$b_1 = 0.966$	0.8192	0	0.5736
		$b_2 = 0.973$	0	1	0			$b_2 = 0.946$	0	1	0
		$b_3 = 1.012$	-0.6115	0	0.7912			$b_3 = 1.005$	-0.5736	0	0.8192
whence $10^{35}\theta_1 = 0.057$; $10^{12}{}_mK = 0.24$.						whence $10^{35}\theta_1 = 0.032$; $10^{12}{}_mK = 0.135$.					
Model (V)	Principal polarisabilities	$b_1 = 0.962$	1	0	0	Model (VII)	Principal polarisabilities	$b_1 = 0.996$	1	0	0
		$b_2 = 0.973$	0	1	0			$b_2 = 0.946$	0	1	0
		$b_3 = 0.982$	0	0	1			$b_3 = 0.975$	0	0	1
whence $10^{35}\theta_1 = 0.003$; $10^{12}{}_mK = 0.013$.						whence $10^{35}\theta_1 = 0.022$; $10^{12}{}_mK = 0.093$.					

All the ${}_mK$'s thus predicted are less than the small value (1.21×10^{-12}) measured; the nearest is that calculated for (IV), the conformation which seems most reasonable on steric grounds. Very low ${}_mK$'s of non-polar solutes are difficult to determine with precision and their origins are uncertain (*e.g.*, they may arise from θ_3 terms,^{14,15} as in the cases of

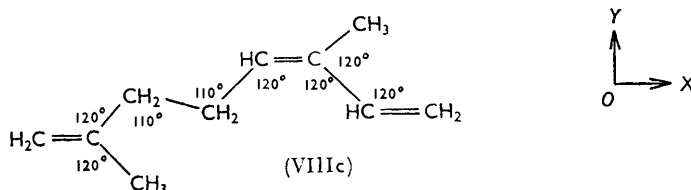
¹⁴ Le Fèvre, Le Fèvre, and Rao, *J.*, 1956, 708.

¹⁵ Le Fèvre and Le Fèvre, *J.*, 1959, 2670.

methane, carbon tetrachloride, and tetrabromide, etc., the apparent mK 's of which are 0.395×10^{-12} , $1.1_5 \times 10^{-12}$ and 7.3×10^{-12} ; they may also in part contain θ_2 terms due to moments now being found for molecules previously considered as non-polar—reports that isobutane¹⁶ has $\mu = 0.132$ D and that even propane¹⁷ has $\mu = 0.083$ D are relevant to the present work.



Ocimene.—The observed mK for this dimer of isoprene is 42.4×10^{-12} ; to achieve such a value by calculation from bond anisotropies the three C=C links must be nearly parallel to one another. Neither of the text-book formulæ (VIIIa) and (VIIIb) can therefore represent accurately the conformation of ocimene as a solute. Internal rotations to produce parallelism can be made in both, but extended planar forms,



likely to provide the highest predictable molar Kerr constants, are only derivable from (VIIIa). Accordingly, as an example of these, we consider model (VIIIc), in which OX and OY are placed so that OX is parallel to the double bonds and OY is perpendicular to OX in the molecular plane. Computations yield the following results:

$$b_1 = 2.186 \text{ (along } OX); \quad \mu_1 = 0.54 \text{ D}$$

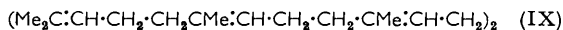
$$b_2 = 1.677 \text{ („ } OY); \quad \mu_2 = 0$$

$$b_3 = 1.417 \text{ („ } OZ); \quad \mu_3 = 0$$

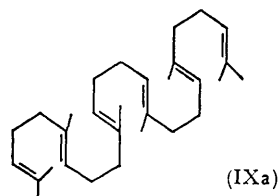
$$\text{whence } 10^{35}\theta_1 = 5.46, \quad 10^{35}\theta_2 = 4.89, \quad \text{and } 10^{12}mK = 43.5.$$

Since the greatest calculable mK is being sought, μ_{res} is applied along OX ; other directions of action or non-planar variants of (VIII) produce lower estimates of mK calc.

Squalene.—This acyclic dihydrotriterpene $C_{30}H_{50}$, having¹⁸ the structure (IX) in which two equal halves of the molecule are



united by isoprene units joined tail-to-tail, was considered to be the all-*trans*-stereoisomer by Nicolaidis and Laves.¹⁹ As a solute it cannot be fully extended since in any such arrangement the double bonds would produce a high anisotropy inconsistent with the $\infty(mK_2)$ actually observed. In fact, squalene has a molar Kerr constant (38.4×10^{-12}) resembling in order of magnitude those⁸ calculated and found (41×10^{-12} , 44×10^{-12}) for cholest-5-ene, a coincidence recalling the role of (IX) as a cholesterol precursor²⁰ in animal organisms, and Robinson's remark²¹ that (IX) can be coiled into a "steroid" arrangement, as in (IXa).



In relation to the last point we note that if squalene is assumed to adopt the stereostructure of cholest-5-ene and appropriate subtractions and additions of bond polarisability data are made in the calculations recorded in ref. 8 for cholest-5-ene (the process is simplified by regarding the polarisabilities of the bonds being interchanged or removed

¹⁶ Maryott and Birnbaum, *J. Chem. Phys.*, 1956, **24**, 1022.

¹⁷ Lide, *J. Chem. Phys.*, 1960, **33**, 1514.

¹⁸ Karrer and Helfenstein, *Helv. Chim. Acta*, 1931, **14**, 78.

¹⁹ Nicolaidis and Laves, *J. Amer. Chem. Soc.*, 1954, **76**, 2596.

²⁰ Heilbron, Kamm, and Owens, *J.*, 1926, 1630; Channon, *Biochem. J.*, 1926, **20**, 400; Bloch and Woodward, *J. Amer. Chem. Soc.*, 1953, **75**, 2023; Bloch and Langdon, *J. Biol. Chem.*, 1953, **200**, 135.

²¹ Robinson, *Chem. and Ind.*, 1934, **53**, 1062.

as equally distributed over b_1 , b_2 , and b_3), then, if μ_{res} acts in the b_1 direction, we have for squalene:

$$\begin{aligned} b_1 &= 5.493; & 10^{35}\theta_1 &= 3.18 \\ b_2 &= 5.307; & 10^{35}\theta_2 &= 4.68 \\ b_3 &= 4.908; & 10^{12}{}_mK \text{ calc.} &= 33.1 \end{aligned}$$

The ${}_mK$ so reached is fairly close to that from experiment (38.4×10^{-12}). However, the result may be fortuitous because squalene, being acyclic, would probably be less flat than a steroid—the tendency for C-H links on the C-C bonds 4-5, 8-9, 12-13, 16-17, and 20-21 to be staggered being a responsible factor. A model of form (IX) constructed by making symmetrical rotations in opposite directions about the five C-C bonds just mentioned yields a helix for which a polarisability ellipsoid of revolution appears adequate. Accordingly, from the experimental quantities in Table 2, we have $\theta_1 + \theta_2 = 9.132 \times 10^{-35}$, $b_1 + 2b_2 = 15.714 \times 10^{-23}$, and $b_1 - b_2 = \pm 0.504 \times 10^{-23}$; with the positive value of $b_1 - b_2$, an estimate of the molecular semi-axes emerges as $b_1 = 5.574$, and $b_2 = b_3 = 5.070$. If now the b_2 and b_3 semi-axes for 2-methylbut-2-ene (Table 3) are regarded as both equal to their mean (0.855), and a helix is built from six molecules of (I), each less the requisite number of C-H bonds, joined appropriately by five C-C links, a polarisability of 5.574 results when the greater axes of the eleven component ellipsoids are inclined at *ca.* 45° to the helical axis. From a model such an angle appears reasonable.

Squalene.—By arguments parallel to those used with squalene we have (a), when appropriate bond substitutions are made in cholest-5-ene:

$$\begin{aligned} b_1 &= 5.734; & 10^{35}\theta_1 &= 4.02 \\ b_2 &= 5.538; & \theta_2 &= 0 \\ b_3 &= 5.080; & 10^{12}{}_mK &= 17.0 \end{aligned}$$

or (b), if the polarisability ellipsoid is regarded as one of revolution and the observed ${}_mK$ and R_D are treated accordingly: $\theta_1 = 5.303 \times 10^{-35}$, $b_1 + 2b_2 = 16.018$, and $b_1 - b_2 = \pm 0.668$, whence (for the positive value of $b_1 - b_2$) $b_1 = 5.784$ and $b_2 = b_3 = 5.116$. The anisotropy of squalene must, since the molecule is saturated, be largely caused by the twenty-three carbon-carbon bonds in the main chain. A helical model is readily constructed in which the helix axis is roughly perpendicular to the six C-Me bonds and *ca.* 40° to each skeletal C-C bond; calculation for such a structure gives $b_1 = 5.8$ and $b_2 = b_3 = 5.1$, fitting the solution (b) above, and of interest in relation to Mumford's postulated helical arrangement²² of n-alkane chains for which angles of 36 – 37° were forecast.

Poly-cis- and Poly-trans-isoprene (Rubber and Gutta-percha).—Apparent dipole moments of rubber in benzene as listed by Wesson⁹ vary between *ca.* 14 and *ca.* 58 D and seem to be affected by milling and other pretreatment; the value 33 D now found for a specimen of $M 936 \times 10^3$ is comparable to the 27–33 D reported by Ostwald and Riedel²³ for milled crepe. Ref. 9 contains no entry for gutta-percha. Recalculated on a monomer molecular-weight basis, the moments of rubber and gutta-percha given in Table 2 become 0.28 and 0.31 D, respectively, *i.e.*, close to the μ observed for (I). The corresponding quotients $\mu^2_{\text{app}}/x\mu_0^2$ (where x is the degree of polymerisation and $\mu_0 = 0.34$ D) are 0.70 and 0.82, suggesting that the methylbutene units are differently hindered in the two macromolecules.

Rubber and gutta-percha are the first polyisoprenes for which negative molar Kerr constants have been noted. If their conformations as solutes are flexed versions of those,

²² Mumford, J., 1952, 4897.

²³ Ostwald and Riedel, *Kolloid-Z.*, 1932, 59, 150.

basically helical,²⁴ which occur in the solid state, we may assume for the dissolved species polarisability ellipsoids for which $b_1 \neq b_2 = b_3$; if also μ_{res} acts parallel to b_1 , the data in Table 2 yield differences ($b_1 - b_2$) of -2.714 and -2.764 for the two polymers, respectively; division by the degrees of polymerisation then shows gutta-percha to be slightly more anisotropic than rubber.

The present results are qualitatively as expected for polyisoprenes built from isomeric di-isoprene units, disposed as illustrated in Figs. 56, 57, and 61 of ref. 25, which are less extended and less planar in rubber (identity period 8.2 \AA) than in gutta-percha (identity period 8.7 \AA).

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²⁴ Natta and Corradini, *J. Polymer. Sci.*, 1959, **39**, 29; Bunn, *Proc. Roy. Soc.*, 1942, *A*, **180**, 40, 67, 82; "Chemical Crystallography," Clarendon Press, Oxford, 1946, pp. 317—329; Jeffrey, *Trans. Faraday Soc.*, 1944, **40**, 517; Robertson, *Ann. Reports*, 1942, **39**, 108; Fraga, *J. Polymer. Sci.*, 1959, **41**, 522; Fisher, *Proc. Phys. Soc.*, 1953, **66**, *B*, 7.

²⁵ Meyer, "Natural and Synthetic High Polymers," Interscience Publ., Inc., New York, Vol. IV, 1942, pp. 129—136.
