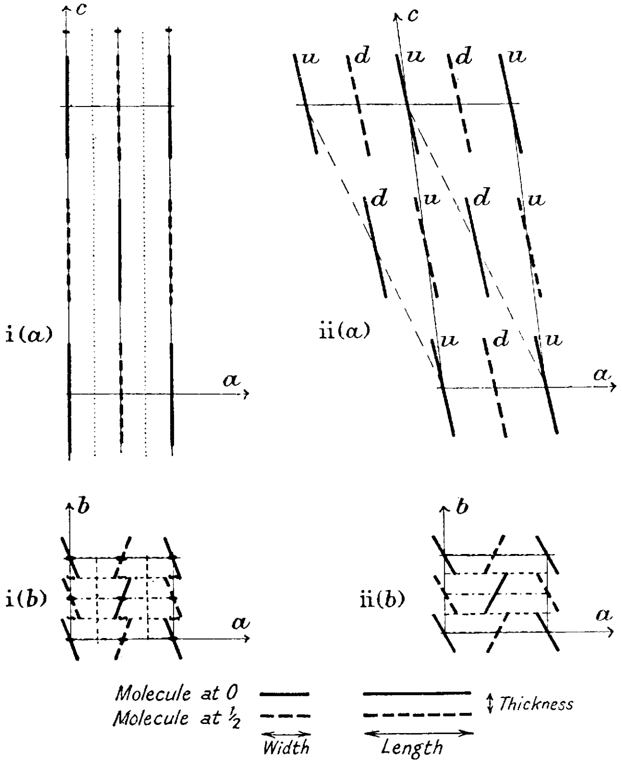
21. *The Structure of Some Hydrocarbons related to the Sterols.*

By J. D. BERNAL and (MISS) D. CROWFOOT.

THE structural formulæ of the sterols and related bile acids and œstrogenic hormones have largely been based on their dehydrogenation to polycyclic aromatic hydrocarbons (see *Ann. Reports*, 1933, **30**, 199). The formulæ are not definitely established in detail, beyond the fact that all contain a phenanthrene nucleus.

In order to elucidate doubtful points, a number of the hydrocarbons derived from sterols have been examined crystallographically by *X*-ray and optical methods, and compared with synthetic hydrocarbons of known structure. The general results are shown in the table. The crystals are all monoclinic or orthorhombic. Most are flat plates with perfect cleavage in the plane of the plate, sometimes diamond-shaped, sometimes elongated along one axis. As this axis proves to be the crystallographic *b* axis in the monoclinic varieties (in which the elongation is most common), it is also called the *b* axis in the orthorhombic forms. The flat face of the crystal is chosen as the *c* plane, and the *c* axis is accordingly at right angles to it in the orthorhombic varieties and slanting at an angle β to it in the monoclinic crystals. From the crystallographically possible β values shown by the *X*-ray measurements, that one is generally chosen which brings *c* most nearly along the γ optical direction (see table). In many cases the plates as crystallised from solution were too small and imperfect for *X*-ray examination (though for $C_{25}H_{24}$ a crystal weighing about 10^{-6} mg. was used), but suitable crystals could always be obtained by crystallisation from the melt by the hot-wire method (Bernal and Crowfoot, *Trans. Faraday Soc.*, 1933, **29**, 1032).

FIG. 1.



The arrangement of molecules in the hydrocarbon crystals.
i. *Orthorhombic type* (Aba) : (*a*) *Projection on* (010) ; (*b*) *projection on* (001).
ii. *Monoclinic type* (Aa) : (*a*) *Projection on* (010); (*b*) *projection on* (001) (*the lines - - - show the cell chosen by Iball in interpreting chrysene, orientation* 1c).

	Name.		Space group.	a.	b.	c.	β.	Probable molecular length, Å.	Optic orientation.
1	Phenanthrene	$C_{14}H_{10}$	*P*2₁/*a*	8·66	6·11	19·24	98°	9·62	Optic axial plane (010); *b* = β, γ nearly along *c*.
2.	1 : 2-Dimethylphenanthrene	$C_{16}H_{14}$	*Aba*	8·28	6·35	21·8	90	10·9	*a* = α, *b* = β, *c* = γ.
3.	1 : 2 : 7-Trimethylphenanthrene	$C_{17}H_{16}$	*Aba*	7·9	6·4	24·4	90	12·2	,, ,, ,,
4.	Retene	$C_{18}H_{18}$	*Aba*	8·54	6·25	23·4	90	11·7	,, ,, ,,
5.	1 : 2-*cyclo*Pentenophenanthrene (stable)	$C_{17}H_{14}$	*B*2₁/*a*	18·2	6·05	21·2	119	11·6	Optic axial plane (010); *b* = β, γ about 6° from *c*.
6.	1 : 2-*cyclo*Pentenophenanthrene (metastable)	$C_{17}H_{14}$	*Aba*	8·10	6·4	22·8	90	11·4	*a* = α, *b* = β, *c* = γ.
7.	Diels's $C_{18}H_{16}$ and γ-methyl-1 : 2-*cyclo*pentenophenanthrene	$C_{18}H_{16}$	*Aba*	8·50	6·25	24·3	90	12·1	,, ,, ,,
8.	Jacobs's $C_{16}H_{14}$	$C_{16}H_{14}$	*Aba*	8·2	6·35	23·7	90	11·8	,, ,, ,,
9.	" Chrysene perhydrur"	?	*Aba*	8·25	6·4	23·4	90	11·7	,, ,, ,,
10.	Chrysene	$C_{18}H_{12}$	*I*2/*c*	8·34	6·18	25·0	115·8	11·4	Optic axial plane (010); *b* = β, γ 10° from *c* in obtuse angle.
11.	2′ : 1′-Naphtha-1 : 2-fluorene	$C_{21}H_{14}$	*Aba*	7·9	6·28	26·8	90	13·4	*a* = α, *b* = β, *c* = γ.
12.	Ruzicka's $C_{21}H_{16}$ from cholic acid	$C_{22}H_{18}$	*Aba*	8·70	6·41	27·2	90	13·6	,, ,, ,,
13.	Methylcholanthrene	$C_{21}H_{16}$	*P*2₁/*c*	4·9	11·3	27·4	116	13·7	Optic axial plane (010); *b* = β, γ 27° from perpendicular to (001).
14.	1 : 2 : 5 : 6-Dibenzanthracene	$C_{22}H_{14}$	*P*2₁	7·84b	6·59a	14·17	103·5	13·75	*b* = α, γ perpendicular to (001).
15.	Picene	$C_{22}H_{14}$	*Aba*	8·21	6·16	28·8	90	14·4	*a* = α, *b* = β, *c* = γ.
16.	Ruzicka's $C_{25}H_{20}$ from gypsogenin	$C_{25}H_{20}$	*P*2₁	8·46	6·48	16·0	114	15·2	*b* = β, γ about 12° from perpendicular to (001).
17.	5-Methyl-8-*iso*propyl-2′ : 1′-naphtha-1 : 2-fluorene	$C_{25}H_{22}$	*P*2₁/*c*	13·15	8·69	30·8	96	15·9	*b* = β, γ 16° from perpendicular to (001).
18.	Diels's $C_{25}H_{24}$ from cholesterol	$C_{25}H_{22}$	*P*2₁/*a*	22·02	6·16	13·45	96	17·2	*b* = β, γ 39° from perpendicular to (001).
19.	Ruzicka's $C_{26}H_{26}$ from ergosterol (stable)	$C_{26}H_{24}$	*P*2₁/*a*	24·10	6·15	13·45	103	19·0	*b* = β, γ 46° from perpendicular to (001).
20.	Ruzicka's $C_{26}H_{26}$ from ergosterol (metastable)	$C_{26}H_{24}$	*Pcn*	15·8	6·43	39·2	90	19·6	*a* = α, *b* = β, *c* = γ.
21.	Ruzicka's $C_{27}H_{28}$ from phytosterols	$C_{27}H_{26}$	*Pcn*	13·4	7·7	39·2	90	19·6	,, ,, ,,
22.	Cholesterylene	$C_{28}H_{46}$	*P*2₁2₁2₁	15·85	7·66	19·25	90	20·5	,, ,, ,,
23.	Cholestane	$C_{28}H_{48}$	*P*2₁	11·2	11·0	20·5	110	20·5	*b* = β, γ 6° from perpendicular to (001).

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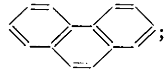
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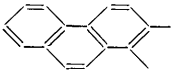
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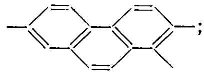
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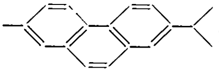
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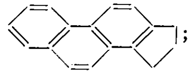
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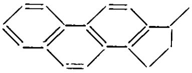
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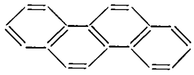
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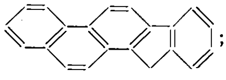
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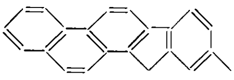
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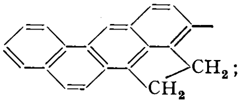

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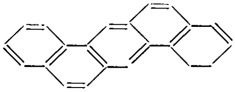
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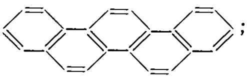
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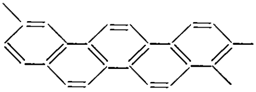
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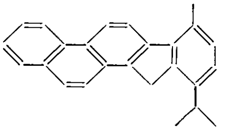
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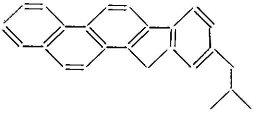
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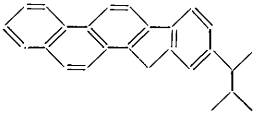
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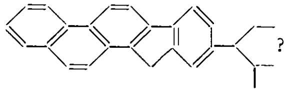
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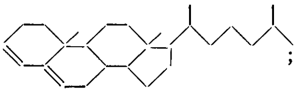
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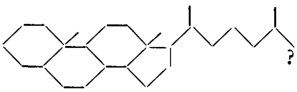
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It is at once apparent that all the hydrocarbons examined, except methylcholanthrene (13) and the methyl*iso*propylnaphthafluorene (17), have in common the two cell dimensions $a \sin \beta$ and b, and differ in c according to the number of carbon atoms they contain. The optical properties indicate that the most highly refractive direction of the molecule lies along or nearly along c (γ), the next most refractive along b (β), and the least is perpendicular to (100) (α). This points to common lath-shaped molecules of width approximately 6 Å. and thickness 4 Å. packed together in parallel bundles with their lengths (γ) along the c axis, widths (β) along the b, and thicknesses (α) in the a planes as shown in Fig. 1. Phenanthrene, chrysene, and picene belong to the series, and we may take it to represent the mode of packing of the $\alpha\beta$ polycyclic, condensed-ring hydrocarbons. The length of the molecule determines the c axis, and in the higher compounds is approximately $2{\cdot}1n + 4{\cdot}4$, where n is the number of condensed rings. The substitution of 5- for 6-carbon rings will not alter substantially the dimensions of such molecules.

Crystallographically, therefore, the table shows that the hydrocarbons appear in two characteristic forms, a monoclinic with the planes of the rings inclined to the basal c plane, and an orthorhombic where they are approximately parallel to it. These forms are not essentially different, as is shown by the fact that 1 : 2-*cyclo*pentenophenanthrene and Ruzicka's $C_{26}H_{26}$ crystallise in both forms, the orthorhombic being metastable.

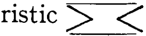
The general arrangement of the molecules in the orthorhombic and the monoclinic form is shown in Fig. 1. Slight variations in the $a \sin \beta$ and b values are due either to inclination of the molecular planes to the (100) plane or to the presence of methyl or other aliphatic groups.

Tetracyclic Hydrocarbons : Diels's Hydrocarbon $C_{18}H_{16}$.—The significant hydrocarbons fall into two groups, tetracyclic and pentacyclic. The former contains *cyclo*pentenophenanthrene, $C_{17}H_{14}$, γ-methyl*cyclo*pentenophenanthrene, and the Diels hydrocarbon, $C_{18}H_{16}$. The problem of determining whether the last two are identical is very difficult, and has not yet been definitely solved.

It was relatively easy to show that the Diels hydrocarbon was not identical with *cyclo*pentenophenanthrene even in its orthorhombic form, for the spacing difference was about 1 Å. or 4% (*Chem. and Ind.*, 1933, **52**, 729). Between Diels's hydrocarbon (D) (Diels, Gädke, and Körding, *Annalen*, 1927, **459**, 1) and the two synthetic γ-*cyclo*pentenophenanthrenes prepared by different methods by Bergmann and Hilleman (B) (*Ber.*, 1933, **66**, 1302) and by Harper, Kon, and Ruzicka (K) (J., 1934, 124) no such difference could be detected. All had the same lattice dimensions within the experimental error (0·5% for a and b, 0·2% for c), the same relative intensities of X-ray reflexions, and the same optic axial angle, 88° ± 2°. This would normally be sufficient to establish their identity, but there were differences in chemical behaviour and in the m. p.'s of addition compounds which suggested that different compounds were involved. Consequently, a more exhaustive morphological, optical, and thermal examination was undertaken. The appearances of the hydrocarbons when crystallised under identical conditions from different solvents were definitely different : D crystallised in diamond-shaped plates, B sometimes in needles but more often in characteristic " christmas-tree " forms, K like D but with more tendency to form imperfect crystals and arborescent growths. These differences may, of course, be significant, but on the other hand they strongly suggest the presence of different impurities in all three samples.

The three sets of trinitrobenzene, trinitrotoluene, and picric acid derivatives were next examined. These were prepared for us by Dr. Kon from his own synthetic hydrocarbon, Bergmann's hydrocarbon, and from a specimen of very specially purified Diels hydrocarbon sent to us by Prof. Diels.

The trinitrobenzene compounds exist in two forms. One from solution is monoclinic, needle-shaped, elongated along (c), with (010) well developed and an extinction corresponding to the slow vibration 81° from c in the obtuse angle. No difference could be observed between the trinitrobenzene compounds of D, B, and K. From the melt, a metastable plate-like form crystallised, also monoclinic with (010) well developed but with the slow extinction direction making an angle 75° from c in the obtuse angle. Again no difference could be observed. The metastable form melts some degrees below the stable, and is converted into it very slowly at temperatures near the m. p. (see below).

The trinitrotoluene compounds are triclinic and offer, therefore, far more basis for comparison. Crystallised from alcohol, they show distinct differences in habit; B appears in characteristic  forms, D in lanceolate needles, often in stellate aggregates, and K is intermediate. Optical examination with the Federow instrument shows, however, that all have the same crystal form and the same direction of their optic axes.

Of all the compounds, the picrates are the most interesting because here the m. p. differences were best defined. The stable form, crystallised from alcohol, was apparently identical in all three preparations, triclinic needles twinned along their length, with the extinction angle corresponding to the optic axial plane making an angle of 8½° to the needle axis. The habits were, however, markedly different, the B picrate growing in separate, well-formed needles, and D and K in leafy aggregates. On melting, differences were even more marked. Both D and K picrates melted at 121—122°, whereas the recrystallised B picrate melted sharply at 128° (as against 120—122° and 130—131° observed by Kon *et al.*). On cooling, all three crystallised in a metastable leafy form, melting sharply in all cases at 117°, apparently monoclinic flattened on (010). The transformation of the metastable into the stable form takes place most readily at about 70°; at room temperatures it is extremely slow. At higher temperatures, however, characteristic differences appear, as observed by the hot-wire method. Whereas the stable form of the B picrate slowly takes the place of the metastable and grows in well-defined needles in the liquid right up to its m. p., those of the D and K picrates can never be made to replace the metastable form just below its m. p. or to grow in the liquid, for decomposition sets in before the change is complete. This suggests very strongly that the last two are not pure compounds.

All the evidence suggests that both Kon's and Bergmann's synthetic preparations and the Diels hydrocarbon are substantially identical, being probably γ-methyl*cyclo*pentenophenanthrene, $C_{18}H_{16}$. It would seem extremely unlikely that different hydrocarbons should be indistinguishable optically and in all three unit cell dimensions, but should also each form three indistinguishable sets of addition compounds in all containing five forms. The observed differences seem to be only those of habit and m. p., and everything points to the presence of impurities, possibly in very small quantities.

Bergmann's hydrocarbon behaves more nearly as a pure compound than either of the other two. The greater resemblance between Kon's and Diels's hydrocarbons than between either of these two and Bergmann's may therefore be due to a greater proportion of impurities in these two preparations.* Differences between the impurities in the two preparations may explain why Diels (private communication) has been unable to prepare from Kon's synthetic hydrocarbon the nitroso-derivative of which he obtained a very small yield from the natural $C_{18}H_{16}$.†

The crystal structure of the $C_{18}H_{16}$ hydrocarbons offers some points of interest. The cell is apparently orthorhombic, 8 × 6 × 24 Å., and the measured density of $1{\cdot}185 \pm 0{\cdot}005$ indicates 4 molecules of weight 232 ± 3 (Calc. for $C_{18}H_{16}$: M, 232). The absent spectra indicate an A face-centred cell, with the probable space-group Aba (or $Abam$ if the slight pyroelectricity found is not a genuine effect). In this space-group, each molecule must possess an axis of symmetry. As no suggested chemical formula for $C_{18}H_{16}$ can give an axis of symmetry, we are consequently forced either (a) to lower the space-group to monoclinic Aa (or $A2/a$), $\beta = 90°$, without any evidence of difference of intensities between $(h\,k\,l)$ and $(h\,k\,\bar{l})$, (b) to assume a statistical distribution of molecules, or (c) to imagine the crystal built of monoclinic units repeatedly twinned on (001) so as to make the c axis a pseudo-dead axis (Fig. 2). The last alternative seems the most probable, but further work on larger and better-formed crystals will be necessary to confirm it. The tendency to

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* (Note added in proof.) The question of the purity of Diels's hydrocarbon has been recently discussed by H. W. Thompson (*Chem. and Ind.*, 1934, **53**, 1027) and J. W. Cook (*ibid.*, p. 1047).

† (Note added in proof.) H. Hilleman has since prepared this nitroso-derivative from his own and Bergmann's preparation (*Ber.*, 1935, **68**, 102), so doubt on this score at least as to the substantial identity of the compounds is removed.

statistical symmetry, which is present in any case, probably explains the frequent occurrence of this type among the condensed-ring hydrocarbons (see Table, Nos. 2, 3, 4, 6, 7, 8, 9, 11, 12, 15) and also the extreme ease with which they form solid solutions with each other, with the consequent difficulty in purification by ordinary methods.

FIG. 2.

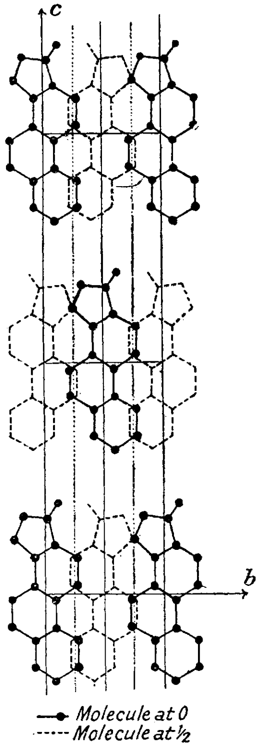


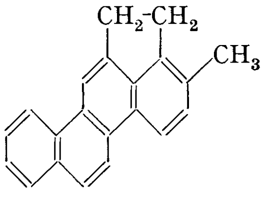
*Diagram to illustrate the crystal structure of γ-methyl*cyclo*pentenophenanthrene projected on* (100). *The unit shown belongs to the space-group* Aa. *To obtain a structure simulating* Aba, *such units may be imagined to be combined in groups by twinning, or individual molecules may, while still occupying the same general positions, be turned statistically to the right and left throughout the structure instead of regularly as in the figure.*

The physical structure of the crystals, however, is clear enough; the analogies to chrysene and to the hydrocarbon $C_{25}H_{20}$ (probably a trimethylpicene) prepared from gypsogenin (Ruzicka, Hösli, and Ehmann, *Helv. Chim. Acta*, 1934, **17**, 442), as well as the optical properties and the strength of the (200) plane, all point to the typical arrangement shown in Fig. 2, the length of the molecule being nearly exactly along *c*, the width not so near to *b*, and the thickness to *a*.

To the C_{18} type belong a number of other hydrocarbons examined, notably 1 : 2-dimethyl- and 1 : 2 : 7-trimethyl-phenanthrene (2 and 3), retene (4) which is extremely similar to Diels's $C_{18}H_{16}$ (7), and Jacobs and Fleck's $C_{16}H_{14}$ (8) (*J. Biol. Chem.*, 1932, **97**, 57). The intermediate *c* spacing of the last, *viz.*, 23·4 Å., might well result from its being a mixed crystal of a compound similar to (2) and (7), which would agree well with Jacobs's later conclusions that this is not a pure compound but a mixture of Diels's $C_{18}H_{16}$ and a dimethylphenanthrene. The obscure compound " chrysene perhydrur " (9) (von Braun and Irmisch, *Ber.*, 1932, **65**, 883) is practically indistinguishable from this and may also be a mixture; further work on this compound would probably throw light on the nature of Diels's hydrocarbon.

Finally, the complete solution of the structure of chrysene (Iball, *Proc. Roy. Soc.*, 1934, **146**, 153) is a satisfactory check on the correctness of the rougher methods used by us in arriving at the structure of the other hydrocarbons.

Pentacyclic Hydrocarbons.—The first point of interest here is the nature of the hydrocarbon $C_{21}H_{16}$ (12) obtained from cholic acid by Ruzicka, Thomann, Brandenburger, Furter, and Goldberg (*Helv. Chim. Acta*, 1933, **17**, 200). It can be seen that it fits into the typical orthorhombic series, lying between naphthafluorene (11) and picene (15). The formula suggested for it by Ruzicka (private communication) is (I), but this seems improbable in view of the totally different structure of methylcholanthrene (13) (II) (Wieland and Dane, *Z. physiol. Chem.*, 1933, **219**, 240; Cook and Haslewood, J., 1934, 428). The crystal structure of this compound as indicated by the table is markedly different from that of all the other hydrocarbons examined, as might be expected from its



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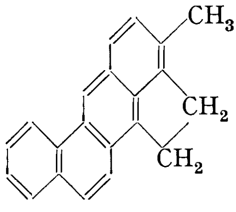

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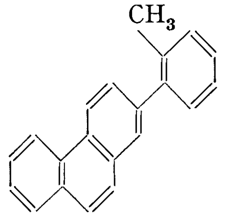
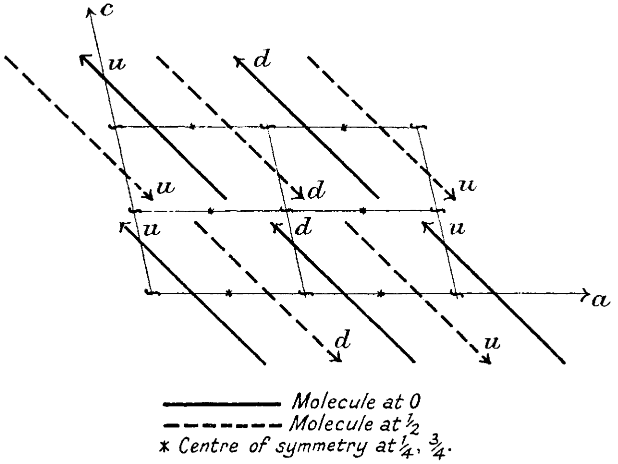


(III.)

possessing three rings sharing one carbon atom. It crystallises in needles, and resembles in most ways the flat molecule rather than the long-chain hydrocarbons. It seems probable that $C_{21}H_{16}$, on the other hand, is one of the latter type, but it is difficult to suggest a formula for it different from that of naphthafluorene. It may possibly be a methylnaphthadiphenyl, $C_{21}H_{16}$ (III), but the density, 1·244 ± 0·002, suggests that the molecular weight is higher than that required by the formula $C_{21}H_{16}$ and closely in agreement with the formula $C_{22}H_{18}$. Although this needs confirmation by more accurate *X*-ray work, the possibility remains that the compound may be a methylnaphthafluorene.

Far more important, however, for the study of the mechanism of dehydrogenation of the sterols are the hydrocarbons, $C_{25}H_{24}$, first obtained from cholesterol by Diels (*loc. cit.*), and $C_{26}H_{26}$ and $C_{27}H_{28}$, prepared by Ruzicka *et al.* from ergosterol and from a mixture of phytosterols respectively (*Helv. Chim. Acta*, 1933, **17**, 200). As the formulæ of these three compounds have given rise to much dispute, it seemed important to make a complete study. [$C_{25}H_{24}$ had been examined in 1932, but as only extremely small crystals (*ca.* 10^{-6} mg.) were available it was impossible to be certain of the results, though they have since been confirmed.]

FIG. 3.



Molecular arrangement in the monoclinic form of $C_{26}H_{26}$.

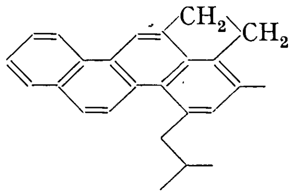
$C_{25}H_{24}$ and $C_{26}H_{26}$ crystallise from solution in similar but distinct forms. Both are lath-shaped, monoclinic crystals elongated along *b*, but the faces are much better developed in the second compound. The cell dimensions (see table), together with the observed densities, *viz.*, 1·195 ± 0·003 and 1·158 ± 0·003, lead to cells containing 4 molecules of molecular weights 327 ± 7 and 341 ± 5, respectively (Calc.: 324, 338, respectively). Thus there can no longer be any doubt that the numbers of carbon atoms in the molecules are correctly assigned. The positions of the molecules in the cell are fixed by the direction of the highest vibration direction γ; they make angles 39° and 46° respectively to the normal to the *c* plane. From these and the cell dimensions, the lengths of the molecules can be determined as 17·2 and 19·0 Å., respectively (see Fig. 3). From the melt, $C_{25}H_{24}$ recrystallises in the same form, but $C_{26}H_{26}$ on rapid cooling shows a metastable, plate-like, orthorhombic variety (20), with the molecules parallel to the *c* axis and a crystal structure rather more complicated than, but essentially similar to, that of $C_{18}H_{16}$. The value of the axial length *c*, 39·2 Å. (2 × 19·6), confirms the values found from the monoclinic variety.

$C_{27}H_{28}$ crystallises directly from solution in small diamond-shaped plates which are orthorhombic or pseudo-orthorhombic and show exactly the same type of arrangement as that found in the metastable orthorhombic variety of $C_{26}H_{26}$. The length of *c*, which defines the length of the molecules, is 2 × 19·6 Å., very little different from that found for $C_{26}H_{26}$, but there are marked differences in the *a* and *b* dimensions and in the intensities of the various planes. The crystal structures of the two hydrocarbons $C_{26}H_{26}$

and $C_{27}H_{28}$ evidently differ mainly in the arrangement of the molecules at right angles to the *c* axis.

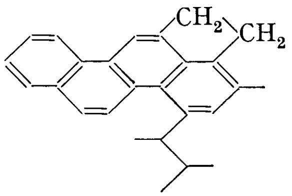
The molecular lengths deduced above dispose at once of certain formulæ for these compounds, *e.g.*, (IV*a*) and (IV*b*), proposed by Ruzicka * (cf. $C_{21}H_{16}$), or (V*a*) and (V*b*), proposed by Cook (private communication) even if in the latter a methyl group is dropped in both cases to agree with the new confirmations of the molecular weights. The first pair of formulæ is excluded as being much too short and broad (cf. methylcholanthrene, above); the latter pair is better as regards breadth, but definitely too short, as shown by the measurements, 15·9 Å., of Cook's synthetic 5-methyl-8-*iso*propyl-2′ : 1′-naphtha-1 : 2-fluorene (17), and 2 × 16·0 Å. of the (probable) trimethylpicene prepared from gypsogenin by Ruzicka (16). In the former case, the effect of the laterally inserted *iso*propyl group is shown by the anomalous crystal structure, and by the fact that the melt can be supercooled to room temperature.

(IV*a*.)



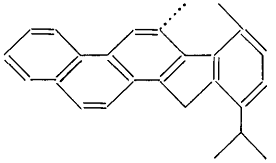
$C_{25}H_{24}$ (calc. length, *ca.* 13·5 Å.).

(IV*b*.)



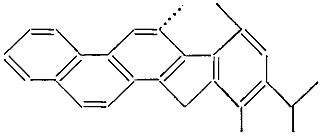
$C_{26}H_{26}$ (calc. length, *ca.* 13·5 Å.).

(V*a*.)



$C_{26}H_{24}$ (calc. length, 16·1 Å.).

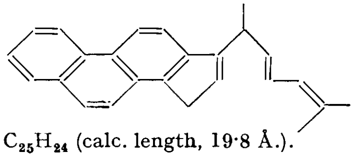
(V*b*.)



$C_{27}H_{26}$ (calc. length, 17·5 Å.).

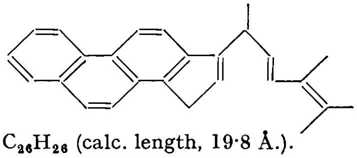
Some tentative ideas as to the probable formulæ can be put forward on the basis of the crystallographic evidence. As seen by the comparison with cholestane (21), the cell length is not more than 1 or 2 Å. shorter than in the sterols themselves; consequently, the chain must be preserved fairly intact. The simplest formulation is based on dehydrogenation of the chain without new ring formation (VI). Such structures may not be acceptable on chemical grounds; moreover, they give rather too long molecules. Breaking of ring D (VII) gives a possibility of forming a six-membered ring with or without the formation of a new five-membered ring, (IX), (X), or (VIII); (IX) and (X), which are indistinguishable by preliminary *X*-ray examination, seem the most probable, as some such formulæ would explain both the spectral evidence and the formation of a monoketone, which (VI) and (VIII) would not. (IX) can most easily be imagined to be formed from the original sterol skeleton. In any case, the existence at the ends of these molecules of three different side chains such as the *iso*butyl, αβ-dimethylpropyl, and β-methyl-α-ethylpropyl groups in the formulæ (VI)—(X) is strongly suggested by the *X*-ray evidence. This shows that the main change in passing from the cholesterol to the ergosterol series is one of inclination of the molecules, whereas in passing from the ergosterol to the phytosterol series it is a variation in the mutual arrangement of the molecular widths and thicknesses. A change of the first kind

(VI*a*.)



$C_{25}H_{24}$ (calc. length, 19·8 Å.).

(VI*b*.)



$C_{26}H_{26}$ (calc. length, 19·8 Å.).

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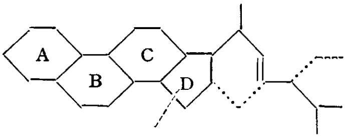
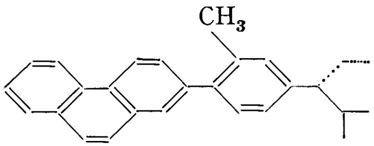
* The formulæ originally proposed by Ruzicka *et al.* (*Helv. Chim. Acta*, 1933, **16**, 822) are also excluded, but as these have since been withdrawn (*ibid.*, 1934, **17**, 214), they are not discussed here.

generally indicates a change in a group near one end of the molecule, whilst that of the second kind is easily understandable where the alteration in the end group is such as markedly to

(VII.)

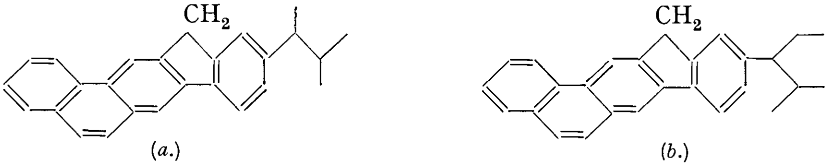




(VIII.)

$C_{25}H_{24}$, $C_{26}H_{26}$, $C_{27}H_{28}$ (calc. length, 18·8 Å.).

(IX.)



(a.) (b.)

(a) $C_{25}H_{22}$, $C_{26}H_{24}$; (b) $C_{27}H_{26}$ (calc. length, 19·0 Å.).

(X.)

(a.) (b.)

(a) $C_{25}H_{22}$ (calc. length, 18·4 Å.); (b) $C_{26}H_{24}$, $C_{27}H_{26}$ (calc. length, 19·0 Å.).

increase one of these molecular dimensions, as in the proposed phytosterol formula [cf. (IX*b*), Fernholz, *Annalen*, 1933, **507**, 128]. The correct formula can only be established if the study is extended to the derivatives of these hydrocarbons.

Although this study of hydrocarbons is by no means complete, the essential similarities of the crystal structures and the comparative methods of arriving at molecular dimensions already justify the value of such *extensive* crystallographic surveys. The more substances studied in this way, the more diverse and certain will be the deductions drawn from the crystallographic data.

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