SOME OBSERVATIONS ON THE OPTICAL PROPERTIES OF LONG CHAIN NORMAL PARAFFINS

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ABSTRACT

This paper presents the results of optical studies of the crystals of long chain normal paraffins. The studies were restricted to crystals grown from solvent solution at ordinary temperatures; polymorphic crystal forms obtained under other conditions are not considered.

It is shown that all long chain n-paraffin crystals, including very pure synthetic compounds and those occurring in nature, are optically active and invariably dextrorotatory. It is further shown that the crystals are normally orthorhombic, approaching hexagonal symmetry. No monoclinic crystals have been found.

The cause of the optical activity is discussed. The writer holds that the zig-zag type of molecular chain, currently believed to exist in the long chain n-paraffins, cannot cause the observed optical activity. A spiral molecular chain for these compounds is proposed as a working theory. Such a spiral chain is believed to account for the observed optical rotation.

INTRODUCTORY STATEMENT

The present paper deals with the crystal structure of normal paraffins within the wax range: that is, the homologous series of n-paraffins above $C_{15}H_{32}$, which are waxy solids at ordinary temperatures. The observations here summarized, and which are the basis of the paper, were made on n-paraffin crystals ranging from C_{21} to C_{32}, inclusive. These were crystallized on glass microslides from a solvent solution at ordinary temperatures, between 20°C. and 25°C. The crystals studied ranged from very pure individual n-paraffins to mixtures of two or three n-paraffins differing by one or a few carbon atoms. All materials studied were "pure" to the extent that non-paraffin impurities were absent, or present in such small quantities as not to affect materially the crystallization.

All optical observations were made with a petrographic microscope, and except where stated otherwise, were made at ordinary air temperatures. The light source was a 10 watt lamp with Corning "Daylight" filter. Observations and measurements of crystals using controlled higher-than-ordinary temperatures were made with a Leitz-Weygand heating stage, the temperatures being estimated to the nearest 0.1°C. with a probable error in most observations of ± 0.2°C. Crystal interfacial angles were determined by averaging at least five readings, the probable

error of a single reading being about $\pm 0.12°$, and of the mean, about $\pm 0.05°$.

The primary objective of this paper is to present the results of the writer's microscopic observations of n-paraffin crystals and his interpretation of the molecular and crystalline structures of the long chain normal paraffin series, based on these observations. These studies have been carried out intermittently over a period of four years, and have involved the preparation and examination of more than two thousand microslides of paraffin waxes from ninety five different sources. It is the writer's belief that the results of these studies are worth recording, if only to attempt to clear up some of the apparently contradictory observations to be found in an extensive literature on the subject. Furthermore, certain optical properties of n-paraffins described in the present paper are difficult if not impossible to explain if the molecule of the long chain n-paraffin has the generally accepted zig-zag form, as interpreted from x-ray studies.

To prevent possible misunderstanding, it is emphasized that the n-paraffin crystals described in this paper are exclusively those grown on a glass microslide from a solvent solution (carbon tetrachloride, benzene, toluene, or xylene) at ordinary temperatures well below the melting points. The same compounds, crystallized under different conditions, show quite different crystalline forms. This fact is largely responsible for the confusion one finds in reviewing the many published descriptions of paraffin crystals. The present paper does not attempt to cover the subject of polymorphism in n-paraffin crystals, or the causes thereof.

EXTERNAL CRYSTAL FORM OF NORMAL PARAFFIN

The form and optical orientation of the typical n-paraffin crystal are shown in Fig. 1. The crystallization is generally orthorhombic, but ranges from orthorhombic to hexagonal. In the common form the pinacoid {001} and the rhombic prism {110} predominate. The pinacoid {010} is occasionally developed. The pinacoid {100} occurs rarely, but has not been observed where the pinacoid {010} is developed.

The crystals are small. The long, or b-axis direction of the rhombic plate rarely is found to exceed 0.7 mm., and the usual length for the larger crystals on the average slide is from 0.1 mm. to 0.5 mm. The average thickness, in the c-axis direction, is of the order of 0.005 to 0.01 mm.

Euhedral crystals of a very pure[1] n-paraffin are nearly perfect in form,

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[1] Normal paraffin wax compounds of 100% purity probably do not exist. Paraffins graded as "c.p." may contain up to several per cent of other members of the same homologous series. The term "very pure" as used throughout this paper indicates a compound probably at least 98% pure.

the corresponding interfacial angles in all crystals being nearly the same. Mix crystals of two or more *n*-paraffins, or crystals of a single *n*-paraffin containing impurities, are generally more or less distorted and show con-
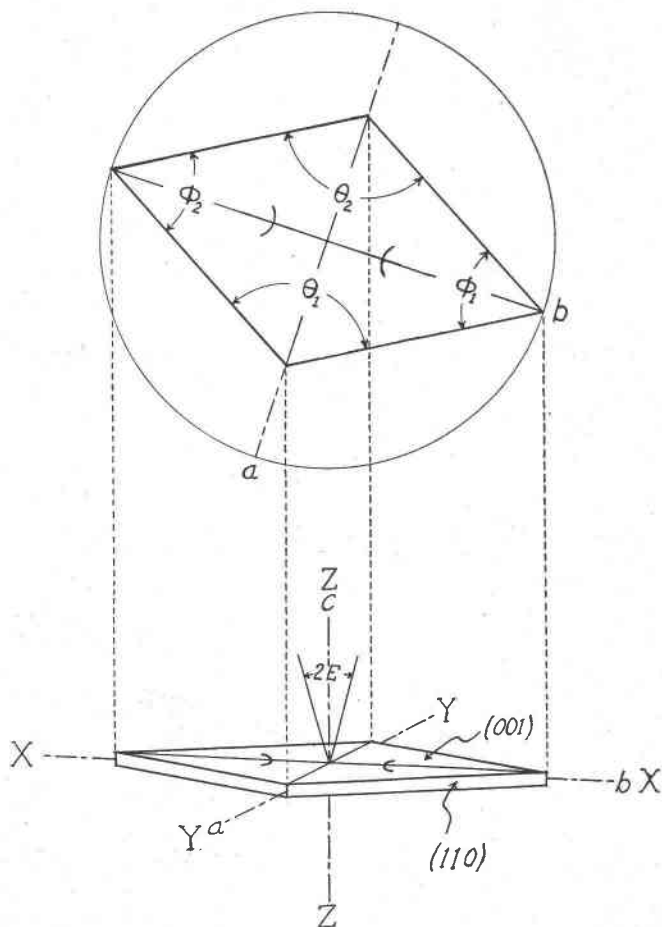

FIG. 1. Form and Optical Orientation of the Orthorhombic *n*-Paraffin Crystal.

In its simplest form, as illustrated, the crystal is a thin rhombic plate. In the figure, the thickness of the plate is exaggerated. It should be noted that since the angular measurements are made with the microscope and depend on the interior angles of the rhombic plate, all descriptive data are given in terms of these angles. The obtuse interior angle is designated as θ, and the acute interior angle as ϕ. Thus θ is equivalent to the conventional interfacial angle $(110) \wedge (1\bar{1}0)$, while ϕ is equivalent to $(110) \wedge (\bar{1}10)$.

siderable variation in interfacial angles, both within the same crystal and among different crystals in a single preparation.

The acute interior angles (ϕ in Fig. 1) are more variable within a single

crystal than are the obtuse interior angles, θ. In crystals of very pure
n-paraffins, $\phi_1 = \phi_2$ (approximately) and $\theta_1 = \theta_2$ (approximately). In mix
crystals and in crystals of impure n-paraffin, as a general observation
$\phi_1 \neq \phi_2$, whereas $\theta_1 = \theta_2$ (approximately). In other words, the b-axis of the
crystal tends to remain an axis of symmetry; the a-axis does not.

The range in variation of ϕ angles and the relative frequencies of oc-
currence of different values of ϕ within the observed range are shown on
the chart (Fig. 2). This chart shows the variations found from about 800
individual measurements of ϕ angles made on approximately 400 differ-
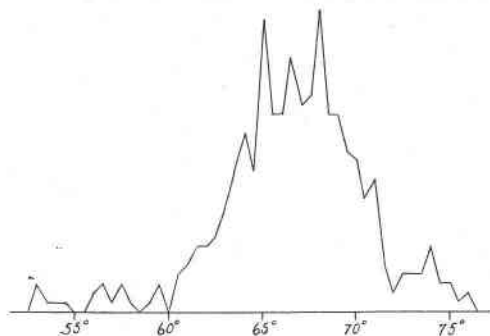ent crystals. To interpret this chart correctly, it should be kept in mind

FIG. 2. Frequencies of Occurrence of Various Values of n-Paraffin Crystal Angles (ϕ).
Data: 800 measured ϕ angles on 400 crystals from 10 different sources. The angles were
measured to the nearest $0.1° \pm 0.05°$, and were plotted on this chart to the nearest $0.5°$.

that the relative frequencies of ϕ angles shown pertain only to the 400
crystals from 10 different sources which were measured to obtain the data
for this particular frequency curve. Similar measurements on crystals
from other sources, or on a much larger selection of n-paraffins from all
natural and synthetic sources would probably show frequency curves dif-
fering from that in Fig. 2.

It should also be kept in mind that the frequency curve in Fig. 2 shows
the frequencies of individual ϕ angles; not the means of ϕ_1 and ϕ_2 for the
different crystals. In a single crystal the difference between ϕ_1 and ϕ_2
has been found to be as great as 20°, though the average difference is
much less.

Several interesting features are evident from an inspection of Fig. 2.
The frequency curve declines rapidly to 60° (the angle for a hexagonal
crystal form), and remains low for all values less than 60°. Frequency
peaks, in order of importance, are seen at 68°, 65°, 66.5°, 64°, 74°, and
71°. The peak at 74° represents very pure Octacosane ($C_{28}H_{58}$). The re-
mainder of the data incorporated in the chart are from mix crystals of
refined n-paraffins from petroleum sources.

In general, the entire range of ϕ values will not be found in mix crystals from any single source. Each sample of paraffin from a different source shows a characteristic frequency curve of ϕ angles, usually distinguishable in its form from ϕ-frequency curves of samples from other sources.

Numerous observations of both pure and mix crystals show that the range of ϕ values in a pure individual n-paraffin is quite limited, and much greater in the mix crystals. For example, a very pure n-Octacosane showed a sharp ϕ-frequency peak at about 74.25°, and a range of ϕ values from 73.5° to 75.5°. A sample of pure n-Dotriacontane ($C_{32}H_{66}$) showed a peak at 68° and a range from 65.5° to 69.5°. An equi-molar mixture of pure Octacosane and fairly pure Nonacosane showed a broad peak at 68° and a range from 63.5° to 75.5°. Typical samples of mix crystals, refined from petroleum sources, showed one or more frequency peaks, usually not sharp, and ranges in ϕ values in some cases as great as 15° or 20°.

The evidence indicates clearly that the spread or range in ϕ values for any given sample is related to the purity of the material, or to the number of individual n-paraffins present in the mixture. Although no exact relationships have been determined, it may be stated that the spread of ϕ values varies inversely as the degree of purity of the material crystallized. With carefully controlled molar mixtures of very pure n-paraffins it may prove possible to establish a mathematical relationship between the interfacial angles of the crystal and the molar percentages of n-paraffins comprising the mixture. The writer has been unable to make such a study because he has been unable to obtain samples of more than one n-paraffin of sufficient purity.

Twins

The long chain n-paraffins crystallized from solution at ordinary temperatures, exhibit a variety of twins. The most commonly observed twinning planes are {100}, {110}, {310}, and {010}, listed in order of frequency of occurrence. Twinning apparently occurs in other directions, but much less frequently.

Micro-twinning is apparently responsible in many instances for curved {110} faces observed in n-paraffin crystals. In the majority of these instances, the curvature of the {110} faces is convex outward, but the reverse curvature is common in crystals of n-paraffin from certain sources.

Curved faces may also be produced where impurities are present in the solution, or in mix crystals containing several n-paraffins. Curvature is also common in crystals of the lower melting point members of the n-paraffin series when the temperature during crystallization is within 8° or 10°C. below the melting point.

It is sometimes difficult to determine whether the curved faces are the

result of twinning, or of warping of the crystal structure produced by impurities, or of other factors. It has been observed that freshly formed perfect crystals may in the course of time develop curved or irregular faces. This is apparently the result of resorption produced by relatively low melting point amorphous wax or oil, which makes up the residual matrix surrounding the paraffin crystals after the solvent has evaporated. This feature is particularly noticeable where relatively low melting point crystals have not been stored in a cool place.

In addition to twinning, a common feature of *n*-paraffin crystals is the formation, by parallel growth on the {001} face, of one or more rhombic plates of successively smaller dimensions. These are usually more or less concentrically arranged, so that the entire crystal has the appearance of a very flat step pyramid.

Occasionally, and particularly in pure *n*-Octacosane, the successive steps or tiers of rhombic plates, instead of having a concentric arrangement, are superimposed in such a manner as to present the appearance of a spiral arrangement,[2] and in such cases, the pseudo-spirals may appear right-handed of left-handed, with no statistical evidence to indicate a tendency toward either direction.

BEHAVIOR IN PLANE POLARIZED LIGHT

In plane polarized light the pure crystals are colorless, translucent to transparent. They show no sign of pleochroism. When crystallized from solution on the microslide beneath a cover glass, the rhombic plates are so thin that a reduced or an oblique light is usually necessary to make them visible. The refractive indices of the crystals are commonly only slightly different from the index of the surrounding matrix. This matrix is composed of amorphous waxy materials, and shows few or no indications of crystalline structure.

In the case of extremely pure single members of the *n*-paraffin series, however, practically the entire area of the microslide preparation is crystalline. In such cases, it is unusual to observe euhedral crystals, formed free of interference from neighbors, and the true boundaries of crystals are difficult to observe without the use of crossed nicols.

BEHAVIOR BETWEEN CROSSED NICOLS

Between crossed nicols in parallel rays (without use of condenser lens) the crystals behave differently, depending upon whether the preparation is of a single very pure *n*-paraffin on the one hand, or on the other a mix-

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[2] This form of parallel growth with a spiral pattern differs from the spiral structure in certain paraffin crystals described by Prof. Chas. M. Heck, North Carolina State College, Raleigh (Heck,1936).

ture of two or more pure *n*-paraffins, or from one to several *n*-paraffins containing impurities. In general, pure preparations of a single *n*-paraffin compound show fairly marked double refraction in the *c*-axis direction, whereas the mix crystals and the impure preparations are usually feebly anisotropic, or practically isotropic (uniaxial).

Interference colors are invariably first order gray, even in the pure unmixed compounds. This is true for the thickest crystals that have been observed. The insertion of a gypsum plate effectively enhances the colors.

The following characteristics in parallel light between crossed nicols have been observed without exception in all *n*-paraffin crystals which are appreciably biaxial:

1. The faster ray vibrates approximately parallel to *b*.

2. Extinction is approximately symmetrical, but as will be described later, it is in some instances noticeably asymmetrical, and the extinction angle varies slightly with different crystals.

3. Double refraction characteristically varies within a single crystal where the thickness in the *c*-axis direction is variable. Many crystals are thicker in the center and thin out toward the margins, being roughly of the form of a flattened pyramid. In such crystals, the central portion may be rather strongly anisotropic, and the marginal zone apparently isotropic. This observation suggests that many crystals appear isotropic because of their very slight thickness.

4. When the *b*-axis of the rhombic plate is rotated into the "northwest" quadrant (with reference to the vibration planes of the nicols) the crystals show stronger double refraction than when the *b*-axis is rotated to the "northeast" quadrant. In thick, strongly anisotropic crystals, or in crystals of a single very pure *n*-paraffin, this phenomenon is not conspicuous, and might be missed if one were not looking for it. In the more feebly anisotropic crystals, and particularly in very thin crystals, this feature is striking. Such crystals, during a complete rotation of the microscope stage, may show double refraction only twice; both when the *b*-axis of the crystal is in the "northwest" quadrant. When the *b*-axis is in the "northeast" quadrant, there is either a very faint appearance of double refraction, or the crystal remains dark. There is nearly always complete extinction when the *b*-axis is parallel to the plane of the lower nicol. When the *b*-axis is parallel to the plane of the upper nicol, extinction is often incomplete. When the *b*-axis is oriented with the plane of the lower nicol, extinction is almost always symmetrical. When the *a*-axis is oriented with the plane of the lower nicol, however, extinction is often observed to be slightly asymmetrical. Wherever the angular positions of extinction and of maximum double refraction have been measured carefully, they have been found to be shifted or rotated slightly in a counter-clockwise direction from their normal positions (with the possible exception, previously noted, when the *b*-axis is parallel to plane of lower nicol).

    In order to investigate more thoroughly the nature of this anomalous behavior, the microslides were in many cases placed up-side-down on the microscope stage, and the identical crystals observed again in the inverted position. The phenomenon remained unchanged, with maximum double refraction still in the "northwest" position, and the positions of extinction and of maximum double refraction shifted slightly counterclockwise.
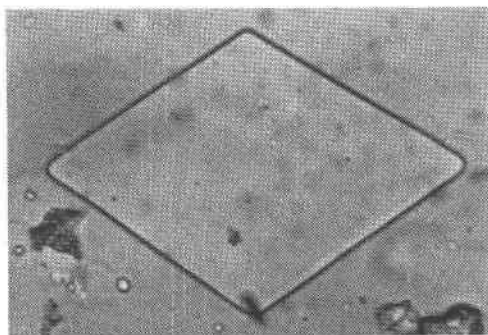
Fig. 3   Fig. 4

Fig. 3. Photomicrograph in plane polarized light of a typical *n*-paraffin mix crystal of about 56°C. melting point, occurring in petroleum (Panhandle, Texas). Magnification ×415.

Fig. 4. Photomicrograph in polarized light of crystals of a pure synthetic *n*-paraffin (*n*-Dotriacontane, $C_{32}H_{66}$). Crossed nicols, with parallel light. Magnification 48×. Vibration planes of the nicols are parallel to edges of the photograph; P-P' being "north-south" and A-A' being "east-west."

The crystals seen in the photograph are all oriented with their *c*-axes "vertical" (normal to plane of the paper) and with their *b*-axes (long diagonal of the rhombic plate) oriented at random in the "horizontal" plane (plane of the paper). It will be observed that those crystals with *b*-axis aligned in the "northwest" quadrant show relatively strong double refraction, whereas those with *b*-axis parallel to vibration plane of either nicol or aligned in the "northeast" quadrant are dark, or show relatively weak double refraction. This anomalous behavior is explained as an effect of the optical rotatory power of the *n*-paraffins.

BEHAVIOR IN CONVERGENT POLARIZED LIGHT

The interference figure is biaxial positive. Because of the invariable orientation of the crystals on the microslide with the *c*-axis in the vertical position, the interference figure always seen is the acute bisectrix figure. The isogyres show no accompanying isochromatic curves, due to the relatively small double refraction $(\beta-\alpha)$, and to the thinness of the crystals.

Mix or impure crystals show small optic angles, and in many cases the interference figure appears to be practically uniaxial. In pure unmixed *n*-paraffins, values of 2E have been observed as large as 41°. The usual range of 2E for distinctly biaxial crystals is between 20° and 40°. Among the mix and impure crystals, the 2E angles range generally from 0° to 10° or 15°. Both in the strongly biaxial and in the approximately or apparently uniaxial crystals, the sign of the interference figure is invariably positive. No *n*-paraffins of opposite sign have been observed.

The writer has been unable to determine accurately the refractive indices of *n*-paraffin crystals in the three crystal directions. In the in-

variable orientation of the crystals on the microslide, only the β and α indices may be measured conveniently, and these two indices are usually nearly equal. Measurements of these have shown a range of values from 1.50 to 1.52. If the average of β for all the observed paraffins is assumed to be 1.51, then the observed range for distinctly biaxial crystals of $2E = 20°$ to 40° would correspond to the values $2V = 13°$ to 26°.

The interference figure is always central in the field of view, and shows no displacement when the microscope stage is rotated. Thus the acute bisectrix is parallel to the optical axis of the microscope, and normal to the (001) face of the crystal. No evidence of the slightest inclination of the acute bisectrix has been observed in any of the many n-paraffin crystals from all sources, both natural and synthetic. Because of the impossibility of thus detecting a slight inclination of the acute bisectrix, these observations do not necessarily prove that every crystal studied was either orthorhombic or hexagonal. The observations do, however, show that none of the strongly monoclinic crystal forms reported from x-ray studies, are to be found among the long chain n-paraffins crystallized from solution at temperatures well below transition and melting points.

As would be expected, in view of the previously described asymmetrical behavior of n-paraffin crystals between crossed nicols with parallel light, the behavior in convergent polarized light is also anomalous. Without any observed exception, even in the purest n-paraffins, the axial angle (2E) is definitely larger when the b-axis of the crystal is oriented in the "northwest" quadrant. This asymmetry is usually but not invariably more pronounced in those crystals showing 2E values somewhat below the average for all crystals studied. The degree of the asymmetry is fairly constant for all crystals from any one sample or source. This statement is particularly true of pure, unmixed n-paraffins.

Careful measurements of the axial angles of 24 crystals from 15 different sources, ranging from very pure n-paraffins to mixtures and impure preparations, and including both natural and synthetic n-paraffins, showed the following results:

2E(N.W.)—Range 17.8° to 41.6°; arithmetic mean $= 30.2°$.
2E(N.E.) —Range 15.3° to 38.9°; arithmetic mean $= 25.0°$.
2E(N.W. and N.E.)............arithmetic mean $= 27.6°$.

Maximum asymmetry measured in a mix crystal; 2E(N.W.) $= 30.9°$; 2E(N.E.) $= 20.4°$.
Minimum asymmetry measured in a pure crystal; 2E(N.W.) $= 40.7°$; 2E(N.E.) $= 38.9°$.
Minimum asymmetry measured in a mix crystal; 2E(N.W.) $= 22.1°$; 2E(N.E.) $= 20.4°$.

All determinations of 2E on individual crystals represent means of repeated measurements. The probable errors of the means are in most cases less than $\pm 0.5°$.

Interpretation of Anomalous Behavior in Polarized Light

The previously described anomalous behavior of n-paraffin crystals between crossed nicols shows that these crystals are optically active. The observations furthermore show that all the crystals thus far examined are dextrorotatory.

The dextrorotatory action of the n-paraffin crystal is illustrated graphically in Fig. 5. The left diagram (Fig. 5a) represents a crystal with the b-axis oriented at 45° in the "northwest" quadrant; the right diagram (Fig. 5b) another crystal with the b-axis oriented at 45° in the "northeast" quadrant. In both diagrams lines PP′ and AA′ represent the vibration directions of the lower and upper nicols respectively. In each dia-
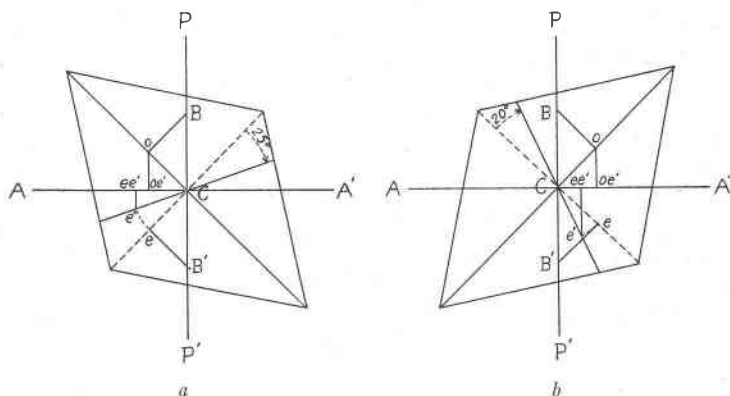

Fig. 5. Optical Rotation of n-Paraffin Crystal Between Crossed Nicols.

gram the b-axis of the crystal is shown by a solid line; the a-axis by a dashed line (cf. Fig. 1). The projection of the vertical c-axis on each diagram at the intersection of the a and b axes, and is designated by the letter C. The c-axis of the crystal on each diagram coincides with the optical axis of the microscope. The distances $CB = CB'$ represent the amplitude of the plane polarized ray emerging from the lower nicol.

When this polarized ray enters the crystal, it is split into two polarized rays, the ordinary, or (o) ray and the extraordinary, or (e) ray. If the n-paraffin crystal were optically inactive, the (o) ray would vibrate through the crystal in a direction parallel to the b-axis, and the (e) ray would vibrate parallel to the a-axis.

An optically active dextrorotatory crystal would produce a clockwise rotation of the vibration direction of one or of both rays. Observations of n-paraffin crystals indicate that the amount of rotation suffered by the (o) ray is usually small or negligible. For greater simplicity, therefore,

the (*o*) ray in Figs. 5*a* and 5*b* is assumed to have undergone no rotation. The clockwise rotation of the (*e*) ray is shown by a solid line in both diagrams. The amount of rotation is about 25° in Fig. 5*a* and about 20° in Fig. 5*b*.

At the 45° position the component amplitude of the (*o*) ray which emerges from the crystal is represented by the distance C–o, found by dropping a perpendicular from B to the *b*-axis. A perpendicular to AA′ is then dropped from the point (o) to point (oe′) on AA′. Then the distance C–oe′ represents the component amplitude of the (*o*) ray which emerges from the upper nicol.

The (*e*) ray, which like the (*o*) ray, originates the instant the plane polarized light enters the crystal from below, vibrates initially parallel to the *a*-axis (dashed lines in Figs. 5*a* and 5*b*). The component amplitude of the (*e*) ray while passing through the crystal is represented by the distance C–e, found by dropping a perpendicular to the *a*-axis from the point B′. In passing through the crystal the plane of vibration of the (*e*) ray is rotated in a clockwise direction, so that on emerging from the upper surface of the crystal the ray has changed its vibration direction from C–e to C–e′. A perpendicular to AA′ dropped from (e′) to (ee′) gives the distance C–ee′, which is the component amplitude of the rotated (*e*) ray which emerges from the upper nicol. The sum of the components C–oe′ and C–ee′ gives the total amplitude of the combined rays emerging from the upper nicol.

It may be visualized from Figs. 5*a* and 5*b* that as the dextrorotatory crystal is rotated on the microscope stage between crossed nicols, the sum of the components of the two emergent rays (oe′ and ee′) will vary greatly, and the pattern of the variation will differ from that of an optically inactive crystal. The pattern will also depend on the amount and direction of rotation of either or both rays emerging from the crystal.

To illustrate the effect of optical activity, the two curves in Fig. 6 show the changes in relative intensity of transmitted light as the crystal is rotated (between crossed nicols) through 180° in a clockwise direction, starting (on the left) with the *b*-axis parallel to the vibration plane of the upper nicol. The dashed line curve is that of an optically inactive crystal. The solid line curve is that of a *n*-paraffin crystal in which the (*o*) ray has undergone no rotation, and the (*e*) ray has undergone a clockwise rotation of 20°. The curves need not be extended as they are repeated over each 180° rotation of the crystal.

The solid line curve (for an optically active crystal) in Fig. 6 illustrates qualitatively several observations of the anomalous behavior of *n*-paraffins in parallel polarized light which have been described previously.
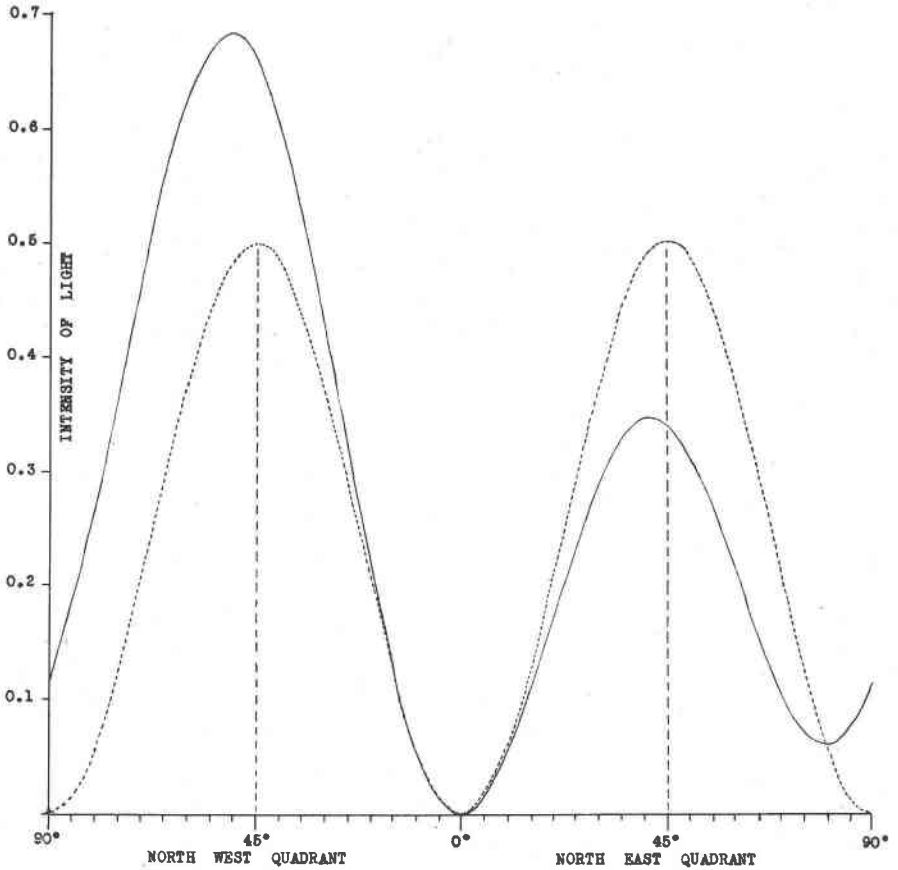
FIG. 6. Orientation of *b*-Axis of Crystal vs. Light Intensity.
Dashed Line Curve; r=0°
Solid Line Curve;   r(o) =0°
                     r(e) = +20°

These are:

1. Light intensity is invariably greater with the *b*-axis at 45° in the "northwest" quadrant than at 45° in the "northeast" quadrant.

2. Extinction is often incomplete and slightly asymmetrical with the *b*-axis in the "east-west" position.

3. Extinction is usually complete and symmetrical when the *b*-axis is in the "north-south" position.

4. Positions of maximum light intensity and positions of extinction (where measurably asymmetrical) are always shifted counter-clockwise from their respective normal positions.

5. In the case of a thin crystal, or one with weak double refraction, the light intensity maximum in the "northeast" quadrant would not be observed, and the crystal would appear to remain dark through 180° of rotation on the microscope stage.

The solid line curve in Fig. 6 is intended to illustrate only qualitatively what actually happens. It is not intended to imply that only the extraordinary ray is rotated; and it may be assumed that both the (*e*) and (*o*) rays undergo amounts of rotation which vary with the structure and thickness of each individual crystal. However, observations suggest that the (*e*) ray is rotated more than is the (*o*) ray in the great majority of *n*-paraffin crystals.

In order to check further the theoretical asymmetry shown in Fig. 6 against actual behavior of the *n*-paraffin crystal in polarized light, a single crystal was selected, and a number of repeated measurements made and averaged. The crystal selected was a fairly large distinctly biaxial mix crystal, the melting point of which was later found to be about 61° C. The axial angles (2E) were 27.4° (N.W.) and 24.8 (N.E.). The results of the measurements are recorded in Table 1.

TABLE 1

Obs. No.	Light filter used	Approx. wave length of incident light-peaked at:	λ (N.W.)	λ (N.E.)	Sum	No. of repeated measurements	Probable error of mean
1(a)	Red shade yellow Corning No. 3480	Above 610 mμ	48.0°			10	±0.6°
1(b)	Red shade yellow Corning No. 3480	Above 610 mμ		36.2°	84.2°	10	±0.6°
2(a)	None	Approx. 589 mμ	48.4°			10	±0.5°
2(b)	None	Approx. 589 mμ		43.8°	92.2°	10	±0.3°
3(a)	Dark blue green Corning No. 4303	Below 520 mμ	48.3°			10	±0.7°
3(b)	Dark blue green Corning No. 4303	Below 520 mμ		45.0°	93.3°	10	±0.4°

Light source was 10 watt tungsten lamp with Corning "Daylight" glass.

In this table, the angle λ is the angle between the plane of the lower nicol and the *b*-axis of the crystal when the crystal is rotated to the position of maximum light intensity in the quadrant indicated.

The results shown in Table 1 agree qualitatively with the theoretical requirements illustrated in Fig. 6. Thus it is evident that in dextrorotatory crystals the peaks of light intensity are displaced in a counter-

clockwise direction. Still another feature brought out in Table 1 is the indication that the longer the wave length of the transmitted light, the greater the counter-clockwise shift of the light intensity maximum in the "northeast" quadrant.

It is obvious from the preceding observations that it would be possible to determine with fair accuracy the amount of optical rotation in a *n*-paraffin crystal by measuring accurately, with monochromatic light, the positions of extinction and of light intensity maxima, and the relative peak intensities. To determine the specific rotation, the thickness of the crystal would have to be measured. Thus it would be possible, and of interest, to compare the specific optical rotation of a paraffinic petroleum or petroleum fraction with the calculated specific rotation of *n*-paraffin crystals extracted from the same petroleum.

Cause of Optical Activity of *N*-Paraffin

It has been pointed out that whereas the observed optical asymmetry of the *n*-paraffin crystal between crossed nicols is often quite pronounced in the impure and mix crystals, it is still clearly present in the purest synthetic *n*-paraffin crystals. It is therefore highly probable that this optical activity is caused by the internal structure of *n*-paraffin, and not necessarily by the presence as impurities of some foreign organic compounds, as seems generally to have been assumed in the case of paraffinic petroleums.

In the above connection, Gruse and Stevens (1942) state: "Optical rotatory power is exhibited by nearly all crude oils. The majority of them are dextro-rotatory; some are laevo-rotatory; and only a few appear to be inactive. The optical activity is not uniformly distributed throughout the distillation range of the crude but is usually a maximum for the intermediate fractions. Curiously, the maximum occurs at about the same boiling point for all crude types, 250° to 300° C. at 12 mm. Hg., but no extensive data have been collected on this point. No activity has been observed in fractions boiling below 200° C. at atmospheric pressure. The decrease in activity above the maximum may be partly due to racemization by heat. The existence of optical rotation of oils has given much weight to the organic theories of the origin of petroleum."

Of course a considerable number of organic compounds, known or believed to be present in petroleum, could cause the observed optical activity. It is perhaps significant, however, that the range of crude oil fractions showing the maximum optical activity corresponds in a general way with the range of fractions which in paraffinic crudes contain most of the long chain *n*-paraffin waxes. The fact that the majority of crude

oils are dextrorotatory is likewise significant. Absence of optical activity in a crude oil might be due to racemization, or it might be due to absence of optically active constituents, such as long chain n-paraffins. The laevo-rotatory activity of some crude oils may be caused by the presence of laevorotatory hydrocarbons. At least, the evidence presented in the present paper would seem to show that the laevorotatory activity, exhibited by some crude oils, cannot be due to the presence of n-paraffins.

It has been shown by Müller (1928, 1929) that the molecules of the long chain n-paraffins are arranged with their long axes parallel to the c-axis of the crystal, and the ends of the molecules lie in planes normal to the c-axis. Müller (*ibid.*) and others (Piper *et al.*, 1931; Kolvoort, 1938; Gray, 1943) have also shown that under certain conditions at least some members of the n-paraffin series may have the long axes of the molecules inclined to the c-axis and to the {001} planes.

In the present paper it has been shown that when n-paraffin crystals form from solvent solutions at ordinary temperatures well below transition and melting points, the molecular chains must be vertical, or parallel to the c-axis of the crystal, and that the crystals are primarily orthorhombic. Under the conditions specified, no definitely monoclinic crystals have been observed.

It appears that nothing in the packing arrangement or attitude of the n-paraffin chains in forming the crystal unit cells and the lattice can explain the observed optical activity. If the optical activity is not caused by the presence of foreign material in the inter-molecular spaces of the lattice, then it can only be produced by the internal structure of the n-paraffin molecule.

Müller (1928) working with one or two perfect crystals of very pure n-Nonacosane, carried out the only complete x-ray study that has been made of any long chain n-paraffin. This work has become classical, and Müller's conclusions on the structure of the long chain n-paraffin molecule and crystal lattice have become generally accepted.

Briefly stated, Müller found the n-paraffin molecular chain to be a zigzag form, in which the carbon atom centers all lie in one plane, and in that plane, form two vertical rows on opposite sides of, and equidistant from the zig-zag chain axis. Instead of the carbon-carbon bonds forming, one with the next, the tetrahedral angle of $109° 28'$, as might be expected from the known tetrahedral form of the carbon atomic domain, the zigzag angle was found to be between $76°$ and $92°$. The chain axis was found to be parallel to the c-axis of the crystal, and the zig-zag planes of the molecules were found to lie at an angle to the b-axis of the crystal of somewhere between $23°$ and $30°$. In any single {001} layer of molecules, half

the molecules have their zig-zag planes rotated 23°–30° clockwise; the other half counter-clockwise. In each {001} layer of molecules, the molecules are staggered along rows which are parallel to the *a*-axis. Each row alternately has molecules with zig-zag planes rotated clockwise or with planes all rotated counter-clockwise.

The above described zig-zag molecule and crystal lattice (for orthorhombic crystal forms) have come to be generally accepted as representing the true structure of the long chain *n*-paraffin series. There is nothing in this molecular structure or in this lattice structure which can explain the observed dextrorotatory optical activity of *n*-paraffins, and it is therefore apparent that in some respects, Müller's reconstruction from *x*-ray data must be in error. In general, the results of the optical studies described in the present paper do not disagree with Müller's reconstruction of the crystal lattice. Exception is taken only to Müller's reconstruction of the molecule, on the grounds that the optical observations tend to confirm the essential accuracy of Müller's reconstruction of the crystal lattice, and that neither this lattice arrangement nor the zig-zag form molecule can account for the observed optical rotation.

Spiral Structure of the Long Chain *N*-Paraffin Molecule

As a working theory, subject to confirmation by further investigations, it is suggested that the long chain *n*-paraffin molecule has a spiral structure.

Starting with this basic assumption, which is not new as applied to some other long chain compounds, certain other reasonable assumptions will be made. These are:

1. The diameter of the carbon atom domain, or length of the C-C bond, is 1.54 Å, as in diamond.
2. Adjacent C-C bonds form the tetrahedral angle, 109° 28'. From this assumption, a spiral or solenoidal arrangement of carbon centers is a logical consequence.
3. Of many different geometrically possible tetrahedral spirals, the two simplest arrangements are selected, and from these two, the left handed spiral is chosen. (See photo of model, Fig. 7.)
4. The C-H bonds also form the tetrahedral angle with all other bonds from a common center. This assumption may be unnecessary to explain the optical rotation. It is made merely to complete the picture in an orderly manner.

From the foregoing assumptions, the following relationships and dimensions of the spiral chain (see Fig. 7) have been calculated:

1. The carbon atom centers are spirally arranged around the chain axis, being equally spaced on a left-handed helix, the parametric equations of which are; $x = R \cos \theta$; $y = R \sin \theta$; $z = K\theta$, where $R = 0.534$ Å, $K = 0.5189$, and $\theta = 131° 43.94'$ $(= 2.2991629$ radians).

2. Various dimensions and angles are:
   - (a) Diameter of the helix = 1.068 Å.
   - (b) Cross sectional area of helix = 0.895 (Å)^2.
   - (c) Inclination of C-C bonds to direction of chain axis = 39° 14.035′.
   - (d) Spacing (in direction of chain axis) of successive carbon centers = 1.193 Å.
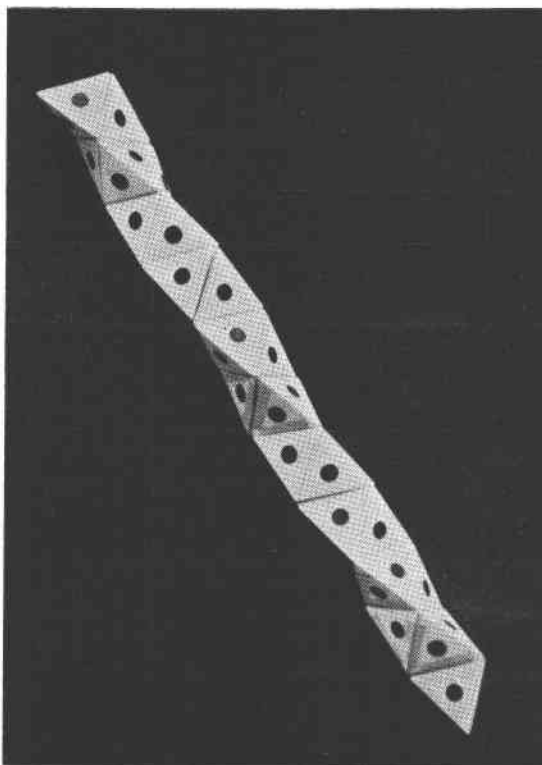

FIG. 7. Model of a spiral molecule of *n*-paraffin (*n*-Octacosane). The centers of the tetrahedrons correspond with the carbon atom centers, which fall on a helical curve. For greater convenience in constructing the model, the carbon-carbon bonds are made to intersect the tetrahedron face centers rather than the corners. The helical arrangement of the carbon atom centers is the same in either arrangement. Positions of the hydrogen atoms are shown by the black dots.

3. The molecule has no plane of symmetry.
4. As is evident from the calculated value of θ, no two carbon centers in a chain of any reasonable finite length lie in vertical alignment. There is, however, an approximate repetition or cycle for every eleventh carbon atom. Thus, C-12 is situated almost vertically below C-1; C-13 below C-2; C-14 below C-3, etc.

A reconstruction of the assumed n-paraffin spiral molecule is shown in Fig. 7, which represents a chain of 28 carbon atoms (n-Octacosane). For convenience in construction, the C–C bonds are made to intersect the tetrahedron face centers, though they could as well be drawn through the tetrahedron corners. The result is the same as long as the bond length of 1.54 Å is retained. The hydrogen atoms are represented on the model by black dots at the centers of the "free" tetrahedron faces. It is seen that

TABLE 2

Measurement	Müller	Spiral Theory	Remarks
Length of C-C Bond	1.8 to 2.0 Å	1.54 Å (exactly)	
Distance between 2 vertical rows	1.2 to 1.6 Å	No rows exist	Diam. of helix = 1.068 Å
Dist. between consecutive centers in either row	2.537 Å ±0.5%	No rows exist	Dist. parallel to chain axis between alternate carbon centers = 2.386 Å
Zig-zag angle	76° to 92°	Tetrahedral angle = 109° 28′	If C–C bonds were projected on plane parallel to chain axis, apparent angle would vary between 109° 28′ and 180°.
Angle between C–C bonds and chain axis direction	44° to 52°	39° 14.035′	Projected on plane as per above, apparent angle would vary between 0° and 39° 14.035′
Angle between zig-zag plane and crystal b-axis	23° to 30°	non-existent	

in addition to the spiral arrangement of the carbon centers, there are six spirals made by the hydrogen atoms in the CH₂ groups It is not necessary to assume that the hydrogen spirals exert any influence in producing the observed optical activity.

For comparison, Table 2 shows the spacings and angular relationships of the carbon centers as reconstructed by Müller from x-ray studies, and as result from the spiral arrangement described above.

According to Müller's calculation of 2.537 Å for the distance between carbon centers along either row of the zig-zag chain, the addition of one carbon atom would increase the chain length by 1.2685 Å ± 0.5%. With a spiral chain of the dimensions described, the corresponding increase in

chain length would be 1.193 Å. It should be noted, however, that Müller's value corresponds to a calculated C–C bond length of about 1.9 Å whereas we have assumed for our spiral chain a bond length of 1.54 Å. If we were to assume a bond length of 1.9 Å for the spiral chain, the addition of one carbon atom would increase the chain length by 1.47 Å.

Whether or not Müller's x-ray data could be re-interpreted to fit a spiral molecule is a question beyond the scope of the present paper. It is, of course, possible that the zig-zag type of chain exists in some n-paraffins, or in all n-paraffins under some conditions. On the other hand, the optical evidence presented appears definitely to favor the spiral form, as it is difficult to visualize how either the zig-zag chain or the lattice structure could produce the observed optical rotation. Several thousand individual n-paraffin crystals from many sources have been studied in polarized light. Among these not a single crystal was observed which failed to show the characteristic indications of optical activity.

Behavior of N-Paraffin Crystals on Heating

Review of Previous Work and Theoretical Considerations

Members of the n-paraffin series, when isolated in a very pure state, may be identified by the melting points, as is well known. The melting points for the series have been shown to lie on a smooth curve. In the case of mixed n-paraffins, Piper and co-workers (1931) showed that the purity of a paraffin sample, or the identities of the two or more paraffins in a mixture, cannot be determined from the melting point alone. However, the same investigators showed from experiments with n-paraffins of known purity, and with known mixtures of these, that the purity of a sample and considerable information about the identities of components in an unknown mixture of n-paraffins can be determined by observing the difference between the transition temperature (on heating) and the melting point. It was also established by these same authors that there is an alternation in transition points (on heating), the differences between the corresponding transition and melting points being from 1°C. to 2°C. greater for n-paraffins with odd-numbered chains than for even-numbered. This alternation was observed through the n-paraffin series within the range from C_{26} to C_{34}.

This alternation in the physical properties of the odd- and even-numbered n-paraffins was cited by Müller as confirmatory evidence supporting his thesis of the zig-zag form of the molecule. From purely geometrical considerations, it would appear that a zig-zag molecular chain would be more in accord with the observed alternation in physical properties than would a spiral chain. It seems possible, however, that this alternation of

properties may be explainable on a chemical basis rather than geometrical.

It is generally agreed that the transition point (on heating) marks the rupture of the inter-chain terminal bonds between adjacent end-to-end molecules. According to Müller, this means that the chains retain their fixed relative positions in the crystal lattice, but are freed to rotate around their axes. It seems more likely that on reaching the transition temperature, the chains are not only freed to rotate on their axes, but also freed to move laterally in any direction normal to the c-axis, and thus to rearrange themselves from an orthorhombic packing into a hexagonal packing. When the temperature is raised to, and beyond the transition point, it is probable that the crystal would change from an orthorhombic to a hexagonal form, and the original ϕ angles of the crystal would change abruptly, decreasing toward the 60° angle as the melting point is approached. Observations supporting this interpretation will be described later.

The n-paraffin molecule has generally been regarded as built up of a series of CH_2 groups, capped at each end by a CH_3 group. On this basis, there should be no alternation of physical properties of odd- and even-numbered members, except for the geometrical difference pointed out by Müller. In a zig-zag chain which is even-numbered the C–C bonds at the ends of the chain are parallel; in the odd-numbered chain they are not.

However, the writer has noted other apparently constant differences between odd- and even-numbered n-paraffins, which are not as readily explainable by the geometrical difference between the odd- and even-numbered molecule. Crystals of even-numbered n-paraffins have larger average ϕ angles than do crystals made up wholly or largely of odd-numbered members of the n-paraffin series. The even-numbered crystals also tend to be more strongly orthorhombic in their symmetry, and to have larger axial angles. These observations are only of qualitative value, and will be checked quantitatively when a sufficient number of pure n-paraffins can be obtained for study. Nevertheless, differences in form, structure, and crystallization habits do exist between odd- and even-numbered crystals, and these differences are more easily visualized as differences in the lattice dimensions than as differences of geometrical form of the molecules.

It is suggested that the alternation of transition points on heating, as well as the above described differences in crystal form, which serve to distinguish the odd from the even members of the n-paraffin series, are caused by chemical differences in the two types of molecule. If we regard the "building blocks" of the n-paraffin chain as C_2H_4 and C_4H_8 groups,

rather than as the conventional CH_2 groups, then we have the basis for assuming a difference in chemical properties between the odd and even molecule.

The evidence supporting this suggestion is indirect. Chibnall and Piper (1934) have shown rather conclusively that all long chain n-fatty acids and primary alcohols found in nature (various plant and insect waxes) have even-numbered chains, whereas all n-paraffin waxes from these natural sources have odd-numbered chains. These authors showed how the metabolic processes within plants might decarboxylate a fatty acid to form a corresponding n-paraffin with one less carbon atom.

It is difficult to explain the synthesis by plants of even-numbered acids and alcohols exclusively unless the plants are assumed to utilize as "building blocks" short straight chain molecules of even number carbon atoms. If we assume that in the plant metabolism long chain odd-numbered n-paraffin are synthesized, and some of them later carboxylated to form even-numbered acids, we are faced with the difficulty of explaining why both odd- and even-numbered paraffins are not found among the plant waxes.

The assumption of primitive "building blocks" with even numbers of carbon atoms, perhaps synthesized during early metabolic processes in plants, would appear to explain the observations of Chibnall and Piper. It is suggested here that these primitive "building blocks" probably included both C_2H_4 and C_4H_8 groups. If only the latter group existed, then it would be difficult to explain why the fatty acids and primary alcohols with 26, 30, and 34 carbon atoms are about as abundant among the plant waxes as are those with 24, 28, and 32 carbon atoms. On the other hand, the C_4H_8 group is the shortest chain which can define a right or a left handed spiral. It has been shown in the present paper that all the n-paraffins are dextrorotatory. If we assume that the primitive "building blocks" were C_2H_4 groups exclusively, then it is necessary also to assume an inherent tendency in these groups to join in a left handed spiral.

If the long chain molecules were all synthesized from original short chain groups, such as C_2H_4, having an even number of carbon atoms, then an odd-numbered n-paraffin may be regarded as having at one end an incomplete or ruptured "building block" (such as a CH_3 group), and at the other end a normal C_2H_5 (or C_4H_9) group. In a crystal lattice of an even-numbered n-paraffin, the inter-molecular bonds of end-to-end molecules would all be between like groups. In a lattice of odd-numbered chains, the end bonds would either all be between unlike groups, or between CH_3 groups in one {001} interface, and between C_2H_5 groups in the next interface, thus alternating throughout the crystal lattice. The latter arrangement would be in agreement with Müller's x-ray findings

that the c-spacing in odd-numbered n-paraffins is equivalent to the length of two molecules, and only equivalent to the length of one molecule in the even-numbered paraffins. The arrangement would also account for the observed alternation of transition points on heating, provided we assume that the CH_3–CH_3 bond is less stable than the C_2H_5–C_2H_5 bond.

Changes in Crystal Form on Heating

Müller (1930, 1932) measured the lattice dimensions of fifteen n-paraffins ranging from C_{18} to C_{44} at different temperatures by means of a series of x-ray photographs. He showed that the dimensions of the (a) and (b) axes of the unit cell changed with change of temperature. His results may be summarized as follows:

1. On heating, the series C_{21} to C_{29} changed from lower symmetry to hexagonal symmetry, the latter being reached just below the melting point.

2. On heating, the series C_{18} to C_{20}, and those above C_{29} tended to approach hexagonal symmetry, but melted before arriving at hexagonal symmetry.

3. C_{21} and C_{23} showed continuous change in (a) and (b) unit cell dimensions with increasing temperature up to the melting point. The n-paraffins C_{24}, C_{25}, C_{26}, C_{27}, C_{29}, C_{30}, C_{31}, C_{34}, and C_{44} showed abrupt transitions between room temperatures and their respective melting points.

The unit cell dimensions of the n-paraffins at different temperatures as determined by Müller may be used to compute the corresponding interfacial angles ϕ of the crystals. Some of Müller's results, thus converted to ϕ angles, are shown on the chart, Fig. 8. Also on the same chart is a curve for the ϕ angles of pure Octacosane (C_{28}) for different temperatures. This curve is based on direct measurements of the crystal on the microscope heating stage, and represents the mean of two series of observations on two different microslides. The two original observed curves, however, are practically identical with the mean shown in Fig. 8. The errors of the observed points on the original curves were estimated to be less than $\pm 0.1°$ for the ϕ measurements, and approximately $\pm 0.2°C$. for corresponding temperatures.

In the first experiment, the crystal temperature was raised from 24.5°C. to 58.5°C. over a period of 3.5 hours at the nearly constant rate of 0.16°C. per minute. In the second experiment, the crystal temperature was raised from 23.5°C. to 56.9°C. over 2.25 hours at the average rate of 0.25°C. per minute.

Both original curves showed two definite transition points with rising temperature. The first (or lower) transition point was at 39.3°C. in each experiment. The second (or upper) and principal transition point was at 57.3°C. in the first experiment, and at 56.6°C. in the second experiment.
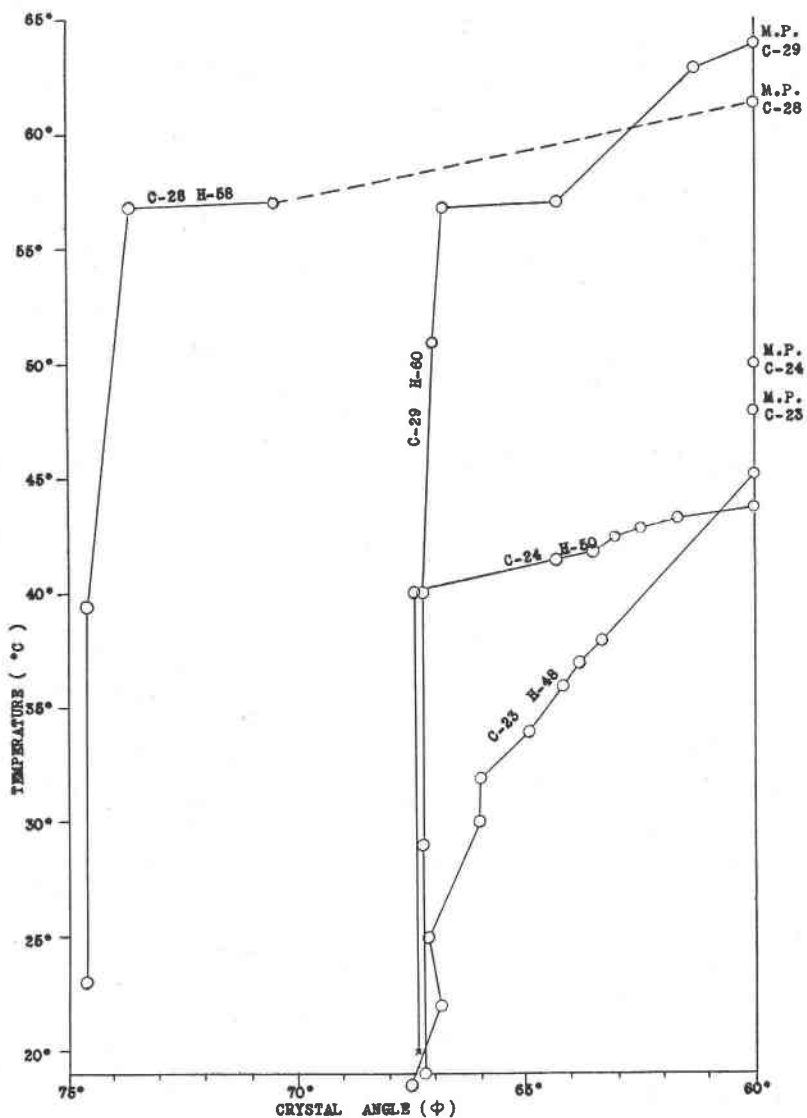
FIG. 8

The mean value, 56.9°C., is shown in Fig. 8. It will be observed that up to the temperature of 39.3°C., no change whatever took place in the crystal angles. From 39.3°C. to about 56.9°C. there was a linear decrease of about 1° in the ϕ angles. At 56.9°C. there was a very sudden decrease of about 3° in the ϕ angles. It will be noted in Fig. 8 that this ϕ-tempera-

ture curve for C_{28}, based on direct measurements of the changing crystal angles, shows a close parallelism to the curve for C_{29}, computed from Müller's x-ray measurements of the unit cell.

In the two experiments on C_{28} crystals, the temperature increase was carried to about 58°C. (3.5°C. below the melting point) and then allowed to decrease at uniform rates to room temperature over periods of two hours and four hours respectively. In each experiment the crystal {110} faces became somewhat irregular or warped at temperatures immediately above 56.9°C. (the upper transition, heating). During cooling below that point, still other irregularities appeared in the crystals, all of which had been completed on cooling to about 50°C. There were no further changes apparent in the crystals on cooling from 50°C. to room temperature.

The changes during cooling were observed between crossed nicols, with gypsum plate. It was evident that the setting of the crystals was accompanied by an irregular reorientation of the lattice structure, and that the changes described were not merely surface or resorption phenomena. After cooling to room temperature, the measured crystals, as well as others on the same microslides, were studied conoscopically. The interference figures were for the most part diffuse, due evidently to the irregularities in the lattice structure. The most significant observation noted, however, was that the dextrorotatory optical activity was still present, though in many instances, the positions of extinction and of maximum double refraction had been shifted varying amounts with respect to the original axes of symmetry of the crystals.

Interpretation of Heating Stage Observations

The interpretations of the foregoing observations are summarized as follows:

1. The first transition on heating (39.3°C. in C_{28} and about 40°C. in C_{29}, from Müller's data) marks a sudden "weakening" of the intermolecular end-bonds, permitting a progressive distortion of the orthorhombic lattice in the direction of hexagonal packing.

2. The second transition (This corresponds to Piper's "First Transition"—see Piper, 1931) represents sudden rupture of the end-bonds of most of the molecules, and the initiation of a "mass movement" of the molecules toward hexagonal packing, as the ϕ angles of the crystal decrease rapidly toward the limiting value of 60°. If it were possible to bring all portions of the lattice to the transition temperature at exactly the same instant, the ideal curve would presumably be "flat" at this temperature. In other words, the ϕ angles would decrease instantly to 60° when the crystal reached the transition temperature. It is also possible that the 60° ϕ angle could be reached by maintaining the crystal at exactly the transition temperature for a sufficient time to allow the molecules to move into the hexagonal pattern.

3. By allowing the crystal to cool before it had reached the melting point and before the entire lattice had reached the hexagonal form, a distorted lattice resulted, consisting of various segments, some orthorhombic, others more nearly hexagonal. This heterogeneity of the lattice is responsible for the observed warped and irregular crystal faces.

4. The fact that the dextrorotatory behavior of the crystals persisted after the crystals had cooled from temperatures above the upper transition point, and in spite of the disarrangements in the lattice structure, confirms the interpretation that the optical activity of *n*-paraffin crystals is produced by the internal structure of the molecule, and not by any peculiar orientation or arrangement of the molecules in the lattice.

5. It will be noticed that Müller's curve for C_{23} (shown in Fig. 8) differs radically from the curves for C_{24}, C_{28}, and C_{29}. As mentioned above, Müller found that C_{21} also behaved in the same manner as C_{23}. Incomplete heating stage observations of mix *n*-paraffin crystals indicate behavior somewhat similar to C_{21} and C_{23}, which suggests that the samples of C_{21} and C_{23} used by Müller may not have been pure compounds.

GROWTH OF *N*-PARAFFIN CRYSTALS FROM SOLUTION

One of the most interesting aspects of the study of normal paraffin crystals, is to be found in observing through the microscope their growth, either from solution at ordinary temperatures, or from the melt. The present paper, however, is concerned only with the crystals formed from solvent solution at temperatures well below melting and transition points. Under such conditions, many observations were carried out with different optical combinations, including plane polarized light, crossed nicols with parallel light (with and without gypsum plate), and conoscopic observations of the interference figure.

A complete summary of these observations would be unnecessarily lengthy, and for present purposes it is sufficient to record only the following observed features, which are believed to have a bearing on the form of the crystal lattice, and the manner in which it is built up from a solvent solution of the paraffin.

1. In oblique or reduced ordinary or plane polarized light, the crystals make their first appearance out of solution as full sized crystals; that is, the rhombic plate has attained its maximum dimensions in the plane of the *a* and *b* axes. The first appearance of the crystal is sudden, because at this stage of growth the crystal is a very thin rhombic plate, and is at the lower limit of visibility. The "suddenness" of appearance is therefore an optical illusion. During the course of minutes, the outline of the crystal becomes progressively clearer. The refractive indices of the crystal are in almost all cases higher than that of the surrounding liquid or amorphous medium.

2. The same phenomena may be observed between crossed nicols, with and without a gypsum plate. With the gypsum plate, the interference colors, ranging between blue and yellow, are seen to increase gradually in intensities, the colors changing with the increase in thickness of each crystal.

3. Conoscopically, the changes observed are similar. The interference figure, during early stages of crystal growth, is invisible, then very faint, and gradually strengthening to normal visibility. During this change, the axial angle remains constant.

4. In the case of twinned crystals, the twins make their appearance simultaneously and in the same manner as described for the single crystal.

The most probable interpretation of the phenomena described above is that the initial stage of the crystal growth is the attachment of molecules to the glass surface (both microslide and cover glass) as a single layer of molecules. The molecular chain axes are normal to the glass surface. The molecules arrange themselves in the orthorhombic packing found in the finished lattice. This primitive layer grows laterally until it attains the full (*a*) and (*b*) dimensions of the completed crystal.

The second and subsequent stages of crystal growth consist in the consecutive additions of identical layers on the primitive layer, the process continuing until stopped by (a) interference of opposite glass surface, (b) interference from adjacent crystals, (c) exhaustion of paraffin in solution, or (d) by evaporation of the solvent and excessive viscosity of the surrounding solution.

CRYSTALLIZATION UNDER OTHER CONDITIONS

It is again emphasized that the foregoing description of the growth of *n*-paraffin crystals applies only to crystallizations from solvent solutions on glass microslides at normal room temperatures which are below the transition and melting points of the compound. The description also applies only to reasonably pure individual or mixed *n*-paraffins, free of oils or other organic materials which inhibit or modify normal growth of the paraffins.

Under other conditions, the method of growth and the final crystal forms of the *n*-paraffins may be different from those we have described. For example, if during growth of a crystal the *c*-axis of the lattice is not parallel to the optical axis of the microscope, change in crystal dimensions may be visible during growth. When crystals are formed out of solvent solution at temperatures between the lower transition and melting points, the lattice may be warped, so that the *c*-axis lies at angles other than vertical. A common habit under these conditions is the formation of "needles." One type of paraffin needle is formed by a rolling up or curling of the {001} layers around the axis of the needle. During growth, these needles are seen to increase rapidly in length and more slowly in width as successive {001} layers are added to the elongate, cigar-shaped body. The long axes of such needles usually lie horizontally on the microslide. The {001} layers are wrapped around the needle in a manner which may be compared to a long stack of conical paper drinking cups, or to the wrapper leaves on a cigar. As viewed through the microscope, the *c*-axis of the distorted layers of the lattice approaches the horizontal position toward the lateral margins of the needle, and the

vertical position toward the median or central portion of the needle. Thus the birefringence seen toward the two lateral margins of the needle is much stronger (γ–β) than that seen along the central axis of the needle (β–α). As observed between crossed nicols, such needles present a characteristic appearance of two bright zones along the margins of the needle, separated by a darker zone extending along the needle axis. Needles of this type are seen in *n*-paraffins which have crystallized from the melt, and sometimes in those crystallized from solvent solution at ordinary temperatures, but with oil, asphalt, or some other organic materials present in the solution as impurities.

The formation of needles of the type described, and many other variations of crystal form and habit have been described in various published papers on the subject (see Heck, 1936; Kolvoort, 1938; Gray, 1943; Rhodes *et al.*, 1927; Tanaka *et al.*, 1928; Ferris *et al.*, 1931). These numerous other crystal forms are rarely or never observed when reasonably pure individual or mixed *n*-paraffins are crystallized under a cover glass on a microslide at ordinary temperatures, employing such solvents as carbon tetrachloride, benzene, toluene, and xylene.

Acknowledgments

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