

Ultraviolet and Infrared Absorption Spectra.—Samples were prepared for absorption studies by coagulation with 500 ml. of ethanol of polymerized lattices from 20 g. of monomer. No antioxidant was added. The polymers were washed with ethanol and dried *in vacuo* at room temperature.

Ultraviolet analyses for styrene content¹⁴ were determined by the method of Meehan.¹⁵

The infrared absorption spectra¹⁴ (Fig. 2) are considered to be identical. The difference at 1580 cm^{-1} is attributed to an experimental error.

Acknowledgment.—The authors are indebted to Dr. David Craig of The B. F. Goodrich Company for helpful suggestions in the preparation of the manuscript and to Dr. B. M. Vanderbilt of Esso Laboratories for a generous supply of piperylene.

Summary

The preparation and properties of *cis*- and *trans*-

(14) Ultraviolet analyses were carried out by Mr. J. S. Nelson and Miss Ruth Johnston. Infrared absorption spectra were determined by Mr. W. B. Treumann and Mrs. J. L. Johnson.

(15) Meehan, *J. Polymer Sci.*, **1**, 175 (1946).

piperylenes (1,3-pentadienes) have been investigated.

The pyrolysis of 2,4-diacetoxypentane results in a mixture of *cis*- and *trans*-piperylenes which can be separated by careful fractional distillation.

Both *cis*- and *trans*- piperylenes are converted to a 14:86-*cis:trans* mixture by refluxing with iodine. Thermal isomerization at 600° results in an approximately 3:4-*cis:trans* mixture. Sulfur and ultraviolet light do not effect isomerization.

The adduct of *trans*-piperylene with acrylonitrile has been shown to be chiefly 2-methyl-1,2,5,6-tetrahydrobenzoxitrile and partly 3-methyl-1,2,3,6-tetrahydrobenzoxitrile. The *cis* isomer does not react with acrylonitrile.

Emulsion polymerization of *cis*-piperylene is much faster than that of *trans*-piperylene, with or without styrene as a comonomer. The polymers are rubbery. Emulsion polymers of the *cis* and *trans* isomers appear to be identical in respect to infrared absorption.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY MEDICAL SCHOOL]

The Structure of the Branched Chain Fatty Acids in Wool Fat. An X-Ray Diffraction Study¹

By SIDNEY F. VELICK

The branched chain fatty acids of wool fat contain, in addition to the usual homologous series of normal acids with even numbered carbon chains, two homologous series of branched chain acids.² One of these, the *iso* series, consists of members with odd numbered carbon chains and a branching methyl group in the penultimate position, the location of which was determined by conversion of the C₁₆ and C₁₈ members to the previously known 17-methyloctadecanoic acid. The second, or so-called *anteiso* series, consists of members with even numbered chains and a branching methyl group in the antepenultimate position. One member of the *anteiso* series, *d*-14-methylhexadecanoic acid, has been synthesized in the optically active form, confirming the proposed structure and configuration.³ In both cases the homology of the remaining members of the series was inferred from the neutralization equivalents, characteristic crystal habits, and orderly sequence of melting points. The present X-ray study was undertaken with the object of establishing homology by independent means, and of investigating the observation that the melting points of the amides, as the series are ascended, do not lie on a smooth curve but exhibit a periodic relationship.

(1) Part of the work reported here was done in 1945 at the Sterling Chemistry Laboratory, Yale University.

(2) A. W. Weitkamp, *THIS JOURNAL*, **67**, 447 (1945).

(3) S. F. Velick and J. English, Jr., *J. Biol. Chem.*, **160**, 473 (1945).

Long chain aliphatic compounds tend to crystallize in the form of thin leaflets with the molecules either perpendicular to the leaflet surface or tilted at characteristic angles.⁴ Consequently the spacings of the crystal planes parallel to the leaflet's surface are functions of the molecular length. If the members of a homologous series form an isomorphous series of crystals, which is usually the case, the spacing increments as the series is ascended are approximately constant or show a simple periodicity which is a function of the arrangement of the chain carbon atoms. Thus the increments in spacing between adjacent members of the normal fatty acid series show a simple alternation which arises from the zig-zag configuration of the tilted chains.⁵ The differences in the orientation of the terminal groups of odd and even members with respect to the chain axis affects not only the spacing increment but also the melting points and is responsible for the well known alternation of melting points between odd and even members of the series.⁶

The Homology of the Iso Acids.—Since both the *iso* and *anteiso* series of acids from wool fat are built up by units of 2 carbon atoms it was to be expected, if the series were homologous and isomorphous, that the long spacings would increase

(4) Th. Schoon, *Z. Physik. Chem.*, **39B**, 385 (1939).

(5) F. Francis and S. H. Piper, *THIS JOURNAL*, **61**, 577 (1939).

(6) T. Malkin, *Trans. Faraday Soc.*, **29**, 977 (1933).

linearly with carbon content. That the series were actually isomorphous was indicated by the characteristic crystal habit. All of the iso acids available gave diffraction patterns containing 15 to 20 orders of long spacing reflection. The observed spacings are listed in Table I. The abso-

TABLE I

CRYSTAL SPACINGS OF THE ISO ACIDS FROM WOOL FAT

	Long spacing, Å.	Observed side spacings, Å.		
		D ₁	D ₂	D ₃
12-Methyltridecanoic	26.8	4.39		2.33
14-Methylpentadecanoic	30.7	4.66	3.76	2.32
16-Methylheptadecanoic	33.8	4.82	3.78	2.33
17-Methyloctadecanoic ⁷	36.2 ⁸			
18-Methylnonadecanoic	37.8	4.66	3.74	2.33
20-Methylheneicosanoic	41.4			2.33
24-Methylpentacosanoic	48.4	4.60	3.78	2.33

lute magnitudes of the spacings are greater than the length of a single molecule and somewhat less than that of two molecules. This indicates the existence of a typical double layer structure in which the molecules are tilted toward the basal planes. Plotted against carbon content of the acids, the spacing relation is seen to be linear with an average increment between members of 3.60 Å.; Fig. 1. Assuming a planar chain configura-

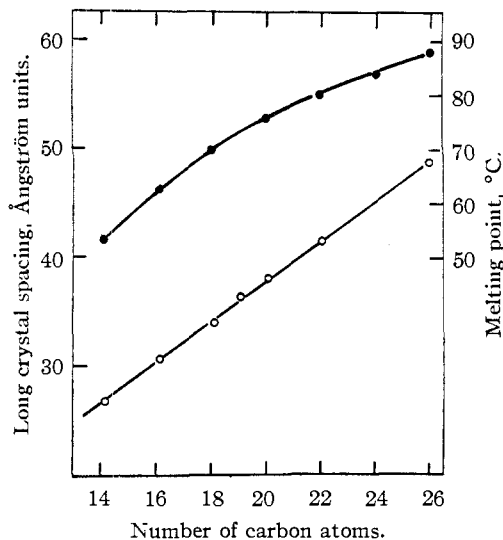


Fig. 1.—The long crystal spacings and melting points of the iso acids from wool fat as a function of the carbon content: O—O, long crystal spacings; ●—●, melting points.

tion, tetrahedral bond angles and a carbon-carbon bond length of 1.54 Å. the observed average spacing increment corresponds to an angle of inclination of approximately 45°. When the spacings are extrapolated back to zero chain carbon atoms, the spacings intercept is 3.7 Å., which is of the

(7) Sample of acid synthesized by J. Cason, *THIS JOURNAL*, **64**, 1106 (1942).

(8) S. F. Velick, *J. Biol. Chem.*, **156**, 101 (1944).

order of magnitude expected for the average layer gap.

The side spacings, D₂ and D₃, remain constant as would be expected in an isomorphous series since they represent lateral spacings of similar chains. However, the variation of spacing D₁, together with the slight deviations in the long spacings from the straight line of closest fit, indicate that the isomorphism of the crystal structures is not perfect.

The intensity distributions of the long spacing reflections are shown diagrammatically in Fig. 2. Insofar as the early odd orders are strong and the early even orders weak with a reversal of this relation in the higher orders, the patterns resemble those of the normal fatty acids and of other long chain acids containing methyl side chains.^{8,9} The individual intensities are the sums of cosine functions of the atomic parameters and vary in a periodic manner with increasing order. As the series is ascended, the shifts in the atomic parameters are relatively small and the form of the function is not altered although new terms are added.

Accordingly the general form of the intensity pattern is maintained but gradual transitions occur in individual orders. The observed results are those expected from the successive insertion of similarly spaced sheets of methylene groups between reflecting planes of a structure which remains otherwise the same. The intensities together with the linear relation of the long spacings and the general correspondence of the side spacings indicate a series of at least approximately isomorphous crystal structures. Evidence is thus provided that the iso acids form a homologous chemical series. The structures of those members which had not been studied chemically in detail are accordingly confirmed.

The Amides.—Since the amide group occupies roughly the same volume as the acid hydroxyl group which it replaces and, like the hydroxyl group, is capable of hydrogen bonding, it was to be expected that the crystal structures of the amides would be similar to those of the free acids. It was therefore surprising that the melting points of the iso amides, instead of falling on a smooth curve as do the even or odd numbered amides in the normal series, showed a peculiar alternating sequence; Fig. 3. The suggestion was made by Weitkamp that an apparent 5 carbon periodicity was exhibited which might be associated with a spiral structure.

That a periodicity exists in the crystal structures of the iso amides is demonstrated by the long crystal spacings; Fig. 3, Table II. However, the periodicity does not appear to be a simple one. There is an exact alternation in spacings in the C₁₄ to C₂₀ region which parallels the region of most pronounced alternation in melting point. Here the periodicity appears to be one of 4 rather than 5 carbon atoms. On both sides of this region the

(9) S. F. Velick, *ibid.*, **154**, 497 (1944).

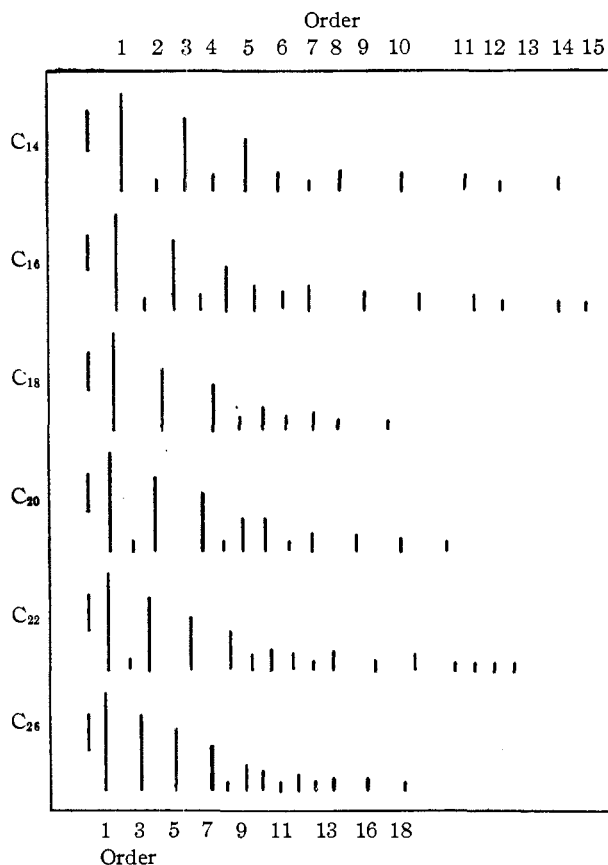


Fig. 2.—Diagram of the long spacing X-ray reflections of the iso acids from wool fat. The visually estimated intensities are indicated by the heights of the lines.

spacings follow different sequences. In the upper range, C_{22} to C_{26} , the spacing curve is almost linear although the slight deviations indicate a possible reversal of the periodicity at C_{22} . A break in the melting point curve also occurs at C_{22} . The melting points of the higher members appear to

TABLE II
THE LONG CRYSTAL SPACINGS OF THE AMIDES OF THE ISO ACIDS

	Formula	Long spacing, Å.
8-Methylnonoic	$C_{10}H_{22}ON$	19.9
10-Methylundecanoic	$C_{12}H_{27}ON$	24.1
12-Methyltridecanoic	$C_{14}H_{31}ON$	27.0
14-Methylpentadecanoic	$C_{16}H_{35}ON$	28.8
15-Methylhexadecanoic ¹⁰	$C_{17}H_{37}ON$	34.2
16-Methylheptadecanoic	$C_{18}H_{39}ON$	35.0
17-Methyloctadecanoic ^{8,9}	$C_{19}H_{41}ON$	36.9
18-Methylnonadecanoic	$C_{20}H_{43}ON$	36.8
20-Methylheneicosanoic	$C_{22}H_{47}ON$	39.9
22-Methylpentacosanoic	$C_{24}H_{51}ON$	43.4
24-Methylpentacosanoic	$C_{26}H_{55}ON$	48.3
26-Methylheptacosanoic	$C_{28}H_{59}ON$	52.5

(10) Amide of acid prepared by Weitkamp by lengthening the next lower natural occurring iso acid.

fall close to a smooth curve which approaches asymptotically the value for an acid of infinite chain length. In the lower region, C_{10} to C_{12} , the spacing periodicity is also interrupted, but since only two points are measured, the form of the curve cannot be determined. The melting point sequence also changes between C_{10} and C_{12} .

If the carbon chains assume the usual planar zig-zag structure in the iso amide series it becomes difficult to account for the observed periodicity in long crystal spacings. It would be necessary that alternate members in the iso series differ in the angle of inclination of the molecules or in the degree of rotation of the molecules about their long axis with respect to the angle of tilt. Although such effects are possible, there is no obvious physical reason why they should occur in a homologous series of molecules the members of which possess the same symmetry. For like reasons the hypothesis that corresponding differences occur in layer gaps, which would also involve crystallographic changes of the above type does not seem justified. Further, if the amides in the C_{14} to C_{20} region or in the C_{20} to C_{26} region actually possess a planar zig-zag structure, in the crystalline state, then the ends of the molecules in adjacent layers would have to be imbricated. This is readily seen by extrapolating the spacing curve back to zero chain length, where the intercept on the spacing axis is negative. In the known aliphatic series where data are available, including the free iso-acids, the intercept so obtained is positive and is of the order of magnitude of the average layer gap found by analysis of single crystals.

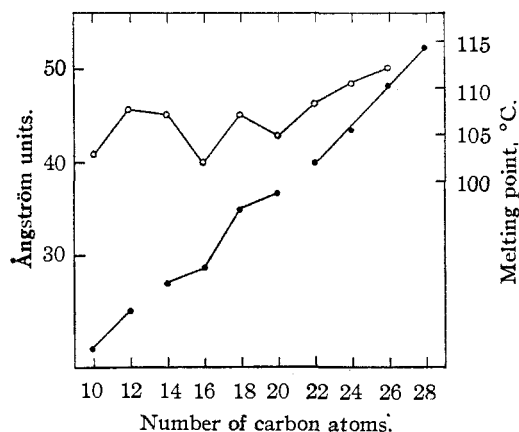


Fig. 3.—The melting points and long crystal spacings of the amides of the iso acids from wool fat as a function of carbon content: ●—●, long crystals spacings; ○—○, melting points.

As an alternative to the well established planar zig-zag structure, it is possible that the hydrocarbon chains assume a spiral configuration. An examination of models reveals that the densest possible spiral shows a 4 carbon periodicity along

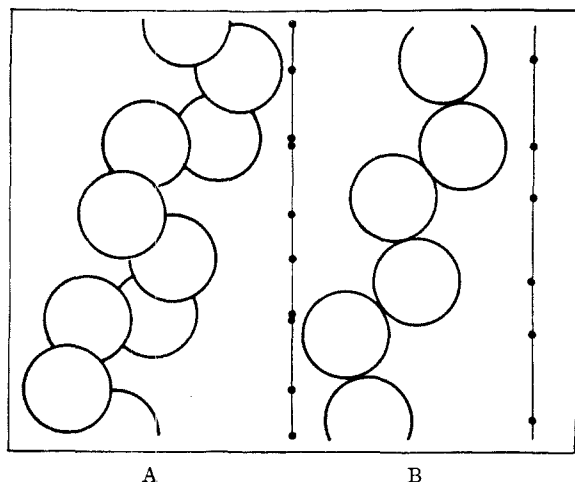


Fig. 4.—A, tilted spiral chain configuration showing four carbon periodicity; B, planar zig-zag configuration showing two carbon periodicity.

the spiral axis, Fig. 4A. When the molecule is tilted, the projections of the carbon centers on the line normal to the reflecting planes show the same periodicity in spacing increments as those observed in the C_{14} to C_{20} region of the amide series. The orientation of the terminal isopropyl groups likewise shows a 4 carbon periodicity, Fig. 5.

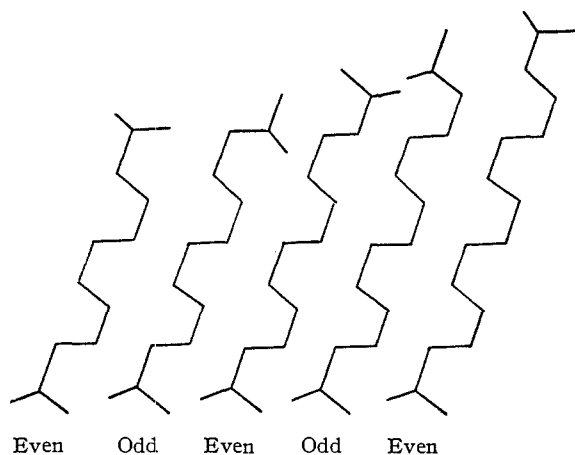


Fig. 5.—Orientation of the terminal isopropyl groups in the spiral configuration.

The resulting crystallographic differences would be sufficient to account for the alternation both of the melting points and the long crystal spacings.

A consideration of the models further reveals that the odd members of the iso amide series might encounter steric difficulties in crystallizing in the spiral form unless the terminal isopropyl groups were rotated from the spiral configuration. If a spiral configuration is actually assumed, the odd members would be expected to form an independent periodic series with the carbamide and isopropyl groups *cis* and *trans* to each other in alternate members. Although not a member of the

natural series, 17-methyloctadecanoic acid has been synthesized, and its long crystal spacing together with that of its amide determined in connection with a previous investigation.⁹ The amide spacing is found to differ from that of the next higher homolog by only 0.1 Å. This is not inconsistent with the spiral model. The next lower odd member, 15-methylhexadecanoic acid, has been prepared by lengthening the chain of the naturally occurring 14-methylpentadecanoic acid. Both the melting points and long crystal spacings of these compounds form independent series. Whether or not they form a periodic series cannot be determined until more members are available.

The approximately linear sequence of the iso amides in the C_{22} to C_{28} region and the smooth melting point curve are superficially indicative of a planar zig-zag structure. However, the negative layer gap, determined on this assumption as previously described, renders the assumption unlikely. Melting points in this region of the series, and higher, cease to be a sensitive index, and there are a sufficient number of variables involved to permit an approximately linear spacing sequence with a spiral chain configuration. The details of the spiral and its packing however cannot be identical with the 4 carbon period proposed for the C_{14} to C_{20} amides.

The intensity distributions of the long spacing reflections of the amides are shown in Fig. 6. In the C_{14} to C_{20} region, the 2nd and 4th orders give evidence of periodicity although the predominant effect is due to the increase in chain length. The C_{19} and C_{20} amides which have almost identical spacings also have very similar patterns differing only in the weak 2nd, 4th and 13th orders and in higher orders which are very sensitive to small structural differences.

The Anteiso Series.—The anteiso acids crystallize with difficulty presumably because of their asymmetry and the absence of a close packing terminal group. The exceedingly small, soft, fragmentary crystals are not readily oriented and give diffraction patterns with much background scattering and a relatively small number of reflections, few of which are identifiable. It does not seem likely that the lattice imperfections are due to the presence of impurities. Weitkamp has discussed the peculiar crystal habit.

The anteiso amides likewise present difficulties. As the chains are lengthened, the crystals are obtained in the form of increasingly long hair-like micro-needles and give increasingly poor diffraction patterns. However, spacings could be determined for the lower members of the series. These are presented in Table III. In spite of the large alternation in melting points, the anteiso amides show a roughly linear spacing sequence. The spacing intercept obtained by backward extrapolation falls close to 4 Å, which is a reasonable value for a planar zig-zag structure. The crystallographic differences responsible for the periodi-

city in melting points are thus not revealed by the long spacings. A spiral structure is not excluded by the spacing sequence because differences in projected chain length may be compensated by periodic shifts in symmetry of the spiral forms and consequent alteration in the mode of packing. The relative intensity diagrams of the anteiso amides are shown in Fig. 7.

None of the simple aliphatic compounds previously subjected to crystallographic structure analyses have exhibited properties which indicate a spiral structure. Such studies have been confined almost entirely, however, to acids, amides, alcohols, ketones, esters, and hydrocarbons with unbranched carbon chains. In general, the modifications imposed by polar substituents on the preferred packing of the planar aliphatic chains has been confined chiefly to the arrangement at the polar layers and the rotation and tilt of the chains. The effect of increasing chain length in a given homologous series does not usually alter the balance of forces sufficiently to cause any but minor changes in crystal structure. Consequently the melting points lie on smooth curves and the long crystal spacings increase linearly.

The presence of a side chain may cause a localized distortion of bond angle in the carbon chain or a weakening of the lateral forces between molecules. Under such conditions, a spiral configuration may yield the crystal structure of minimum energy. This process may be facilitated by increased possibilities for hydrogen bonding in the amide group. The spiral, when imparted by a small, widely spaced disturbing force, may be expected to be less stable than the planar form and sensitive to changes in chain length. Such factors may account for the apparent changes in crystal type as the iso amide series is ascended.

TABLE III

THE LONG CRYSTAL SPACINGS OF SOME ANTEISO ACIDS WITH AMIDES

Substance	Long crystal spacing, Å.	
	Amide	Acid
<i>d</i> -6-Methyloctanoic	19.2	
<i>d</i> -8-Methyldecanoic	23.2	
<i>d</i> -10-Methyldodecanoic	25.9	
<i>d</i> -12-Methyltetradecanoic	29.2	
<i>d</i> -14-Methylhexadecanoic	32.8	33.4
<i>d</i> -16-Methyloctadecanoic		34.2
<i>dl</i> -16-Methyloctadecanoic	35.8	28.0

Spiral structures have been proposed for rubber and polychloroprene,¹¹ polyvinyl chloride, polyisobutylene, polyvinylidene chloride and other linear polymers.¹² The evidence for such forms resides chiefly in the observance of axial identity periods not consistent with a planar zig-zag arrangement. Polyethylene, with no substituents, is planar. However, polyoxymethylene¹² appears to be

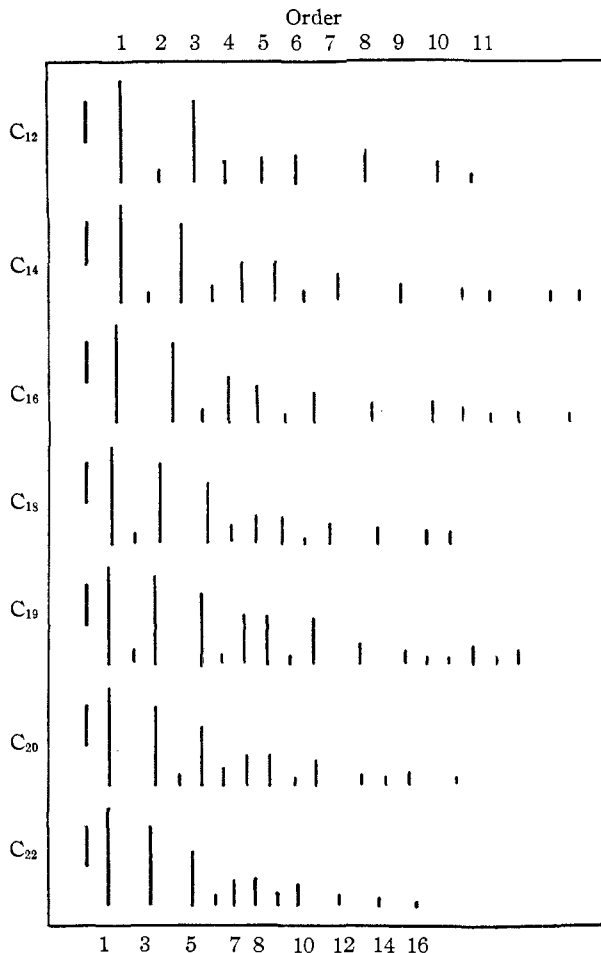
(11) C. W. Bunn, *Proc. Roy. Soc. (London)*, **180A**, 40 (1942).(12) M. L. Huggins, *J. Chem. Phys.*, **13**, 37 (1945).

Fig. 6.—Intensity distributions of the long spacing X-ray reflections of the iso amides. The visually estimated intensities are indicated by the heights of the lines.

spiral, and polyoxyethylene¹² appears to form a non-uniform spiral. Some N-methyl substituted

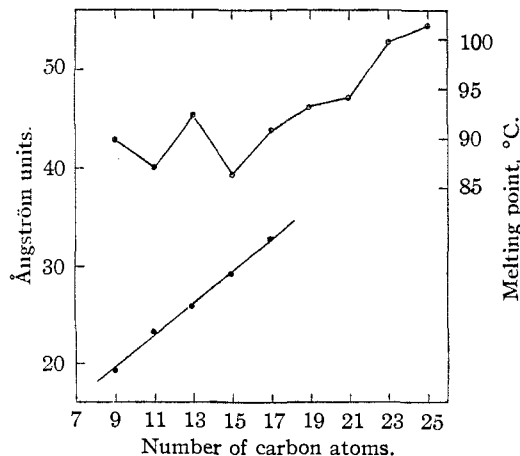


Fig. 7.—The long crystal spacings and melting points of the amides of the anteiso acids from wool fat as a function of carbon content: upper curve, O—O, long crystal spacings; lower curve, ●—●, melting points.

linear polyamides of the nylon type have exhibited abnormally short axial spacings.¹³ The authors have assumed a planar chain configuration and have attributed the shortening to a twisting of the polar groups from the molecular plane and a consequent alternate folding at the polar layer.

It is obvious that structural interpretation of homologous series of monomeric compounds or of fibrous polymers based chiefly on long crystal spacings or axial identity periods, although highly suggestive, are limited. A more detailed analysis is in order.

Experimental

I am indebted to Dr. A. W. Weitkamp and the Research Laboratories of the Standard Oil Company of Indiana for making available the samples of the branched chain fatty acids isolated from wool. The amides used in these studies were prepared from the acids in 50-mg. runs by way of the acid chlorides and ammonia. They were recrystallized from dilute methanol. In all cases the melting points were redetermined and found to agree closely with the values presented by Weitkamp.

The long crystal spacings were obtained from thin films of polycrystalline aggregates. The preparations were mounted on a goniometer-head and oscillated in the X-ray beam at reflection angles of 0 to 20°. A copper target was employed and the radiation was filtered through nickel foil. Exposures ranged from 5 to 15 milliampere hours at about 40 kilovolts. The cylindrical camera had a specimen to film distance of 51.2 mm.

(13) W. O. Baker and C. S. Fuller, *THIS JOURNAL*, **65**, 1120 (1943).

The films of the free acids were prepared by melting a few milligrams of the material between 1 cm. square glass microscope coverslips and allowing the melt to cool slowly from one end in a steep temperature gradient maintained by a hot resistance wire. This procedure accentuated the flat crystal habit and yielded a partially oriented polycrystalline film which remained coherent after removal of one of the cover slips. Identical spacings were obtained from lightly pressed aggregates of crystals obtained directly from solvents. However, diffraction photographs obtained from the latter preparations showed fewer orders and more diffuse scattering.

In contrast, preparations of the amides crystallized from the melt yielded poor diffraction diagrams whereas excellent ones were obtained from pressed crystals from solvents. The latter preparations were slightly solvated and showed small spacing differences from the melted preparations. Since the very small differences were uniform throughout the series, they did not affect the results and were not further investigated. Due to their small size, attempts to obtain rotation and Weissenberg projections of single amide crystals have so far been unsuccessful although it is hoped that such data will eventually be obtained.

Summary

The long crystal spacings of the iso series of fatty acids of wool fat increase linearly with carbon content. Both the spacings and diffraction patterns provide clear evidence of homology. The long crystal spacings of the iso amides show the same peculiar periodic sequence as the melting points. The results are discussed in terms of a spiral chain configuration.

ST. LOUIS, MISSOURI

RECEIVED MAY 15, 1947

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

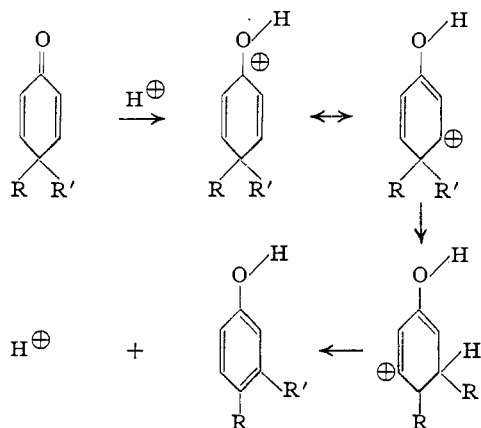
The Dienone-Phenol Rearrangement

By RICHARD T. ARNOLD, JAY S. BUCKLEY, JR., AND JOHN RICHTER.

Rearrangement of semibenzenes into alkylbenzenes has been studied in some detail by v. Auwers and co-workers.¹ These reactions are now regarded as typical examples of pinacol or neopentyl type rearrangements.

In our opinion the dienone-phenol rearrangement observed by Clemo in the conversion of santonin to desmotroposantonin² and more recently by Inhoffen³ and co-workers in the cholestanone and androstenone series is mechanistically the same as the semibenzene-alkylbenzene rearrangement discussed above. These reactions are acid catalyzed and proceed under the same general experimental conditions.

Wilds and Djerassi⁴ recently published the first example of this rearrangement in which the structure of both the starting compound and product of the reaction were established by an independent synthesis.



In this paper is reported a new example which, because of the high yields involved, represents a convenient synthesis of 3,4-dialkyl-1-naphthols. Reaction between γ -methylvalerolactone (I, R = CH₃) and benzene to form 4,4-dimethyl-1-tetralone (II) proceeded smoothly in the presence of

(1) v. Auwers and Ziegler, *Ann.*, **425**, 217 (1921).

(2) Clemo, *J. Chem. Soc.*, 1110 (1930).

(3) Inhoffen, Zuhlsdorf and Huang-Minlon, *Ber.*, **73**, 451 (1940).

(4) Wilds and Djerassi, *THIS JOURNAL*, **68**, 1712 (1946).