might be raised whether here, too, a diradical is formed which readily forms a six-membered ring rather than adding further olefin units. The insensitivity of the Diels Alder reaction to medium and to polar catalysts is in keeping with such a biradical intermediate, while the ineffectiveness of free radical sources as catalysts presents no difficulty since they produce single radicals. On the other hand, the transition state of the Diels–Alder reaction has usually been pictured as involving the simultaneous formation of two new bonds. However, the close parallel between the resonance forms advanced by Woodward[27] for the Diels–Alder reaction and structures such as II suggest that, in either case there is a very close mechanistic parallel between the two.

Acknowledgment.—The author wishes to thank Dr. Frank R. Mayo and Dr. Max Matheson for their interest and advice in the preparation of this paper.

Summary

Kinetic expressions have been developed for the

(27) Woodward, THIS JOURNAL, **64**, 3058 (1942).

over-all rate of copolymerization of two monomers which are in agreement with those of Melville, Noble and Watson,[7] and, which, when the rate of chain initiation is known, contain only one unknown parameter.

Experimental determination of rates of polymerization, using 2-azo-bis-isobutyronitrile as a constant radical source, show reasonable agreement with theory for the systems styrene–methyl methacrylate, styrene–methyl acrylate, and styrene–vinyl acetate.

In both the first two pairs a relatively rapid cross-termination reaction is detected, and is suggested as arising from a "polar effect" in radical coupling reactions parallel to that producing alternation in copolymerization.

Rate measurements of the rates of *uncatalyzed* copolymerization of styrene–methyl methacrylate indicate a bimolecular initiation reaction involving one molecule of each monomer, and more rapid than the bimolecular initiation in either monomer alone. The analogy to the Diels–Alder reaction is pointed out.

Optical, Crystallographic, and X-Ray Diffraction Data for Limonin and Some of its Solvates

BY F. T. JONES AND K. J. PALMER

During attempts to prepare pure limonin (C_{26}-$H_{30}O_8$) by extraction from citrus fruits,[1b] crystalline products were obtained by the addition of methanol to the methylene chloride solution of the purified limonin. A plate type and two prismatic types of crystals were usually present in the fresh product, but the two prismatic types would change to the plate type on standing a day or two in contact with the saturated solution.

Microscopic observation of behavior plus X-ray tests as reported below have shown that the three kinds of crystals are unsolvated limonin and two solvates of limonin. Analyses reported by Emerson[1] show that the two solvates are limonin monomethylene chloride solvate and limonin hemimethylene chloride solvate. The properties of limonin acetic acid solvate are also reported.

Microscopical Examination and Optical Properties.—All data reported below were obtained at 25° except where otherwise noted. Refractive indices were obtained by immersion methods with sodium light. In some cases it was necessary to mount crystals on a stage goniometer in order to obtain the principal refractive indices and

(1a) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(1b) Emerson, THIS JOURNAL, **70**, 545 (1948).

to determine the optic orientation. Table I lists the optical properties of all the compounds except limonin hemimethylene chloride solvate, which is too unstable to determine accurately.

Limonin.—Crystals of this compound are shown in Figs. 1 and 2. When limonin is recrystallized from hot ethanol, methanol, butanol, or acetone, crystals of the stable plate type are obtained, but the habit may vary considerably with rate of growth, nature of the solvent, and presence of impurities. Rapid growth favors the very thin rhomb-shaped plates and hexagonal forms which tend to grow in laminated aggregates (Fig. 1). Slow growth favors the thick plates (Fig. 2) with beveled edges replacing the acute ends of the other type. These two types of crystals were at first thought to be different in composition, but a determination of their optical properties proved that they are identical.

When a cautery needle is held close above the cover glass over a few crystals of limonin, the crystals melt without transformation. The viscous melt becomes vitreous if cooled rapidly, but birefringent bladed crystals will grow if the melt is cooled slowly. Such crystals were not investigated further.

The optical properties reported for limonin by

TABLE I

OPTICAL PROPERTIES OF LIMONIN AND ITS SOLVATES

| Substance | $N^{25}_D{}^\circ$ | | | 2E | 2V calcd. | | Dispersion | Opt. char. | Crystal | |
	α	β	γ		(d)	(e)			Syst.	Class
Unsolvated plates[a]	1.557	1.562	1.582	87°	53°	54°	(r > v) faint	+	Or. Rh.	6
Monomethylene chloride solvate[b]	1.540	1.543	1.551	108°	63°	62°	(r > v) faint	+	Or. Rh.	6
Monoacetic acid solvate[c]	1.543	1.545	1.553	83°	51°	52°	(r > v) mod.	+	Or. Rh.	6

[a] Ax. plane bisects acute plate angle. Bx_0, normal to plate, is α. [b] Ax. plane, Bx_0 and α are lengthwise. Bx_a bisects obtuse edge angle of 101°. Ordinary views give $\beta' = 1.546$. [c] Ax. plane, Bx_a and γ are lengthwise. Bx_a bisects acute edge angle of 75°. Ordinary views give $\beta' = 1.544$. [d] Sin $V = \sin E/\beta$. [e] Cos$^2 V = \alpha^2(\gamma^2 - \beta^2)/\beta^2(\gamma^2 - \alpha^2)$.

Winchell[2] are incomplete. The two indices reported as alpha and gamma were determined on plates similar to those shown in Fig. 1. The index reported as alpha is actually beta. All views show symmetrical extinction. The crystal system is orthorhombic. Class 6, (enantiomorphic), is confirmed by etch figures. This is consistent with the optical activity of limonin. Figure 3 shows the principal views and optic orientation.
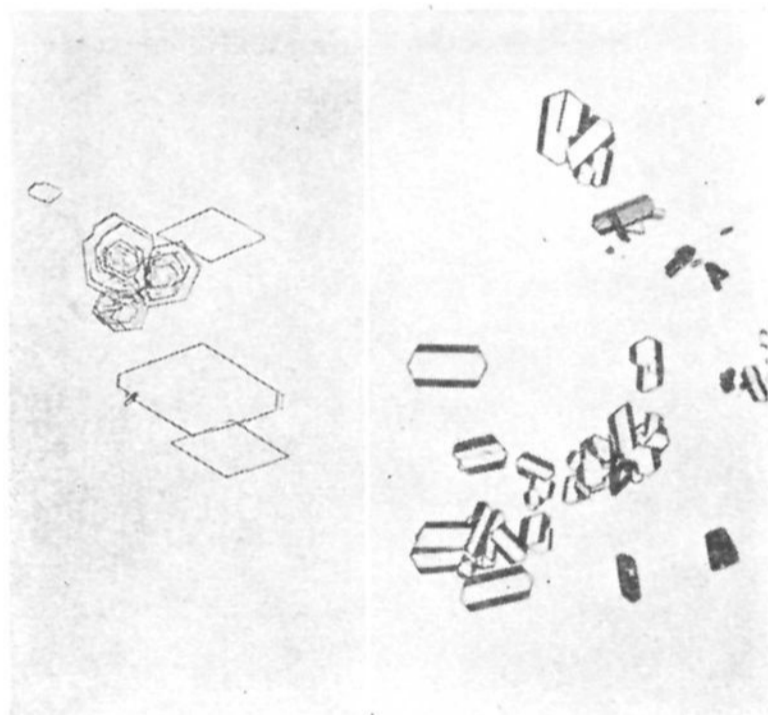
causes the crystals to melt with some bubbling. If the crystals are fresh, they will burst when heated, before melting. The resulting melt behaves like that from unsolvated limonin. When
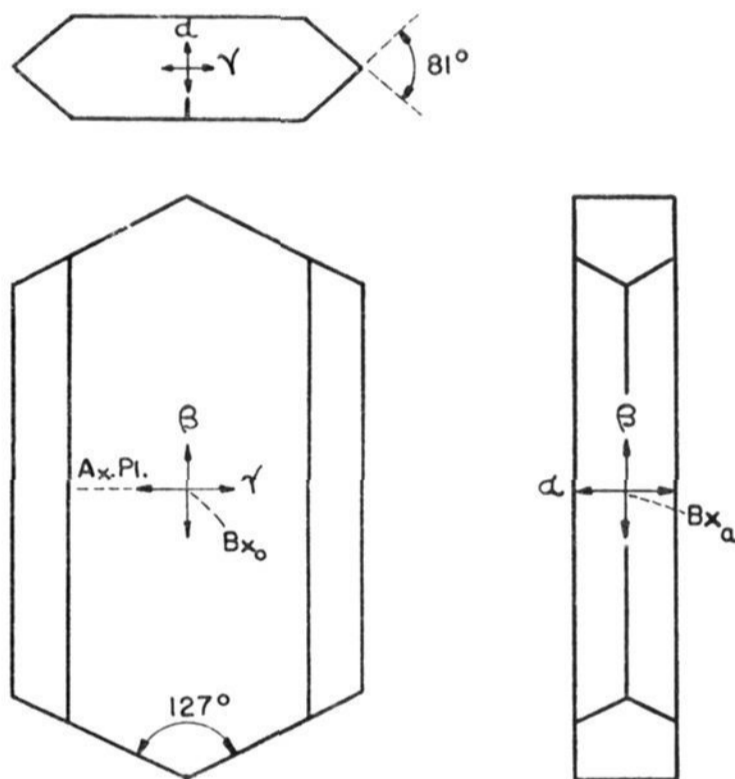

Fig. 3.—Limonin.

Fig. 1.—Limonin from alcohol rapid crystallization.

Fig. 2.—Limonin from butanol slow crystallization.

placed in immersion oil the clear crystals develop a more highly birefringent outer layer which slowly increases in thickness until a completely transformed pseudomorph of the original crystal re-

Limonin Monomethylene Chloride Solvate.—Limonin solvated with one mole of methylene chloride forms colorless prismatic crystals which are five to ten times as long as they are wide, depending on conditions of growth. The crystals are similar in appearance to those shown in Fig. 4. When these crystals are left uncovered at room temperature overnight the clear crystals begin changing to white, opaque, porcelain-like, pseudomorphs of the original crystals. The transformation usually begins at one or two spots or on one end and creeps through the crystal in a few hours. If these transforming crystals are heated with a cautery needle, the transformation will be completed in a few seconds. Further heating

(2) Winchell, "Optical Properties of Organic Compounds," University of Wisconsin Press, Madison, Wisconsin, 1943.
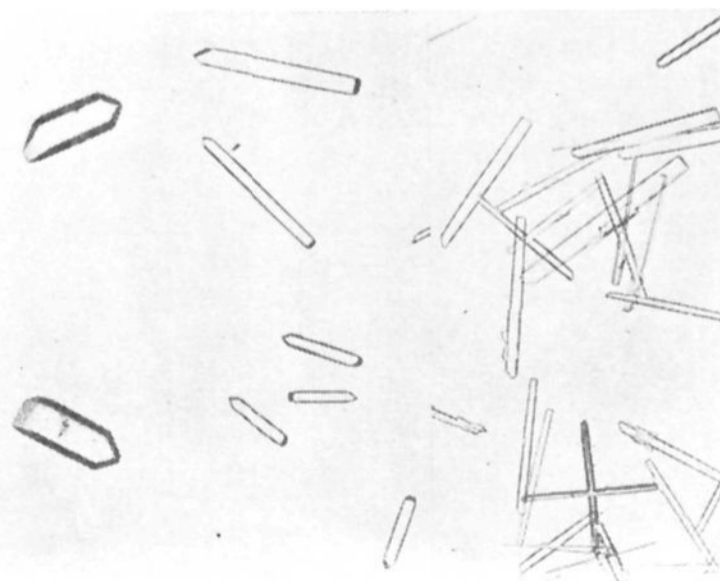

Fig. 4.—Limonin–acetic acid solvate.

mains. This process requires a day or two at room temperature. The new phase is assumed to be unsolvated limonin resulting from loss of methylene chloride. X-Ray powder diffraction tests made on the procelain-like pseudomorph prove that it is unsolvated limonin. A few crystals of the fresh solvate crushed in a drop of water become crusted over in a few minutes and crystals of the unsolvated limonin like those shown in Fig. 2 grow among the fragments.

All of the observations above led to the conclusion that the prismatic crystals were an unstable solvate. The analysis reported by Emerson[1b] confirmed this conclusion and provided the composition.

The birefringence is weak for ordinary views. The slow ray is always crosswise of the crystals. The extinction is symmetrical for all views. Crystals lying on a prism face show an interference figure intermediate between the acute bisectrix and the optic normal. The crystal system is orthorhombic.

Limonin Hemimethylene Chloride Solvate.— Limonin thought to be solvated with one-half mole of methylene chloride forms colorless, prismatic crystals similar in appearance to those shown in Fig. 4. These crystals behave like those of the monomethylene chloride solvate except that they lose their methylene chloride of crystallization more rapidly under corresponding conditions. The new phase which appears on the periphery when these crystals stand in oil has a much higher birefringence and the slow ray in the new phase is crosswise instead of lengthwise, as it is in the original crystal. Extinction is symmetrical for all views. These crystals can be distinguished from the monomethylene chloride solvate by their very weak birefringence and the fact that their slow ray is lengthwise instead of crosswise. The refractive index of the slow ray in the ordinary view before noticeable transformation has occurred is 1.542 ± 0.002. The interference figure obtained from this view was too hazy and indistinct to permit certain recognition of the optic orientation, but the axial plane was probably lengthwise and inclined to the axis of the microscope. The crystal system is orthorhombic.

Limonin–Monoacetic Acid Solvate.—Recrystallization of limonin from glacial acetic acid yielded crystals of the solvate previously reported.[3] These crystals (Fig. 4) are similar in appearance to the methylene chloride solvates; however, they did not show any signs of loss of solvate after standing uncovered for a week at room temperature. Decomposition to opaque white pseudomorphs was observed after a month in air but not in a closed container. They did not change noticeably in oil during determination of their refractive indices. When warmed in water on a slide, they did decompose slowly, as indicated by the appearance of crystals like those of Fig. 2 and by crusting over of the original crystals.

(3) Geissman and Tulagin, *J. Org. Chem.*, **11**, 760 (1946).

The birefringence is moderate for ordinary views of crystals lying on a prism face. Such views give interference figures showing the axial plane lengthwise of the crystal and slightly inclined from the optic normal toward the obtuse bisectrix. The slow ray is lengthwise of the crystal. End views, when obtainable, show symmetrical extinction and give acute bisectrix interference figures by conoscopic observation. The crystal system is orthorhombic.

If any of the three solvates is obtained in preparative work, it can be converted to the stable plate type crystals of limonin by recrystallizing from hot methanol or by warming crushed crystals in a drop of water on a microscope slide, thus making recognition certain.

X-Ray Diffraction Data.—X-Ray diffraction photographs of single crystals of limonin and limonin monoacetic acid solvate have been taken with a Weissenberg camera. Copper radiation ($\lambda = 1.542$ Å.) filtered through a thin nickel foil was used. The X-ray data obtained have been summarized in Table II, which includes the dimensions of the unit cell and the refractive index parallel to each crystallographic axis. It also in-

TABLE II

X-RAY DIFFRACTION DATA ON LIMONIN AND ITS MONO-ACETIC ACID SOLVATE

Space Group D_2^4—P $2_12_12_1$; 4 molecules per unit cell for both.

Substance	Unit cell, Å. units			Density, g./cc.	
	a	b	c	Calcd.	Obs.
Limonin	14.53//α	17.75//γ	8.88//β	1.364	1.366
Monoacetic acid solvate	12.75//β	16.85//α	12.40//γ	1.318	1.328

cludes the space group, number of molecules per unit cell, density as determined by flotation in an ethylene bromide–toluene mixture, and value of the calculated density. Density of the solvate was calculated on the basis of one molecule of acetic acid per limonin molecule. The good agreement between calculated and observed densities shows that this assumption must be correct.

The best chemical evidence indicates that limonin has one carboxyl group, at least two (and probably three) lactone groups, and two (and probably three) ether groups.[1b] In addition there are probably two carbon–carbon double bonds. The comparatively low values of the refractive indices suggests that there is no extensive conjugation in the molecule. This premise is supported by the low absorption in the ultraviolet region.[1b]

The value 8.88 Å. for the c axis suggests that the limonin molecule is comparatively flat. From the fact that only the c axis spacing increases in the acetic acid solvate, it is also apparent that the polar group responsible for the solvation (probably the carboxyl group) projects out in the c axis direction.

In order to aid in the identification of limonin

and its acetic acid solvate, the interplanar spacings and visually estimated intensities were obtained from X-ray powder photographs but are omitted in order to save space.

Acknowledgment.—We wish to thank Dr. O. H. Emerson for the pure limonin and the limonin solvates, and Merle Ballantyne for the X-ray photographs.

Summary

Optical and crystallographic data are given for limonin, limonin monomethylene chloride solvate and limonin monoacetic acid solvate. Partial data are given for limonin hemimethylene chloride. The unit cell size, space group, and density are given for limonin and limonin monoacetic acid solvate.

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Surface Tensions and Refractive Indices of the Perfluoropentanes

BY GILSON H. ROHRBACK AND GEORGE H. CADY

Considerable interest has recently been shown in the physical properties of fluorocarbons for the testing and advancing of theories of the liquid state. It is known that the value of many of the properties related to the intermolecular forces are much lower than in the corresponding hydrocarbons, *viz.*, surface tension, viscosity, dispersion, etc. Careful measurements of such quantities for the perfluoropentanes should be of particular interest as these compounds are liquid at room temperature and are not as yet too complicated in structure for application to theory.

This research is a continuation of the program of the determination of physical properties of the perfluoropentanes; densities, melting points, transition temperatures and viscosities having been previously measured.[1]

Experimental

Indices.—Refractive indices were determined at 15° for the compounds n-C_5F_{12}, iso-C_5F_{12}, cyclo-C_5F_{10}, as well as for the two mono-hydrogen compounds n-C_5HF_{11}[1a] and cyclo-C_5HF_9. In order to obtain dispersion values, a wide range of wave lengths in the visible region was employed. Since the indices were too low to be measured by the refractometers available, a hollow prism containing the liquid to be studied was mounted in a spectroscope and the refractive index measured by the method of minimum angle of deviation. All readings were taken in a room cooled to 15°, each sample being allowed to stand for about one-half hour inside the prism, to which an airtight cap had been fitted, before measurements were commenced.

The magnitude of the angle of the prism was determined directly by measuring the angle of the reflected light from its inner faces. The value so determined was 60°06′. As a check on this value the n_D indices of water and carbon tetrachloride were determined using this prism. The comparison with the readings using an Abbe refractometer on the same samples as well as with literature values are as follows:

	Prism	Abbe	Literature	Temp., °C.
H_2O	1.3327	1.3326	1.3326[2]	24
CCl_4	1.4583	1.4582	1.4582[3]	24

Surface Tension.—The surface tension was measured by the capillary rise method. Due to its very small mag-

nitude a capillary was chosen with a diameter of only 0.1614 mm. A uniform section of this tubing was selected by the usual method of observing the length of a mercury bead. An operating section of about 8 cm. was marked off with scribed markings and the tube was calibrated by observing the rise of pure water in the capillary. A total of ten determinations within the marked section gave an average rise of 18.43 cm. at 21.8°; the mean variation from this value being 0.014 cm. Using the expression $\gamma = 75.68 - 0.138t$[4] as a standard, the radius of the tube was calculated to be 0.0807 mm. Similar calculation using benzene as the reference liquid ($\gamma_{20°} = 28.80$[5]) gave a value which was 0.25% higher, while direct measurements by a weighed mercury bead yielded a radius 0.3% lower. Therefore, because of the reliability of the water sample in both purity and surface tension value, the radius was taken to be 0.0807 mm.

After calibration the capillary was cut and fitted into the apparatus as pictured in Fig. 1. Since Richards and Coombs[6] had previously shown that the tube containing the main bulk of the liquid should be at least 3.3 cm. wide in order to make the liquid rise negligible, tube A was made 4.1 cm. in diameter; a loaded glass sinker was included to diminish the volume of liquid required. The capillary was well held into the smaller side tube by means of a tight fitting rubber sleeve which further permitted the capillary to be raised and lowered for measurements at various levels within the calibrated region. The top end of the capillary was vented back into the main chamber by means of a looped rubber tube which allowed easy vertical movement in the side-arm. The entire apparatus could be evacuated and filled by distillation.

After filling, the apparatus was mounted in a thermostat. The height of the liquid in the large tube of the apparatus and in the capillary was read by means of a cathetometer.

Four compounds were thus examined for capillary rise over varying temperature ranges from 0 to 45°, the upper value being determined in each case by the boiling point. In addition to the three perfluoropentanes, n-C_7F_{16}[6a] was also examined for comparison purposes.

Experimental Results

Indices.—The results of the several runs are recorded in tabular form in Table I with the plot of the same data given in Fig. 2.

(4) W. D. Harkins, Chapter VI, A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, New York, N. Y., 1945.

(5) W. D. Harkins and F. L. Brown, THIS JOURNAL, **41**, 503 (1919).

(6) T. W. Richards and L. B. Coombs, *ibid.*, **37**, 1656 (1915).

(6a) This sample of perfluoro-n-heptane was generously furnished by R. D. Fowler, Johns Hopkins University. It was redistilled through an 82-plate column, only the middle cut being used in this research.

(1) L. L. Burger, Thesis, University of Washington, 1948.

(1a) Very probable H is on second carbon.

(2) L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. of Standards*, **20**, 419 (1938).

(3) E. Pohlaronini, *Bull. Soc. Chim. Belg.*, **36**, 533 (1927).