ing between the silver atoms and the oxygen atoms is staggered in such a way that there are strong forces in both the *b* and *c* directions. This is in agreement with the observed growth of the crystals.

A preliminary report on the structure of silver carbonate[3] follows: Laue and rotation pictures showed the crystals to be monoclinic with a_0 = 4.83 Å., b_0 = 9.52 Å., c_0 = 3.23 Å., β = 92.7°, z = 2 (calcd. 1.99). The probable space group is C_2^2-$P2_1$. Patterson and Fourier analysis of (*hk*0) data gives positions for the silver atoms and probable positions for the carbonate groups. The silver atoms are surrounded by deformed tetrahedra of oxygen atoms at about 2.3 Å. The binding is somewhat similar to that in potassium silver carbonate, there being a staggered arrangement of bonds between the silver and oxygen atoms.

The table given by Helmholz and Levine[10] can now be extended:

Table III

Compound	Ag-O,[a] Å.	Radius Sums		Color
		Ionic	Covalent	
$AgClO_3$[11]	2.51	2.46	2.19	Colorless
Ag_2SO_4	2.50	2.46	2.19	Colorless
$KAgCO_3$	2.42	2.46	2.19	Colorless
Ag_3PO_4	2.34	2.46	2.19	Yellow
Ag_3ASO_4	2.34	2.46	2.19	Deep red
Ag_2CO_3	2.30	2.46	2.19	Yellow
Ag_2O	2.06		2.02	Brown-black

[a] Average distance.

The correlation between the color and the bond distance is in reasonable accord with the rule of Pitzer and Hildebrand.[4] In view of the nature of the absorption process,[12] it seems probable that the *change* in absorption when, for example, silver is substituted for sodium in salts of these acids, rather than the color of the silver salt itself, should serve as a criterion for the amount of covalent character, in crystals of the type considered here. The apparent discrepancies in Table III of potassium silver carbonate and silver arsenate can be explained on this basis, and would lead, in the case of silver arsenate, to the reasonable conclusion that the tendency of the arsenate group to share electrons is greater than that of the phosphate group.

Summary

The crystal structure of potassium silver carbonate has been determined. The crystal is orthorhombic holohedral, with a_0 = 20.23 Å., b_0 = 5.75 Å., c_0 = 5.95 Å. The space group is D_{2h}^{27}-*Ibca*. The Ag-O bond distance was found to be 2.42 Å., and this is discussed in relation to other silver salts, including silver carbonate, for which a preliminary structure is given. The application of the rule of Pitzer and Hildebrand to the probable nature of this bond is also discussed.

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[10] L. Helmholz and R. Levine, This Journal, **64**, 354 (1942).

[11] I. Naray-Szabo and J. Pocza, *Z. Krist.*, **104**, 28 (1942).

[12] G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice Hall, New York, N. Y., 1939, Chapter VI.

Pasadena, Calif. Received October 11, 1943

[Contribution from the Chemical Laboratory of the University of Missouri]

Normal and Pseudo Structures of 8-Benzoyl-1-naphthoic Acid and Derivatives[1,2]

By H. E. French and J. E. Kircher

An earlier paper from this Laboratory[3] gave evidence for both the symmetrical and the unsymmetrical forms for 1,8-naphthalyl dichloride. This work has now been extended to the 8-benzoyl-1-naphthoic acid and certain of its derivatives.

8-Benzoyl-1-naphthoic Acid.—This acid was prepared by the method of Mason.[4] Upon crystallization from ethanol, 70% acetic acid, or chloroform, we obtained a product melting at 110°, as reported by Mason. From xylene, cyclohexane or toluene, the substance melted at 129–130°, checking the melting point reported by Knapp.[5] A sample of the 110° melting material heated to 90° for four hours under a watch glass was found to melt at 154°. From all of these samples, material of melting point 110° or 129–130° could be obtained by crystallization from the proper solvent.

Absorption curves were plotted for the acids melting at 110° and 129°, in chloroform solution, and for the 129° variety after refluxing in cyclohexane solution for twenty-four hours. The curves were all of the same form, with maximum and minimum points in the same regions. These maximum and minimum points are given in Table I. These curves for the acid are similar to the curve for diphenylnaphthalide, and bear no resemblance to the curve for dibenzoylnaphthalene which shows only one minimum and one maximum. Data for these curves are also given in Table I.[6]

Diphenylnaphthalide, ditolylnaphthalide and naphthalic anhydride, all of which have a ring structure across the 1,8 positions, were found to

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[1] This paper is a summary of part of the thesis material submitted by Dr. Kircher to the graduate faculty of the University of Missouri.

[2] The material in this paper was presented at the meeting of the American Chemical Society at Detroit, Mich., in April, 1943.

[3] French and Kircher, This Journal, **63**, 3270 (1941).

[4] Mason, *J. Chem. Soc.*, **125**, 2116, 2119 (1924).

[5] Knapp, *Monatsh.*, **67**, 332 (1936).

[6] The spectroscopic data were determined by Dr. Victor Ells, University Spectroscopist for the University of Missouri.

TABLE I

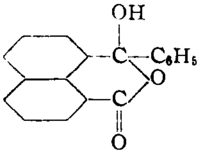
MAXIMUM AND MINIMUM POINTS FOR 8-BENZOYL-1-NAPHTHOIC ACID AND DERIVATIVES

Compound	Min., Å.	Max.	Min.	Max.	Min.	Max.
110° acid in chloroform	2710			3115	3252	3289
129° acid in chloroform	2718			3120	3246	3297
129° acid in cyclohexane, reflux 24 hr.	2661			3081	3221	3252
Acid chloride	2730	2961	3000	3074	3214	3251
Diphenyl-naphthalide	2675			3092	3215	3275
Pseudo ester	2655			3085	3200	3259
Normal ester	2700	2946				
Diethyl naphthalate	2665	2950				
1,8-Dibenzoyl-naphthalene	2754	2910				

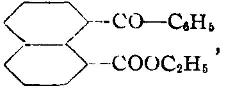
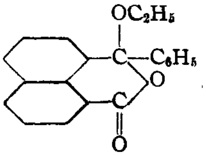
Absorption spectra measurements were made in cyclohexane solution unless otherwise noted.

show a blue fluorescence under ultraviolet light, while the ethyl ester of 8-benzoyl-1-naphthoic acid and 1,8-diethylnaphthalate, which do not possess this closed structure, appear gray-white under the ultraviolet lamp. The samples of 8-benzoyl-1-naphthoic acid of various melting points all showed the blue fluorescence, as did 8-toluyl-1-naphthoic acid.

It is concluded from the evidence of absorption spectra and ultraviolet fluorescence that the acid in solution is very largely, if not completely, in the form of the cyclic compound of the structure



Ethyl Derivatives of 8-Benzoyl-1-naphthoic Acid.—Mason[4] prepared the acid chloride by the action of thionyl chloride on the acid of melting point 110°. The chloride was crystallized from benzene, and melted at 125–127°, and gave with ethyl alcohol an ethyl derivative melting at 166°. We repeated these reactions and obtained results which corresponded to those of Mason.

We also obtained an ethyl derivative by the action of the silver salt of the acid on ethyl iodide. This ethyl derivative melted at 134°. A mixture of the two ethyl derivatives gave a melting point depression of 15°. Without question the derivative melting at 134° was the normal ester,  $-CO-C_6H_5$, $-COOC_2H_5$, and the product obtained from the crystallized acid chloride and ethyl alcohol possessed some other structure, probably that of the pseudo ester  Analyses for carbon and hydrogen showed the two compounds to be isomeric.

The normal ester, melting at 134°, gave the gray-white fluorescence of the open compounds, under the ultraviolet light, while the pseudo ester, melting at 166°, showed the blue fluorescence characteristic of the closed structure across the 1,8 positions.

Experiment with a known mixture showed that nearly quantitative separation of the two isomers could be accomplished by chromatographic adsorption on alumina from a benzene–petroleum ether solution. The crude product from the reaction of ethyl alcohol on the recrystallized chloride was dissolved in the benzene–petroleum ether mixture and passed through the column of alumina. As in the case of the known mixture, the isomer melting at 134° was adsorbed in the first layer, and fluoresced gray-violet, while the isomer melting at 166° was adsorbed in the second layer, and fluoresced light blue. In these experiments the high melting ester predominated.

In certain experiments the chloride was prepared by the usual reaction but, instead of crystallizing from benzene, the excess of thionyl chloride was distilled off and the brown oil remaining was treated with absolute alcohol. The reaction here was very vigorous, quite unlike those in which the recrystallized acid chloride were used. When chromatographed, the same two ethyl derivatives were obtained, but with the low melting form predominating. The acid chloride used in these experiments was prepared in some cases from acid melting at 110° and in other cases from acid melting at 130°. The results, however, corresponded throughout as shown in the following table.

TABLE II

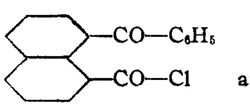
ETHYL DERIVATIVES OF 8-BENZOYL-1-NAPHTHOIC ACID

M. p., °C., acid	Reagent for chloride	M. p., °C., chloride	% ratio of isomers m. p. 166°/ m. p. 134°
110	$SOCl_2$	oil	15/85
110	$SOCl_2$	oil	5/95
110	$SOCl_2$	125	87/13
130	$SOCl_2$	oil	23/77
130	PCl_3	oil	33/67
130	$SOCl_2$	125	96/4

The recrystallized acid chloride with benzene and aluminum chloride gave diphenylnaphthalide in yields of from 25 to 50% of theoretical. No dibenzoylnaphthalene could be isolated from any of these reactions. When the acid chloride was used in the form of an oil, only hydrogen chloride and tars were obtained.

The absorption curve for the true ester corresponded to those of the diethylnaphthalate and the 1,8-dibenzoylnaphthalene, while the curve for the pseudo ester corresponded to that for the diphenylnaphthalide (see Table I). It is evident, then, that the ethyl derivative melting at 134° is the true ester and the one melting at 166° is the pseudo ester.

8-Benzoyl-1-naphthoyl Chloride.—As shown in Table II, the ratio of pseudo ester to the true ester in the reaction between the acid chloride and ethyl alcohol, can be practically inverted at will. There seems to be no doubt as to the existence of two chlorides represented by the formulas



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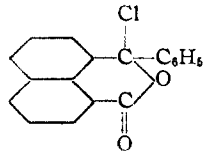

II

As pointed out in an earlier section of this paper, these chlorides differ in physical properties, one being an oil and the other a crystalline solid, as well as in the rates with which they react with ethyl alcohol. The recrystallized compound, no doubt represented by Formula II, yields diphenylnaphthalide in the Friedel–Crafts reaction, while the isomeric compound yields only tars and hydrogen chloride under the same conditions. The absorption curve for the chloride recrystallized from benzene was plotted and the maximum and minimum points are given in Table I. These points occur in the regions which characterize both the closed structures, such as diphenylnaphthalide, and the open structures, such as diethylnaphthalate. Results from the Friedel–Crafts reaction suggest the presence of the closed structure chiefly.

Experimental

The 8-benzoyl-1-naphthoic acid and its chloride were prepared by the method of Mason.[4] The diphenylnaphthalide was prepared as previously described.[5]

8-Benzoyl-1-ethyl Naphthoate.—Five grams of benzoylnaphthoic acid was dissolved in an excess of ammonium hydroxide after which the excess of ammonia was removed by boiling. To the neutral solution was added a slight excess of silver nitrate solution, and the white silver salt was filtered and dried.

The silver salt was placed in a 250-cc. conical three-neck flask equipped with reflux condenser and stirrer, and 17 cc. of ethyl iodide was added slowly. A vigorous reaction took place with the precipitation of silver iodide. After the reaction had subsided, the mixture was refluxed for thirty minutes. The silver iodide was repeatedly extracted with 20 cc. portions of boiling ethyl alcohol. On concentration of the solution the ester crystallized as white needles, m. p. 134°; yield, nearly quantitative.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.94; H, 5.26. Found: C, 78.43; H, 5.49.

8-Benzoyl-1-ethyl Naphthoate from the Acid Chloride.—Four grams of benzoylnaphthoic acid was treated with 4 cc. of thionyl chloride. After the initial vigorous reaction, the mixture was heated over a water-bath for thirty minutes, when the excess of thionyl chloride was distilled off, leaving an oily residue. To the residue 100 cc. of absolute alcohol was slowly added, whereupon a vigorous reaction took place. The solution was refluxed for an hour and then concentrated to 50 cc., and the white crystalline product filtered off. This solid material was then dissolved in benzene and chromatographed on alumina, after the addition of enough petroleum ether (b. p. 70–80°) to make the solution nearly saturated. The first major layer fluoresced gray-violet with only a small band showing a blue fluorescence. The gray-violet band was treated with alcohol and the material which crystallized melted at 128–130°. Repeated crystallizations from alcohol brought the melting point up to 134°; average yield 60%. *Anal.* Calcd. for $C_{20}H_{16}O_3$: C, 78.94; H, 5.26. Found: C, 79.22; H, 5.50. From the small layer showing blue fluorescence, the 3-phenyl-3-ethoxynaphthalide was obtained in about a 10% yield on extraction with alcohol.

3-Phenyl-3-ethoxynaphthalide.—The chloride of benzoylnaphthoic acid was prepared and crystallized from benzene as directed by Mason. The chloride was then treated with absolute ethyl alcohol, approximately 10 cc. per gram of chloride being used. There was practically no evolution of heat. The mixture was refluxed for approximately an hour. The chloride went into solution with some difficulty. Upon cooling the pseudo ester crystallized in colorless crystals melting at 166°. The average yield from several runs was about 60%. *Anal.* Calcd. for $C_{20}H_{16}O_3$: C, 78.94; H, 5.26. Found: C, 78.91; H, 5.43. In addition to the pseudo ester small amounts of the normal ester, melting at 134°, were also obtained.

1,8-Diethyl Naphthalate.—The silver salt of naphthalic acid was prepared by adding a slight excess of silver nitrate in aqueous solution to a solution of the sodium salt of the acid. A considerable excess of ethyl iodide was added as described in the preparation of 8-benzoyl-1-ethyl naphthoate. After the initial reaction had subsided the mixture was refluxed for one hour. The precipitated silver iodide was heated with ethyl alcohol and filtered, then washed repeatedly with 20 cc. portions of alcohol. The combined alcoholic solutions were concentrated and diluted with water. Upon cooling, the ester crystallized as white crystals, m. p. 54°.

1,8-Dibenzoylnaphthalene.—Two grams of 9,10-diphenylacenaphthene glycol[7] was dissolved in 50 cc. of dry benzene and a suspension of lead tetraacetate in benzene was added over a period of one hour, at room temperature. The solution was then refluxed for thirty minutes on the water-bath. After filtration the benzene was removed under reduced pressure. The solid material thus obtained was crystallized from dilute ethyl alcohol. The pure product melted at 186°.

Summary

1. 8-Benzoyl-1-naphthoic acids having melting points of 110, 129, and 154° have been obtained as allotropic forms. They are readily interconverted. The evidence points to the pseudo acid structure for the compound in solution.

2. The normal and pseudo ethyl derivatives of the acid as well as two forms for the acid chloride have been prepared.

Columbia, Mo. Received September 10, 1943

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[7] Bachmann, This Journal, 58, 1118 (1936).