

The following premises have emerged from the above discussion as a basis for the complete picture of the positions of the molecules of diphenyl derivatives. The diphenyl molecule is symmetrical about a center; dimesityl and hexachlorodiphenyl have no symmetry. The molecules in all cases lie with their length parallel or at a slight tilt to the *c* axis. The rings of carbon atoms are in each case probably staggered and have a thickness which is constantly 4.3 for the derivatives and 4.1 for diphenyl itself. The width across the ring is 5.6 for diphenyl, 7.9 for hexachlorodiphenyl and 8.1 for dimesityl and its diamino derivative. The respective lengths of these compounds are 9.5, 10.75, 11.1 and 11.3.

Discounting the staggering for the moment, there are the possibilities that the two rings may lie in the same plane, in planes at small angles to each other, or at right angles. The space considerations do not favor the first. The facts that the molecules are asymmetric and that they occupy the spaces given in the preceding paragraph lead to the conclusion that the two rings are in planes turned from each other at an angle of not greater than 45° in the 2,2',6,6'-derivatives of diphenyl, while the rings in diphenyl itself are coplanar.

Summary

1. Unique solutions of the crystal structure for diphenyl and five of its derivatives have been determined by rotating and oscillating crystal methods.
2. The possible size, shape and position of the molecules of these compounds are discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

SYNTHESIS OF QUINOLINE COMPOUNDS. VI. PREPARATION OF CERTAIN ACYLAMINO DERIVATIVES OF 8-HYDROXYQUINOLINE

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RECEIVED JULY 17, 1930

PUBLISHED JANUARY 12, 1931

The acyl derivatives of aminohydroxyquinoline described in this paper were prepared in connection with a study of the bactericidal action of quinoline compounds.

Experimental

The aminohydroxyquinoline (1 mole) and acetic anhydride (1.1 moles) were allowed to react in ether solution for three days at room temperature in the presence of finely ground sodium acetate, with occasional stirring. The ether was then evaporated and sufficient water was added to dissolve the sodium acetate. The product was filtered, washed and finally recrystallized. The yields were very good.

In general, these quinoline derivatives are sparingly soluble in water and ether, fairly soluble in benzene and very soluble in alcohol and chloroform. Their salts with mineral acids can be crystallized from alcohol and they are all soluble in water except the hydrochloride of 7-iodo-5-acetamino-8-hydroxyquinoline, which undergoes hydrolysis with separation of free base.

TABLE I

HYDROXYQUINOLINE DERIVATIVES

No.	Quinoline derivative	Form	Solvent	M. p., °C.
1	7-Iodo-5-acetamino-8-hydroxy-	Colorless needles	EtOH	212
2	5-Acetamino-8-hydroxy-	Colorless prisms	CHCl ₃	218-219
3	5-Acetamino-6-hydroxy-	Colorless needles	EtOH	278 (dec.)
4	7-Acetamino-5-methyl-8-hydroxy-	Pale yellow prisms	EtOH	203-204
5	7-Acetamino-5-methyl-8-acetoxy-	Colorless columns	C ₆ H ₆	222
6	5-Methyl-8-methoxy- ^a	Viscous yellow oil	B. p. 298-302 (773 mm.)	
7	7-Amino-5-methyl-8-hydroxy- ^d	Yellow prisms	Ether	141-142
8	5-Benzoylamino-8-hydroxy- ^e	Colorless plates	EtOH	237-238
9	7-Benzoylamino-5-methyl-8-benzoyloxy- ^f	Colorless columns	C ₆ H ₆	181

No.	Formula	Analyses, %		Name	Salt form	M. p., °C.
		Calcd.	Found			
1	C ₁₁ H ₉ O ₂ N ₂ I	N, 8.54	8.23	Hydrochloride	Yellow needles	196 (dec.)
2	C ₁₁ H ₁₀ O ₂ N ₂	N, 13.86	13.69	Acid sulfate	Yellow needles	263 (dec.)
3	C ₁₁ H ₁₀ O ₂ N ₂	N, 13.86	13.54	Acid sulfate	Colorless columns	...
4	C ₁₂ H ₁₂ O ₂ N ₂	N, 12.96	13.00	Neut. sulfate	Yellow needles	180
5	C ₁₄ H ₁₄ O ₃ N ₂	N, 10.85	11.02	Acid sulfate	Yellow plates	183
6	C ₁₁ H ₁₁ ON	Picrate ^b	Yellow needles from alc.	180-181
				Chloroplatinate ^c	Yellow prisms	224 (dec.)
7	C ₁₀ H ₁₀ ON ₂	C, 68.97	68.90	Picrate	Red needles from EtOH; dec. at 215-220° without melting	
		H, 5.75	5.56			
		N, 16.09	16.11			
8	C ₁₅ H ₁₂ O ₂ N ₂	N, 10.60	10.57	Acid sulfate	Yellow needles from EtOH	225-227 (dec.)
9	C ₂₄ H ₁₈ O ₃ N ₂	C, 75.39	75.54
		H, 4.71	4.83			
		N, 7.33	7.26			

^a Made by refluxing a methyl alcohol solution (30 cc.) of 5-methyl-8-hydroxyquinoline (15.9 g.) with methyl iodide (14.2 g.) and potassium hydroxide (5.6 g.).

^b Calcd. for C₁₁H₁₁ON·C₆H₅O₇N₃: C, 50.75; H, 3.48; N, 13.93. Found: C, 50.89; H, 3.74; N, 14.17. ^c Calcd. for (C₁₁H₁₁ON·HCl)₂PtCl₄: C, 34.92; H, 3.17; Pt, 25.82. Found: C, 34.68; H, 3.24; Pt, 25.78. ^d Prepared by reduction of 7-nitroso-5-methyl-8-hydroxyquinoline (4.2 g.) in glacial acetic acid (60 g.) by means of stannous chloride (12 g.) in concentrated hydrochloric acid (42 cc.); cf. Ganelin and Kostanecki, *Ber.*, 24, 3979 (1891).

^e Obtained in 91% yield by interaction of equimolecular amounts of 5-amino-8-hydroxyquinoline and benzoyl chloride in cold pyridine solution. ^f Prepared from 7-amino-5-methyl-8-hydroxyquinoline and benzoyl chloride in ether solution (at room temperature) in the presence of sodium acetate.

I desire to express my hearty thanks to Professor Hata for the interest which he has kindly taken in this work.

Summary

5-Acetamino-6-hydroxy-, 5-acetamino-8-hydroxy-, 7-iodo-5-acetamino-8-hydroxy- and 7-acetamino-5-methyl-8-hydroxyquinoline have been prepared and characterized.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE REDUCTION OF NAPHTHALENE BY ALKALI METALS IN LIQUID AMMONIA¹

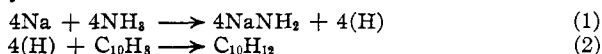
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RECEIVED JULY 26, 1930

PUBLISHED JANUARY 12, 1931

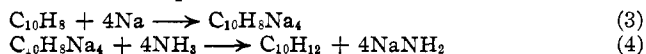
The reaction between sodium and naphthalene in liquid ammonia solution was first investigated by Lebeau and Picon² and the products which they obtained at 15° were sodium amide and tetrahydronaphthalene. These facts are equally open to two different interpretations.

I. It may be assumed that the naphthalene was reduced by nascent hydrogen generated by a reaction between the alkali metal and the solvent.



This hypothesis is analogous to that advanced by Kekulé, Kolbe, von Baeyer and others³ to explain reductions of organic substances with sodium amalgam and water.

II. The formation of tetrahydronaphthalene may also be attributed to a solvolytic action of the solvent upon an organo-alkali compound which was formed as an intermediate product.



This assumption is analogous to an alternative theory of amalgam reduction recently proposed by Willstätter, Seitz and Bumm.⁴

This reaction, therefore, is of especial interest as a test case for indicating the possibilities of wider application of the two general hypotheses.

Dipotassium⁵ and dilithium⁶ derivatives of naphthalene have been pre-

¹ Paper presented at the Cincinnati meeting of the American Chemical Society, September, 1930.

² Lebeau and Picon, *Compt. rend.*, **158**, 1514 (1914).

³ (a) Kekulé, *Ann. Suppl.*, **1**, 129 (1861); (b) Herrmann, *Ann.*, **132**, 75 (1864) (an account of work done in Kolbe's laboratory); (c) von Baeyer, *ibid.*, **269**, 145, 170, 174 (1892).

⁴ Willstätter, Seitz and Bumm, *Ber.*, **61**, 871 (1928).

⁵ Berthelot, *Ann.*, **143**, 98 (1867); *Ann. Suppl.*, **5**, 370 (1867); *Ann. chim.*, [4] **12**, 157, 205 (1867).

⁶ Schlenk and Bergmann, *Ann.*, **463**, 83 (1928).