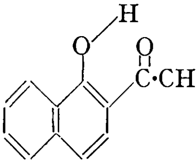
106. *Studies in Chelation. Part VI. Hydroxy-derivatives of Acetylnaphthalenes, Benzonitrile, and Carboxylic Esters.*

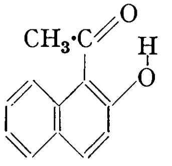
By Wilson Baker and G. N. Carruthers.

Hydroxyacetylnaphthalenes.—The method described in the preceding paper for detecting fixed double and single links in the aromatic nucleus of hydrindene has now been applied to the case of naphthalene. Much evidence has accumulated to show that naphthalene almost invariably reacts as if the bond between carbon atoms 1 and 2 was double, and that between carbon atoms 2 and 3 was single (for a summary of such evidence see Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1935, **57**, 1459), and that this applies to both rings simultaneously is shown by the remarkable behaviour of 2 : 7-dihydroxy-1 : 8-dialkylnaphthalenes, and 2 : 6-dihydroxy-1 : 5-dialkylnaphthalenes which do not couple with diazotised amines and whose allyl ethers do not undergo thermal rearrangement (Fieser and Lothrop, *loc. cit.*). This evidence definitely points to the symmetrical formula for naphthalene (as shown in formulæ I—IV) possessing a double bond common to the two rings. Nevertheless, an *op*-directing group in position 2 in the naphthalene nucleus does occasionally direct an entering substituent into position 3, thus indicating the possibility of a double bond between carbon atoms 2 and 3; examples are (1) the action of carbon dioxide on sodium β-naphthoxide at 280—290°, giving 2-hydroxy-3-naphthoic acid (Schmitt and Burkard, *Ber.*, 1887, **20**, 2702), (2) the bromination of 1-bromo-*p*-toluenesulphon-2-naphthalide in position 3 in pyridine solution (Bell, J., 1932, 2732), and (3) the production in poor yield of a bromobenzohydrindone by ring closure of 1-bromo-2-β-naphthylpropionyl chloride (Mayer and Sieglitz, *Ber.*, 1922, **55**, 1859). The physical evidence as to the structure of naphthalene is conflicting; for a brief discussion of previous work see Hampson and Weissberger (J., 1936, 331). These authors themselves conclude, as a result of the measurement of the dipole moments of chlorinated naphthalenes, that the C–Cl bonds are directed as from the centre of the rings, and that " if there is any fixation of the single and double bonds in naphthalene it is not revealed in the direction of the substituents." On the other hand, Bergmann and Hirshberg (J., 1936, 331), from a study of the dissociation constants of the chloronaphthoic acids, infer that the bond C_1 to C_2 is not identical with the bond C_2 to C_3, and Fries, Bestian, and Klauditz (*Ber.*, 1936, **69**, 715) conclude, from a comparison of the optical properties of *o*-divinylbenzene and naphthalene, that the symmetrical structure is most probably correct.

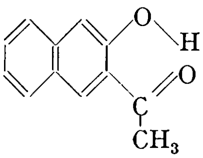
In order to see if any difference between the links C_1 to C_2 and C_2 to C_3 could be detected by chelation between hydroxyl and acetyl groups (which has been shown to depend on a double bond between the carbon atoms bearing these groups; for references, see preceding paper), the properties of the four isomeric hydroxyacetylnaphthalenes (I—IV) were investigated. If the symmetrical structure shown in (I—IV), which seems to be the most probable and is usually regarded as being due to the tendency for both rings to become as completely aromatic as possible, is quite rigid, it is clear that 2-acetyl-1-naphthol (I) and 1-acetyl-2-naphthol (II) should behave like typically chelated compounds, but that 3-acetyl-2-naphthol (III) should be non-chelated. To provide a reference compound which could not be chelated, the properties of 4-acetyl-1-naphthol (IV) also were examined. The following table gives some of the physical properties of these compounds:



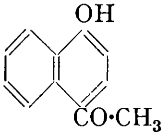
(I.)



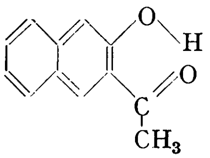
(II.)



(III.)



(IV.)



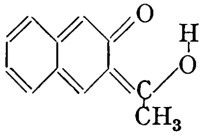
(V.)

	M. p., dry.	M. p., wet.	Depression.	Critical solution temp.
2-Acetyl-1-naphthol (I)	101°	99°	2°	>255°
1-Acetyl-2-naphthol (II)	64	62	2	*ca.* 234
3-Acetyl-2-naphthol (III)	112	106	6	>255
4-Acetyl-1-naphthol (IV)	197	153	44	*ca.* 212

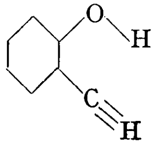
The only conclusion which can be drawn from these figures is that all three *o*-hydroxyacetylnaphthalenes (I), (II), and (III) are highly chelated compounds. 3-Acetyl-2-naphthol (III) shows a slightly greater depression of the melting point under water than (I) and (II), but on the other hand its critical solution temperature is higher than that of (II). Owing to darkening and decomposition above 250°, the critical solution temperatures of (I) and (III) could not be reached. The great difference between (I), (II), and (III) and the non-chelated compound (IV) is very striking.

The interpretation of the result in the case of 3-acetyl-2-naphthol (III) may mean that chelation between the hydroxyl and the acetyl group is sufficiently powerful to overcome the normal symmetrical arrangement of the naphthalene valencies, so that the molecule must assume the asymmetrical distribution of the bonds as shown in (V) in which one of the rings is *o*-quinonoid. In this connection, it is perhaps significant that 3-acetyl-2-naphthol (III and V) alone amongst the isomeric acetylnaphthols is a highly coloured compound, being bright yellow, and the fact that its methyl ether, in which chelation is impossible, is colourless points to the conclusion that the colour is due to some disturbance of the normal naphthalene structure set up by the process of chelation. On the other hand, it shows none of the properties of a true *o*-quinonoid compound—with bromine it yields a *monobromo*-derivative and not a tetrabromide, and it does not combine additively with maleic anhydride. Again, it would be difficult to account for the fact that 2 : 3-dihydroxynaphthalene does not yield a quinone on oxidation (see Marckwald, *Annalen*, 1893, **274**, 331; 1894, **279**, 1; Fries and Schimmelschmidt, *Ber.*, 1932, **65**, 1502; Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 5219) if 3-acetyl-2-naphthol actually possessed a fixed *o*-quinonoid structure. The explanation of these facts will probably ultimately be found in the phenomenon of resonance (Pauling and Wheland, *J. Chem. Physics*, 1933, **1**, 362; Sherman, *ibid.*, 1934, **2**, 488); the naphthalene molecule is conceived as a hybrid in which the symmetrical structure (as in I—IV) is the most important, followed in importance by the two asymmetrical structures (as in V). *o*-Quinonoid structures such as (V) and (VI) may be possible as important components of a resonance hybrid (a third component of which is III) which are not possible as the fixed structure of a molecule that does not exhibit resonance (*e.g.*, the unknown naphtha-2 : 3-quinone).

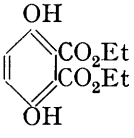
Hydroxybenzonitriles.—Examination of the physical properties of the three isomeric hydroxybenzonitriles has been made in order to find out if the *o*-compound (VII) is capable of chelation. The substance might contain a hydrogen bond between the oxygen atom and the nitrogen atom which carries the necessary lone pair of electrons; if this were so, then (VII) should possess abnormal physical properties compared with the *m*- and the *p*-isomer in which chelation is impossible (as is the case with nitrophenols, hydroxybenzaldehydes, etc.). Experiment showed clearly that the *o*-compound (VII) is in no way abnormal compared with the *m*- and the *p*-compound, as is shown in the following table:



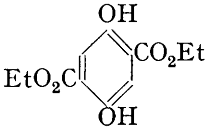
(VI.)



(VII.)



(VIII.)



(IX.)

	M. p., dry.	M. p., wet.	Depression.
o-Hydroxybenzonitrile	94·5°	42°	52·5°
m- ,, ...	82	31	51
p- ,, ...	113	61	52

It must, therefore be concluded that *o*-hydroxybenzonitrile is completely non-chelated. a conclusion which has also been reached by Hendricks, Wulf, Hilbert, and Liddel (*J. Amer. Chem. Soc.*, 1936, **58**, 1991), who found that it shows absorption in the infra-red characteristic of the hydroxyl group. They regard the non-chelation of this compound as due to the linear nature of the -C≡N group, owing to which the distance between the nitrogen and oxygen atoms must be rather more than 3 A., a distance greater than the normal length (about 2·6 A.) of a hydrogen bond between oxygen atoms, or between oxygen and nitrogen, a view with which the present authors are in agreement.

Hydroxy-carboxylic Esters.—Evidence as to whether chelation between the carboxylic ester grouping and hydroxyl depends upon the presence of a double bond between the two intermediate carbon atoms is conflicting. (1) In the aliphatic series there is strong evidence that the carbon–carbon double bond is essential. A direct comparison of the b. p.'s of acetoacetic ester (79°/18 mm.*) and β-hydroxybutyric ester (81°/18 mm.) does not appear to support this, but it must be remembered that, even at ordinary pressure, a considerable drop in the b. p. occurs in passing from an unsaturated ester $CHR{:}CH{\cdot}CO_2Et$ to the saturated ester $CH_2R{\cdot}CH_2{\cdot}CO_2Et$; where R is a simple alkyl group, the difference is on the average about 17°. Hence, if β-hydroxybutyric ester were chelated, it should have a b. p. of the order of 20° *lower* than that of acetoacetic ester, whereas in fact its b. p. is slightly higher. The general properties of β-hydroxybutyric ester leave no doubt that it is non-chelated: it is a somewhat viscous liquid, totally miscible with water, and gives no chelate metallic derivatives, properties which stand in strong contrast to those of acetoacetic ester. (2) In the aromatic series the fact that β-resorcylic acid and ester substitute in position 5 and not in position 2 would appear to indicate that fixation of the Kekulé forms as a result of such chelation does not take place as in the case of *o*-hydroxycarbonyl compounds (Baker, J., 1934, 1689), but such evidence is valueless if the reagent which is used to bring about the substitution is capable of combining with the carboxylic ester grouping (cf. the nitration of resacetophenone, discussed by Baker, *loc. cit.*, p. 1686). (3) Owing to the uncertainty of the evidence in the aromatic series, certain dihydroxydicarboxylic esters were examined, one of which should be doubly chelated if chelation fixes a double bond in the ring, and the others only singly chelated, just as in the case of 2 : 4- and 4 : 6-diacetylresorcinols (Baker, J., 1934, 1684). The compounds prepared were *ethyl quinol-*2 : 3*-dicarboxylate* (VIII), ethyl quinol-2 : 5-dicarboxylate (IX), and ethyl resorcinol-4 : 6-dicarboxylate. Attempts to prepare ethyl resorcinol-2 : 4-dicarboxylate were unsuccessful. If the double bonds are fixed by chelation, then (VIII) should be

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* This is actually the b. p. of the equilibrium mixture present under the particular experimental conditions, but this does not affect the reasoning which follows, as the b. p. of the pure enolic form (β-hydroxycrotonic ester) will be *lower* than this.

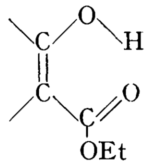
fully chelated, and (IX) and ethyl resorcinol-4 : 6-dicarboxylate incompletely chelated, which is not borne out by the depression of the m. p.'s of the substances under water :

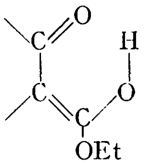
	M. p., dry.	M. p., wet.*	Depression.
Ethyl quinol-2 : 3-dicarboxylate (VIII)	85°	68°	17°
,, ,, -2 : 5- ,, (IX)......................	133	126	7
,, resorcinol-4 : 6-dicarboxylate	140	132	8

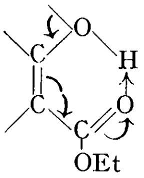
* It was ascertained that no hydrolysis occurred during these determinations.

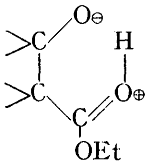
The evidence appears to show that (VIII), contrary to expectation, is less chelated than the other two esters.

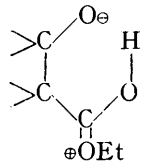
It is difficult to explain these facts. From the behaviour of β-hydroxybutyric ester and acetoacetic ester, it seems probable that the chelate form of the latter is a resonance hybrid mainly derived from the two forms shown in the partial formulæ (X) and (XI), corresponding to the older formula (XII). Other components of the resonance hybrid not dependent upon a carbon–carbon double bond are "zwitterion" forms (XIII) and (XIV) (recalling the mechanism of the association of simple hydroxylic substances, see Sidgwick, *Ann. Reports*, 1934, **31**, 42), which, however, appear to be of little importance in the aliphatic series, but may be of greater importance in the aromatic series.


(X.)


(XI.)


(XII.)


(XIII.)


(XIV.)

EXPERIMENTAL.

2-Acetyl-1-naphthol (I), prepared as described by Witt and Braun (*Ber.*, 1914, **47**, 3219) and crystallised several times from alcohol, formed very pale yellowish-green needles, m. p. 101°.

1-Acetyl-2-naphthol (II), prepared according to Fries (*Ber.*, 1921, **54**, 711) and purified by steam-distillation and finally by two crystallisations from light petroleum (b. p. 40—60°), formed almost colourless rhombic prisms, m. p. 64°.

2-*Methoxy*-3-*naphthoic Acid.*—2-Hydroxy-3-naphthoic acid (10 g.), dissolved in a mixture of acetone (100 c.c.) and water (100 c.c.), was warmed and shaken with successive small portions of methyl sulphate (in all 30 c.c.) alternately with 20% aqueous potassium hydroxide. The solution was now made strongly alkaline, heated for 2 hours on the water-bath, cooled, diluted, and acidified with hydrochloric acid. The 2-methoxy-3-naphthoic acid crystallised from dilute alcohol in pale yellow plates (9 g.), m. p. 133° (cf. Werner and Seybold, *Ber.*, 1904, **37**, 3661).

2-*Methoxy*-3-*naphthoyl Chloride.*—The foregoing acid (13·5 g.) was refluxed with thionyl chloride (60 c.c.) for 1 hour, and the product distilled, finally under diminished pressure. The acid chloride (11·5 g.), b. p. 197°/15 mm., separated from light petroleum (b. p. 60—80°) in pale yellow plates, m. p. 57° (cf. Fries and Schimmelschmidt, *Ber.*, 1925, **58**, 2839).

3-*Acetyl*-2-*naphthol* (III).—2-Methoxy-3-naphthoyl chloride was converted by the action of methylzinc iodide into 2-methoxy-3-acetylnaphthalene, and thence by demethylation with aluminium chloride into 3-acetyl-2-naphthol, following the directions of Fries and Schimmelschmidt (*loc. cit.*). The naphthol was crystallised four times from light petroleum (b. p. 60—80°) and obtained in bright yellow plates, m. p. 112°.

4-*Acetyl*-1-*naphthol* (IV).—This was prepared from α-naphthyl methyl ether *via* 1-methoxy-4-acetylnaphthalene, which was then demethylated with aluminium chloride (Witt and Braun, *loc. cit.*). It was crystallised three times from aqueous alcohol and obtained as very pale yellow needles, m. p. 197°.

1(?)-*Bromo*-3-*acetyl*-2-*naphthol.*—3-Acetyl-2-naphthol (1 g.) in glacial acetic acid (10 c.c.) was treated with a solution of bromine (2·6 g.) in acetic acid (25 c.c.). After 24 hours, the yellow crystalline powder which had separated was collected, and crystallised from acetic acid, forming bright yellow leaflets, m. p. 150° (Found, in material dried over potassium hydroxide at 100° : Br, 30·1. $C_{12}H_9O_2Br$ requires Br, 30·2%).

o-, m-, *and* p-*Hydroxybenzonitriles.*—These compounds were all prepared from the oximes of the corresponding hydroxy-aldehydes by dehydration with acetic anhydride. The *o*-compound was crystallised from benzene–light petroleum (b. p. 60—80°), and the *m*- and the *p*-compound from carbon tetrachloride.

β-*Hydroxybutyric Ester*.—This was prepared by the catalytic hydrogenation of acetoacetic ester (Lease and McElvain, *J. Amer. Chem. Soc.*, **1933**, **55**, 806), the product being freed from unchanged acetoacetic ester by shaking its ethereal solution with dilute sodium hydroxide; the solution was then dried with sodium sulphate and distilled. β-Hydroxybutyric ester gives no chelate copper derivative with copper acetate.

Ethyl Quinol-2 : 3-*dicarboxylate* (VIII).—Quinol-2 : 3-dicarboxylic acid (Thiele and Meisenheimer, *Ber.*, 1900, **33**, 675; Thiele and Günther, *Annalen*, 1906, **349**, 48) (5 g.) was refluxed for 8 hours with 3% absolute-alcoholic hydrogen chloride (100 c.c.). The bulk of the alcohol was removed by distillation, and the diluted residue, after treatment with excess of sodium bicarbonate solution, yielded to ether an oil which solidified on standing. It separated from a large volume of light petroleum (b. p. 60—80°) in needles, m. p. 85° (Found : C, 56·7; H, 5·6. $C_{12}H_{14}O_6$ requires C, 56·7; H, 5·5%).

Ethyl Quinol-2 : 5-*dicarboxylate* (IX).—This was prepared similarly from quinol-2 : 5-dicarboxylic acid (Brunner, *Annalen*, 1907, **351**, 321), and separated from alcohol in pale yellow needles, m. p. 133° (cf. Schmid, *Monatsh.*, 1911, **32**, 443).

Ethyl Resorcinol-4 : 6-*dicarboxylate*.—This ester, prepared in 35% yield in a similar manner from resorcinol-4 : 6-dicarboxylic acid, refluxing being continued for 12 hours, separated from alcohol in colourless needles, m. p. 140° (Errera, *Ber.*, 1899, **32**, 2789, gives m. p. 137°).

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