# 1*H*-Benzo[*de*]cinnoline and 8-Hydroxy-1-naphthonitrile

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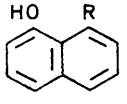
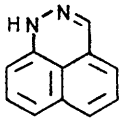
8-Hydroxy-1-naphthaldehyde reacts with hydrazine to give 1*H*-benzo[*de*]cinnoline; some reduction to 8-methyl-1-naphthol also takes place. The oxime of 8-hydroxy-1-naphthaldehyde does not cyclise analogously to an oxazine; instead dehydration to the nitrile occurs.

In continuation of a study of the condensation of 8-hydroxy-1-naphthyl ketones with hydrazine,[1] 8-hydroxy-1-naphthaldehyde (1) has been found to yield the unsubstituted 1*H*-benzo[*de*]cinnoline (6), although with some concomitant reduction to 8-methyl-1-naphthol (2), which was also made by hydrogenating 8-hydroxymethyl-1-naphthol (3).

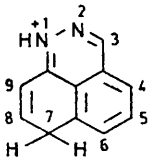
The u.v. spectrum of 1*H*-benzo[*de*]cinnoline (6) shows similar and reversible shifts in trifluoroacetic and in



(1) R = CHO
(2) R = Me
(3) R = $CH_2$·OH
(4) R = CN
(5) R = $CO_2$·$CH_2$·$CH_2$·OH

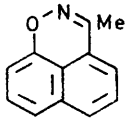


(6)



$CF_3CO_2^-$

(7)



(8)

concentrated hydrochloric acids, but not in dilute hydrochloric acid: n.m.r. spectroscopy shows that in trifluoroacetic acid the salt is formed by *C*-protonation on a carbocyclic ring, of the type shown in structure (7). 3-Methyl-1*H*-benzo[*de*]cinnoline [1] gives a similar salt in trifluoroacetic acid.

Treatment of the oxime of 8-hydroxy-1-naphthaldehyde with boiling ethylene glycol, conditions previously employed for preparing the oxazine (8) from the corresponding oxime,[1] did not give the naphtho[1,8-*de*]-oxazine; instead a mixture of 8-hydroxy-1-naphthonitrile (4) and its solvolysis product, the hydroxy-ester (5), was obtained. Cold acetic anhydride, which converted the oxime of 2,8-dihydroxy-1-naphthaldehyde into an oxazine,[2] also gives only the nitrile from the oxime of the aldehyde (1). Dehydration occurs so readily that with alkaline solutions of hydroxylamine the nitrile is formed directly, instead of the oxime.

## EXPERIMENTAL

*Condensation of 8-Hydroxy-1-naphthaldehyde* (1) *with Hydrazine.*—8-Hydroxy-1-naphthaldehyde (227 mg),[3] ethylene glycol (20 ml), and hydrazine hydrate (98—100%; 2 ml) were boiled under reflux, under a stream of nitrogen, for 3 h, any water formed being allowed to distil out. Cooling and diluting with water (40 ml) precipitated 1H-*benzo*[de]*cinnoline* (6) (108 mg) as bronze needles, m.p. 148—151° (Found: C, 78·1; H, 4·9; N, 16·6. $C_{11}H_8N_2$ requires C, 78·6; H, 4·8; N, 16·7%); $\nu_{max.}$ ($CS_2$) 3400, 3270, and 1635 $cm^{-1}$; $\lambda_{max.}$ (EtOH) 261, 332sh, 341, 421, and 441sh nm (log ε 3·99, 4·01, 4·02, 3·15, and 3·11); $\lambda_{max.}$ ($CF_3$·$CO_2H$) 268 and 343 nm (log ε 4·06 and 3·72); τ ($CDCl_3$) 1·84br (1H, s, exchangeable), 2·7—3·0 (4H, m), 3·2 (1H, dd, *J* 9 and 1·5 Hz), 3·4 (1H, dd, *J* 6 and 2·5 Hz), and 3·9 (1H, dd, *J* 7 and 1 Hz); *m/e* 168 (100%, $M^+$), 141 (20), 140 (35), 139 (20), 115 (9), 114 (22), and 113 (18), *m** 118·2 (168 → 141), 116·7 (168 → 140), 92·2 (141 → 114), and 91·2 (140 → 113).

The filtrate from 1*H*-benzo[*de*]cinnoline, on extraction with benzene, gave a gum (107 mg) that was separated on a silica preparative thin-layer plate (20 × 20 × 0·2 cm) developed with benzene–ethyl acetate (1 : 4). As well as more 1*H*-benzo[*de*]cinnoline, $R_F$ 0·3 (12 mg), there was obtained 8-*methyl*-1-*naphthol* (2), $R_F$ 0·5 (60 mg), purified by sublimation at 120° and 0·1 mmHg, then recrystallised from ether–petroleum (b.p. 40—60°) to give prisms (28 mg), m.p. 55—56° (Found: C, 83·7; H, 6·4. $C_{11}H_{10}O$ requires C,

[1] P. H. Lacy and D. C. C. Smith, *J. Chem. Soc.* (*C*), 1971, 747.
[2] R. Adams and D. E. Burney, *J. Amer. Chem. Soc.*, 1941, **63**, 1103.
[3] D. Berry and D. C. C. Smith, *J.C.S. Perkin I*. 1972, 699.

83·5; H, 6·3%); $\lambda_{max.}$ (EtOH) 220, 231sh, 290sh, 301, 309sh, 315, 322sh, and 329 nm (log ε 4·57, 4·49, 3·69, 3·76, 3·66, 3·68, 3·50, and 3·67); $\lambda_{max.}$ (aq. 2N-NaOH) 248, 330sh, and 340 nm (log ε 4·30, 3·88, and 3·91); τ ($CDCl_3$) 2·3—3·0 (5H, m), 3·4 (1H, dd, *J* 8 and 2 Hz), 4·9br (1H, s, exchangeable), and 7·1 (3H, s); *m/e* 158 (34%, $M^+$) and 130 (100%), *m** 107 (158 → 130).

Chemical shifts (τ) of salts in trifluoroacetic acid

| Salt | H-1 | H-3 | H-4, -5, -6 | H-7 | H-8 | H-9 |
|---|---|---|---|---|---|---|
| (7) | *a* | 0·6 [b] | 1·7 [c] | 5·5 [d,e] | 2·4 [f,g] | 2·7 [h,i] |
| 3-Methyl-(7) | *a* | 6·9 | 1·7 [c] | 5·5 [d] | 2·5 [f] | 2·7 [h] |

[a] Exchanging with solvent (and position 2?). [b] 1H, sharp s. [c] 3H, compact m. [d] 2H, broad s. [e] Sharpened by irradiation at τ 2·4 or 2·7. [f] dt, *J* 10 and 4 Hz. [g] Irradiation at τ 5·5 causes the signal at τ 2·4 to collapse to d, *J* 10 Hz. [h] dt, *J* 10 and 1 Hz. [i] Irradiation at τ 5·5 causes the signal at τ 2·7 to collapse to d, *J* 10 Hz.

*Hydrogenation of* 8-*Hydroxymethyl*-1-*naphthol* (3).—The diol (3) [4] (998 mg) in ethyl acetate was shaken with hydrogen over palladium–charcoal (prepared by hydrogenating palladium chloride–hydrochloric acid solution in the presence of charcoal in methanol, then washing the solids with methanol to remove acid); uptake 1 mol. equiv. in 30 min. The solution was filtered, washed, and concentrated to give an oil that was distilled at 120—130° and 0·05 mmHg. The solid distillate (819 mg) crystallised from benzene–petroleum (b.p. 40—60°) to give 8-methyl-1-naphthol (587 mg), m.p. 56—57° (Found: C, 84·1; H, 6·5%), mixed m.p. with the foregoing product 54·5—56·5°.

8-*Hydroxy*-1-*naphthonitrile* (4).—(*a*) 8-Hydroxy-1-naphthaldehyde (100 mg), hydroxyammonium chloride (500 mg), ethanol (10 ml), and aqueous 8% sodium hydroxide (5 ml) were boiled under reflux for 15 min; the mixture was then cooled, acidified (HCl), and concentrated under reduced pressure. The crystals which separated were collected, washed, and dried (yield 100 mg; m.p. 192—195°) and shown by t.l.c. to consist mainly of the nitrile (4). Sublimation at 160° and 0·1 mmHg followed by recrystallisation gave 8-*hydroxy*-1-*naphthonitrile*, as prisms (22 mg), m.p. 200—201° (from methanol–1,1,1-trichloroethane) (Found: C, 78·3; H, 4·1; N, 8·0. $C_{11}H_7NO$ requires C, 78·1; H, 4·1; N, 8·3%); $\nu_{max.}$ ($CHCl_3$) 3480, 3300, and 2220 $cm^{-1}$; $\lambda_{max.}$ (EtOH) 251, 320sh, 332, and 350sh nm (log ε 4·46, 3·54, 3·61, and 3·46); $\lambda_{max.}$ (aq. 2N-NaOH) 266, 328sh, 343, and 382 nm (log ε 4·32, 3·34, 3·51, and 3·46); τ [$(CD_2)_3CO$] 0·3br (1H, s, exchangeable), 1·9 (1H, dd, *J* 8 and 2 Hz), 2·1 (1H, dd, *J* 7 and 2 Hz), 2·4—2·7 (3H, m), and 2·9 (1H, dd, *J* 6 and 3 Hz); *m/e* 169 (100%, $M^+$), 141 (32), 140 (43), 115 (10), 114 (74), and 113 (51), *m** 117·5 (169 → 141), 92·2 (141 → 114), 91·2 (140 → 113), and 77 (169 → 114).

(*b*) The same procedure as in (*a*), but with aqueous N-sodium hydroxide (5 ml), gave, after concentration, grey needles of the *oxime* (78 mg), m.p. 179—180° (from methanol) (Found: C, 70·5; H, 4·8; N, 7·8. $C_{11}H_9NO_2$ requires C, 70·6; H, 4·8; N, 7·5%). The oxime (100 mg) in ethane-1,2-diol (10 ml) was boiled under nitrogen for 1 h; the solution was then poured into water (50 ml) and the precipitate was collected, washed, and dried. Separation on a silica preparative thin-layer plate (20 × 20 × 0·2 cm) developed with benzene–ethyl acetate (1 : 4) gave 8-hydroxy-1-naphthonitrile, $R_F$ 0·4 (35 mg), and 2-*hydroxyethyl* 8-*hydroxy*-1-*naphthoate* (5), $R_F$ 0·1 (53 mg), m.p. 138—140° (Found: C, 66·5; H, 5·2. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%); $\nu_{max.}$ ($CHCl_3$) 3630, 3200, 1722, and 1673 $cm^{-1}$; $\lambda_{max.}$ (MeOH) 239, 255sh, 300, 313, and 325 nm (log ε 4·46, 3·87, 3·69, 3·69, and 3·65); $\lambda_{max.}$ ($CHCl_3$) 315sh, 325, and 350sh nm (log ε 3·47, 3·48, and 3·27); $\lambda_{max.}$ (methanolic NaOH) 255 and 341 nm (log ε 4·37 and 3·81); τ [$(CD_3)_2CO$] 0·4br (1H, s, exchangeable), 2·1 (1H, dd, *J* 8 and 2 Hz), 2·3—2·7 (4H, m), 3·0 (1H, dd, *J* 7 and 2 Hz), 5·6 (2H, t, *J* 5 Hz), 6·2 (t, *J* 5 Hz), and 6·8br (1H, s, exchangeable); *m/e* 232 (5%, $M^+$) and 170 100%).

(*c*) The oxime of 8-hydroxy-1-naphthaldehyde (100 mg) in acetic anhydride (5 ml) was kept for 6 h at room temperature, then stirred with water to hydrolyse acetic anhydride. An ethyl acetate extract, washed (aq. $NaHCO_3$), dried ($Na_2SO_4$), and concentrated, yielded 8-hydroxy-1-naphthonitrile (63 mg).

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[4] R. J. Packer and D. C. C. Smith, *J. Chem. Soc.* (*C*), 1967, 2194.