949. *Polycyclic Cinnoline Derivatives. Part XI.*[1] *The Nitration of Benzo*[c]*cinnoline and Some Methylbenzo*[c]*cinnolines, and the Ultraviolet Absorption of Derived Amines.*

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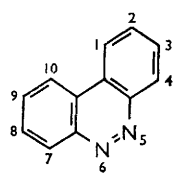
Benzo[*c*]cinnoline, on nitration, gives 1- and 4-nitrobenzo[*c*]cinnoline. 3-Methylbenzo[*c*]cinnoline is mononitrated in positions 1, 4, and 10, 1,10-dimethylbenzo[*c*]cinnoline in position 4, 2,9-dimethylbenzo[*c*]cinnoline in position 1, and 3,8-dimethylbenzo[*c*]cinnoline in position 4. The ultraviolet absorption spectra of aminobenzo[*c*]cinnoline derivatives may be used to diagnose the position of the amino-group.

Smith and Ruby [2] nitrated benzo[*c*]cinnoline (I) with nitric acid in sulphuric acid at 0° and 25°, and showed that the major product was 1-nitrobenzo[*c*]cinnoline. They suggested that the minor (*x*-nitro-)product was the 3-nitro-isomer. Arcos, Arcos, and Miller [3] reported that the nitration of benzo[*c*]cinnoline at 70—80° gave another mononitro-benzo[*c*]cinnoline, which they called the *y*-nitro-derivative, and apparently, at this temperature, none of the 1- or *x*-isomer. Those authors showed that the amine derived from the *x*-nitro-compound was not 3-aminobenzo[*c*]cinnoline, which they prepared by reduction of 2,4,2′-trinitrobiphenyl and of 4-amino-2,2′-dinitrobiphenyl. The *x*- and the *y*-nitrobenzo[*c*]cinnoline appeared then to be the 2- and the 4-, or the 4- and the 2-isomer.



(I)

We studied the nitration of benzo[*c*]cinnoline at several temperatures between 0° and 100°. Contrary to other reports,[4] we find that the 1- and the *x*-isomer can be separated quantitatively from benzene solution by chromatography on alumina. Only these isomers were obtained and the yield, about 59% of the 1- and 15% of the *x*-isomer, was not appreciably affected by the temperature. Further experiments proved that nitration at 70° was almost complete after 10 minutes. The *y*-nitrobenzo[*c*]cinnoline of Arcos, Arcos, and Miller [3] was presumably a mixture of the 1- and the *x*-isomer. Their product melted at 141—142°, whilst the mixture of 1- and *x*-isomer that we obtained melted over the range 137—141°.

An oil that is eluted after these isomers contains no nitrobenzo[*c*]cinnoline, as the ultraviolet spectrum of the product from the catalytic hydrogenation of the oil showed no peaks characteristic of an aminobenzo[*c*]cinnoline. The *x*-nitro-compound of Arcos, Arcos, and Miller was either the 2- or the 4-isomer. 2-Nitrobenzo[*c*]cinnoline was synthesised to establish the orientation.

2-*Nitrobenzo*[c]*cinnoline*.—Arcos, Arcos, and Miller [3] could not reduce 5-amino-2,2′-dinitrobiphenyl to a cinnoline derivative. We therefore examined possible methods for

[1] Part X, *J.*, 1962, 1812.
[2] Smith and Ruby, *J. Amer. Chem. Soc.*, 1954, **76**, 5807.
[3] Arcos, Arcos, and Miller, *J. Org. Chem.*, 1956, **21**, 651.
[4] Ruby, *Diss. Abs.*, 1953, **13**, 669 (University microfilm, Ann Arbor, Michigan, No. 5497).

forming the benzo[*c*]cinnoline ring system which did not involve the reduction of a 2,2′-dinitrobiphenyl derivative.

An attempt to cyclise a 2-amino-2′-nitrobiaryl failed. 2-Amino-5,2′-dinitrobiphenyl was produced by nitrating 2-acetamido-2′-nitrobiphenyl and hydrolysing the product. The identity of the product was established by deaminating it to 2,3′-dinitrobiphenyl. When refluxed with sodium hydroxide in methanol it did not give the expected 2-nitrobenzo[*c*]cinnoline *N*-oxide but, instead, gave polymeric material.

2-Nitrobenzo[*c*]cinnoline was eventually made by oxidising 2,2′-diamino-5-nitrobiphenyl, 2,9-dinitrobenzo[*c*]cinnoline *N*-oxide having been previously prepared from 2,2′-diamino-5,5′-dinitrobiphenyl.[5] Nitration of 2,2′-di(acetamido)biphenyl gave the 5-nitro-derivative, the structure of which was shown by further nitration to the 5,5′-dinitro-compound. Hydrolysis of 2,2′-di(acetamido)-5-nitrobiphenyl gave 2,2′-diamino-5-nitrobiphenyl, which on oxidation with the theoretical amount of sodium perborate in acetic acid gave 2-nitrobenzo[*c*]cinnoline.

The properties of 2-nitrobenzo[*c*]cinnoline and its derived amine differed from those of *x*-nitrobenzo[*c*]cinnoline. The latter must thus be 4-nitrobenzo[*c*]cinnoline and this assignment has been confirmed by Smith [6] who measured its dipole moment.

The Nitration of Some Methylbenzo[c]*cinnolines.*—One monomethyl- and three dimethyl-benzo[*c*]cinnolines were nitrated at room temperature for 30 min. with nitric acid in the quantity calculated to yield a mononitro-derivative. Each gave one or more nitration products, which were separated and purified by chromatography. No attempt was made to establish the orientation of the methylnitro-derivatives by chemical methods because of the difficulty of synthesising the numerous reference compounds. A previous study [1] of the ultraviolet absorption spectra of all the mononitro- and amino-benzo[*c*]cinnolines indicated that, whereas little information about the orientation of the nitro-group could be obtained from the spectra of the nitrobenzo[*c*]cinnolines, the spectra of the aminobenzo[*c*]cinnolines were characteristic of the orientation. Substituent methyl groups have little effect on ultraviolet absorption spectra [1] provided that they do not cause steric hindrance, so it was expected that the aminomethylbenzo[*c*]cinnolines could be similarly differentiated. The methylnitro-compounds were therefore reduced catalytically to the corresponding amines.

TABLE 1.

Long-wavelength absorption bands of aminobenzo[*c*]cinnolines.*

Position of NH_2	$\lambda_{max.}$ (mμ) in EtOH	HCl	Protonation shift	log ε in EtOH	HCl	Protonation increment
1	412	508	96	3·3	2·8	−0·5
2	386	442	56	4·2	4·55	0·35
3	440	505	65	3·4	3·5	0·1
4	448	575	127	3·55	3·6	0·05

* Data from Corbett, Holt, Hughes, and Vickery, *J.*, 1962, 1812.

The orientation of the amine is characteristised (Table 1) by: (1) The position of the long-wavelength bands, the wavelengths varying with the position of the amine group in the order $4 > 3 > 1 > 2$ when ethanol is the solvent and $4 > 1 > 3 > 2$ when hydrochloric acid is the solvent. (2) The shift of these bands (protonation shift) when acid replaces ethanol as solvent, varying with the position of the amino-group in the order $4 > 1 > 3 > 2$. (3) The change in intensity of the long-wavelength peaks when the solvent is changed from ethanol to acid (protonation increment), varying with the position of the amine in the order $2 > 3 > 4 > 1$.

3-*Methylbenzo*[c]*cinnoline.*—This compound was prepared by the crossed Ullmann reaction between 4-bromo-3-nitrotoluene and *o*-bromonitrobenzene, followed by reduction

[5] Corbett and Holt, *J.*, 1961, 3695.
[6] Smith, personal communication.

of the resulting 4-methyl-2,2′-dinitrobiphenyl with lithium aluminium hydride to give the cinnoline as yellow crystals (m. p. 101°). On nitration, 3-methylbenzo[*c*]cinnoline gave three mononitro-derivatives (*x*-, *y*-, and *z*-), separable from benzene solution by chromatography on alumina. These were reduced catalytically to the amines.

The *x*-amino-compound was identified as 4-amino-3-methylbenzo[*c*]cinnoline since solutions in ethanol and in 0·1N-hydrochloric acid gave long-wavelength absorption peaks in positions within 2 or 3 mμ of those of 4-aminobenzo[*c*]cinnoline and the protonation shift was within 2 mμ. The protonation increment was 0·1, close to that for 4-aminobenzo[*c*]cinnoline, but this value alone is not completely diagnostic since 3- and 4-aminobenzo[*c*]cinnoline have nearly the same value (0·1 and 0·05, respectively). Details of the spectra of this and other amines are given in Tables 2 and 3.

The *y*- and the *z*-amino-compound in ethanol and in 0·1N-hydrochloric acid both gave similar values for the long-wavelength absorption peaks and the protonation shift. The values were very close to the corresponding values for 1-aminobenzo[*c*]cinnoline. The protonation increment in both cases was negative and the 1-isomer is the only aminobenzo[*c*]cinnoline which gives a negative protonation increment. It is deduced then that one of these compounds is 1-amino-3- and the other 1-amino-8-methylbenzo[*c*]cinnoline.

These results indicate that the products of nitration of 3-methylbenzo[*c*]cinnoline are 3-methyl-1-nitro-, 3-methyl-4-nitro-, and 8-methyl-1-nitro-benzo[*c*]cinnoline.

TABLE 2.

Long-wavelength absorption bands of aminomethylbenzo[*c*]cinnolines.

Position of Me	Position of NH_2 Designated	Deduced	$\lambda_{max.}$ (mμ) in EtOH	HCl	Protonation shift	log ε in EtOH	HCl	Protonation increment
3	*x*	4	449	578	129	3·6	3·7	0·1
3	*y*	1 or 10	415	515	100	3·4	2·9	−0·5
3	*z*	10 or 1	412	514	102	3·3	2·9	−0·4
2, 9	*x*	1	410	504	94	3·4	3·2	−0·2
3, 8	*x*	4	450	576	126	3·6	3·7	0·1
1, 10	4 (known)	4	465	594	129	3·5	3·6	0·1

TABLE 3.

Short-wavelength absorption bands (mμ) for aminomethylbenzo[*c*]cinnolines (log ε in parentheses).

Position of NH_2	Me	Solvent	Group I	*x*	Group II	*y*
1(10)	3	EtOH	227(4·5), 240s(4·4)	—	302(4·2)	342s(3·5)
(*y*-isomer)		HCl	— 247(4·5)	—	314(3·9)	380(3·4)
10(1)	3 †	EtOH	226(4·4), 246(4·3)	—	301(4·2)	346s(3·4)
(*z*-isomer)		HCl	— 247(4·5)	—	314(4·1)	380(3·5)
1	2, 9	EtOH	230(4·4), 248(4·4)	—	305(4·3)	340s(3·6)
		HCl	225(4·5), 258(4·3)	—	328(4·1)	395(4·0)
4	3	EtOH	— 242(4·6)	—	305(4·2)	340s(3·8)
		HCl	232(4·4), 250s(4·3)	270(4·2)	316(4·1)	378(3·7)
4	3, 8	EtOH	— 250(4·6)	—	305(4·2)	340(3·8)
		HCl	— 252(4·4)	270(4·2)	317(4·1)	379(3·5)
4	1, 10	EtOH *	237(4·3), 250s(4·3)	—	320(3·85)	370(3·5)
		HCl *	— 248(4·1)	282(4·0)	344(3·7)	371(3·5)

s = Shoulder. * Values from Corbett, Holt, Hughes, and Vickery, *J.*, 1962, 1812. † The compound here designated 10-NH_2-3-Me is properly called the 1-amino-8-methyl derivative.

2,9-*Dimethylbenzo*[c]*cinnoline.*—Only one product, designated 2,9-dimethyl-*x*-nitrobenzo[*c*]cinnoline (m. p. 149—150°), was isolated on nitration of 2,9-dimethylbenzo[*c*]cinnoline. On reduction, *x*-amino-2,9-dimethylbenzo[*c*]cinnoline (m. p. 243°) was obtained; this and its cation showed peaks at long wavelengths closely similar to those

given by 1-aminobenzo[*c*]cinnoline. The protonation shift differed by only 2 mμ. The protonation increment was negative. The amine must be 1-amino-2,9-dimethylbenzo[*c*]-cinnoline. Apparently 2,9-dimethylbenzo[*c*]cinnoline is nitrated to give only the 1-nitro-derivative.

3,8-*Dimethylbenzo*[c]*cinnoline*.—This compound gave one product on nitration, designated 3,8-dimethyl-*x*-nitro- (m. p. 282°). The amine obtained by catalytic reduction and its ion had long-wavelength peaks within 1—2 mμ of those in the spectra of 4-amino-benzo[*c*]cinnoline. The protonation increment was 0·1, which also suggested the 4-amino-isomer.

1,10-*Dimethylbenzo*[c]*cinnoline*.—This compound gave a single mononitro-derivative which further nitration converted into 1,10-dimethyl-4,7-dinitrobenzo[*c*]cinnoline, whose structure had been proved by Theilacker and Baxmann.[7] The first nitration product must, then, be 1,10-dimethyl-4-nitrobenzo[*c*]cinnoline.

Catalytic hydrogenation of the mononitro-compound gave the amine. It was known that 1,10-dimethylbenzo[*c*]cinnoline shows anomalies in its absorption spectra because steric interference of the two methyl groups produces a twisted structure. As compared with, say, 3-methylbenzo[*c*]cinnoline there is a loss of fine structure, a considerable shift towards the red in the Group II and Group III bands. Similar shifts occur in the spectra of other 1,10-disubstituted benzo[*c*]cinnolines. Anomalies of the same kind are apparent when the spectrum of 4-amino-1,10-dimethylbenzo[*c*]cinnoline is compared with that of 4-amino-benzo[*c*]cinnoline. The Group II band of the dimethyl compound in ethanol and in acid shows a large bathochromic shift, no absorption in the region of the *x*-band, and the Group I, the *y*, and the long-wavelength band occur at longer wavelengths.

The protonation shift (129 mμ compared with 127 mμ for 4-aminobenzo[*c*]cinnoline) again indicates the position of the amino-group. As with 4-amino-3-methylbenzo[*c*]-cinnoline the protonation increment was nearer that of 3-aminobenzo[*c*]cinnoline than that of the 4-isomer.

Discussion.—For electrophilic substitution in a heterocyclic compound the π-electron-energy difference between the transition state and the ground state is given by:

$$\Delta E_\pi = 2\beta(a_{or} + a_{os}) - \sum_i a_{oi}^2 \alpha_i$$

where a_{oi}, a_{or}, and a_{os} are the non-bonding molecular-orbital coefficients for the heteroatom i and the atoms r and s adjacent to the point of attack. β is the difference between the carbon–carbon resonance integral in the parent hydrocarbon between atoms s and the point of attack in the ground state, and the corresponding value in the transition state; α_i is the difference between the coulomb integral of the atom i and a carbon atom in the homocyclic system. If α is the coulomb term for the heteroatom a value of α/3 can be used for adjacent atoms.

Considering benzo[*c*]cinnoline, Dewar and Maitlis [8] used $\alpha_{NH^+} = -40$ kcal. mole^{-1} and $\beta = -4$ kcal. mole^{-1} to calculate the reactivity of positions towards nitration. They obtained $\Delta E_1 = -10$, $\Delta E_2 = -17$, $\Delta E_3 = -11{\cdot}3$, $\Delta E_4 = -14{\cdot}8$, giving the order of reactivity $1 > 3 > 4 > 2$. The observed order was $1 > 4 > 3$ and 2. They assumed that both nitrogen atoms are protonated whereas, since the ultraviolet absorption spectrum of benzo[*c*]cinnoline in 98% sulphuric acid and in 0·1N-hydrochloric acid are similar, only one nitrogen atom is in fact protonated. In the transition state the unstarred nitrogen atom would probably be protonated; in the ground state both nitrogen atoms may share a single proton, as has been suggested for protonated azobenzenes. Mason [9] used an empirical value of −12 kcal. mole^{-1} for α_N.

[7] Theilacker and Baxmann, *Annalen*, 1953, **581**, 117.
[8] Dewar and Maitlis, *J.*, 1957, 2521.
[9] Mason, *J.*, 1958, 674.

The value of β is also uncertain. Values given by Dewar, Mole, and Warford,[10] calculated from the partial rate factors of the nitration of hydrocarbons, were −6 kcal. mole^{-1} in acetic and −4 kcal. mole^{-1} in sulphuric acid. They are not applicable to all hydrocarbons and the application to heterocycles is arbitrary.

The calculated value of β for sp^2-hybridisation in a hydrocarbon is −20 kcal. mole^{-1} and for the Wheland transition state, where the carbon atom under attack will be sp^3-hybridised, it is zero. Therefore, if one assumes that the transition state lies between these extremes, the value of β will be between 0 and −20 kcal. mole^{-1}. Dewar and Maitlis assumed a value of −4 when they forecast the order 1 > 3 > 4 > 2; a value of −7 or lower would give the correct order 1 > 4 > 3 > 2.

The molecular-orbital treatment, can more accurately be applied to the nitration of substituted benzo[*c*]cinnolines if it is assumed that the energy of activation for the various positions of benzo[*c*]cinnoline is in the order 2 > 3 > 4 > 1. Methyl groups should lower the energy of activation by the amount $\sum_i a_{oi}^2 \alpha_{Me}$, where α_{Me} is the difference between the coulomb integral of the substituted carbon atom i and that of carbon. The values for the dimethyl compounds are given in Table 4.

For 1,10-dimethylbenzo[*c*]cinnoline it is the difference between ΔE_π for the 4- and the 2-position which determines the orientation of the nitro-group, as the reduction in the energy of activation of these two positions by the methyl groups is almost equal to, but larger than, that for the 3-position. The theory, therefore, agrees with the experimental evidence that 1,10-dimethylbenzo[*c*]cinnoline is nitrated in the 4-position.

ΔE_π is least for the 1-position, and in 2,9-dimethylbenzo[*c*]cinnoline the energy of activation is lowered most for this position, and so it would be expected that this compound would nitrate in the 1-position, as found experimentally.

From the calculated values for 3,8-dimethylbenzo[*c*]cinnoline the 4-nitro-isomer would be expected as the major product. Experimentally only this was obtained.

TABLE 4.

$\sum_i a_{oi}^2$ for substituted benzo[*c*]cinnolines.

Psn. of attack	1	2	3	4
1,10-Substd.	—	0·375	0·047	0·310
2,9-Substd.	0·346	—	0·190	0·034
3,8-Substd.	0·038	0·166	—	0·310

The methyl group in 3-methylbenzo[*c*]cinnoline should lower the energy of activation for nitration by 0·166α, 0·310α, 0·047α, and 0·038α for the 2-, 4-, 8-, and 10-position, respectively, but should not alter that for the 1-, 7-, and 9-position. Taken in conjunction with the results of the nitration of benzo[*c*]cinnoline and 3,8-dimethylbenzo[*c*]cinnoline, these values suggest the order of reactivity 4 > 1 > 10 > 7, in agreement with experiment. The major isomer is therefore probably 3-methyl-4-nitrobenzo[*c*]cinnoline rather than the 7-nitro-isomer.

EXPERIMENTAL

2-Nitrobenzo[c]*cinnoline.*—(*a*) *Attempted cyclisation of 2-amino-2′,5-dinitrobiphenyl.* 2-Amino-2′-nitrobiphenyl was prepared by Badger and Sasse's method [11] and acetylated with acetic anhydride. The acetamido-compound (0·62 g.), m. p. 155—157° (lit.,[12] 159—160°), after crystallisation from benzene and then ethanol, in sulphuric acid (10 ml.) was treated with potassium nitrate (0·163 g.) at <10°. After 1 hr. at room temperature, water (10 ml.) was added and the solution refluxed for 3 hr. The solution was neutralised and the precipitate filtered off, washed, and recrystallised from ethanol and then from benzene. 2-Amino-2′,5-dinitrobiphenyl formed yellow rods, m. p. 170° (Found: C, 55·4; H, 3·5; N, 16·45. $C_{12}H_9N_3O_4$ requires C, 55·6; H, 3·5; N, 16·2%). The orientation of the compound was proved by its

[10] Dewar, Mole, and Warford, *J.*, 1956, **3581.**
[11] Badger and Sasse, *J.*, 1957, 4.
[12] Purdie, *J. Amer. Chem. Soc.*, 1941, **63**, 2276.

deamination to 2,3′-dinitrobiphenyl. The nitroamine (0·1 g.) in methanolic N-sodium hydroxide (10 ml.) was refluxed for 3 hr. Polymeric material was formed which had a high m. p. and could not be crystallised.

(*b*) *Oxidation of 2,2′-diamino-5-nitrobiphenyl.* 2,2′-Di(acetamido)biphenyl (1·9 g.) in concentrated sulphuric acid (20 ml.) was treated with potassium nitrate (0·72 g.) added in small portions, with stirring, at 0°. The mixture was left at room temperature for 2 hr., then poured on ice. The product was recrystallised twice from benzene, to give *2,2′-di(acetamido)-5-nitrobiphenyl*, m. p. 234—236° (Found: N, 13·7. $C_{16}H_{15}N_3O_4$ requires N, 13·4%). Further nitration of the product gave 2,2′-di(acetamido)-5,5′-dinitrobiphenyl, identical with a sample prepared by Sako's method.[13]

2,2′-Di(acetamido)-5-nitrobiphenyl (1 g.) was refluxed for 3 hr. in 50% aqueous sulphuric acid. The solution was basified and the precipitate filtered off, washed with water, and dried at room temperature. The dry solid was dissolved in acetic acid (10 ml.), and sodium perborate (1 g.) in acetic acid (10 ml.) was added. The mixture was kept at 40° for 2 hr., then evaporated to low bulk. After being poured into water, the precipitate was collected, dried, and chromatographed on alumina in benzene. The eluate was evaporated and the product recrystallised from benzene, to give *2-nitrobenzo*[c]*cinnoline* (0·14 g.) as yellow needles, m. p. 260—261° (Found: C, 64·3; H, 2·85; N, 18·75. $C_{12}H_7N_3O_2$ requires C, 64·1; H, 3·1; N, 18·7%).

Nitration of Benzo[c]*cinnoline.*—Benzo[*c*]cinnoline (0·2 g.) in concentrated sulphuric acid (2 ml.) was treated with nitric acid (*d* 1·42; 0·065 ml.) in sulphuric acid (0·75 ml.), and the mixture was kept at 25°, 50°, 70°, or 100° for 2 hr. or at 70° for 10 min. The solution was poured on ice, and water was added to make the volume 100 ml., sufficient to precipitate the nitrocompounds quantitatively but not benzo[*c*]cinnoline. The precipitate was filtered off on a tared crucible, washed with water, dried, and weighed. A small weighed amount of the precipitate was dissolved in benzene and filtered through a tared crucible and then through an alumina column (2·0 × 0·75 cm.). The material was eluted with benzene until the eluate was no longer yellow. The eluate was evaporated and the weight and m. p. of the residue were determined. The total weight of pure mixed isomers was then calculated. The mixed isomers were chromatographed in benzene on alumina (15 × 0·75 cm.). The first fractions contained 1-nitrobenzo[*c*]cinnoline, m. p. 161° (lit., 161°), and 4-nitrobenzo[*c*]cinnoline, m. p. 232° (lit., 230°) was obtained from later fractions by elution with acetone. The 1 : 4-isomer ratio (4 : 1 w/w) appeared to be independent of temperature between 25° and 100°. Smith and Ruby [2] found a ratio of 5 : 1 at 0°.

4-Methyl-2,2′-dinitrobiphenyl.—4-Bromo-3-nitrotoluene, m. p. 31—33° (lit., 34°), was prepared as described by Hodgson and Walker.[14] A mixed Ullmann reaction with *o*-bromonitrobenzene and 4-bromo-3-nitrotoluene gave the unsymmetrical biphenyl, m. p. 93—94° (lit.,[15] 93—95°).

3-Methylbenzo[c]*cinnoline.*—4-Methyl-2,2′-dinitrobiphenyl (2 g.) was dissolved in benzene (150 ml.) and ether (100 ml.), and lithium aluminium hydride (2 g.) in ether (50 ml.) was added. The mixture was refluxed for 1 hr. and the excess of hydride decomposed with water. Evaporation left an oil which was distilled. The fraction of b. p. 186°/1 mm. solidified and recrystallised from ethanol, to give *3-methylbenzo*[c]*cinnoline* (1 g.), m. p. 101° (Found: C, 80·2; H, 5·2; N, 14·3. $C_{13}H_{10}N_2$ requires C, 80·4; H, 5·2; N, 14·4%).

Nitration of Some Methylbenzo[c]*cinnolines.*—The methylbenzo[*c*]cinnoline was added to the quantity of nitric acid (*d* 1·5) calculated to give mononitration, in an excess of sulphuric acid. The solution was left at room temperature for 30 min., then poured on ice, and water was added until precipitation ceased. The precipitate was filtered off, washed with water, dried, dissolved in benzene, and filtered through alumina. A small portion of the solution was diluted with benzene and chromatographed on alumina (20 × 0·75 cm.) to separate isomers, if more than one was present. Only 3-methylbenzo[*c*]cinnoline gave more than one nitro-compound. In this case the column was eluted first with benzene which gave a product of m. p. 128—134°. This was recrystallised twice from benzene, to give *8-methyl-1-nitrobenzo*[c]*cinnoline* (or the 3-methyl-1-nitro-isomer), m. p. 134°. Elution of the column with benzene–acetone gave a product of m. p. 254—258°, and final elution with acetone gave transparent yellow crystals, m. p. 276—278°. The last set recrystallised from benzene–acetone to give *3-methyl-4-nitrobenzo*[c]*cinnoline*,

[13] Sako, *Mem. Coll. Eng. Kyushu Imp. Univ.*, 1932, **6**, 327.
[14] Hodgson and Walker, *J.*, 1933, 1620.
[15] Baker, Barton, and McOmie, *J.*, 1958, 2658.

m. p. 278°. The product from benzene–acetone was fractionally crystallised from ethanol, to give a mixture of 3-*methyl*-1-*nitrobenzo*[c]*cinnoline*, m. p. 197°, and 3-methyl-4-nitrobenzo[*c*]-cinnoline. Therefore, 3-methylbenzo[*c*]cinnoline (2·39 g.) gave 3-methyl-4-nitro- (0·35 g.), m. p. 278° (Found: C, 64·1; H, 4·0; N, 18·0. $C_{13}H_9N_3O_2$ requires C, 65·0; H, 3·7; N, 17·5%), 8-methyl-1-nitro- (0·12 g.), m. p. 197° (Found: C, 65·7; H, 3·4; N, 17·6%), and 3-methyl-1-nitro-benzo[*c*]cinnoline (0·14 g.), m. p. 134° (Found: C, 64·0; H, 3·4; N, 17·5%).

The bulk solutions of the other nitro-compounds were fractionally crystallised and the following methylnitro-compounds obtained: 1,10-Dimethylbenzo[*c*]cinnoline (0·504 g.) gave the 4-*nitro-compound* (0·3 g.), m. p. 132° (Found: 64·9; H, 4·2; N, 16·0. $C_{14}H_{11}N_3O_2$ requires C, 66·5; H, 4·4; N, 16·6%). 2,9-Dimethylbenzo[*c*]cinnoline (0·30 g.) gave the 1-*nitro-compound* (0·29 g.), m. p. 187° (Found: C, 66·9; H, 4·3; N, 16·8%). 3,8-Dimethylbenzo[*c*]cinnoline (0·724 g.) gave the 4-*nitro-compound* (0·52 g.), m. p. 282° (Found: C, 66·9; H, 4·6; N, 16·1%).

Preparation of Amino-compounds.—The nitrobenzo[*c*]cinnolines in ethanol (*ca.* 150 ml.) were hydrogenated at atmospheric pressure with platinum oxide. When hydrogen ceased to be absorbed, the solutions were filtered and evaporated and the residues filtered in benzene through alumina. The filtrates were concentrated and the products recrystallised from ethanol. By this method were obtained: 1 Amino-, m. p. 167° (lit., 167°), orange needles, 4-amino-, m. p. 198° (lit., 198°), gold leaflets or orange needles, and 2-*amino-benzo*[c]*cinnoline*, m. p. 223°, brown blades (Found: C, 72·1; H, 4·4; N, 21·1. $C_{12}H_9N_3$ requires C, 73·9; H, 4·6; N, 21·6%). 1-*Amino*-3-*methyl*- (or the 1-amino-8-methyl isomer), m. p. 143—144°, dark brown (Found: C, 73·9; H, 5·4. $C_{13}H_{11}N_3$ requires C, 74·7; H, 5·27%), 1-amino-8-methyl- (or the 1-amino-3-methyl isomer), m. p. 154°, yellow (insufficient for analysis), 4-*amino*-3-*methyl*-, m. p. 165—166°, brown (Found: C, 73·5; H, 5·1; N, 20·6%), 4-*amino*-1,10-*dimethyl*-, m. p. 74—75°, black with a metallic glint (Found: C, 74·8; H, 6·0; N, 17·9. $C_{14}H_{13}N_3$ requires C, 75·4; H, 5·84; N, 18·8%), 1-*amino*-2,9-*dimethyl*-, m. p. 243°, golden (Found: C, 74·7; H, 6·1; N, 18·9%), and 4-*amino*-3,8-*dimethyl-benzo*[c]*cinnoline*, m. p. 172°, dark orange (Found: C, 74·3; H, 6·09; N, 19·0%). 3-Aminobenzo[*c*]cinnoline was prepared by reduction of 2,4,2′-trinitrobiphenyl, according to the method of Arcos, Arcos, and Miller,[3] as yellow-brown crystals, m. p. 165° (lit., 163—165°).

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