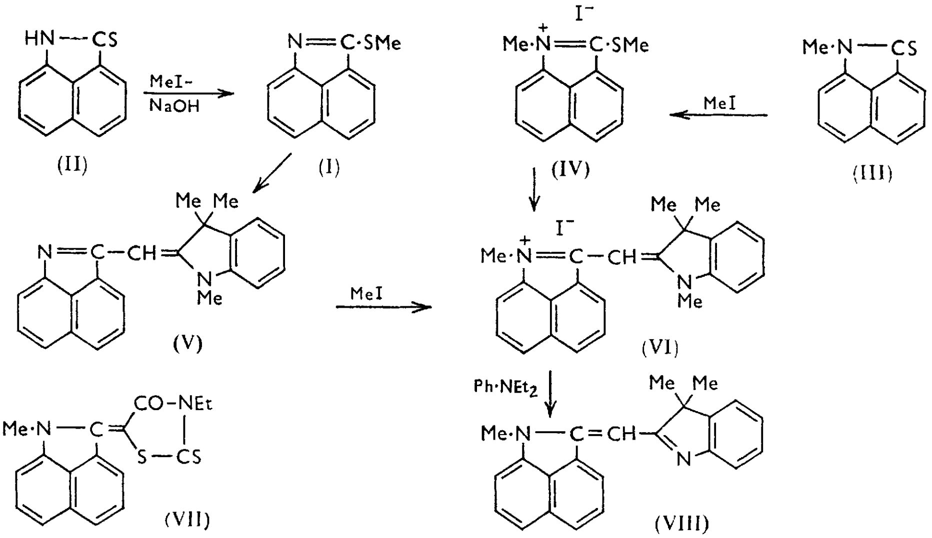
309. *The Reactivity of the Alkylthio-group in Nitrogen Ring Compounds. Part III.** *2-Methylthiobenz*[cd]*indole and its Methiodide.*

By G. E. Ficken and J. D. Kendall.

The preparation of 2-methylthiobenz[*cd*]indole and of its methiodide is described. Both compounds possess a reactive methylthio-group, and cyanine bases and dyes have been prepared. The light absorption of these is discussed.

In Part II * we described the smooth reaction of 3,3-dimethyl-2-methylthio-3*H*-indole with quaternary salts of nitrogen heterocycles possessing reactive methyl groups to form cyanine bases. It was therefore of interest to examine the related 2-methylthiobenz[*cd*]indole (I).

We have prepared this sulphide from thionaphthostyril (II), a compound first prepared by Dokunikhin and Gaeva[1] by reaction of α-naphthyl isothiocyanate with aluminium chloride. We have prepared both (II) and its *N*-methyl derivative (III) by reaction of naphthostyril and *N*-methylnaphthostyril respectively with phosphorus pentasulphide in pyridine; a similar method has recently been described by Dokunikhin and Gaeva[2] for the preparation of both (II) and (III). Whereas thionaphthostyril reacted with methyl iodide to give the hydriodide of 2-methylthiobenz[*cd*]indole, from which the base (I) was liberated by sodium hydroxide, the *N*-methyl-thione (III) gave 1-methyl-2-methylthiobenz[*cd*]indolium iodide (IV) with methyl iodide.



Both 2-methylthiobenz[*cd*]indole and its methiodide were found to possess highly reactive methylthio-groups and gave cyanine bases and true cyanine dyes respectively by reaction with quaternary salts of nitrogen heterocycles possessing reactive methyl groups. Thus, with 1,2,3,3-tetramethyl-3*H*-indolium iodide the base (V) and cyanine (VI) were obtained; the latter was also formed by reaction of the base (V) with methyl iodide. In its reactions with reactive methyl quaternary salts the sulphide (I) appears to be distinctly more reactive than any alkylthio-compound hitherto described. Whereas 3,3-dimethyl-2-methylthio-3*H*-indole requires a temperature of about 150° for this type of

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* Part II, preceding paper.

[1] Dokunikhin and Gaeva, *J. Gen. Chem.* (*U.S.S.R.*), 1954, **24**, 1871; *Chem. Abs.*, 1955, **49**, 13,239.

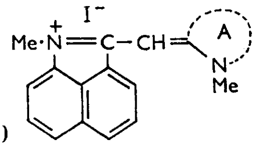
[2] *Idem*, *J. Gen. Chem.* (*U.S.S.R.*), 1958, **28**, 2670; *Chem. Abs.*, 1959, **53**, 9183.

reaction (preceding paper), and a similar temperature was used in the examples described by Hamer *et al.*,[3] compound (I) underwent a vigorous reaction when fused with 2,3-dimethylbenzothiazolum toluene-*p*-sulphonate at 100°. In the preparation of base (V), reaction occurred in boiling ethanolic solution in presence of a base.

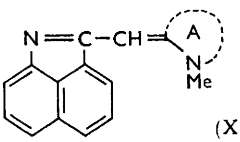
The quaternary methiodide (IV) gave merocyanines, *e.g.*, (VII), by reaction with heterocyclic ketomethylene compounds. Compounds of similar type, but lacking an alkyl group on the benz[*cd*]indole nitrogen atom, have been prepared by Dokunikhin and Gaeva [4] by reaction of thionaphthostyril with ketomethylene compounds.

Dequaternisation of cyanine (VI) in refluxing diethylaniline gave a base which, being different from base (V), must be assigned structure (VIII). Since, as explained in the previous paper, dequaternisation appears to occur at the more basic nitrogen atom of an unsymmetrical cyanine, this result implies that the benz[*cd*]indole nucleus is less basic than 3*H*-indole. This conclusion was confirmed by application of Brooker's rule [5] that in an isomeric pair of bases the one carrying the alkyl group on the more basic nitrogen will absorb at the higher wavelength. In fact bases (V) and (VIII) absorbed at 5150 and 4900 Å respectively (cf. Table), thereby confirming the weaker basicity of benz[*cd*]indole than of 3*H*-indole.

The light absorption data are recorded in the Table for some cyanines (IX) and bases (VIII and X), the bases in both neutral and acid solution. The Δ^H and Δ^{Me} functions are as defined in the preceding paper. Since the absorption bands are in most cases rather broad with flat maxima, there is a possible error of up to ±20 Å in some of the $\lambda_{max.}$ values. The nuclei are arranged in the Table in order of increasing basicity. It is seen that as the basicity of A increases, the values for bases of structure (X) tend to decrease, in agreement with the results for the analogous series (X) in the preceding paper. In the latter series the Δ^{Me} values are still positive, and only one Δ^H value is just negative, even for the most strongly basic nuclei A. In series (X) of the present paper however, the Δ



(IX)



(X)

Light absorption of cyanines and bases, $\lambda_{max.}$ and log ε.

Nucleus A [a]	Cyanine (IX)	Base (X)		Δ^H	Δ^{Me}
		Neutral	Acid		
3,3-Dimethyl-3*H*-indole	5350 [b]	5150 [c]	5300	150	200
	4·47	4·36	4·58		
2-Benzothiazole	5450	5200	5340	140	250
	4·52	4·47	4·75		
2-Quinoline	5600	5620	5580	−40	−20
	4·56	4·55	4·76		
4-Methyl-2-thiazole	5190	5640	5180	−460	−450
	4·47	4·34	4·55		
	(4900)	(5320)	(4880)	(−440)	(−420)
	(4·45)	(4·43)	(4·57)		
4-Quinoline	5960	6200	5770	−430	−240
	4·58	4·53	4·77		
		(5860)		(−90)	(10)
		(4·57)			
Base (VIII)		4900	5460	560	450
		4·43	4·44		

[a] As in Part II, the nuclei are named in the simplest possible form; the names do not strictly apply to either (IX) or (X). [b] Cyanine (VI). [c] Base (V).

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[3] Hamer, *J.*, 1940, 799; Beilenson, Hamer, and Rathbone, *J.*, 1945, 222.
[4] Dokunikhin and Gaeva, *Khim. Prom.*, 1958, **3**, 126; *Chem. Abs.*, 1958, **52**, 11,427.
[5] Brooker, Sprague, Smyth, and Lewis, *J. Amer. Chem. Soc.*, 1940, **62**, 1116.

values become definitely negative when A is 2-quinoline, and are quite strongly negative when A is 4-methyl-2-thiazole and 4-quinoline. These constitute further examples of the "reversed halochromism" discussed by Brooker *et al.*,[5] which arises when the dequaternised nitrogen of the base is very feebly basic compared with the other nitrogen atom. For the 4-quinoline base, the large deviations are shown only by the band of longer wavelength, which has a slightly lower intensity than the shorter-wavelength band. The thiazole base also shows a similar two-banded spectrum, but here the spectra of the acidified base and of the cyanine also show two bands, the separation being fairly constant (~300 Å).

Comparison of the spectra given in these two papers shows that replacement of the 3,3-dimethyl-3*H*-indole nucleus by the benz[*cd*]indole nucleus, in a cyanine or a base, causes a bathochromic shift of 900—1300 Å. These shifts are considerably greater than those (100—250 Å) accompanying the replacement of the 4*H*-3,1-benzothiazine nucleus by the naphtho[1,8]-*m*-thiazine nucleus in a series of carbocyanines and bases.[6]

EXPERIMENTAL

Thionaphthostyril (II).—Naphthostyril [7] (17·8 g.), phosphorus pentasulphide (12·0 g.), and pyridine (50 ml.) were refluxed together for 75 min. The resulting solution was decanted from a little tar into warm water (250 ml.), and the mixture was warmed on the steam-bath for 1 hr. On cooling, the oil gave a solid, which crystallised from ethanol to yield thionaphthostyril (17·4 g., 89%) as brown prisms, m. p. 156·5—157·5° (Found: S, 17·5. Calc. for $C_{11}H_7NS$: S, 17·3%). Dokunikhin and Gaeva [1] give m. p. 156·6—157·6°.

2-*Methylthiobenz*[cd]*indole* (I).—A solution of thionaphthostyril (12·4 g.) in acetone (80 ml.) was refluxed for 30 min. with methyl iodide (5·0 ml.). The product (18·9 g.) which separated crystallised from methanol, to give 2-*methylthiobenz*[cd]*indole hydriodide* as golden-brown plates, m. p. 216° (decomp.), slight decomposition with evolution of methanethiol occurring during the crystallisation (Found: I, 38·3. $C_{12}H_{10}NIS$ requires I, 38·8%). A suspension of the crude hydriodide (18·2 g.) in cold ethanol (50 ml.) was treated with cold 10% aqueous sodium hydroxide (25 ml.), the solid rapidly dissolving. The resulting brown solution was diluted immediately with water, the oil which separated was taken up in chloroform, and the solution was washed with water and dried (Na_2SO_4). Evaporation of the chloroform left a dark brown oil (9·9 g.) which was sufficiently pure for use in the preparation of dye bases. 2-*Methylthiobenz*[cd]*indole* formed a yellow oil, b. p. 192°/0·6 mm., which solidified to yellow crystals, m. p. 53—55°, slowly darkening (Found: S, 16·1. $C_{12}H_9NS$ requires S, 16·1%). The *picrate*, prepared in ethanol and crystallising from ethyl acetate in long yellow needles, had m. p. 190° (Found: S, 7·4. $C_{18}H_{12}O_7N_4S$ requires S, 7·5%).

N-*Methylnaphthostyril*.—This was prepared from 8-bromo-1-naphthoic acid essentially by Rule and Brown's method for naphthostyril.[7] The bromo-acid (30·5 g.) was dissolved in 27% aqueous methylamine (450 ml.) containing concentrated nitric acid (7·0 ml.), and the solution refluxed with potassium chlorate (0·6 g.) and copper bronze (0·6 g.) for 3 hr. After cooling, the oil which had separated was taken up in chloroform, and the dried (Na_2SO_4) extract was evaporated to leave an oil which solidified on trituration with light petroleum (b. p. 60—80°). Recrystallisation of the solid (11·9 g.) from cyclohexane gave *N*-methylnaphthostyril as yellow crystals, m. p. 76·5—78°. Dokunikhin and Gaeva give m. p. 77—79·2° for material prepared by methylation of naphthostyril.

1-*Methyl*-2-*thiobenz*[cd]*indoline* (III).—A mixture of *N*-methylnaphthostyril (10·2 g.), phosphorus pentasulphide (7·5 g.), and pyridine (20 ml.) was refluxed for 2 hr., and the resulting solution warmed with water for 30 min. Acidification of the mixture with hydrochloric acid precipitated a solid, which crystallised from ethanol (300 ml.) to yield 1-methyl-2-thiobenz[*cd*]indoline (8·5 g.) as orange-yellow needles, m. p. 124·5—125° (Found: S, 15·9. Calc. for $C_{12}H_9NS$: S, 16·1%). A further crop (1·6 g.) of slightly less pure material was obtained by concentration of the mother-liquors. Dokunikhin and Gaeva [2] give m. p. 127·2—130·4°.

1-*Methyl*-2-*methylthiobenz*[cd]*indolium Iodide* (IV).—1-Methyl-2-thiobenz[*cd*]indoline (5·5 g.) was refluxed with ether (25 ml.) and methyl iodide (25 ml.) for 6 hr. The solid which separated was washed with ethyl acetate and had m. p. 115—117° (decomp.) (4·82 g.); the mother-liquors

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[6] Hamer and Rathbone, *J.*, 1943, 487.
[7] Rule and Brown, *J.*, 1934, 137.

from the reaction yielded a further quantity (3·35 g.) of slightly less pure material when refluxed for a further 6 hr. with methyl iodide. Crystallisation from methanol was accompanied by slight decomposition but gave 1-*methyl*-2-*methylthiobenz*[cd]*indolium iodide monohydrate* as olive-green needles, m. p. 116—118° (decomp.) (Found: I, 35·2; S, 8·9. $C_{13}H_{14}ONIS$ requires I, 35·3; S, 8·9%).

Cyanine Bases (X).—(a) *By fusion.* 2-Methylthiobenz[*cd*]indole (1·00 g.) and 2,3-dimethylbenzothiazolium toluene-*p*-sulphonate (1·38 g.) were fused together on the steam-bath, an immediate vigorous evolution of methanethiol occurring. After about 1 min. the mixture had completely solidified, and was then refluxed for 1 hr. with pyridine (10 ml.). The solid which separated on cooling was washed successively with a little cold pyridine and boiling ethanol, and the product (1·73 g.) crystallised from methanol (250 ml./g.) to give 2-2′-*benz*[cd]-*indolylmethylene*-3-*methylbenzothiazoline toluene*-p-*sulphonate* (1·15 g., 58%) as deep red needles with a blue reflex, m. p. 300—301° (decomp.) (Found: S, 12·95. $C_{27}H_{22}O_3N_2S_2$ requires S, 13·2%). This material (1·56 g.) was warmed with chloroform and dilute aqueous sodium hydroxide until dissolution was complete. The chloroform layer was washed with water and dried (Na_2SO_4) and then evaporated to dryness, to give a solid which was extracted (Soxhlet) with benzene. The extracts deposited a solid (0·76 g.) which crystallised from benzene (260 ml./g.) to yield 2-2′-*benz*[cd]*indolylmethylene*-3-*methylbenzothiazoline* (0·55 g.) as purple-brown needles, m. p. 279° (Found: S, 10·2. $C_{20}H_{14}N_2S$ requires S, 10·2%).

A mixture of 1,2-dimethylquinolinium toluene-*p*-sulphonate (1·6 g.) and 2-methylthiobenz-[*cd*]indole (1·0 g.) was fused on the steam-bath and then boiled in pyridine as before. The resulting solution was poured into 10% aqueous sodium hydroxide, and the tar which separated was taken up in chloroform. The chloroform extract was washed with water, dried (Na_2SO_4), concentrated, and then chromatographed on activated alumina. Elution of the main band with chloroform, followed by evaporation of the eluate, gave a solid (0·6 g.), from which 2-2′-*benz*[cd]-*indolylmethylene*-1,2-*dihydro*-1-*methylquinoline* (0·17 g.) was obtained as purple needles, m. p. 223°, by crystallisation from benzene (Found: C, 85·9; H, 5·3. $C_{22}H_{16}N_2$ requires C, 85·7; H, 5·2%). Similarly prepared was 4-2′-*benz*[cd]*indolylmethylene*-1,4-*dihydro*-1-*methylquinoline*, deep green crystals, m. p. 256°, from 2-methoxyethanol (Found: C, 86·0; H, 5·7. $C_{22}H_{16}N_2$ requires C, 85·7; H, 5·2%).

(b) *In solution.* 2-Methylthiobenz[*cd*]indole hydriodide (1·64 g.), 1,2,3,3-tetramethyl-3*H*-indolium iodide (1·51 g.) and anhydrous sodium acetate (1·4 g.) were refluxed together in ethanol (20 ml.) for 6 hr. The solid (1·80 g.) obtained by pouring the resulting solution into water crystallised from ethanol (60 ml.), to yield 2-2′-*benz*[cd]*indolylmethylene*-1,3,3-*trimethylindoline hydriodide* (0·99 g.), deep green needles, m. p. 241—242° (decomp.) (Found: C, 61·2; H, 4·5. $C_{23}H_{21}N_2I$ requires C, 61·1; H, 4·7%). Treatment of this material with sodium hydroxide and chloroform yielded the *base* (V), deep green needles, m. p. 137—137·5°, from cyclohexane (Found: C, 85·0; H, 6·4. $C_{23}H_{20}N_2$ requires C, 85·15; H, 6·2%). Similarly prepared was 2-2′-*benz*[cd]*indolylmethylene*-3,4-*dimethylthiazoline hydriodide* (49%), deep purple-blue needles, m. p. 282—283° (decomp.) (from 2-methoxyethanol; 50 ml./g.) (Found: I, 31·3. $C_{17}H_{15}N_2IS$ requires I, 31·3%); the *base* prepared from it formed green plates, m. p. 270°, from benzene (Found: C, 73·2; H, 5·4. $C_{17}H_{14}N_2S$ requires C, 73·35; H, 5·1%).

Cyanines (IX).—(a) *From quaternary salt* (IV). A mixture of 1-methyl-2-methylthiobenz-[*cd*]indolium iodide (1·00 g.), 1,2,3,3-tetramethyl-3*H*-indolium iodide (0·88 g.), and fused sodium acetate (0·80 g.) in ethanol (20 ml.) was refluxed for 3 hr. The solid which separated on chilling of the solution was collected and washed with a little cold ethanol. (1-*Methyl*-2-*benz*[cd]*indole*)(1,3,3-*trimethyl*-2-3H-*indole*)*methincyanine iodide* (VI) (0·59 g., 43%) had m. p. 245—246° (decomp.), unchanged by crystallisation from ethanol (25 ml./g.) from which it formed brown plates with a bronze reflex (Found: I, 25·7. $2C_{24}H_{23}N_2I,C_2H_6O$ requires I, 25·9%). Similarly prepared were: (1-*methyl*-2-*benz*[cd]*indole*)(1-*methyl*-2-*quinoline*)*methincyanine iodide* (39%), clusters of green needles, m. p. 266—267° (decomp.), from methanol (60 ml./g.) (Found: I, 27·2. $2C_{23}H_{19}N_2I,CH_4O$ requires I, 27·2%); (1-*methyl*-2-*benz*[cd]*indole*)(1-*methyl*-4-*quinoline*)*methincyanine iodide* (71%), green needles, m. p. 283°, from methanol (85 ml./g.) (Found: I, 27·7. $2C_{23}H_{19}N_2I,CH_4O$ requires I, 27·2%); (1-*methyl*-2-*benz*[cd]*indole*)-(3,4-*dimethyl*-2-*thiazole*)*methincyanine iodide* (46%), purple needles, m. p. 267° (decomp.), from methanol (110 ml./g.) (Found: I, 29·3. $2C_{18}H_{17}N_2IS,CH_4O$ requires I, 29·1%).

(b) *By quaternisation of bases* (X). Dye base (V) was fused on the steam-bath for 3 hr. with an excess of methyl toluene-*p*-sulphonate. A solution of the product in ethanol was treated with an aqueous potassium iodide solution, to precipitate the dye, which after crystallisation from ethanol was identical in m. p. and mixed m. p. with dye (VI) prepared as in (a). A mixture of 2-2′-benz[*cd*]indolylmethylene-3-methylbenzothiazoline (0·30 g.) and methyl toluene-*p*-sulphonate (2·0 g.) was fused at 200° for 20 min., and the product in methanol was treated with an aqueous solution of sodium bromide. The precipitate was collected, washed with water, and crystallised from methanol (25 ml.), to give (1-*methyl*-2-*benz*[cd]*indole*)(3-*methyl*-2-*benzothiazole*)*methincyanine bromide* (0·19 g.), purple-brown, m. p. 297—298° (decomp.) (Found: Br, 18·6. $2C_{21}H_{17}N_2BrS,CH_4O$ requires Br, 18·8%).

Merocyanines.—A mixture of 1-methyl-2-methylthiobenz[*cd*]indolium iodide (1·00 g.), 3-ethyl-2-thiothiazolid-4-one (0·47 g.) and anhydrous sodium acetate (0·80 g.) was refluxed for 2 hr. in ethanol (20 ml.). The chilled solution deposited a solid (0·25 g.), which from benzene (15 ml.) formed 3-*ethyl*-5-(1-*methyl*-2-*benz*[cd]*indolinylidene*)-2-*thiothiazolid*-4-*one* (VII) (0·17 g.), red plates, m. p. 209—211° (Found: S, 19·5. $C_{17}H_{14}ON_2S_2$ requires S, 19·65%), $\lambda_{max.}$ 5280 Å (log ε 4·59). Similarly prepared from 1,3-dimethyl-2-thiohydantoin was 1,3-*dimethyl*-5-(1-*methyl*-2-*benz*[cd]*indolinylidene*)-2-*thioiminazolid*-4-*one*, deep blue needles, m. p. 212—213° (from benzene; 65 ml./g.) (Found: S, 10·25. $C_{17}H_{15}ON_3S$ requires S, 10·4%), $\lambda_{max.}$ 5420 Å (log ε 4·08).

Dequaternisation of Cyanine (VI).—Finely powdered dye (VI) (0·58 g.) and redistilled *NN*-diethylaniline (15 ml.) were refluxed together for 20 min. After removal of the amine by steam-distillation, the solid product was collected, washed with water, dried, and chromatographed in chloroform solution on activated alumina. The red band was eluted, and the eluate was evaporated to dryness, to leave a solid which was washed with light petroleum (b. p. 60—80°) and crystallised from benzene–cyclohexane. 2-(3,3-*Dimethyl*-2-3H-*indolyl*)-*methylene*-1-*methyl*-*benz*[cd]*indoline* (VIII) (35 mg.) was obtained as green crystals, m. p. 202—203°, from benzene–cyclohexane (Found: N, 8·5. $C_{23}H_{20}N_2$ requires N, 8·6%).

The absorption spectra were measured as in the preceding paper. Since some of the bases tended to show the spectrum of the acidified form in ethanolic solution (cf. Brooker *et al.*[5]), 10% aqueous sodium hydroxide solution (1 drop) was added to the solution (100 ml.) before the spectrum of the unprotonated form was measured.

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