recrystallizations (200 cc. per g.). The dye formed beautiful prisms with a greenish-bronze reflex; m. p. above 300°. dec., with sintering from 275°.

Anal. Calcd. for $C_{23}H_{22}I_2N_2$: I, 43.76. Found: I, 43.56.

1',2 - Diethyl - 4' - methylthia - 2' - cyanine iodide (IX) was obtained from V in similar fashion to III, using 1-methylbenzothiazole etho-*p*-toluenesulfonate. The yield of crude product was 84%, and 45% after two recrystallizations (125 cc. per g.). The orange-yellow needles had m. p. 276–277.5°, dec.

Anal. Calcd. for $C_{22}H_{23}IN_2S$: I, 26.76. Found: I, 26.86.

The maximum absorption is at 4800 Å.

1',2 - Diethyl - 4 '- methyl - 3,4 - benzothia - 2' - cyanine iodide (X) was obtained similarly using 2-methyl-*β*-naphthothiazole etho-*p*-toluenesulfonate. The yield of product was 57% before and 42% after recrystallization (325 cc. per g.). The minute reddish-orange needles had m. p. 272–274°, dec.

Anal. Calcd. for $C_{26}H_{25}IN_2S$: I, 24.21. Found: I, 24.19.

The dye has its maximum absorption at 5000 Å. There is an indefinite secondary band with its head at about 4800 Å.

1,1' - Diethyl - 2' - iodo - 4 - methyl - 2,4' - cyanine Iodide (XI).—2-Iodolepidine ethiodide (4.25 g.; 2 mols), triethylamine (1.5 cc.; 2.1 mols) and ethyl alcohol (25 cc.) were refluxed for twenty minutes. Dye separated from the hot reaction mixture; yield 71% (44%; 140 cc. per g.). After a further recrystallization (yield 20%) the greenish-bronze crystals had m. p. 231–232°, dec.

Anal. Calcd. for $C_{24}H_{24}I_2N_2$: C, 48.49; H, 4.07; I, 42.73. Found: C, 48.65; H, 4.10; I, 42.37.

Summary

1. Both the methyl groups in 2,4-dimethylquinoline ethiodide can undergo condensation with 2-iodoquinoline ethiodide and there results a cyanine dye of a new type containing three quinoline nuclei. The same dye is formed when 2,4-diiodoquinoline ethiodide is condensed with quinaldine ethiodide and also when 1,1'-diethyl-2'-methyl-2,4'-cyanine iodide is condensed with 2-iodoquinoline ethiodide.

2. The absorption curve of the new dye is unusual. It consists of two distinct bands separated by a trough of almost complete transmission. This is probably due to the unusual structure of the dye, for the molecule contains linkages characteristic of three distinct cyanine dye types.

3. 2,4-Diiodoquinoline ethiodide condenses with 1-methylbenzothiazole etho-*p*-toluenesulfonate to give a trinuclear dye containing one quinoline and two benzothiazole nuclei. The absorption curve of this dye likewise consists of two distinct bands and bears a very close resemblance to the sensitizing curve of the dye for silver chloride, thus affording a particularly striking example of this relationship.

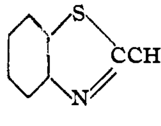
ROCHESTER, N. Y. RECEIVED OCTOBER 5, 1936

[CONTRIBUTION NO. 582 FROM THE KODAK RESEARCH LABORATORIES]

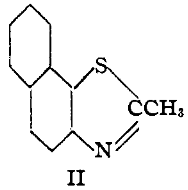
Studies in the Cyanine Dye Series. VIII. Dyes Derived from 2-Methylphenanthro-[9,10]-thiazole

BY G. H. KEYES AND L. G. S. BROOKER

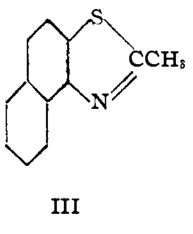
Certain cyanine dyes derived from 1-methylbenzothiazole (I) are well known, and in the search for effective photographic sensitizers, cyanines have been prepared from the methyl-*α*- and *β*-naphthothiazoles (II and III, respectively)[1,2,3] some of which dyes proved to be of considerable value. It was accordingly felt to be of interest to attempt to prepare dyes from 2-methylphenanthro-[9,10]-thiazole (IV), since this base may be considered to bear a similar relationship to II (or III) as III (or II) bears to I.



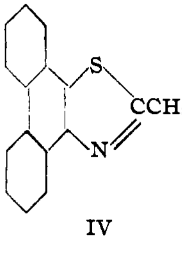
I



II



III



IV

The method used for preparing IV was a modi-

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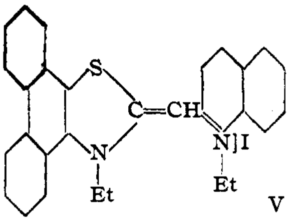
(1) Brooker, U. S. Patent 1,935,696; 1,969,444.

(2) Hamer, *J. Chem. Soc.*, 2598 (1929).

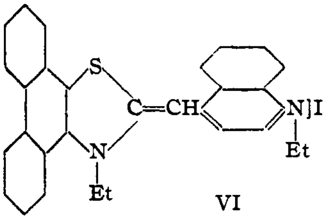
(3) Brooker and White, THIS JOURNAL, **57**, 547, 2480 (1935).

fication of that used by Jacobson[4] for the preparation of 2-methyl-β-naphthothiazole, 9-acetaminophenanthrene[5] being converted into the thioacetamino compound by treatment with phosphorus pentasulfide in hot dry toluene, and this being oxidized to the base by potassium ferricyanide in cold dilute alkaline solution. The pure base was obtained as nearly colorless needles with m. p. 145–147°, but the yield was only about 0.25%, calculated from the phenanthrene used as starting material.

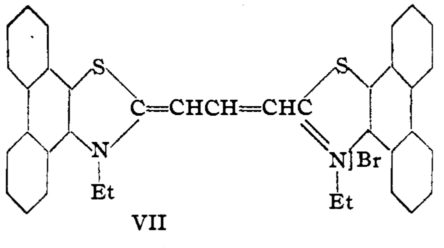
The metho- and etho-*p*-toluenesulfonates of the base were prepared by heating with the appropriate sulfonic esters, but the base reacted with these even more slowly than 2-methyl-β-naphthothiazole. Heating at high temperatures, too, had to be avoided on account of the tendency to decompose on the part of the esters, particularly the ethyl ester. From the appropriate *p*-toluenesulfonates the methiodide and ethiodide of the base were obtained and analyzed, but these salts were sparingly soluble and the *p*-toluenesulfonates themselves were chosen for submitting to certain dye condensations. From the etho-*p*-toluenesulfonate there was thus obtained 1′,2-diethyl-3,4,5,6-dibenzothia-2′-cyanine iodide (V), 1′,2-diethyl-3,4,5,6-dibenzothia-4′-cyanine iodide (VI) and 2,2′-diethyl-3,4,3′,4′,5,6,5′,6′-tetrabenzothiacarbocyanine bromide (VII) by condensation with 2-iodoquinoline ethiodide, quinoline ethiodide and ethyl orthoformate, respectively. In no case was the yield of dye high, and this is probably due in part to the presence in the ether-washed etho-*p*-toluenesulfonate employed of hydro-*p*-toluenesulfonate, formed by the union of the base with *p*-toluenesulfonic acid resulting from the decomposition of the sulfonic ester by elimination of ethylene.



V



VI



VII

It is interesting to compare dyes V, VI and VII with the related simpler dyes derived from I, II and III. In the thia-2′-cyanine series, the 1′,2-diethyl dyes derived from I, II and III are all known,[1,2] but in the present work the yields of those derived from II and III have been improved by the use of triethylamine.[6]

In the thia-4′-cyanine series, the dye derived from I, 1′,2-diethylthia-4′-cyanine iodide, was first described by Braunholtz and Mills[7] but we have obtained it in greatly increased yield by using excess of quinoline ethiodide and of potassium hydroxide in its preparation. High yields of the dyes from II and III were similarly obtained.

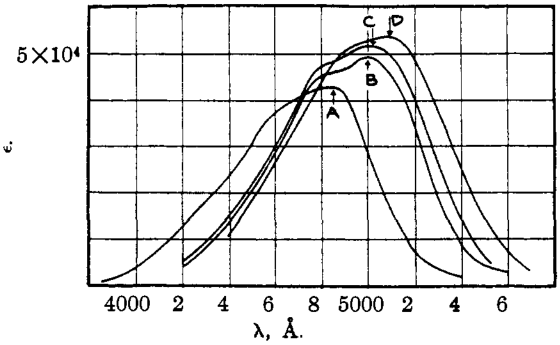


Fig. 1.—Absorption curves: A, 1′,2-diethylthia-2′-cyanine iodide; B, 1′,2-diethyl-5,6-benzothia-2′-cyanine iodide; C, 1′,2-diethyl-3,4-benzothia-2′-cyanine iodide; D, 1′,2-diethyl-3,4,5,6-dibenzothia-2′-cyanine iodide (V).

The absorption curves of the thia-2′-cyanines are given in Fig. 1, those of the thia-4′-cyanines in Fig. 2, and those of the thiacarbocyanines in Fig. 3. In all cases the molecular extinction coefficient, ε, is plotted against the wave length, λ, in Å. In all three series, A, B, C and D indicate the curves of the dyes derived from I, II, III and IV, respectively, and the maxima are indicated by arrows.

The wave lengths of maximum absorption of the

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(4) Jacobson, *Ber.*, **20**, 1897 (1887).

(5) Schmidt and Strobel, *ibid.*, **34**, 1461 (1901).

(6) Brooker and Keyes, THIS JOURNAL, **57**, 2488 (1935).

(7) Braunholtz and Mills, *J. Chem. Soc.*, **121**, 2004 (1922).

dyes are given in the table, the differences between adjacent values being given also.

TABLE OF ABSORPTION MAXIMA, IN Å.

	A		B		C		D
Fig. 1	4850		5000		5025		5100
		150		25		75	
Fig. 2	5025		5215		5225		5300
		190		10		75	
Fig. 3	5575		5925		5950		6125
		350		25		175	

It has been shown previously that, in the thiacarbocyanine series, dyes derived from β-naphthothiazole have their maximum absorption nearer the red, in general, than the corresponding dyes derived from α-naphthothiazole,[3] and this rule is now seen to hold in the thia-2′-cyanine and thia-4′-cyanine series also.

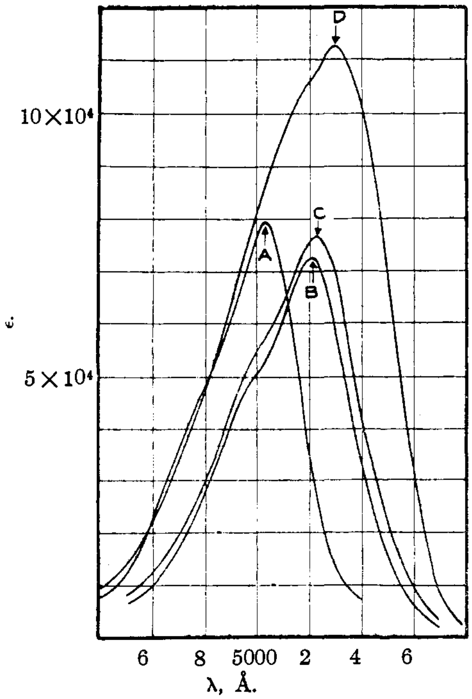

Fig. 2.—Absorption curves: A, 1′,2-diethylthia-4′-cyanine iodide; B, 2′,2-diethyl-5,6-benzothia-4′-cyanine iodide; C, 1′,2-diethyl-3,4-benzothia-4′-cyanine iodide; D, 1′,2-diethyl-3,4,5,6-dibenzothia-4′-cyanine iodide (VI).

A second generalization is that in every case a dye containing the phenanthro-[9,10]-thiazole nucleus has its absorption band nearer the red end of the spectrum than either of the corresponding dyes derived from a naphthothiazole. It is worthy of notice, however, that the shift produced when the benzothiazole nucleus (or nuclei) of a dye is replaced by α-naphthothiazole is at least twice as great as that produced when the β-naphthothiazole nucleus (or nuclei) of the dye in the same series is replaced by phenanthro-[9,10]-thiazole, although in both these processes the lighter nuclei of the two pairs have been weighted in the same way.

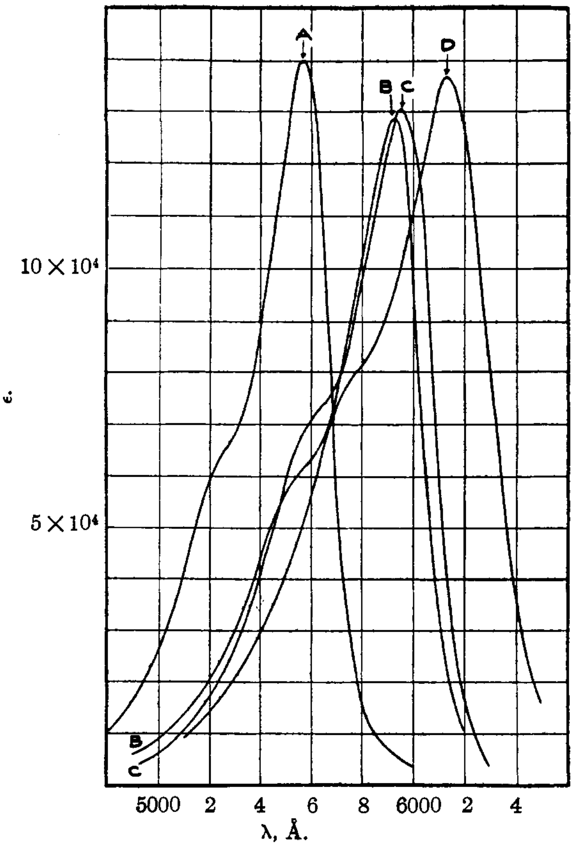

Fig. 3.—Absorption curves: A, 2,2′-diethylthiacarbocyanine iodide; B, 2,2′-diethyl-5,6,5′,6′-dibenzothiacarbocyanine bromide; C, 2,2′-diethyl-3,4,3′,4′-dibenzothiacarbocyanine bromide; D, 2,2′-diethyl-3,4,3′,4′,5,6,5′,6′-tetrabenzothiacarbocyanine bromide (VII).

Within each series the curves show a very marked resemblance to one another. Thus the four curves in Fig. 1 are all of the same general shape, there being in each case a principal band with a pronounced secondary band nearer the region of shorter wave length. The maximum values for ϵ lie very close together, also, and the same holds true, with one exception, for the curves in the other two figures. In Fig. 2 there is again a secondary band nearer the blue in each case, and curves A, B and C have maximum values of ϵ which are close together, but the value for D is considerably higher. The maximum value of ϵ for a thia-4′-cyanine is markedly higher than for the corresponding thia-2'-cyanine, and is highest of all for the corresponding thiacarbocyanine (Fig. 3). The curves in Fig. 3 have sharp maxima and there are again secondary bands nearer the blue.

The dyes were tested photographically after incorporation in a bromide emulsion. In the thia-2'-cyanine series (as in the thiacarbocyanine series[3]) the β-naphthothiazole derivative was a stronger sensitizer than the α-derivative but V is weaker than either of these. The thia-4'-cyanines which are derivatives of II and III are sensitizers for the green portion of the spectrum[8] with maxima at about 5400 Å., and each gives a second, less well-defined maximum nearer the blue. Here again the β-naphthothiazole derivative is the stronger sensitizer of the two. Dye VI sensitizes to about 6400 Å. for a moderate exposure, but the band is very flat and it is difficult to find a maximum.

The sensitizing action of the thiacarbocyanine dyes derived from II and III has already been described.[2,3] The dye VII is a relatively poor sensitizer. Its action extends to 6900 Å., but there is a decided gap between the regions of ordinary and of extra-sensitivity. The maximum effect is at 6550 Å., but even at this wave length VII is markedly inferior to either of the 2,2'-diethylthiacarbocyanines derived from the methyl naphthothiazoles, although their sensitizing maxima lie nearer to the blue.

We again wish to thank Dr. L. A. Jones and Mr. E. E. Richardson for the absorptions (which were all determined for methyl alcoholic solutions) and Dr. L. T. Hallett for the analyses except those marked by an asterisk which were kindly provided by Dr. S. F. Darling.

Experimental

9-Nitrophenanthrene, m. p. constant at 112.5–114.5°, was prepared by the method of Schmidt and Heinle[9] who give m. p. 116–117°. The yield of pure product was 4.5%.

9-Aminophenanthrene, m. p. 132–133°, was obtained in a yield of 27% using Schmidt and Strobel's method.[5] These authors claim a yield of 93–99% of product with m. p. 135–136°. They also state that the base darkens in air, but we find it to be quite stable when pure.

Anal. Calcd. for $C_{14}H_{11}N$: C, 87.00; H, 5.74; N, 7.25. Found: C, 86.75*; H, 5.45*; N, 7.24.

9-Acetaminophenanthrene was obtained by the following modification of Schmidt and Strobel's method, which avoids using a large excess of acetic anhydride. The 9-amino compound (4.8 g.; 1 mol) was dissolved in glacial acetic acid (60 cc.), heated on a steam-bath, acetic anhydride (3 g.; 1.2 mols) added, and the whole heated at 100° for forty-five minutes. The product separated on cooling (5 g.; 86%) and was a nearly colorless crystalline powder with m. p. 204–208° which was sufficiently pure for the next stage. On recrystallization from methyl alcohol (75 cc. per g.) the m. p. was raised to 213–215° (Schmidt and Strobel give m. p. 207–208° with sintering from 205°).

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.66; H, 5.57; N, 5.96. Found: C. 81.5*; H, 5.6*; N, 6.02.

9-Thioacetaminophenanthrene.—Jacobson[4] prepared thioacetyl-α-naphthylamine by fusing acetyl-α-naphthylamine with phosphorus pentasulfide. Hantzsch[10] improved on Hofmann's similar method for the preparation of thioacetamide[11] by using benzene in the reaction and in the following we used toluene.

9-Acetaminophenanthrene (5 g.; 1 mol) was dissolved in gently refluxing dry toluene (300 cc.), pyridine (1 cc.) was added (this improved the yield markedly) followed by finely powdered phosphorus pentasulfide (4.7 g.; 1 mol) with good mechanical stirring. Heating and stirring were continued for two hours, and the toluene was decanted from the sticky residue and extracted with hot 5% caustic soda solution. The chilled extract was acidified carefully with acetic acid and the thioacetyl compound separated as a brownish solid. This was redissolved in alkali and reprecipitated in the cold. (The moist product at this stage was sufficiently pure for conversion to IV.) After drying the yield was 61%. It was recrystallized from methyl alcohol (charcoal) (yield 20%) and formed buff-colored crystals with m. p. 181–182°, dec., not raised by further recrystallization.

Anal. Calcd. for $C_{16}H_{13}NS$: C, 76.45; H, 5.22; N, 5.58. Found: C, 76.4*; H, 5.1*; N, 5.56.

2-Methylphenanthro-[9,10]-thiazole.—A run of crude 9-thioacetaminophenanthrene was dissolved in dilute caustic soda and the solution chilled and aqueous potassium ferricyanide added until an excess was present as indicated by a permanent yellow color. The base which separated as a solid was extracted with ether, the extract dried over anhydrous potassium carbonate and the solvent removed; yield 53%, calculated from the acetyl compound. The base was recrystallized from methyl alcohol (yield 29%).

Anal. Calcd. for $C_{16}H_{11}NS$: C, 77.05; H, 4.45; N, 5.62. Found: C, 77.0*; H, 4.6*; N, 5.59.

2-Methylphenanthro-[9,10]-thiazole Methiodide.—The base (0.5 g.; 1 mol) and methyl p-toluenesulfonate (0.37 g.; 1 mol) were heated at 120–130° for one week. The solid product was dissolved in boiling methyl alcohol (30 cc.) and potassium iodide (0.66 g.; 2 mols) in water (10 cc.) was added to the filtered solution. The methiodide separated and was washed with acetone and dried; yield 0.4 g. (46%). The salt separated from methyl alcohol (25 cc.) as a nearly colorless crystalline powder with m. p. 206–208°, dec., after two further recrystallizations.

Anal. Calcd. for $C_{17}H_{14}INS$: I, 32.45. Found: I, 32.51.

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(8) Brooker, U. S. Patent 1,861,836; Brooker and Kodak Ltd., British Patent 378,445; Kodak-Pathé, French Patent 713,486.

(9) Schmidt and Heinle, *Ber.*, **44**, 1488 (1911).

(10) Hantzsch, *Ann.*, **250**, 264 (1888).

(11) Hofmann, *Ber.*, **11**, 340 (1878).

2-Methylphenanthro-[9,10]-thiazole Ethiodide.—Equimolecular proportions of base (1 g.) and ethyl *p*-toluenesulfonate (0.8 g.) were heated at 130–140° for ten days. A hot aqueous extract (40 cc.) of the solid product was treated with hot aqueous potassium iodide (1.4 g. in 10 cc.). The ethiodide was precipitated (0.4 g.; 24%) and was recrystallized from methyl alcohol (10 cc.; charcoal); yield 18.5%. The melting point, 202–204°, dec., of the cream-colored crystalline powder was unaltered after a second recrystallization.

Anal. Calcd. for $C_{18}H_{16}INS$: I, 31.32. Found: I, 30.86.

In the dye condensations the crude etho-*p*-toluenesulfonate of the base was washed with ether and then used without further purification.

1′,2-Diethyl-5,6-benzothia-2′-cyanine iodide was obtained in a yield of 86% before and 70% after recrystallization when triethylamine was used to effect the condensation. The corresponding yields given by Hamer,[3] who used potassium hydroxide, are 44 and 30%. We find that the m. p. is 287–289°, dec.

1′,2-Diethyl-3,4-benzothia-2′-cyanine iodide was obtained similarly in a yield of 70% before and 55% after recrystallization; Hamer gives 36 and 24%.

1′,2-Diethylthia-4′-cyanine iodide was obtained by the interaction of 1-methylbenzothiazole ethiodide (1 mol), quinoline ethiodide (1 mol) and sodium ethylate (1.2 mols) by Braunholtz and Mills[7] who obtained the pure dye in a yield of 9–13%. By using potassium hydroxide (1 mol) for the condensation our yields were 19.5% before and 15.5% after recrystallization from methyl alcohol (55 cc. per g.). Kaufmann and Vonderwahl[12] have shown that in a very similar preparation, that of Ethyl Red (1,1′-diethyl-2,4′-cyanine iodide), the yield of dye was much improved by using 100% excess of quinoline ethiodide. In the present case, use of 2 mols of quinoline ethiodide resulted in the yield of pure dye being raised to 19%, but by using 2 mols of potassium hydroxide also, the much more marked increase of yield to 59% was obtained. Use of 3 mols of quinoline ethiodide and of potassium hydroxide gave a yield of 63% of pure dye, the yield being calculated in all cases from the 1-methylbenzothiazole ethiodide.

1′,2-Diethyl-5,6-benzothia-4′-cyanine iodide was obtained similarly from 1-methyl-α-naphthothiazole etho-*p*-toluenesulfonate (1 mol) using 100% excess of quinoline ethiodide and of potassium hydroxide; yield 51% before and 45% after recrystallization from methyl alcohol (350 cc. per g.). After a further recrystallization (yield 39%) the scarlet needles had m. p. 285–288°, dec.

Anal. Calcd. for $C_{25}H_{23}IN_2S$: I, 24.87. Found: I, 24.76.

1′,2-Diethyl-3,4-benzothia-4′-cyanine iodide was obtained similarly, yield 33% before and 27% after recrystallization. After two further recrystallizations (yield 21%) from methyl alcohol (175 cc. per g.) the dye formed beautiful reddish-brown needles (transmitted light) with a metallic green reflex; m. p. 248–250°, dec.

Anal. Calcd. for $C_{25}H_{23}IN_2S$: I, 24.87. Found: I, 24.76.

1′,2 - Diethyl - 3,4,5,6 - dibenzothia - 2′ - cyanine Iodide (V).—2 - Methylphenanthro - [9,10] - thiazole etho-*p*-toluenesulfonate (0.9 g.; 1 mol) was condensed with 2-iodoquinoline ethiodide (0.82 g.; 1 mol) in absolute ethyl alcohol (30 cc.) using triethylamine (0.4 g.; 2 mols), the mixture being refluxed for one-half hour; yield 0.15 g. (13%) and 0.09 g. (8%) after recrystallization from methyl alcohol (180 cc.). The dull-red crystals had m. p. 248–250°, dec.

Anal. Calcd. for $C_{29}H_{25}IN_2S$: I, 22.66. Found: I, 22.28.

1′ - Ethyl - 2 - methyl - 3,4,5,6 - dibenzothia - 2′ - cyanine iodide was prepared similarly; yield 45% before and 18% after recrystallization from methyl alcohol (1800 cc. per g.). The bright red crystalline powder had m. p. 244–246°, dec.

Anal. Calcd. for $C_{28}H_{23}IN_2S$: I, 23.24. Found: I, 22.91.

The absorption of this dye resembles that of V, but the maximum lies at 5050 Å.

1′,2 - Diethyl - 3,4,5,6 - dibenzothia - 4′ - cyanine Iodide (VI).—2 - Methylphenanthro - [9,10] - thiazole etho - *p* - toluenesulfonate (1.1 g.; 1 mol) was condensed with quinoline ethiodide (0.7 g.; 1 mol) in absolute ethyl alcohol (25 cc.) using potassium hydroxide (0.14 g.; 1 mol) and refluxing for forty-five minutes; yield 10% before and 7% after recrystallization from methyl alcohol (1130 cc. per g.). The dull reddish-brown crystals had m. p. 244–247°, dec.

Anal. Calcd. for $C_{29}H_{25}IN_2S$: I. 22.66. Found: I, 22.43.

This reaction was carried out before the advantage of using excess of quinoline ethiodide and potassium hydroxide in thia-4′-cyanine condensations was discovered, but the experiment was not repeated owing to lack of material.

2,2′ - Diethyl - 3,4,3′,4′,5,6,5′,6′ - tetrabenzothiacarbocyanine Bromide (VII).—2-Methylphenanthro-[9,10]-thiazole etho-*p*-toluenesulfonate (1.75 g.; 2 mols) was refluxed with pyridine (25 cc.) and ethyl orthoformate (1.2 g.; 2 mols) for forty-five minutes. The dye was precipitated as the bromide; yield 0.077 g. (6%). After recrystallization from dichloroethylene (Soxhlet) the yield was 4%. The minute dark bronze crystals had m. p. 200–202°, dec.

Anal. Calcd. for $C_{37}H_{29}BrN_2S_2$: C, 68.80; H, 4.53. Found: C, 68.97; H, 4.34.

Summary

1. Weighting the benzothiazole nucleus with a fused-on benzene residue gives α- or β-naphthothiazole nuclei, and these are present in photographic sensitizers of value. Repetition of the weighting process leads to the phenanthro-[9,10]-thiazole nucleus, and dyes containing this nucleus have been prepared in the hope that they would also be effective sensitizers.

2. 2-Methylphenanthro-[9,10]-thiazole has

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[12] Kaufmann and Vonderwahl, *Ber.*, **45**, 1413 (1912).

been synthesized and from it the corresponding 1′,2-diethylthia-2′- and -4′-cyanine iodides and the 2,2′-diethylthiacarbocyanine bromide.

3. In no case was a dye derived from the new base a powerful sensitizer. The thiacarbocyanine, for example, was considerably inferior even at the wave length at which it conferred maximum sensitivity, to the corresponding dyes derived from the methyl-α- and β-naphthothiazoles.

4. In every case the dyes derived from 2-methylphenanthro-[9,10]-thiazole absorb nearer the red than the corresponding dyes derived from the methylnaphthothiazoles.

ROCHESTER, N. Y. RECEIVED OCTOBER 5, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Carbonyl Sulfide. The Heat Capacity, Vapor Pressure, and Heats of Fusion and Vaporization. The Third Law of Thermodynamics and Orientation Equilibrium in the Solid

BY J. D. KEMP AND W. F. GIAUQUE

At the present time the most important problem in connection with the third law of thermodynamics relates to the circumstances under which false equilibrium complicates the practical application of this law. When either the third or the second law of thermodynamics is combined with experimental data to permit the evaluation of some desired quantity, it is implied that the observations were made under conditions of true equilibrium with respect to all processes under consideration.

Recent low temperature investigations have shown that lack of equilibrium exists in the cases of hydrogen, water and their deuterium analogs, carbon monoxide, nitric and nitrous oxides. For each of the above substances the entropy may be accurately calculated from spectroscopic data and it has been possible to give a satisfactory quantitative explanation of the discrepancy between the calorimetric and the spectroscopic values. Carbon monoxide, nitrous oxide (NNO) and nitric oxide (N_2O_2) enter the crystalline state without discrimination between the molecular orientation positions of carbon, nitrogen or oxygen in the crystal lattice. These neighboring atoms in the periodic system are very similar in size and it seems desirable to carry out experiments in which the possibility of lack of discrimination is investigated with more dissimilar atoms.

Linear, unsymmetrical, polyatomic molecules offer a particularly simple case since it is evident that only the two positions corresponding to a rotation of 180° are possible within a crystal lattice. The substance selected for investigation was the linear molecule, carbonyl sulfide (SCO). The measurements to be presented show that the practical application of the third law gives the correct entropy. However, thermal equilibrium was obtained with great difficulty in a considerable region below the melting point, as might be expected if the molecules were beginning to acquire random orientation in the equilibrium state at these temperatures.

Carbonyl Sulfide.—Carbonyl sulfide was made by dropping C. P. concentrated sulfuric acid into a saturated water solution of C. P. potassium sulfocyanate. All solutions were boiled and the preparation line was evacuated with a mercury diffusion pump to eliminate air. The gas was bubbled through a 33% sodium hydroxide solution and collected in a bulb cooled by liquid air. The last traces of water were removed by passing the gas through a tower containing phosphorus pentoxide. Generous first and last fractions were discarded, leaving about 425 cc. of liquid carbonyl sulfide. The gas was then bubbled through some of its own liquid for further purification, a procedure similar to that employed by Gray[1] and by Johnston and Giauque.[2] The final purification was effected by the use of a vacuum jacketed fractionating column; 135 cc. of purified liquid carbonyl sulfide remained after these treatments.

By means of the premelting effects which are superimposed on the heat capacity just below the melting point, it was possible to estimate that the final preparation contained less than one part in twenty thousand of liquid-soluble solid-insoluble impurity.

Apparatus.—A vacuum calorimeter assembly similar to that described by Giauque and Wiebe[3] was used for the measurements. A full description of a similar calorimeter has been given by Giauque and Egan.[4] The calorimeter, which has been given the laboratory designation Gold Calorimeter IV, weighed 443 g. It was 4 cm. in

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[1] Gray, *J. Chem. Soc.*, **87**, 1601 (1905).

[2] Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

[3] Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

[4] Giauque and Egan, *J. Chem. Phys.*, January (1937).