cedure similar to that employed for the α-form, the β-form of 2-methyl-2-carbomethoxy-9-methoxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid[12] was converted to the acephenanthrylene in 50% yield. It was crystallized from ethyl acetate; m.p. 173–174°. The ultraviolet absorption spectrum and that of the α-form were identical.

*Anal.* Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 74.18; H, 6.21.

**Acknowledgment.**—This work was supported by a grant No. C-1585 from the National Cancer Institute, U. S. Public Health Service. Dr. E. J. Rosenbaum of the Sun Oil Co. gave valuable assistance with the infrared spectra.

PHILADELPHIA, PA.

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[CONTRIBUTION FROM LINWOOD LABORATORY, REMINGTON RAND DIVISION, SPERRY RAND CORPORATION]

# Cyanine Dyes. I. Absorption of Cyanines Derived from Pyranothiazole and Thiopyranothiazoles[1]

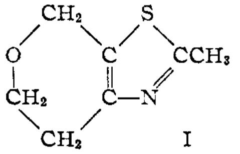
BY ROBERT H. SPRAGUE

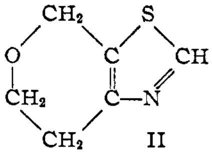
RECEIVED JULY 27, 1956

Three new thiazole bases have been prepared by condensing thioacetamide with 3-bromotetrahydro-4-pyrone, 3-bromotetrahydro-1-thio-4-pyrone and 2-bromotetrahydro-1-thio-3-pyrone. Quaternary salts of the products have given rise to new cyanine dyes, some of which are powerful photographic sensitizers. The absorptions of the new dyes are compared with those of similar dyes from benzothiazole and tetrahydrobenzothiazole.

The well known synthesis of 2-methylthiazoles by condensation of thioacetamide with α-haloketones[2] has been employed to prepare thiazole bases from 3-bromotetrahydro-4-pyrone, 3-bromotetrahydro-1-thio-4-pyrone and 2-bromotetrahydro-1-thio-3-pyrone.

Thus 3-bromotetrahydro-4-pyrone was treated with thioacetamide giving 2-methyl-6,7-dihydro-4-H-pyrano[4,3d]thiazole (I). Although (I) has not been reported in the literature, the corresponding unsubstituted thiazole II has been prepared by Sorkin and Erlenmeyer[3] by condensing thioformamide with 3,5-dibromotetrahydro-4-pyrone. The enol forms of the reactants condense with elimination of water and hydrobromic acid.


I


II

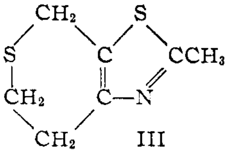
Since the product contained no bromine, Erlenmeyer postulated that the extra bromine atom in the five position of the pyrone ring was eliminated by "reductive splitting" and replaced by hydrogen.

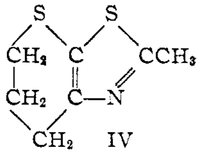
Erlenmeyer isolated only the 3,5-dibromo ketone on treatment of tetrahydro-4-pyrone with N-bromosuccinimide (36% yield, m.p. 156–157°); however, attempts to repeat his work in this Laboratory led to a mixture of the dibromo derivative with a monobromo compound, in which the latter predominated. The mixture was purified by vacuum distillation giving a 24% yield of 3-bromotetrahydro-4-pyrone in the form of a colorless liquid (b.p. 76–80° at 2 mm.) which darkened rapidly and solidified on standing.

In a second experiment the crude product was recrystallized from ethanol without previous distillation resulting in a small yield of the dibromo compound melting at 159–161°.

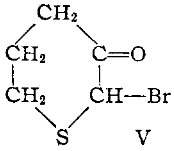
Both products condensed readily with thioacetamide in ethanol solution. Contrary to Erlenmeyer's findings in the analogous thioformamide reaction, a bromine-substituted thiazole was obtained from the dibromopyrone. The bases gave crystalline quaternary salts with ethyl iodide and were analyzed in this form.

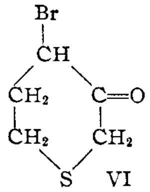
Bromination of tetrahydro-1-thio-4-pyrone[4] with N-bromosuccinimide gave a very unstable bromoketone, which nevertheless could be condensed with thioacetamide at low temperature. The product, 2-methyl-6,7-dihydro-4-H-thiopyrano[4,3d]thiazole (III), formed quaternary salts with alkyl halides which were very reluctant to crystallize. However, a crystalline hydrochloride was obtained on saturating a solution of the base in ether with hydrogen chloride and this derivative was used for analysis.


III


IV

A base IV, isomeric with III, was similarly prepared by condensing thioacetamide with the bromoketone derived from tetrahydro-1-thio-3-pyrone.[5] Of the two possible monobromo derivatives of the latter the product isolated is believed to be the 2-bromo compound V, rather than the 4-bromo isomer VI, for the following reasons:


V


VI

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[1] Presented in part before the Organic Division, American Chemical Society, at Minneapolis, Minn., Sept. 12, 1955.

[2] A. Hantzsch, *Ann.*, **250**, 265 (1889).

[3] E. Sorkin and H. Erlenmeyer, *Helv. Chim. Acta*, **31**, 96 (1948).

[4] G. M. Bennett and I. V. D. Scorah, *J. Chem. Soc.*, 196 (1927).

[5] E. H. Fehnel, THIS JOURNAL, **74**, 1569 (1952).

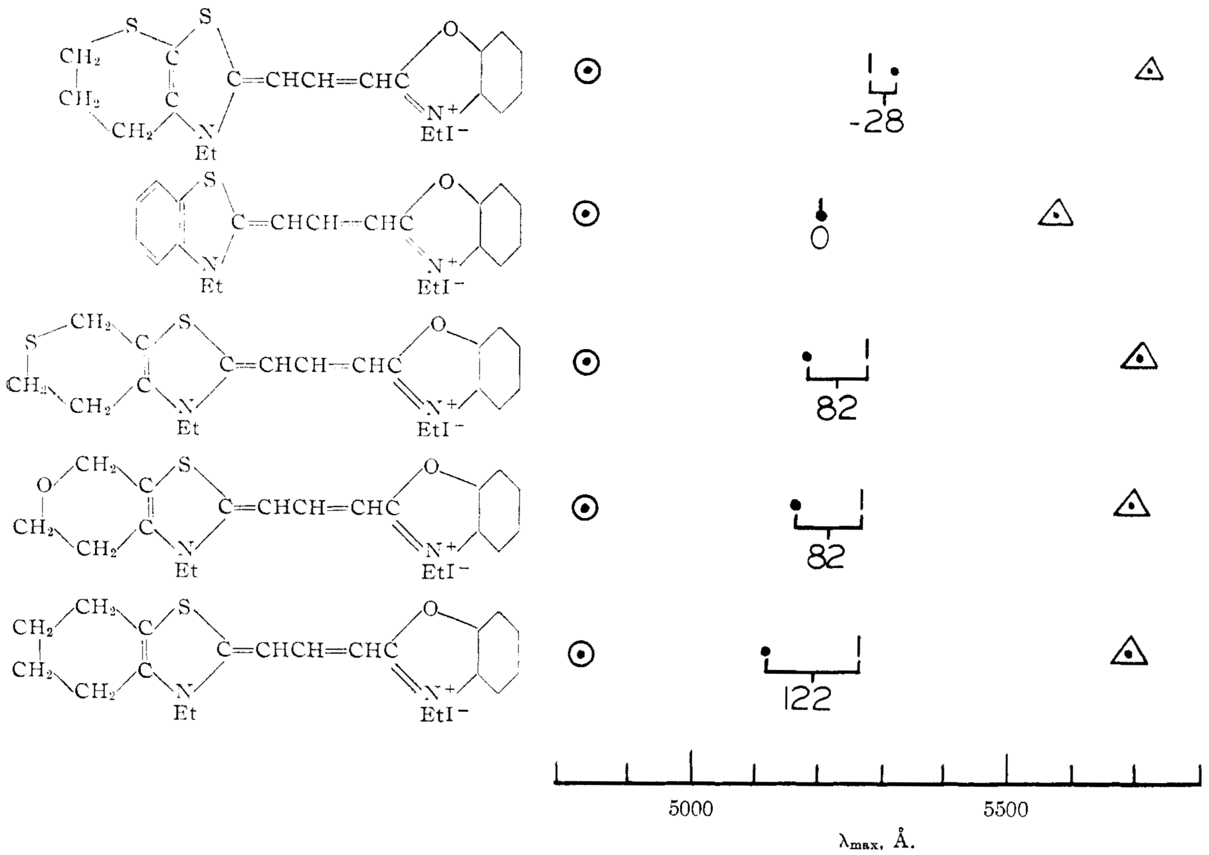
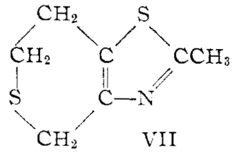


Fig. 1.—Values of $\lambda_{max.}$ of unsymmetrical carbocyanines and related symmetrical dyes: ●, unsymmetrical dye; ⊙, symmetrical oxacarbocyanine (VIII); ◬, second related symmetrical dye; ⊥, indicates arithmetic mean between ⊙ and ◬; deviation is indicated by ⊤ and its magnitude is shown in Å.

It has been noted by several workers that the sulfur atom in the system $-S-\overset{|}{\underset{H}{C}}-$ has a considerable proton-releasing effect on the attached carbon atom.[6–8] This would enhance the activity of the 2-carbon atom, already activated by the 3-carbonyl group, causing the bromine to enter in that position. Furthermore, the thiazole bases derived from V and VI would have the structure IV and VII, respectively. It seems probable that dyes derived from VII would closely resemble in color those from III, since in each the sulfur atom is insulated from the thiazole ring by at least one methylene group on each side.


VII

However, in structure IV the sulfur atom is situated adjacent to that in the thiazole ring and therefore might be expected to participate in the resonating system responsible for the color of dyes containing this nucleus. As detailed below, it was found that dyes derived from IV differ markedly in color from the corresponding dyes derived from III, while there is little difference between similar dyes from III and I. Consequently, it seems highly probable that the new base has the structure IV and therefore its precursor has the structure V. There was no indication that IV was a mixture of two isomers, since the distilled product crystallized readily and quaternary salts prepared from it were sharp melting solids.

Several representative dyes of the various cyanine types were prepared from quaternary salts of the new bases.

## Discussion of Absorptions of Dyes

Striking differences are noted when the absorptions of the dyes from the new bases are compared with the corresponding data from tetrahydrobenzothiazole and benzothiazole, using the convenient technique developed by Brooker, *et al.*, in their studies of color and constitution.[9]

Brooker has shown that the color of unsymmetrical cyanine dyes of various types appears to be de-

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(6) R. B. Woodward and R. H. Eastman, THIS JOURNAL, **68**, 2232 (1946).

(7) H. Gilman and F. J. Webb, *ibid.*, **62**, 987 (1940).

(8) E. Rothstein, *J. Chem. Soc.*, 1550, 1553, 1558 (1940).

(9) (a) L. G. S. Brooker, R. H. Sprague, C. P. Smyth and G. L. Lewis, THIS JOURNAL, **62**, 1116 (1940); (b) L. G. S. Brooker, F. L. White, G. H. Keyes, C. P. Smyth and P. F. Oesper, *ibid.*, **63**, 3192 (1941); (c) L. G. S. Brooker and R. H. Sprague, *ibid.*, **63**, 3203 (1941); (d) L. G. S. Brooker and R. H. Sprague, *ibid.*, **63**, 3214 (1941); (e) L. G. S. Brooker, G. H. Keyes and W. W. Williams, *ibid.*, **64**, 199 (1942); (f) L. G. S. Brooker and R. H. Sprague, *ibid.*, **67**, 1869 (1945); (g) L. G. S. Brooker, *et al.*, *ibid.*, **67**, 1875 (1945); (h) L. G. S. Brooker, R. H. Sprague and H. W. J. Cressman, *ibid.*, **67**, 1889 (1945); (i) L. G. S. Brooker, F. L. White and R. H. Sprague, *ibid.*, **73**, 1087 (1951); (j) L. G. S. Brooker, *et al.*, *ibid.*, **73**, 5332 (1951).

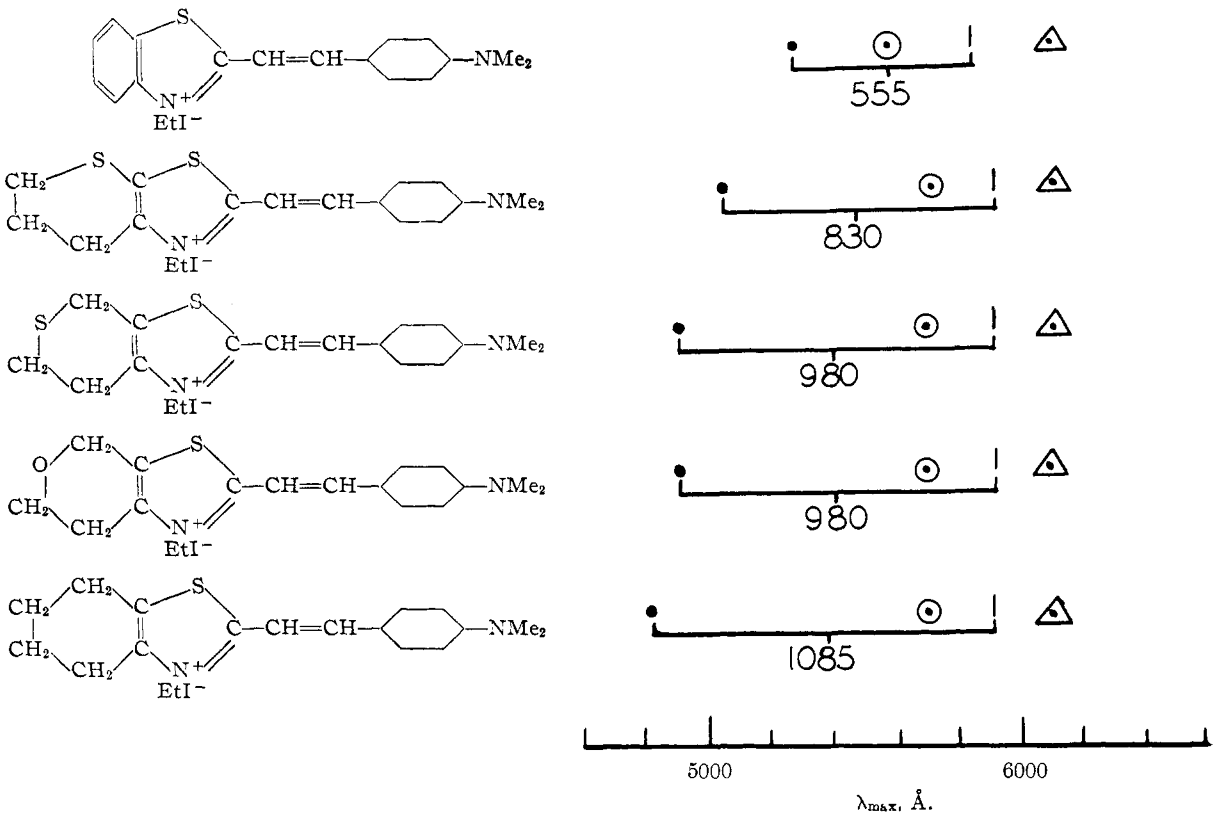
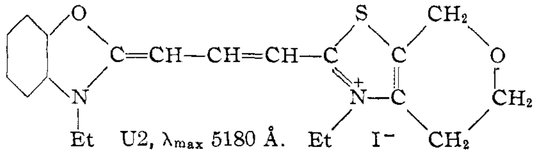
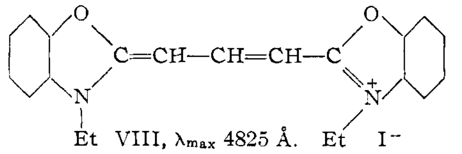


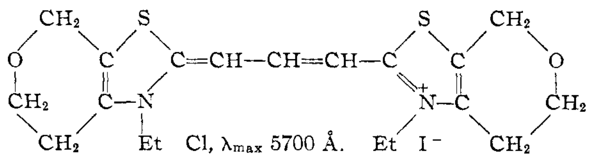
Fig. 2.—Values of $\lambda_{max}$ of $p$-dimethylaminostyryl dyes and related symmetrical dyes: ●, styryl dye; ⊙, symmetrical carbocyanine; ◬, Michler hydrol blue; ⊥, arithmetic mean between ⊙ and ◬; deviation is indicated by ⊤ and its magnitude is shown in Å. For a detailed study of similar dyes see Brooker, *et al.*[9g]

pendent largely on the relative basicity of the heterocyclic rings involved.

For example, the unsymmetrical oxapyranothiazolocarbocyanine (U2) may be considered the structural cross of the symmetrical oxacarbocyanine (VIII) and the symmetrical pyranothiazolocarbocyanine (C1).


U2, $\lambda_{max}$ 5180 Å.


VIII, $\lambda_{max}$ 4825 Å.


C1, $\lambda_{max}$ 5700 Å.

If the component rings are of comparable basicity, the absorption maximum of U2 should be midway between the maxima of the parent dyes, *i.e.*, at 5262 Å. Since the absorption maximum of U2 was found to be 5180 Å., the difference of 82 Å. (called by Brooker the "deviation") indicates that one of the rings is more basic than the other. The corresponding dye from tetrahydrobenzothiazole (U1) gives a similar difference of 122 Å., while the dye from benzothiazole was found by Brooker and co-workers to have zero deviation.[9h] These data together with those for the two isomeric thiopyranothiazole dyes are plotted in Fig. 1.

It already has been pointed out by Brooker[9g,i] that tetrahydrobenzothiazole is considerably more basic than benzothiazole, and since the pyranothiazole and thiopyranothiazoles are structurally very similar to the former, it might be expected that they would closely resemble it in basicity. From Fig. 1 it is seen that the deviations of U2 and U3 are indeed very close to U1 and lie between those of U1 and the corresponding benzothiazole dye. However, dye U4, which is isomeric with U3, has a negative deviation and thus the thiopyrano[3,2d]thiazole nucleus appears to be considerably less basic than tetrahydrobenzothiazole and very similar to benzothiazole, small negative deviations usually being regarded as equivalent to zero.[9j]

On the other hand, data shown in Fig. 2 for the $p$-dimethylaminostyryl series and in Fig. 3 for the pyrrolocarbocyanine series indicate a different order of basicity. In Fig. 2 all three of the new dyes S1, S2 and S3 show deviations lying between those of the tetrahydrobenzothiazole and benzothiazole dyes, S3 again being the least basic of the three but still considerably more basic than benzothiazole. The same order is observed in Fig. 3, the resem-

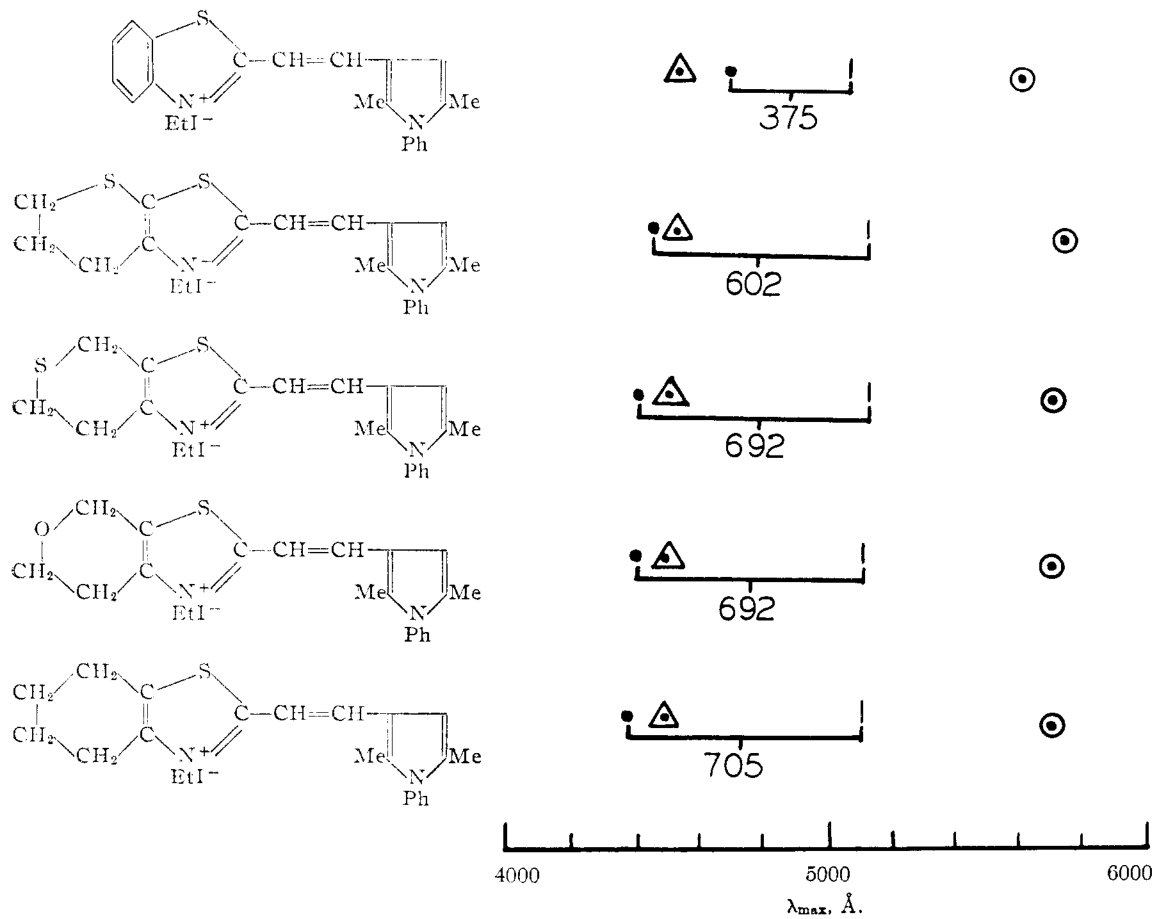
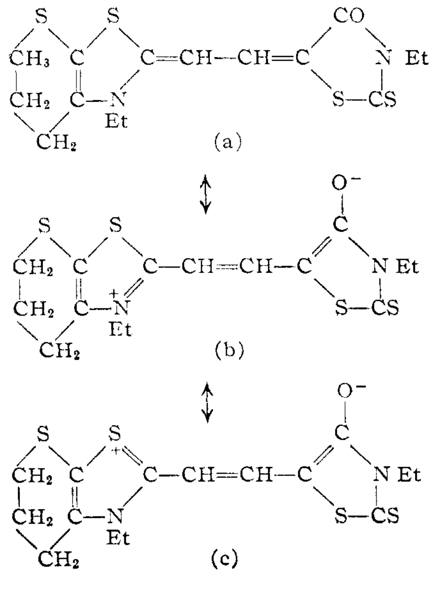


Fig. 3.—Values of $\lambda_{max}$ of unsymmetrical pyrrolocyanines and related symmetrical dyes: ●, unsymmetrical dye; ◬, symmetrical cyanine with two pyrrole nuclei; ⊙, second symmetrical cyanine; ⊥, arithmetic mean between ⊙ and ◬; deviation is indicated by ⊤ and its magnitude is shown in Å. For a detailed study of pyrrolocyanines see Brooker and Sprague.[9f]

blance to tetrahydrobenzothiazole being even more marked than in the styryl series.

It is, therefore, all the more interesting to find that in the merocarbocyanine series, as shown in Fig. 4, the order of basicity is reversed, the thiopyrano[3,2d] nucleus now appearing to be more basic than tetrahydrobenzothiazole. It is noteworthy that in all four series pyrano[4,3d]thiazole and thiopyrano[4,3d]thiazole consistently show the same relative basicity, *i.e.*, somewhat less basic than tetrahydrobenzothiazole, with very slight differences, if any, between themselves.



It seems probable that the different behavior of the thiopyrano[3,2d]thiazole is attributable to the stabilizing effect of the adjacent sulfur atom on the resonating system. This effect could operate through an inductive mechanism or possibly through direct participation of the sulfur atom in charged structures. Thus in the merocarbocyanine M3, for which the principal resonance structures are (a), (b) and (c), the electron-attracting sulfur atom might be expected to stabilize (c) resulting in increased basicity and lessened deviation.

In the absence of such an effect the deviation of M3 would be expected to be somewhere between that of the pyranothiazole dye (70 Å.) and the benzothiazole dye (210 Å.) possibly 100 Å. The observed figure of 30 Å. is thus at least 70 Å. less than the expected value.

Too much emphasis on the results shown in Fig. 4 is perhaps not justified since, as Brooker has already stated,[9j] this series does not lend itself readily to differentiation between highly basic nuclei. Nevertheless a difference of 70 Å. between the ob-

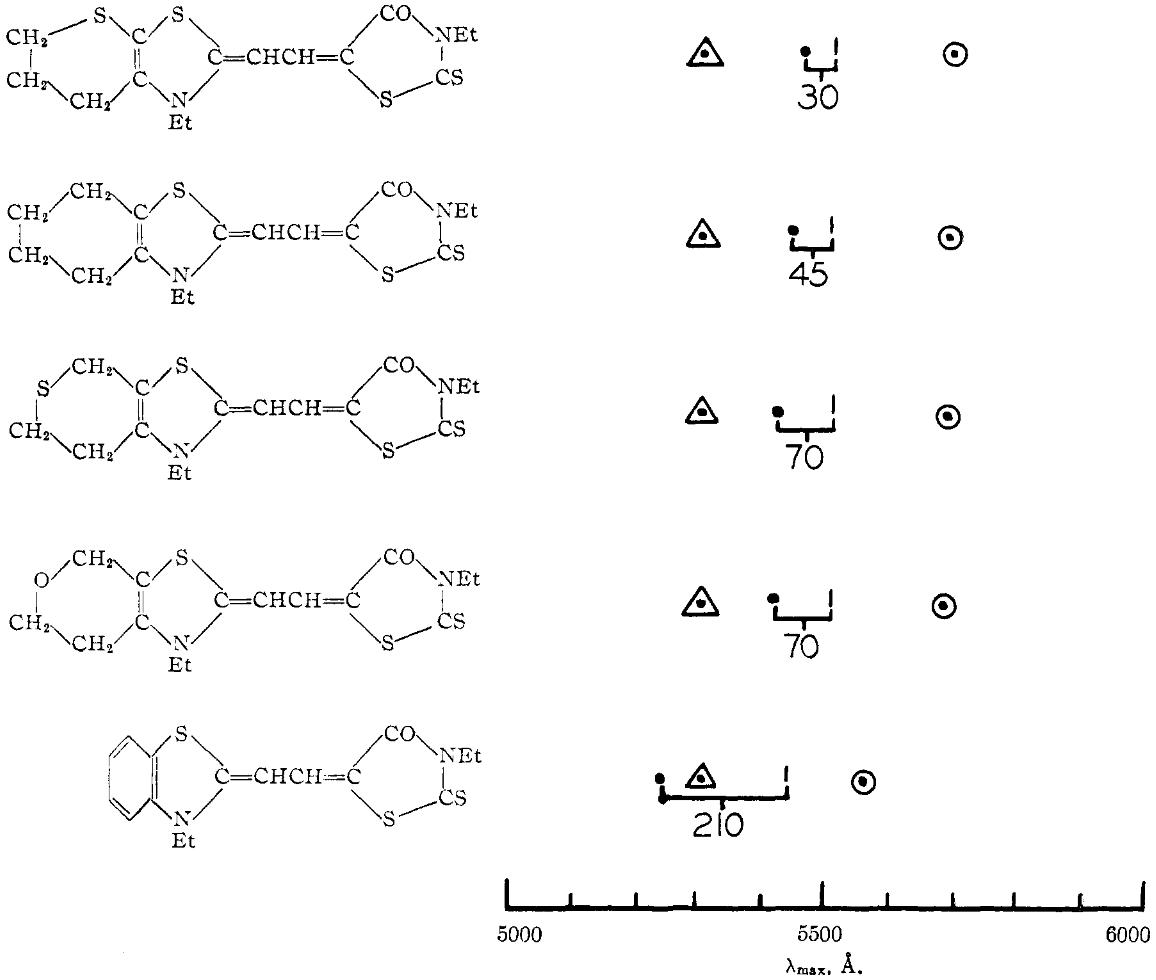


Fig. 4.—Values of $\lambda_{max}$ of merocarbocyanines derived from 3-ethylrhodanine and related symmetrical dyes: ●, merocarbocyanine; ⊙, symmetrical carbocyanine; ◬, symmetrical dye with two rhodanine nuclei (oxonol); ⊥, arithmetic mean between ⊙ and ◬; deviation is indicated by ⊤ and its magnitude is shown in Å. For a detailed study of the merocarbocyanines see Brooker, *et al.*[9j]

served and predicted deviations for M3 is undoubtedly significant and can be explained as suggested above.

## Experimental[10]

**Quaternary salts used are:** QS1, 1-ethyl-2-methyl-6,7-dihydro-4-H-pyrano(4,3d)thiazolium iodide; QS2, 1-ethyl-2-methyl-6,7-dihydro-4-H-thiopyrano(4,3d)thiazolium ethyl sulfate; QS3, 1-ethyl-2-methyl-6,7-dihydro-5-H-thiopyrano(3,2d)thiazolium ethyl sulfate; QS4, 2-(2-acetanilidovinyl)-3-ethylbenzoxazolium iodide; QS5, 1-ethyl-2-methyl-6,7-dihydro-5-H-thiopyrano(3,2d)thiazolium iodide; QS6, 1-ethyl-2-methyl-4,5,6,7-tetrahydrobenzothiazolium *p*-toluenesulfonate.[11]

Other reactants are: R-1, ethyl orthoformate; R-2, *p*-dimethylaminobenzaldehyde; R-3, 5-acetanilidomethylene-3-ethylrhodanine[9j]; R-4, 2,5-dimethyl-1-phenyl-3-pyrrolecarboxaldehyde.[9f]

Details of the preparation of new dyes are given in Table I. These include symmetrical carbocyanines (designated by C), unsymmetrical carbocyanines (U), *p*-dimethylaminostyryl dyes (S) and merocarbocyanines (M). The names of the dyes are given in Table II. In the syntheses the reactants were heated in the solvent indicated for the specified time. The yield of purified dye is given after two crystallizations from the solvent shown in the table.

Details of the preparation of the new bases and their quaternary salts follow.

**3-Bromotetrahydro-4-pyrone.**—Tetrahydro-4-pyrone[3] (30 g., 1 mol), N-bromosuccinimide (54 g., 1 mol) and 200 ml. of dry $CCl_4$ were refluxed with stirring under strong ultraviolet light for 20 minutes. A violent reaction occurred after an induction period of 15 minutes. The mixture was chilled, filtered, the solvent evaporated on the steam-bath and the residue distilled under reduced pressure. The fraction boiling at 60–80° at 2 mm. (21 g.) was redistilled. The product was thus obtained as a colorless liquid boiling at 76–80° at 2 mm., yield 13 g., 24%. On standing, the material rapidly darkened to a pinkish-brown and it was therefore used at once in the preparation of the thiazole base. In a later experiment it was found that distillation of the somewhat unstable bromo compound was unnecessary for use in the thiazole condensation. Using the crude bromo derivative an over-all yield of 20% of thiazole was obtained in a large run from 253 g. of tetrahydropyrone.

**2-Methyl-6,7-dihydro-4H-pyrano(4,3d)thiazole (I).**—3-Bromotetrahydro-4-pyrone (13.0 g., 1 mol), thioacetamide (5.5 g., 1 mol) and absolute ethanol (25 ml.) were heated to boiling under reflux. After the initial vigorous reaction subsided, the mixture was refluxed for 1 hr. The mixture was evaporated nearly to dryness, and the residue was extracted repeatedly with warm dilute HBr. The chilled extract was basified with dilute $NH_4OH$ solution and the oily product was taken up in ether. The ether solution was dried with $K_2CO_3$, evaporated and the residue was distilled under reduced pressure. The product was

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[10] Melting points are uncorrected. Microanalyses are by Schwarzkopf Microanalytical Laboratory, New York, N. Y.

[11] L. G. S. Brooker and F. L. White, U. S. Patent 2,336,843.

TABLE I

DETAILS OF DYE SYNTHESES

| Dye no. | Reactants, g | | | | Medium, ml. | | Re-fluxed, min. | Yield, % | Solvent, ml./g. | | M.p., °C. | Formula | Analyses, % Calcd. | Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Symmetrical carbocyanine dyes | | | | | | | | | | | | | | |
| C1 | QS1 | 3.1 | R1 | 3.0 | $C_5H_5N$ | 25 | 90 | 6 | MeOH | 200 | Above 300 | $C_{19}H_{25}IN_2O_2S_2$ | I, 25.17 | 25.05 |
| C2 | QS2 | 12.8 | R1 | $14.0^a$ | $C_5H_5N$ | 35 | 75 | $6^b$ | EtOH | 400 | 246–247 | $C_{19}H_{25}ClN_2O_4S_4$ | S, 25.19 | 25.04 |
| C3 | QS3 | 6.5 | R1 | 6.0 | $C_5H_5N^a$ | 32 | 90 | $0.3^b$ | EtOH | 330 | 233–234 | $C_{19}H_{25}ClN_2O_4S_4$ | S, 25.19 | 24.99 |
| Unsymmetrical carbocyanine dyes | | | | | | | | | | | | | | |
| U1 | QS6 | 3.5 | QS4 | 4.34 | $C_5H_5N$ | 17 | 15 | 20 | MeOH | 55 | $239–240^e$ | $C_{21}H_{25}IN_2OS$ | I, 26.45 | 26.36 |
| U2 | QS1 | 9.3 | QS4 | $13.0^a$ | $C_5H_5N$ | 90 | 15 | 74 | MeOH | 50 | 259–260 | $C_{20}H_{23}IN_2O_2S$ | I, 26.32 | 26.14 |
| U3 | QS2 | 9.8 | QS4 | $13.0^a$ | EtOH | 50 | 5 | $23^c$ | MeOH | 43 | 244–246 | $C_{20}H_{23}IN_2OS_2$ | I, 25.48 | 25.66 |
| U4 | QS3 | 3.25 | QS4 | $4.3^a$ | EtOH | 25 | 5 | $29^c$ | MeOH | 67 | 246–247 | $C_{20}H_{23}IN_2OS_2$ | I, 25.48 | 25.53 |
| U5 | QS1 | 1.55 | R4 | $1.0^d$ | EtOH | 15 | 15 | 61 | MeOH | 300 | Above 300 | $C_{22}H_{25}IN_2OS$ | I, 25.78 | 25.75 |
| U6 | QS2 | 3.25 | R4 | $2.0^d$ | EtOH | 35 | 5 | 3 | EtOH | 70 | 245–246 | $C_{22}H_{25}IN_2S_2$ | I, 24.97 | 24.95 |
| U7 | QS5 | 1.1 | R4 | $0.7^d$ | EtOH | 10 | 5 | 44 | EtOH | 28 | 229–231 | $C_{22}H_{25}IN_2S_2$ | I, 24.97 | 24.89 |
| *p*-Dimethylaminostyryl dyes | | | | | | | | | | | | | | |
| S1 | QS1 | 1.6 | R2 | $1.5^d$ | EtOH | 15 | 60 | 59 | MeOH | 35 | 233–235 | $C_{18}H_{23}IN_2OS$ | I, 28.70 | 28.80 |
| S2 | QS2 | 2.45 | R2 | $1.15^d$ | EtOH | 15 | 30 | 4 | EtOH | 125 | 247–249 | $C_{18}H_{23}IN_2S_2$ | S, 13.99 | 13.78 |
| S3 | QS5 | 1.1 | R2 | $0.5^d$ | EtOH | 10 | 15 | 67 | MeOH | 75 | 256–257 | $C_{18}H_{23}IN_2S_2$ | I, 27.70 | 27.90 |
| Merocarbocyanine dyes | | | | | | | | | | | | | | |
| M1 | QS1 | 1.6 | R3 | $1.5^a$ | EtOH | 25 | 15 | 49 | MeOH | 1200 | 234–235 | $C_{15}H_{18}N_2O_2S_3$ | N, 7.91 | 8.18 |
| M2 | QS2 | 3.25 | R3 | $2.94^a$ | EtOH | 35 | 30 | 5.4 | MeOH | 125 | 231–232 | $C_{15}H_{18}N_2OS_4$ | S, 34.61 | 34.58 |
| M3 | QS5 | 1.1 | R3 | $1.0^a$ | $C_5H_5N$ | 10 | 5 | 20 | MeOH | 1000 | 235-236 | $C_{15}H_{18}N_2OS_4$ | S, 34.61 | 34.48 |

[a] Plus triethylamine as condensing agent. [b] After conversion to perchlorate. [c] After conversion to iodide. [d] Plus piperidine as catalyst. [e] Brooker and White, U. S. Patent 2,336,843 give m.p. 247–248°. The dyes appear as follows: C1, blue-black powder; C2, dark green needles with golden reflex; C3, dull blue powder; U1 and U2, magenta needles with silver reflex; U3, dull purple powder; U4, bright orange crystals; U5, brownish-orange crystals; U6, dull orange crystals; S1, bright red needles; S2, brown needles with metallic reflex; S3, large garnet prisms; M1, tiny red needles with silver reflex; M2, dark red crystals with blue reflex; M3, minute dark green needles with golden reflex.

TABLE II

OPTICAL DATA

| Dye no. | Dye name | $\lambda_{max}$, Å. Obsd., MeOH | Calcd. | Deviation, Å. |
|---|---|---|---|---|
| | Symmetrical carbocyanine dyes | | | |
| C1 | 1,1′-DiEtbis-(6,7-dihydro-4H-pyrano(4,3d)thiazolo)-carbocyanine iodide | 5700 | | |
| C2 | 1,1′-DiEtbis-(6,7-dihydro-4H-thiopyrano(4,3d)thiazolo)-carbocyanine perchlorate | 5700 | | |
| C3 | 1,1′-DiEtbis-(6,7-dihydro-5H-thiopyrano(3,2d)thiazolo)-carbocyanine perchlorate | 5720 | | |
| | Unsymmetrical carbocyanine dyes | | | |
| U1 | 3,3′-DiEt-4′,5′,6′,7′-tetrahydro-oxathiacarbocyanine iodide | 5140 | 5262 | 122 |
| U2 | 1′,3-DiEt-6′,7′-dihydro-4′H-oxapyrano(4,3d)thiazolocarbocyanine iodide | 5180 | 5262 | 82 |
| U3 | 1′,3-DiEt-6′,7′-dihydro-4′H-oxathiopyrano(4,3d)thiazolocarbocyanine iodide | 5180 | 5262 | 82 |
| U4 | 1′,3-DiEt-6′,7′-dihydro-5′H-oxathiopyrano(3,2d)thiazolocarbocyanine iodide | 5300 | 5272 | −28 |
| U5 | 1-Et-2′,5′-DiMe-1′-Ph-6,7-dihydro-4H-pyrano(4,3d)thiazolo-3′-pyrrolocarbocyanine iodide | 4400 | 5092 | 692 |
| U6 | 1-Et-2′,5′-DiMe-1′-Ph-6,7-dihydro-4H-thiopyrano(4,3d)thiazolo-3′-pyrrolocarbocyanine iodide | 4400 | 5092 | 692 |
| U7 | 1-Et-2′,5′-DiMe-1′-Ph-6,7-dihydro-5H-thiopyrano(3,2d)thiazolo-3′-pyrrolocarbocyanine iodide | 4500 | 5102 | 602 |
| | *p*-Dimethylaminostyryl dyes | | | |
| S1 | 2-*p*-Me2N-styryl-1-Et-6,7-dihydro-4H-pyrano(4,3d)thiazolium iodide | 4900 | 5880 | 980 |
| S2 | 2-*p*-Me2N-styryl-1-Et-6,7-dihydro-4H-thiopyrano(4,3d)thiazolium iodide | 4900 | 5880 | 980 |
| S3 | 2-*p*-Me2N-styryl-1-Et-6,7-dihydro-5H-thiopyrano(3,2d)thiazolium iodide | 5060 | 5890 | 830 |
| | Merocarbocyanine dyes | | | |
| M1 | 3-Et-5-[(1-Et-6,7-dihydro-4H-pyrano(4,3d)(1H)thiazolylidene)-ethylidene]-rhodanine | 5440 | 5510 | 70 |
| M2 | 3-Et-5-[(1-Et-6,7-dihydro-4H-thiopyrano(4,3d)(1H)thiazolylidene)-ethylidene]-rhodanine | 5440 | 5510 | 70 |
| M3 | 3-Et-5-[(1-Et-6,7-dihydro-5H-thiopyrano(3,2d)(1H)thiazolylidene)-ethylidene]-rhodanine | 5490 | 5520 | 30 |

obtained as a nearly colorless strong smelling oil which boiled at 110 to 115° at 15 mm., yield 4.5 g., 40%.

**1-Ethyl-2-methyl-6,7-dihydro-4H-pyrano(4,3d)thiazolium Iodide** (QS1).—The base (2.1 g., 1 mol) was refluxed with ethyl iodide (5 g., 1 mol + 150% excess) for 24 hr. The crystalline product was crushed under acetone, chilled and filtered. The nearly colorless crystals melted with decomposition at 142–143°, yield 3.5 g., 83%.

*Anal.* Calcd. for $C_9H_{14}INOS$: I, 40.80; N, 4.50; S, 10.30. Found: I, 40.84; N, 4.21; S, 10.18.

**7-Bromo-2-methyl-6,7-dihydro-4H-pyrano(4,3d)thiazole,**—3,5-Dibromotetrahydro-4-pyrone[3] (3.1 g., 1 mol), thioacetamide (1.5 g., 1 mol + excess) and absolute ethanol (25 ml.) were refluxed for 2 hr. The alcohol was evaporated and the residue was extracted with dilute HCl. The acid solution was washed with ether to remove tarry material, filtered and basified with $NH_4OH$. The oily product was taken up in ether, dried with $K_2CO_3$ and distilled. The product was a pale yellow oil boiling at 140–145° at 15 mm., yield 0.3 g., 9%.

**7-Bromo-1-ethyl-2-methyl-6,7-dihydro-4H-pyrano(4,3d)-thiazolium Iodide.**—The base (0.3 g., 1 mol) and excess ethyl iodide were refluxed for 6 hr. The oily brown precipitate crystallized on standing overnight. The crystals were collected, washed with acetone and recrystallized from absolute ethanol. The pale orange crystalline product melted at 164–168° dec., yield 50 mg., 10%.

*Anal.* Calcd. for $C_9H_{13}BrINOS$: N, 3.59; S, 8.22. Found: N, 3.69; S, 8.40.

**2-Methyl-6,7-dihydro-4-H-thiopyrano(4,3d)thiazole (III).**—Twenty grams of tetrahydro-1-thio-4-pyrone,[4] 30.5 g. of N-bromosuccinimide and 50 ml. of dry $CCl_4$ were gently warmed under reflux on the steam-bath until a violent reaction set in. The mixture was chilled in an ice-bath, filtered from succinimide and the filtrate was evaporated under water-pump vacuum until the $CCl_4$ was removed. The crude 3-bromo-tetrahydro-1-thio-4-pyrone thus obtained is unstable and must be used at once.

The product from the above reaction was diluted with 25 ml. of absolute ethanol, 12 g. of thioacetamide was added and the mixture was kept at 0° for 24 hr. followed by standing at room temperature for 3 days. The alcohol was distilled off under water-pump vacuum and the brown residue was extracted with 3% hydrochloric acid. After extracting the acid solution with ether to remove tarry impurities, the solution was made alkaline with $NaHCO_3$ and the oily base was taken up in ether. The ether solution was dried with anhydrous $K_2CO_3$, evaporated and the product was distilled under reduced pressure. The product was a pale yellow oil boiling at 125–135° at 8 mm. The yield was 5.0 g., 17%.

**2-Methyl-6,7-dihydro-4H-thiopyrano(4,3d)thiazole Hydrochloride.**—The base (16 g.) in absolute ether (500 ml.) was saturated with dry hydrogen chloride at 0°. The solvent was decanted from the sticky precipitate, and the latter was stirred with 150 ml. of acetone until crystallization occurred. After filtration and washing with acetone, the product was recrystallized from 100 ml. of absolute ethanol. The pale yellow crystals had m.p. 180–181°, yield 12.0 g., 62%.

*Anal.* Calcd. for $C_7H_{10}ClNS_2$: C, 40.43; H, 4.85; N, 6.74; S, 30.87. Found: C, 40.65; H, 4.88; N, 6.70; S, 31.00.

**1-Ethyl-2-methyl-6,7-dihydro-4H-thiopyrano(4,3d)thiazolium Ethyl Sulfate** (QS2).—For use in the dye syntheses, equimolecular proportions of the base and freshly distilled ethyl sulfate were heated at 110 to 115° for 5 minutes. The viscous product was used without purification.

**2-Methyl-6,7-dihydro-5H-thiopyrano(3,2d)thiazole** (IV).—Twenty-five grams (1 mol) of tetrahydro-1-thio-3-pyrone[5] was added to a mixture of 38.2 g. (1 mol) of N-bromosuccinimide and 50 ml. of dry carbon tetrachloride. After the initial vigorous reaction, the mixture was refluxed for 5 minutes. The mixture was chilled, the succinimide filtered and the filtrate evaporated as far as possible under reduced pressure. The product was mixed with 15.0 g. (1 mol) of thioacetamide and 100 ml. of absolute ethanol and allowed to stand at 0° for 3 hr., then overnight at room temperature and finally refluxed for 2 hr. The base was isolated and purified the same as IV above and was obtained as a pale yellow oil, b.p. 90 to 92° at 0.5 mm. The product crystallized on chilling. The yield was 13.4 g., 36%.

**1-Ethyl-2-methyl-6,7-dihydro-5H-thiopyrano(3,2d)thiazolium Ethyl Sulfate** (QS3).—The base was heated with ethyl sulfate the same as in the preparation of QS2 and the crude product was used in the dye syntheses.

**1-Ethyl-2-methyl-6,7-dihydro-5H-thiopyrano(3,2d)thiazolium Iodide** (QS5).—The base (10.0 g., 1 mol) was refluxed with ethyl iodide (20 g., 100% excess) for 16 hr. The crystalline product was crushed under ether, washed on the filter with acetone and dried. The yield of light tan crystals was 13.0 g., 68%. For analysis the product was recrystallized twice from absolute ethanol (10 ml. per g.). The pure material had m.p. 150–153° dec. *Anal.* Calcd. for $C_9H_{14}INS_2$: I, 38.80; N, 4.28; S, 19.60. Found: I, 38.51; N, 4.11; S, 19.52.

Absorption data for the new dyes are given in Table II.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

# Some Methyl Derivatives of *p*-Quaterphenyl[1]

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Condensation of *p*-terphenyl-4-yllithium and 4,4′-biphenylenedilithium with 2-, 3- and 4-methylcyclohexanone, followed by dehydration, has been used to synthesize monomethyltetrahydro-*p*-quaterphenyls and dimethyloctahydro-*p*-quaterphenyls, respectively. The corresponding *p*-quaterphenyl derivatives are formed by dehydrogenation with chloranil. The effect of structure on melting points and on solubilities is discussed.

Chain-type polyaryls have been shown to be superior solutes in liquid solution scintillators.[2–4] The use of hydrocarbons as solutes reaches a limit with *p*-terphenyl because those of higher molecular weight are limited by their sparing solubility in the commonly employed aromatic solvents. The introduction of methyl groups on the terminal rings of *p*-quaterphenyl seemed a direct method of surmounting this limitation in view of an expected decrease in melting point and increase in solubility corresponding to the reduction of symmetry. Also, of significance is the conclusion of Hayes, Ott and Rogers[3] that methyl groups do not generally cause an appreciable change in the scintillation ability of the solute.

Table I shows that this expectation was justified. It is interesting to note the marked correspondence of melting point and solubility in toluene through this series. Among the completely aromatic compounds the one outstanding increase in melting point occurs with the 4,4‴-dimethyl compound (125° higher than the 3,3‴-isomer), and this is accompanied by a drop to nearly complete insolubility. The 4-methyl derivative is rather unusual in that it melts higher than the more symmetrical parent hydrocarbon (320°) while it is slightly more soluble. The series of compounds containing cyclohexene rings exhibits the same trends but in more pronounced fashion. While the melting points are somewhat unreliable because of decomposition of those melting above 200°, it is evident that the close grouping of melting points in the three monomethylated compounds is a reflection of a similar situation in the completely aro-

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(2) H. Kallman and M. Furst, *Nucleonics*, **8**, No. 3, 32 (1950).

(3) F. Hayes, D. Ott and B. Rogers, *ibid.*, **13**, No. 12, 38 (1955).

(4) F. Hayes, D. Ott and V. Kerr, *ibid.*, **14**, No. 1, 42 (1956).