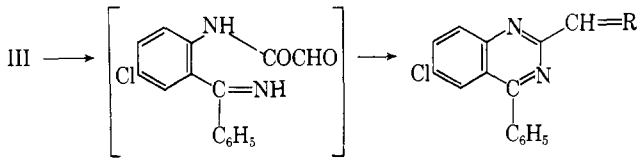
Walker[6] recently has described a treatment of the oxime of 2-benzoyl-4-chlorooxaniloyl chloride with phosphorus oxychloride to afford 6-chloro-4-phenylquinazolin-2(1H)-one. Since the properties ascribed to this compound differed from those of a preparation made in this laboratory by two independent methods,[7] it seemed more likely to us that a Beckmann rearrangement had taken place, *followed* by cyclization and decarboxylation to give 6-chloro-3-phenylquinazolin-4(3H)-one (V). In order to test this hypothesis, 5-chloroanthranilic acid was fused with formanilide to yield V in an unambiguous way. Compound V melted at 182–184° and absorbed in the infrared at 5.97, 6.20, and 6.28 μ (Nujol). Walker gave m.p. 185° and infrared bands at 5.97, 6.20, and 6.26 μ.

In addition to those reported earlier,[1] still another rearrangement has been observed with III. Heating in acetic acid afforded 6-chloro-4-phenylquinazoline-2-carboxaldehyde (VI). Compound VI with hydrazine gave a hydrazone (VII) that was also obtainable directly from hydrazine and III. Methylamine was observed also to bring about this ring contraction leading to the methylimine (VIII) of the aldehyde. The structure of VI was proved easily by elemental analysis, positive Tollens test, and infrared and n.m.r. data (5.81 μ; δ = 10.1 p.p.m.), as well as its oxidation to the known 6-chloro-4-phenylquinazoline-2-carboxylic acid.[8]



VI, R = O
VII, R = NNH_2
VIII, R = NCH_3

Experimental[9]

4-Benzoyl-6-chloro-3,4-dihydroquinoxalin-2-(1H)-one (IV).—A mixture of 5.0 g. of I, 15 ml. of phosphorus oxychloride, and 50 ml. of chloroform was heated under reflux for 0.5 hr. until the solid had dissolved. The resultant dark reaction mixture was concentrated to dryness *in vacuo*. The residue was recrystallized from acetonitrile to afford 1.3 g. of IV, m.p. 255–257°; λ_{max}^{KBr} 3.15, 6.01 μ; δ = 4.56 p.p.m. (s, 2H).

Anal. Calcd. for $C_{15}H_{11}ClN_2O_2$: C, 62.81; H, 3.81; Cl, 12.37; N, 9.77. Found: C, 62.34; H, 3.85; Cl, 12.30; N, 9.87.

Hydrolysis of IV in refluxing 4 *N* sodium hydroxide for 10 min., followed by acidification, gave 6-chloro-3,4-dihydroquinoxalin-2(1H)-one, m.p. 180–182°. Crowther, *et al.*,[4] reported m.p. 184°.

Compound IV (0.3 g.) in 10 ml. of ethanol containing 0.5 ml. of 4 *N* sodium hydroxide was hydrogenated in the presence of palladium–charcoal (5%). After filtering from the catalyst, the solution was diluted to precipitate 4-benzoyl-3,4-dihydroquinoxalin-2(1H)-one, m.p. 204–206°. There was no depression upon mixing with a sample prepared according to the procedure of Motylewski.[5]

6-Chloro-3-phenylquinazolin-4(3H)-one (V).—A mixture of 17.5 g. of 5-chloroanthranilic acid and 12.1 g. of formanilide was fused at 130–150° for 15 min. The melt, which solidified on cooling, was dissolved in alcohol and the resultant solution was diluted with water. The precipitate so obtained was collected and recrystallized from ethanol to give 3 g. of V, m.p. 182–184°; λ_{max}^{Nujol} 5.97, 6.20, 6.28 μ.

Anal. Calcd. for $C_{14}H_9ClN_2O$: C, 65.50; H, 3.53; Cl, 13.82. Found: C, 65.58; H, 3.80; Cl, 14.00.

6-Chloro-4-phenylquinazoline-2-carboxaldehyde (VI).—A mixture of 10.0 g. of III and 100 ml. of acetic acid was heated under reflux for 10 min., then cooled, and diluted with water. The resultant precipitate was recrystallized from an alcohol–water mixture, then hexane, and finally acetonitrile. Compound VI (6 g.) was obtained as a light yellow solid, m.p. 176–178°; λ_{max}^{KBr} 5.81 μ; δ = 10.1 p.p.m. (s, 1H).

Anal. Calcd. for $C_{15}H_9ClN_2O$: C, 67.04; H, 3.38; Cl, 13.20; N, 10.43. Found: C, 67.01; H, 3.36; Cl, 13.12; N, 10.38.

Alkaline oxidation of VI with dilute potassium permanganate afforded 6-chloro-4-phenylquinazoline-2-carboxylic acid, m.p. 212–214°, identical with an authentic sample.[8]

6-Chloro-4-phenylquinazoline-2-carboxaldehyde Hydrazone (VII).—A solution of 1.5 g. of III, 50 ml. of ethanol, and 3.0 ml. of hydrazine hydrate (85%) was heated under reflux for 0.5 hr. Upon cooling 0.8 g. of product was collected. Recrystallization from isopropyl alcohol gave VII, m.p. 166–167°. An identical compound was prepared by treating VI with hydrazine.

Anal. Calcd. for $C_{15}H_{11}ClN_4$: C, 63.88; H, 3.93; Cl, 12.57; N, 19.86. Found: C, 63.72; H, 3.72; Cl, 13.00; N, 19.90.

6-Chloro-4-phenylquinazoline-2-carboxaldehyde Methylimine (VIII).—A mixture of 3.0 g. of III, 50 ml. of ethanol, and 15 ml. of 30% aqueous methylamine that had refluxed for 1 hr. was diluted with 100 ml. of water. The precipitate was collected and recrystallized from cyclohexane. There was obtained 1.7 g. of VIII, m.p. 153–154°.

Anal. Calcd. for $C_{16}H_{12}ClN_3$: C, 68.20; H, 4.29; Cl, 12.59; N, 14.91. Found: C, 68.27; H, 4.20; Cl, 12.60; N, 15.18.

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(6) G. N. Walker, *J. Org. Chem.*, **27**, 1929 (1962).
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(9) The melting points are uncorrected.

Electron Spin Resonance Spectra of the Negative Ions of Phenothiazine and Some of Its Derivatives[1]

M. BRUIN, F. BRUIN, AND F. W. HEINEKEN

Physics Department, American University of Beirut, Lebanon

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Continuing earlier work on thiazine and oxazine dye radicals,[2] we have obtained well-resolved spectra of phenothiazine, 3,7-diaminophenothiazine (Lauth's violet), 3,7-bis(dimethylamino)phenothiazine (methylene blue), and 7-dimethylaminophenothiazin-3-one (methylene violet).

Previously[2] the radicals were produced in various alkaline and acid solutions. The four spectra discussed later were obtained from radicals produced in *p*-dioxane with the sodium mirror technique at room temperature. The hyperfine structure lines observed had an average width of 0.07 gauss. A section of the spectrum of Lauth's violet between the central line and one outer component of the central nitrogen triplet is shown in Fig. 1. This section is typical for all spectra recorded.

(1) Work supported by the (U. S.) National Science Foundation, the Research Corporation, and by the Rockefeller Fund of the School of Arts and Sciences of the American University of Beirut.

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TABLE I

SPLITTING CONSTANTS IN GAUSS OF TRIPLETS DUE TO NUCLEAR SPINS OF NITROGEN (N) AND RING PROTONS (H)[a]

	Position					
Free radical of	1,9 (H)	2,8 (H)	3,7 (H)	4,6 (H)	5	10
Anthracene	2.74	1.57	1.57	2.74	5.56 (H)	5.56 (H)
Phenazine	1.93	1.61	1.61	1.93	5.14 (N)	5.14 (N)
Thianthrene	*b*	1.62	1.62	*b*	0 (S)	0 (S)
Phenothiazine	2.82	0.81	3.80	1.00	0 (S)	7.10 (N)
Lauth's violet	2.77	1.53	*c*	0.93	0 (S)	7.50 (N)
Methylene blue	2.66	1.36	*c*	0.88	0 (S)	7.08 (N)
Methylene violet	2.73	1.46	*c*	0.90	0 (S)	7.29 (N)

[a] For assignments see text. [b] Not observed. [c] Not completely resolved.

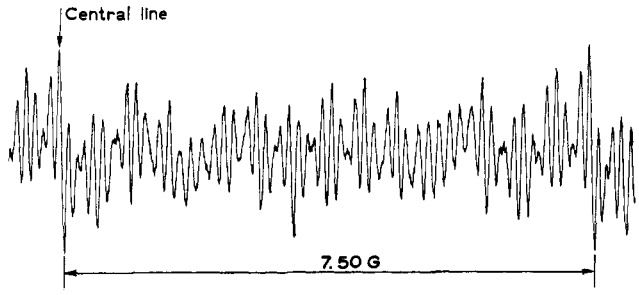
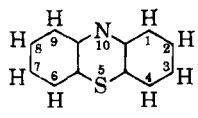


Fig. 1.—Section of the spectrum of Lauth's violet between the central line and one outer component of the central nitrogen triplet.

Recording and analyzing the spectra were hampered by (a) the instability of the free radicals, (b) the many hyperfine structure lines involved, and (c) the pronounced asymmetry of the spectra. This asymmetry, for which theoretical arguments have been given,[3] was most prominent for 7-hydroxyphenoxazine-3,10-dione (resazurin), and will not be discussed further here.

The splittings due to the central nitrogen atom could be determined with higher precision than previously[2]. In addition new splitting constants, due to various protons, were found and are collected in Table I. The inaccuracy in the values is $\leq 5\%$. Data on anthracene in tetrahydrofuran,[4] phenazine in either tetrahydrofuran or dimethoxyethane,[5] and thianthrene in sulfuric acid[6] are included for comparison. Our measurements on these radicals served as a check on the new results. The numbering used in Table I is as follows.



The assignment for the splitting due to the nitrogen atom in position 10 is unique. Comparison of phenothiazine with the phenazine data shows that replacement of nitrogen by sulfur in position 5 notably increases the spin density in position 10. Furthermore appreciable changes are introduced in various proton splittings. For thianthrene in sulfuric acid an incompletely resolved spectrum has been reported,[6] showing five lines at about 1.62 gauss spacing, attributed to the 2,3,7,8 protons. Since the largest proton triplet splitting occurring in phenothiazine is absent in the radicals substituted at the 3,7-positions, one may tentatively assign the largest splitting in phenothiazine to these positions. The other splittings are tentatively assigned by comparison with those of anthracene and phenazine. However, due to the addition of the auxochromic groups, the whole relative spin density pattern in the benzene rings may, of course, have changed, so that the proton splitting assignments are still ambiguous.

The last three substituted radicals of Table I show consistent splittings not only among themselves, but also when compared to a number of other radicals. These were 3-amino-7-dimethylaminophenothiazine (azure A), 3-dimethylamino-7-diethylamino-8-methylphenoxazine (capri blue GN), and 7-hydroxyphenoxazine-3,10-dione (resazurin). These are not included in the analysis, because of less detailed resolution of their spectra.

The splittings shown in Table I by themselves do not fully represent the observed details of the substituted phenazine spectra. To account for all lines observed, one has to assume additional splittings of about 0.5 gauss, which appear to be due to protons of the auxochromic groups. These splittings could not be fully analyzed.

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Electron Density and Nucleophilic Substitution in the Purine Ring

B. PULLMAN

Université de Paris, Institut de Biologie Physico-Chimique 13, rue Pierre Curie, Paris 5ème, France

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In a recent paper in this journal, Sutcliffe and Robins[1] draw attention to some discrepancies between electron density calculations and experimental observations relative to the nucleophilic substitution in the purine ring. Without questioning the results of these authors concerning the possible occurrence in the course of

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