[CONTRIBUTION FROM THE MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT DIVISION, WRIGHT–PATTERSON AIR FORCE BASE, OHIO]

Infrared Spectra of Some 1,3,5-Triazine Derivatives

BY HERBERT K. REIMSCHUESSEL* AND NEIL T. MCDEVITT

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The infrared absorption spectra of a series of triazine derivatives have been obtained from 2–15 μ. Absorption bands at 6.4, 6.65 and 6.9 μ have been assigned to vibrations arising from the triazine ring system.

The synthetic methods are described for these triazine derivatives which have not been reported previously.

Introduction

Over the past ten years the infrared spectra of some triazine derivatives have been reported[1–3] and the fundamental frequencies of the parent 1,3,5-triazine[2,4] molecule determined. Padgett and Hamner[5] recently reported a series of thirty-five 1,3,5-triazine derivatives, with melamine and substituted melamines being the majority of the compounds presented. A comparison of these spectra with 1,3,5-triazine led these authors to assign the strong broad absorption at 6.4 μ to the infrared active in-plane vibrations of the triazine system. The 5.9 and 6.1 μ bands were assigned to the internal deformation vibration of the NH_2 group. However, due to the broad absorption at 6.4 μ, in this particular series of triazine derivatives, it is difficult to see any detail in the ring vibration bands.

This paper presents the infrared spectra of a series of twelve newly synthesized 1,3,5-triazine derivatives along with some previously synthesized triazine compounds. The authors intend to show the in-plane ring deformation vibrations of these compounds and to present these data for identification purposes.

Discussion

In order to elucidate the 6–7 μ region, all the triazine derivatives that were soluble in carbon tetrachloride and carbon disulfide were recorded as solution spectra. They were combined on the same chart in order to form a continuous spectrum of a single compound. The potassium bromide wafers were prepared with a small amount of matrix in order to form a thin window. In this manner the solid sample gave more detail in the 6–7 μ region and the Christiansen[6] effect was suppressed to an extent.

The parent 1,3,5-triazine has two strong absorption bands at 6.4 and 7.1 μ. These bands have been established[2,3] as originating from the in-plane ring vibrations of the triazine ring. Triazine also exhibits a strong band at 13.6 μ and a medium strong band at 14.8 μ. These bands are assigned to the carbon–hydrogen wagging and out-of-plane ring vibration, respectively.

The solution spectra show well defined absorption bands. The spectrum of cyanuric chloride differs from the parent 1,3,5-triazine with respect to all absorption bands. The strong bands appear at 6.65, 7.9, 11.7 and 12.5 μ. The 6.65 μ band is due to the in-plane ring vibration of this triazine ring system, with a small band appearing at 6.9 μ. The 11.7 μ band is probably due to the carbon–chlorine stretching vibration. This stretching vibration has been shifted to shorter wave lengths, and is probably due to the *m* position of the chlorine atoms. The 12.5 μ band is assigned as the out-of-plane ring vibration, analogous to the 14.8 μ band in the parent triazine. Replacing one chloro group with a methyl group, on cyanuric chloride, shifts the 6.65 μ band to 6.5 and splits the band at 7.9 μ. With a phenyl group in place of a chloro group a band appears at 6.5 μ with the 6.65 μ band remaining constant and the intensity of the 6.9 μ band increasing. The 11.7 μ band remains constant in the dichloro substituted triazines. In the other solution spectra (6–11) the in-plane ring modes of the triazine ring system can be seen at 6.4, 6.65 and 6.9 μ. However, the spectrum of 2-chloro-4,6-dimethoxy-*s*-triazine shows only a small shoulder band at 6.65 μ and the 6.9 μ band has shifted to 6.8 μ.

Most of the solution spectra of the triazine compounds contain a phenyl group and it is difficult to differentiative between the absorptions due to the triazine ring and phenyl ring. Both ring systems are capable of exhibiting bands in the 6–7 μ region. There is no doubt that the phenyl ring has absorption bands overlapping the triazine ring absorptions in this region. The slight shoulder band at 6.25 μ can be seen clearly in most of the spectra of the triazine derivatives containing a phenyl group. This band does not seem to be present in the nonbenzene derivatives, so it can be attributed to the in-plane ring vibration of the monosubstituted benzene. The assignment of any other bands in this region due primarily to the phenyl group is complicated by the overlapping of the ring absorptions. However, the absorption bands at 6.4, 6.7 and 6.9 μ, which are present in the solution spectra containing phenyl groups, are also present in the spectra of cyanuric chloride and 2,4,6-triethyl-*s*-triazine.[2] Therefore, we can assume that the phenyl groups, if present, only intensify these absorptions and are not primarily responsible for them. The other region of interest is that above 12 μ. The 2-methyl-4,6-dichloro-*s*-triazine spectrum has a small band appearing at 12.2 μ, while the 12.5 μ band has shifted to 12.6 μ. In the spectrum of 2-phenyl-4,6-dichloro-*s*-triazine the intensity of the 12.2 μ band increases and the 12.5 μ band seems to shift to

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* Allied Chemical, Hopewell, Va.

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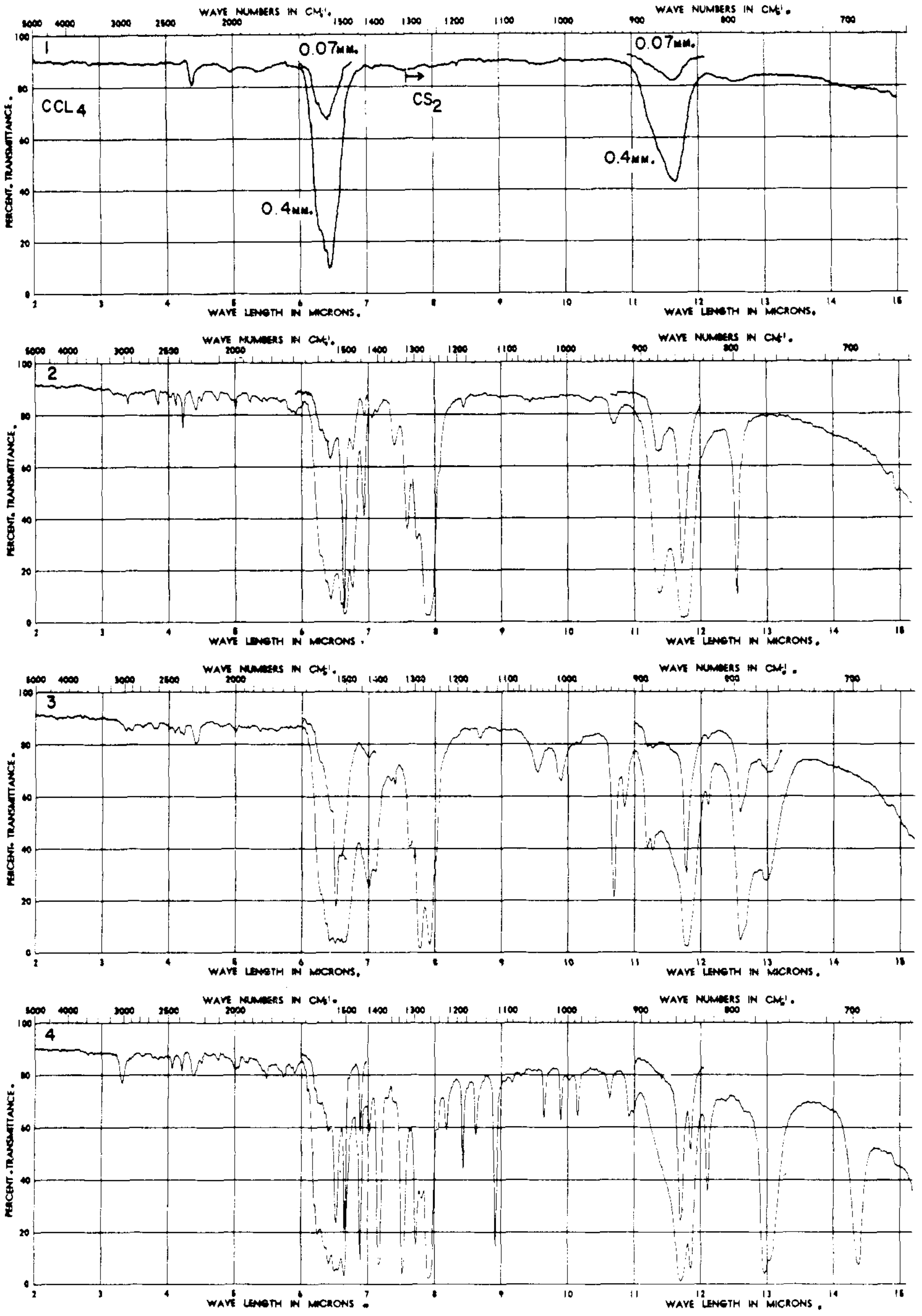

Fig. 1.—Solution spectra: 1, solvent-reference; 2, 2,4,6-trichloro-*s*-triazine; 3, 2-methyl-4,6-dichloro-*s*-triazine; 4, 2-phenyl-4,6-dichloro-*s*-triazine.

13 μ coinciding with the phenyl out-of-plane CH deformation vibrations. With monophenyl substitution the 12.2 μ band does not seem to vary to any great extent. However, with two phenyl rings or a carboxy group present this band is displaced to longer wave lengths. The second band of the phenyl CH deformation vibration remains steady between 14.2–14.4 μ.

The absorption spectra of the non-soluble crystalline triazine derivatives can be seen in spectra A-I. Spectrum A shows the shift in wave length of the triazine ring vibrations when hydroxy groups are ring substituents. This compound exhibits a broad absorption band from 3.1 to 3.7 μ indicating some hydrogen bonding; also the band at 5.8 μ shows that this compound is partially in its tautomeric ketone structure. However, the ring absorption band at 6.7 μ remains constant. Due to the absence of hydrogen bonding and tautomeric forms in most of the compounds in this triazine series, the solid spectra show more detail in the 6–7 μ region than the melamine derivatives. The internal deformation vibration of the primary and secondary amine groups can be seen at 6.1–6.2

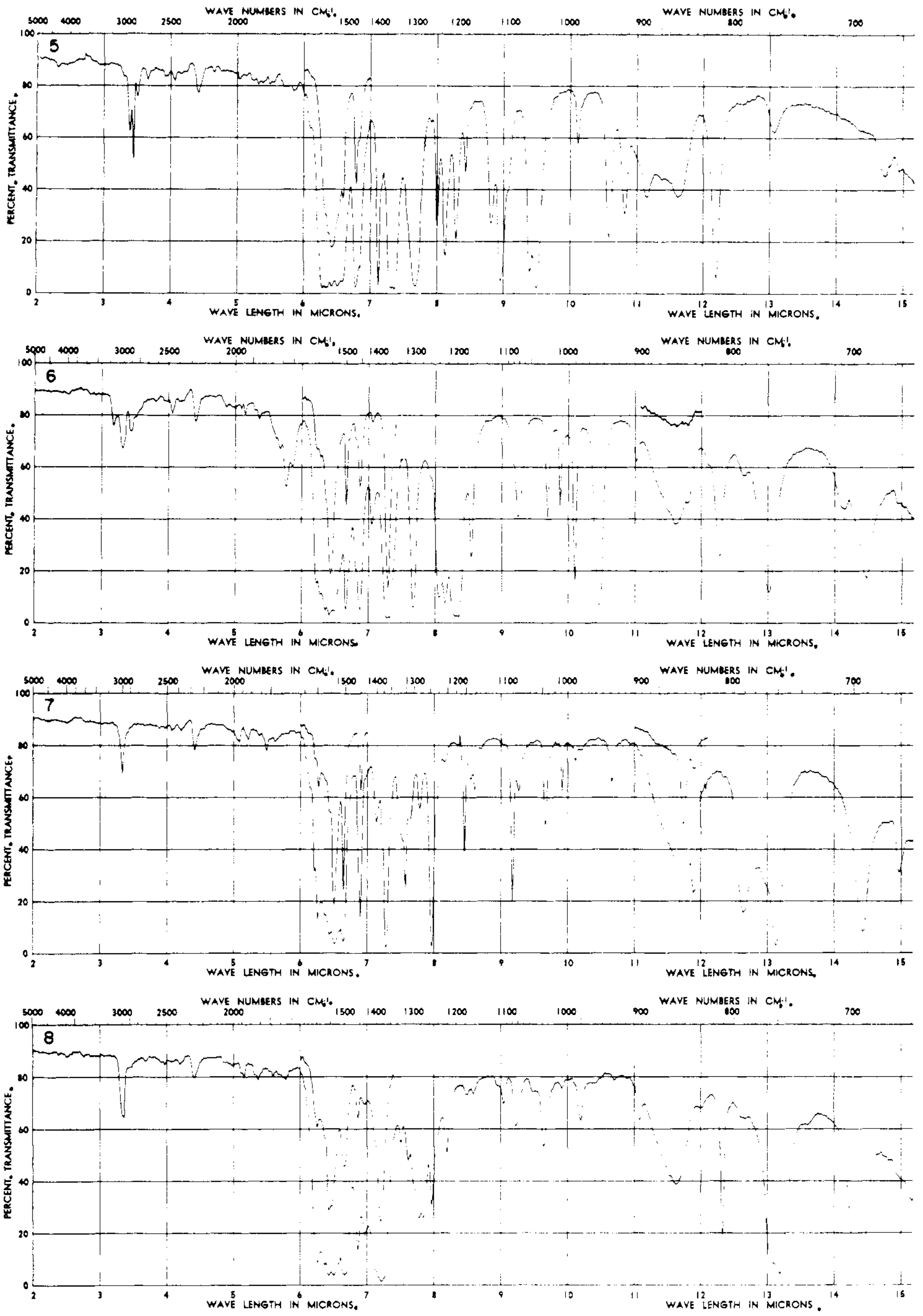

Fig. 2.—Solution spectra: 5, 2-chloro-4,6-dimethoxy-*s*-triazine; 6, 2-chloro-4,6-diphenoxy-*s*-triazine; 7, 2,4-diphenyl-6-chloro-*s*-triazine; 8, 2-methyl-4,6-bis-(diphenylamino)-*s*-triazine.

μ in spectra B, C, D and E. The benzene ring vibration again appears at 6.25 μ in the phenyl substituted derivatives. Due to the nature of the groups on the triazine ring in the potassium bromide spectra, the 6.4, 6.65 and 6.9 μ bands vary in intensity and position. The 12.1–12.2 μ band is probably the out-of-plane triazine ring vibration in this group of derivatives and remains fairly constant in most of the potassium bromide spectra. The carboxy and hydroxy substitution on the triazine ring shifts the 12.1 μ band to 12.7 μ and can be seen in spectrum G. All of the phenyl substituted derivatives exhibit a consistent band at 12.7–12.8 μ.

Experimental

Syntheses of Triazines.[7] The following six triazine derivatives were prepared by methods described in the literature: 2-methyl-4,6-dichloro-*s*-triazine,[8] 2-phenyl-4,6-dichloro-*s*-triazine,[9] 2,4-diphenyl-6-chloro-*s*-triazine,[9] 2-chloro-

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[7] Microanalyses by Huffman Microanalytical Laboratories, P. O. Box 125, Wheatridge, Colo.

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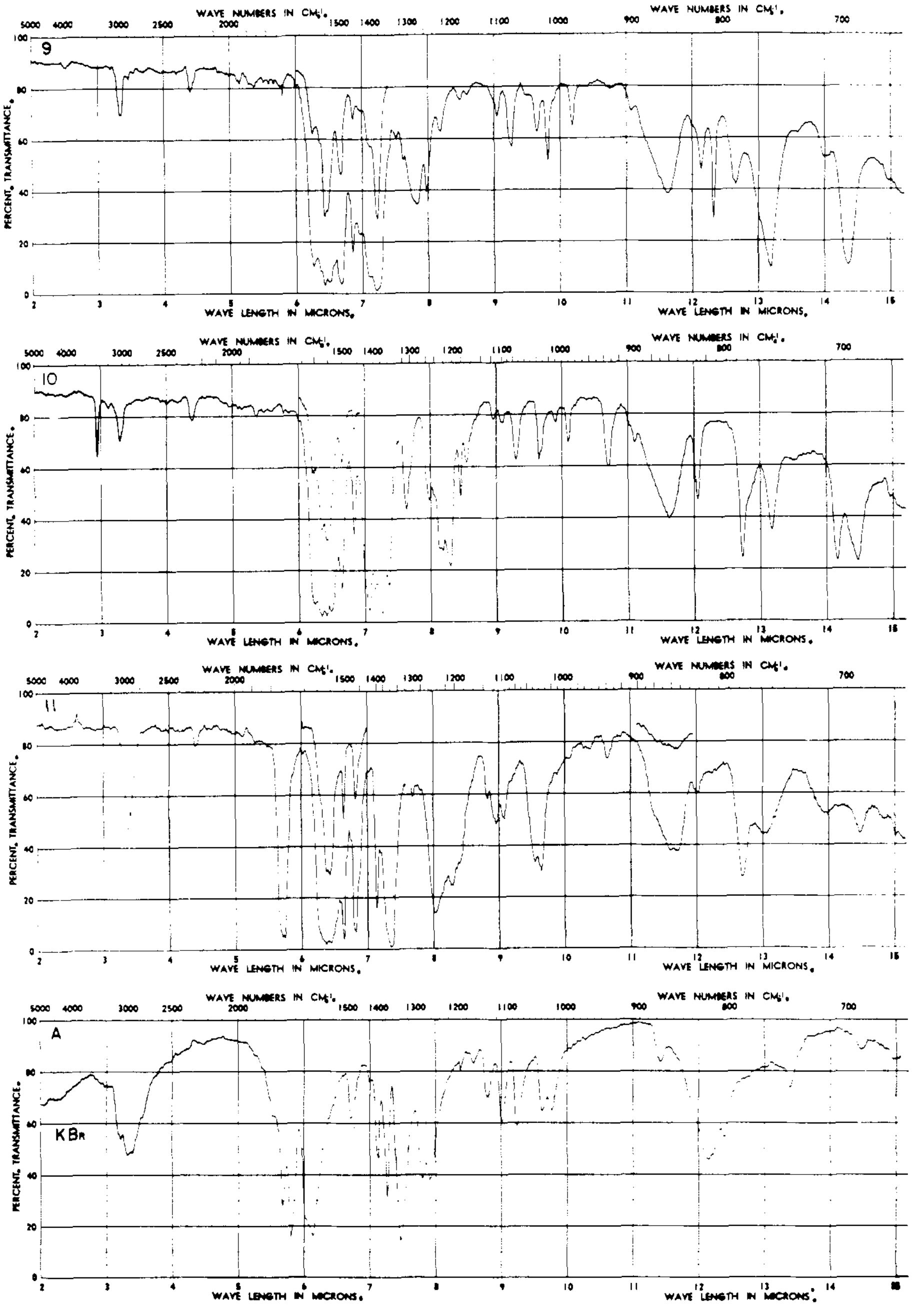

Fig. 3.—Solution spectra: 9, 2-bromomethyl-4,6-bis-(diphenylamino)-*s*-triazine; 10, N-phenyl-2-phenyl-6-phenoxy-4-amino-*s*-triazine; 11, 2-dicarboethoxyphenylmethyl-4,6-dimethoxy-*s*-triazine; KBr spectra: A, 2-dicarboethoxymethyl-4,6-dihydroxy-*s*-triazine.

4,6-dimethoxy-*s*-triazine,[10a] 2-chloro-4,6-diphenoxy-*s*-triazine[10b] and 2-dicarboethoxymethyl-4,6-dihydroxy-*s*-triazine.[11]

2-Carboethoxy-cyano-methyl-4,6-dihydroxy-*s*-triazine.—Sodium (3.5 g.) was dispersed in toluene. After replacing the toluene by anhydrous ether, 22.6 g. of ethyl cyanoacetate was added to this dispersion. The temperature was allowed to rise to 30–35°. Stirring was continued for about 16 hours. After this time 18 g. of cyanuric chloride was added and the mixture kept at 30° with stirring for 8 hours. The light yellow compound which formed was collected on a filter and washed first with ether and then with water. It was purified by recrystallization from water; yield 14.24 g. (41%), m.p. 190–191°.

Anal. Calcd. for $C_8H_8N_4O_4$: C, 42.86; H, 3.59; N, 25.1. Found: C, 43.0; H, 3.96; N, 25.1.

2-N,N-(β-Hydroxyethyl)-Amino-4,6-dimethoxy-*s*-triazine.—To a solution of 130 cc. of dioxane containing 21.28 g. of 2,2′-iminodiethanol was added dropwise 14.3 g. of 2-chloro-4,6-dimethoxy-*s*-triazine dissolved in 50 cc. of 1,4-dioxane. The resulting reaction mixture was heated for 3 hours under reflux and then allowed to cool. The dioxane solution was decanted from the oily bottom layer. The dioxane was evaporated, the solid residue dissolved in chloroform and the resulting solution washed with water. After drying over calcium chloride, crystallization was initiated by addition of ligroin; yield 18 g. (90%), m.p. 124–126°.

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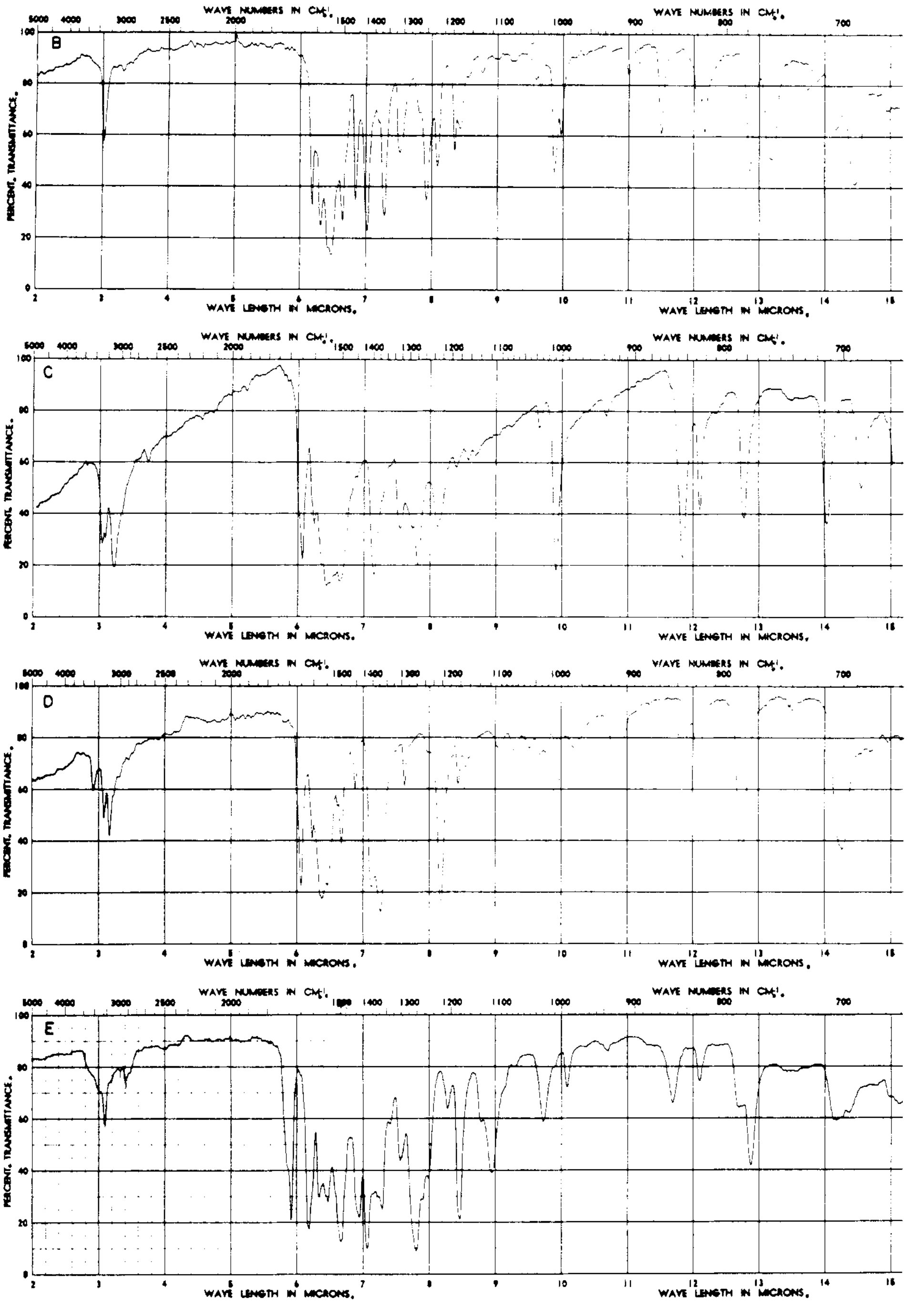

Fig. 4.—KBr spectra: B, N-phenyl-2-phenyl-6-chloro-4-amino-*s*-triazine; C, 2-phenyl-4-amino-6-chloro-*s*-triazine; D, 2-phenyl-4-amino-6-phenoxy-*s*-triazine; E, 2-phenyl-N,N′-bis-(4-carboethoxyphenyl)-4,6-diamino-*s*-triazine.

Anal. Calcd. for $C_9H_{16}N_4O_4$: C, 44.3; H, 6.5; N, 23.0. Found: C, 44.03; H, 6.58; N, 23.11.

2-N,N-Dicyanomethylamino-4,6-dimethoxy-s-triazine.—To a solution of 20 g. of iminodiacetonitrile in dioxane was added a dioxane solution of 17.6 g. of 2 chloro-4,6-dimethoxy-*s*-triazine. The mixture was heated under reflux for 8 hours. After cooling, it was filtered. The dioxane was evaporated leaving a solid material. This was purified by recrystallization from *n*-propyl alcohol; yield 9.4 g. (40%), m.p. 150–152°.

Anal. Calcd. for $C_9H_{10}N_6O_2$: C, 46.15; H, 4.27; N, 35.90. Found: C, 46.06; H, 4.24; N, 36.08.

2-Phenyl-4-amino-6-chloro-*s*-triazine.—To a solution of 22.6 g. of 2-phenyl-4,6-dichloro-*s*-triazine, 6 g. of an aqueous (29%) ammonium hydroxide solution was added while keeping the temperature of the mixture at 0°. Upon completion of the addition the reaction was allowed to proceed at room temperature. The mixture was filtered and the volume of the solution reduced. The product crystallized from solution was collected and recrystallized from chloroform; yield 7.1 g. (34%), m.p. 213–215°.

Anal. Calcd. for $C_9H_7N_4Cl$: C, 52.30; H, 3.38; N, 27.11; Cl, 17.19. Found: C, 52.20; H, 3.40; N, 27.18; Cl, 17.38.

2-Phenyl-4-Amino 6-phenoxy-*s*-triazine.—An aqueous solution of 2.9 g. of phenol and 1.4 g. of sodium hydroxide was added to 7.1 g. of 2-phenyl-4-amino-6-chloro-*s*-triazine dissolved in dioxane and the mixture heated under reflux

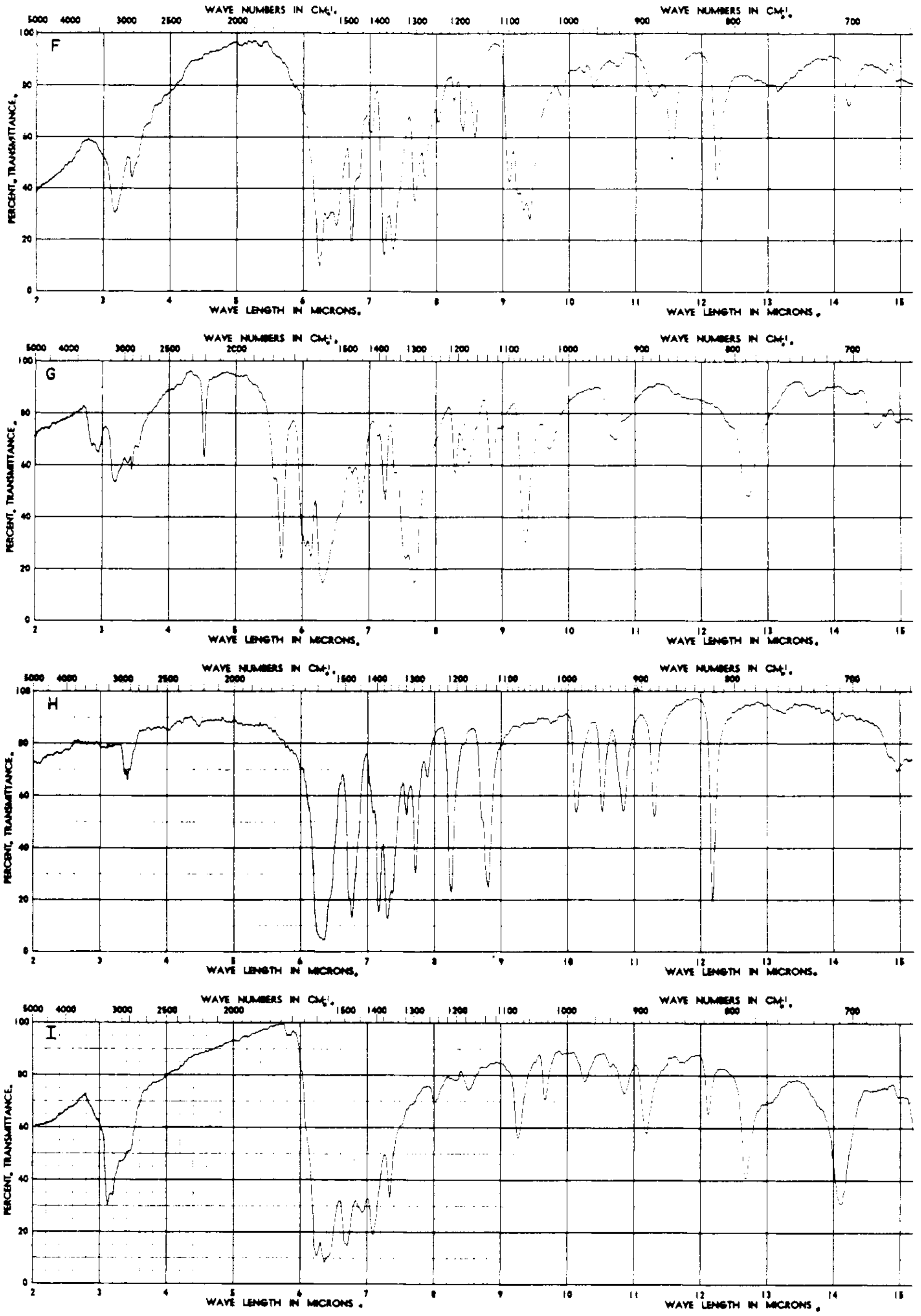

Fig. 5.—KBr spectra: F, 2-N,N-(β-hydroxyethyl)-amino-4,6-dimethoxy-*s*-triazine; G, 2-carboethoxycyanomethyl-4,6-dihydroxy-*s*-triazine; H, 2,4-dimethoxy-6-N,N-dicyanomethylamino-*s*-triazine; I, 2-phenyl-4,6-dihydrazine-*s*-triazine.

for 6 hours. The 2-phenyl-4-amino-6-phenoxy-*s*-triazine crystallized from the cool reaction mixture. After recrystallization of the product from isopropyl alcohol, m.p. 181–183°, yield 3.9 g. (43%).

Anal. Calcd. for $C_{15}H_{12}N_4O$: C, 68.18; H, 4.55; N, 21.21. Found: C, 68.12; H, 4.48; N, 21.54.

N-Phenyl-2-phenyl-6-chloro-4-amino-*s*-triazine.—To a solution of 10 g. of 2-phenyl-4,6-dichloro-*s*-triazine in acetone 8.2 g. of aniline was added while cooling the formed solution in an ice–water-bath. After the addition the mixture was kept at 0° for 30 minutes and then allowed to warm to room temperature and kept there for 3 hours. After filtration the acetone was evaporated and the solid material purified by recrystallization from chloroform–ligroin; yield 5.2 g. (47%), m.p. 163–164°.

Anal. Calcd. for $C_{15}H_{11}N_4Cl$: C, 63.71; H, 3.89; N, 19.82; Cl, 12.57. Found: C, 63.67; H, 3.89; N, 19.65; Cl, 12.91.

N-Phenyl-2-phenyl-6-phenoxy-4-amino-*s*-triazine.—To a solution of 250 cc. of dioxane containing 5 g. of 2-phenyl-4-anilino-6-chloro-*s*-triazine, a solution of 100 cc. of water containing 0.71 g. of sodium hydroxide and 1.66 g. of phenol was added. The mixture was then heated under reflux with stirring for 5.5 hours. Upon cooling, a white solid material separated; it was collected and recrystallized from dioxane; yield 2.2 g. (36%), m.p. 112–114°.

Anal. Calcd. for $C_{21}H_{16}N_4O$: C, 74.12; H, 4.71; N, 16.47. Found: C, 73.93; H, 4.70; N, 16.61.

2-Phenyl-N,N′-bis-(4-carboethoxyphenyl)-4,6-diamino-*s*-triazine.—Phenyl-4,6-dichloro-*s*-triazine (5 g.) dissolved in

50 cc. of *p*-dioxane. This solution was added dropwise to a mixture of 7.4 g. of ethyl *p*-aminobenzoate and 3.8 g. of $NaHCO_3$. The mixture was then refluxed with stirring for 3 hours. At the end of this time the solution was filtered hot to remove the excess of $NaHCO_3$. Upon cooling, crystals separated which were purified by subsequent recrystallization from dioxane; yield 8.1 g. (75.8%), m.p. 229°.

Anal. Calcd. for $C_{27}H_{25}N_5O_4$: C, 67.1; H, 5.5; N, 14.57. Found: C, 67.03; H, 5.22; N, 14.8.

2-Phenyl-4,6-dihydrazine-*s*-triazine.—To a solution of 150 cc. of acetonitrile containing 22.5 g. of 2-phenyl-4,6-dichloro-*s*-triazine, a solution of 100 cc. of ethanol containing 15 g. of hydrazine and 50 cc. of water was added. The mixture was heated for about 30 minutes. After cooling, the precipitate was collected and washed with hot water, ethanol and ether; yield 21 g. (97%), m.p. 182–184°.

Anal. Calcd. for $C_9H_{11}N_7$: C, 49.9; H, 5.05; N, 45.05. Found: C, 49.9; H, 4.99; N, 44.76.

2-Methyl-4,6-bis-(diphenylamino)-*s*-triazine.—A solution of 300 cc. of 1,4-dioxane containing 16.3 g. of 2-methyl-4,6-dichloro-*s*-triazine and 67.6 g. of diphenylamine was heated under reflux for about 5 hours. The reaction mixture was allowed to stand at room temperature overnight. After filtration, about 200 cc. of dioxane was distilled off. The remaining solution was diluted with 100 cc. of chloroform. This resulting solution was washed five times with 100-cc. portions of water, then dried over $CaCl_2$. After addition of ligroin (60–70°), precipitation occurred. The solid material was purified by recrystallization from isopropyl alcohol; yield 40.5 g. (94.5%), m.p. 209–210°.

Anal. Calcd. for $C_{28}H_{23}N_5$: C, 78.2; H, 5.36; N, 16.3. Found: C, 78.14; H, 5.30; N, 16.32.

2-Bromomethyl-4,6-bis-(diphenylamino)-*s*-triazine.—A solution of 100 cc. of carbon tetrachloride containing 10.75 g. of 2-methyl-4,6-bis-N-phenylanilino-*s*-triazine, 0.05 g. of benzoyl peroxide and 5 g. of N-bromo-succinimide was heated under reflux with mechanical stirring for 2 hours. During this time the mixture was irradiated with ultraviolet light. During reaction the succinimide precipitated from solution. After cessation of reaction the succinimide was separated by filtration of the hot solution, washing with carbon tetrachloride and the washings added to the original filtrate. After evaporation of the carbon tetrachloride the remainder was extracted with ligroin. Recrystallization from ligroin afforded the pure 2-bromomethyl-4,6-bis-(diphenylamino)-*s*-triazine; yield 10.5 g. (82%), m.p. 146–148°.

Anal. Calcd. for $C_{28}H_{22}N_5Br$: C, 66.15; H, 4.34; N, 13.80; Br, 15.71. Found: C, 66.46; H, 4.36; N, 13.81; Br., 15.43.

2-Dicarboethoxy-phenylmethyl-4,6-dimethoxy-*s*-triazine.—Sodium (6 g.) was dissolved in 100 cc. of absolute ethanol. The ethanol then was distilled off and the remaining sodium ethoxide pulverized by vigorous stirring. After cooling, 58.5 g. of diethyl phenylmalonate dissolved in 50 g. of diethyl carbonate was added. Stirring was allowed to continue at room temperature until all sodium ethoxide had reacted. The ethanol formed by this reaction was removed by distillation under diminished pressure. A solution of 50 g. of diethyl carbonate containing 50 g. of 2-chloro-4,6-dimethoxy-*s*-triazine was added and the mixture was heated at 100–110° for 8 hours. After standing overnight at room temperature a solution of 2 cc. of glacial acetic acid in 200 cc. of distilled water was then added. The product crystallized from this solution was collected and washed with water, alcohol and ether; yield 61 g. (65%). After recrystallization from ethanol the material melted at 112–113°.

Anal. Calcd. for $C_{18}H_{21}O_6N_3$: C, 57.7; H, 5.6; N, 11.2. Found: C, 57.49; H, 5.62; N, 11.23.

Infrared Spectra. Apparatus.—The infrared investigations were carried out with a Baird associates model B double beam spectrophotometer equipped with a sodium chloride prism. The instrument was calibrated with a polystyrene film to within $\pm 0.05\ \mu$.

Technique.—Mallinckrodt reagent grade carbon tetrachloride and carbon disulfide were used as solvents for the triazine derivatives 2 through 11. Each sample contained 20 mg. per ml. which seemed to be the maximum concentration that could be obtained with this set of derivatives. This limited concentration required that a 0.4-mm. cell be used in order to obtain enough detail in the spectra between 8 and 11 μ. Figure 1,1 shows the absorption bands due to the solvents. In all of the solution spectra carbon tetrachloride was used to 7.6 μ and then carbon disulfide to 15 μ. In the regions where the solvents absorb strongly in the 0.4-mm. cell the spectra were re-run in a 0.07-mm. cell at the same concentration.

The triazine derivatives A through I were not soluble in these solvents and their spectra were recorded as solids in potassium bromide wafers. Between 1 and 1.5 mg. of ground sample was mixed with 200 mg. of infrared quality potassium bromide powder on a Wig-1-Bug[12] and pressed at 10,000 p.s.i. for four minutes. The wafers were 0.4 mm. thick and a 25% transmission screen was used in the reference beam.

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[12] Spex Industries, Scotch Plains, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Stereospecific Lithium Aluminum Hydride Reduction of 2,3-Dimethylquinoxaline and Related Triazanaphthalenes[1]

BY ROY C. DESELMS[2] AND HARRY S. MOSHER

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The lithium aluminum hydride reduction of 2,3-dimethylquinoxaline gives the *cis*-tetrahydro derivative contrary to the previous literature. This is a stereospecific reduction since the reagent does not isomerize the *trans* compound to the *cis*. This reduction is applied to 2,3-dimethyl-1,4,5-triazanaphthalene and 2,3-dimethyl-1,4,6-triazanaphthalene to give the corresponding tetrahydro derivatives which are presumed to have the *cis* configuration. The ultraviolet and infrared spectra of these compounds are reported and discussed.

During a recent study[1] of the synthesis of certain analogs of tetrahydropteroic acid, it became desirable to investigate the selective reduction of some related polyazanaphthalenes to the corresponding tetrahydro derivatives. The pyrazine ring in other fused heterocyclic systems has been preferentially reduced[3,4] and it seemed likely that this could be extended to the pyridopyrazines under study.

It was reported by Bohlmann[5] that the lithium aluminum hydride reduction of 2,3-dimethylquinoxaline gave a product, m. p. 102–103°, which he concluded was the same as the compound of the

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[1] Abstracted in part from the Ph.D. Dissertation of Roy C. De Selms, Stanford Univ., 1959.

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