

action between bromine and stilbene and in the reaction between chlorine and dimethylmaleic acid. It was the purpose of this work to determine if it was possible to prepare cyclic halonium compounds which do not contain iodine as part of the ring system. As a result the present authors have found that diazotized 2-amino-2'-iodobiphenyl is converted into iodonium salts. Similarly it has been found that 2-amino-2'-bromobiphenyl and 2-amino-2'-chlorobiphenyl are converted into bromonium and chloronium compounds, respectively.

All the compounds needed for the investigation were known, but only the acetyl derivative of 2-amino-2'-iodobiphenyl has been characterized.⁷

Experimental⁸

2-Amino-2'-iodobiphenyl (V) was prepared according to Mascarelli and Gatti⁹ who used 2,2'-dinitrobiphenyl as the starting material. The over-all yield of crude 2-amino-2'-iodobiphenyl from 59 g. of the dinitro compound was 20 g. The amine failed to crystallize on long standing and was fractionally distilled; b.p. 197° at 8 mm. The distillate solidified on cooling and after several recrystallizations from ethanol yielded 12 g. of almost white, granular 2-amino-2'-iodobiphenyl; m.p. 81–82°.

Anal. Calcd. for C₁₂H₁₀NI: I, 43.0. Found: I, 42.8, 43.2.

An equally satisfactory starting material for preparing V was 2-amino-2'-acetamidobiphenyl (VI)¹⁰ which was diazotized, treated with potassium iodide, hydrolyzed with hydrochloric acid in ethanol and finally made alkaline and steam distilled. The over-all yield of crude V from VI was about 25%. Compound VI was also used for the preparation of 2-amino-2'-bromobiphenyl (VII) and 2-amino-2'-chlorobiphenyl (VIII) which were known compounds. The over-all yield of crude VII from 41 g. of VI was 22 g. We were unsuccessful in making this compound solidify. The reported m.p. is 46–50°.⁹ For that reason VII was purified as the hydrochloride, m.p. 184–185°, and used as such in subsequent work.

Anal. Calcd. for C₁₂H₁₁NCIBr: Cl, 12.5. Found: Cl, 12.5, 12.5.

The over-all yield of crude VIII from 33 g. of VI was 11 g. It was crystallized from ethanol, m.p. 54°. The reported m.p. is 56–57°.⁹

Preparation of Diphenyleneiodonium Salts.—Three grams of 2-amino-2'-iodobiphenyl was dissolved in boiling 10% hydrochloric acid (180 ml.). On cooling the hydrochloride separated. The mixture was treated at 0–5° with sodium nitrite (1.5 g.) in water (60 ml.). The diazotized solution was allowed to stand at 0–5° for 30 minutes and then treated with urea (1.5 g.). After standing for another 30 minutes potassium iodide (5 g.) in water (20 ml.) was added and the mixture was heated on the steam-bath until the evolution of gas had ceased. During the heating diphenyleneiodonium iodide separated as a brown solid. The mixture was cooled, filtered and the crude salt converted into the nitrate¹¹ which was crystallized from water. The yield was 1.5 g.; decomposition temperature 241–242°.

Anal. Calcd. for C₁₂H₉O₂NI: I, 37.3. Found (Carius): I, 37.5, 37.4.

Sodium chloride was added to some of the nitrate in water. This afforded diphenyleneiodonium chloride which crystallized from water as white needles, decomposing at 292–294°.

Anal. Calcd. for C₁₂H₉ClI: Cl, 11.3. Found (silver nitrate and nitric acid): Cl, 11.3, 11.2.

(7) C. A., 26, 1272 (1932), lists the 2-amino-2'-iodobiphenyl as melting at 129–130°. Evidently this is not the m.p. of the amine but of the acylated derivative.

(8) All melting points and decomposition temperatures are uncorrected.

(9) L. Mascarelli and D. Gatti, *Atti accad. Lincei*, 13, 887 (1931).

(10) S. Sako, *Mem. Coll. Eng. Kyushu Imp. Univ.*, 6, 263 (1932).

(11) A. Wasylewsky, R. K. Brown and R. B. Sandin, *THIS JOURNAL*, 72, 1038 (1950).

Diphenyleneiodonium chloride was also made directly from V by diazotization in hydrochloric acid followed by heating on the steam-bath.

Preparation of Diphenylenebromonium Salts.—The hydrochloride of 2-amino-2'-bromobiphenyl (1.0 g.) was dissolved in boiling 10% hydrochloric acid (40 ml.). The cooled (0–5°) solution was treated with sodium nitrite (0.5 g.) in water (10 ml.). After standing at 0–5° for 30 minutes, urea (0.5 g.) was added. After another 30 minutes, the solution was heated on the steam-bath until the evolution of gas had ceased. The hot reaction mixture was clarified with charcoal, filtered hot, and the filtrate cooled in ice-water. Diphenylenebromonium chloride separated as white needles. After several crystallizations from water the yield was 0.4 g. and it decomposed at 205–207°.

Anal. Calcd. for C₁₂H₉ClBr: Cl and Br, 43.1. Found: Cl and Br (Carius), 42.7.

A small amount of the salt was decomposed by heat. The reaction product was crystallized from ethanol, which afforded white crystals, m.p. 58°. The reported m.p. for 2-bromo-2'-chlorobiphenyl is 58°.⁹ A solution of the salt was treated with potassium iodide. The solid diphenylenebromonium iodide which separated was filtered, and recrystallized from water to give fine yellow crystals, decomposing at 165–170° with the evolution of iodine.

Anal. Calcd. for C₁₂H₉BrI: I, 35.4. Found (silver nitrate and nitric acid): I, 35.3, 35.4.

Preparation of Diphenylenechloronium Iodide.—The preparation of this compound from 2-amino-2'-chlorobiphenyl was the same as described for diphenylenebromonium chloride. However instead of standing for 30 minutes after the urea treatment, the solution was allowed to stand overnight at 5–10°. It was then heated gently on the steam-bath until gas evolution had ceased, cooled to 5–10° and the chloronium iodide precipitated as a brown solid by the addition of solid potassium iodide. The salt was filtered and redissolved in water using a steam-bath as a source of heat, clarified with charcoal and filtered hot. The cold filtrate was treated with solid potassium iodide which afforded the chloronium iodide as a solid which this time was much lighter in color. Three crystallizations from water (steam-bath), afforded diphenylenechloronium iodide as pale yellow needles (darkened in light) which decomposed with some violence at 125–130°. The yield from 1 g. of 2-amino-2'-chlorobiphenyl was 0.4 g.

Anal. Calcd. for C₁₂H₉ClI: I, 40.35, Cl and I, 51.6. Found: I (silver nitrate and nitric acid), 39.9, 40.5; Cl and I (Carius), 51.4.

A small amount of the salt was decomposed by heat. The residue was crystallized from ethanol which yielded white crystals, m.p. 63–64°. The reported m.p. for 2-chloro-2'-iodobiphenyl is 63–64°.⁹

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Factors Involved in the Sharpening of the Ultraviolet Absorption Spectrum of Guanine at Reduced Temperatures¹

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During the course of studies on the effect of low temperatures upon the ultraviolet absorption spectra of various compounds of biological importance, we have noted^{3,4} that the spectra of thin films of sublimate of most of the pyrimidines examined show a considerable degree of sharpening

(1) The work was supported in part by a grant from the American Cancer Society, recommended by the Committee on Growth of the National Research Council, and in part by a grant from the U. S. Public Health Service.

(2) Deceased, January 22, 1951.

(3) J. F. Scott, R. L. Sinsheimer and J. R. Loofbourow, *Science*, 107, 302 (1948).

(4) (a) R. L. Sinsheimer, J. F. Scott, J. R. Loofbourow, *J. Biol. Chem.*, 187, 299 (1950); (b) 187, 313 (1950).

while the spectra of similar preparations of the purines show little or no fine structure even when the temperature of the sample was reduced to that of liquid H_2 . Some of the pyrimidines show an increase in fine structure in the low-temperature spectra upon exposure of the film of sublimate to an atmosphere containing water vapor.⁵

By exposure of sublimed films of purines to high water vapor concentrations we have been able to produce certain spectral changes and to detect a simultaneous change in the order of the molecules comprising the film. Figure 1 demonstrates the changes in the low-temperature ultraviolet absorption spectrum of a thin film of sublimate of guanine (2-amino-6-purine) upon exposure to high water vapor concentration for increasing periods of time.

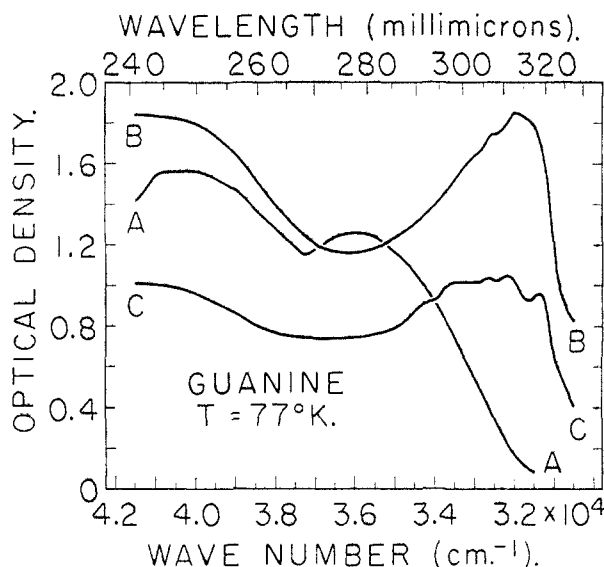


Fig. 1.—Effect of water vapor on the ultraviolet absorption spectrum of a thin film of sublimate of guanine at reduced temperature: curve A, immediately after sublimation; curve B, after 5 min. exposure to 100% humidity at 25°; curve C, after 14 days exposure. Conditions same as for B.

Corresponding changes in the infrared absorption spectrum of a similar but thicker film of the same compound are shown in Fig. 2. The two infrared spectra were obtained with identical conditions of resolution. The sample in this case was at room temperature.

Figure 3 shows the changes produced in the X-ray diffraction pattern of a film of sublimed guanine upon exposure of the film to water vapor. Heating the sublimed films to 60° for four days in a vacuum oven failed to reverse the alteration in the spectra produced by the exposure to water vapor.

Experimental

The details of the method for the preparation of the films of sublimate and for the absorption spectrophotometry have been published elsewhere.^{4,5}

X-Ray Diffraction.—The sublimed material was scraped from the glass slide upon which it had been deposited and the resulting powder placed in a glass capillary tube for X-ray diffraction. A camera with a flat film cassette was used;

(5) R. L. Sinshimer, J. F. Scott and J. R. Loofbourow, *Nature*, **164**, 796 (1949).

specimen-to-film distance, 5 cm.; radiation, nickel filtered $CuK\alpha$ (λ 1.54 Å).

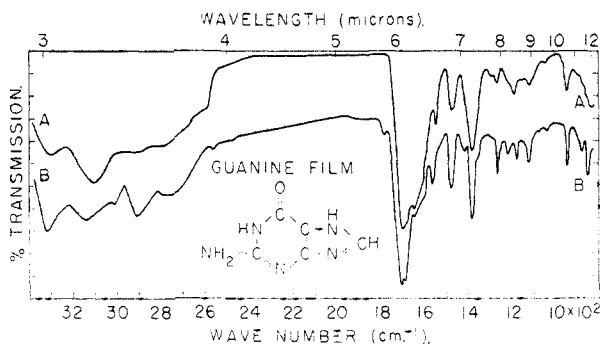


Fig. 2.—Effect of water vapor on the infrared absorption spectrum of a thin film of sublimate of guanine: curve A, immediately after sublimation; curve B, after 5 min. at 100% humidity at 25°. For clarity of presentation curve B has been displaced downward by subtracting 20% from each observed transmission value.

Discussion of Results

The appearance of fine structure in the low-temperature ultraviolet spectrum can be correlated with the changes in the infrared spectra. The latter show a sharpening and splitting of certain absorption bands upon exposure of the film of sublimate to high humidity. In the region of 2900–3300 cm^{-1} new bands appear while there is some splitting of the band in the 1700 cm^{-1} region indicating an alteration in the charge distribution about the double bonds in the molecule. One of the more interesting changes is the splitting of the band in the region of 800–900 cm^{-1} . Blout, *et al.*,⁶ noted that the major difference between the infrared spectrum of a film of sublimate of guanine and of a Nujol mull of the original material was primarily this difference in the band at 800–900 cm^{-1} . The X-ray diffraction pattern shows clearly that exposure of the film to water vapor produces transition from a largely amorphous material to a largely crystalline material. The diffraction maxima of the latter correspond very closely to those reported by Clark.⁷

This evidence suggests that of the factors influencing the degree of sharpening of the ultraviolet absorption spectrum resulting from the reduction of the temperature of the sample,^{4b} the degree of order in the spatial distribution of the fields acting on each absorber is of prime importance. Such spatial order may result when the molecules are arrayed in a crystal lattice. Reduction of the temperature reduces random fluctuations in the fields acting on each absorbing molecule during the period of observation. When conditions of order with respect to both space and time have been produced in the sample then fine structure may appear in the low-temperature ultraviolet absorption spectrum. Hainer and King⁸ have demonstrated the effect of crystallization on the low temperature infrared absorption spectrum.

(6) E. R. Blout, M. Field and R. Karplus, *THIS JOURNAL*, **70**, 194 (1948).

(7) C. Clark, Ph.D. thesis, Dept. of Zoology, Columbia Univ., New York, N. Y., 1950.

(8) R. M. Hainer and G. W. King, *Nature*, **166**, 1029 (1950).

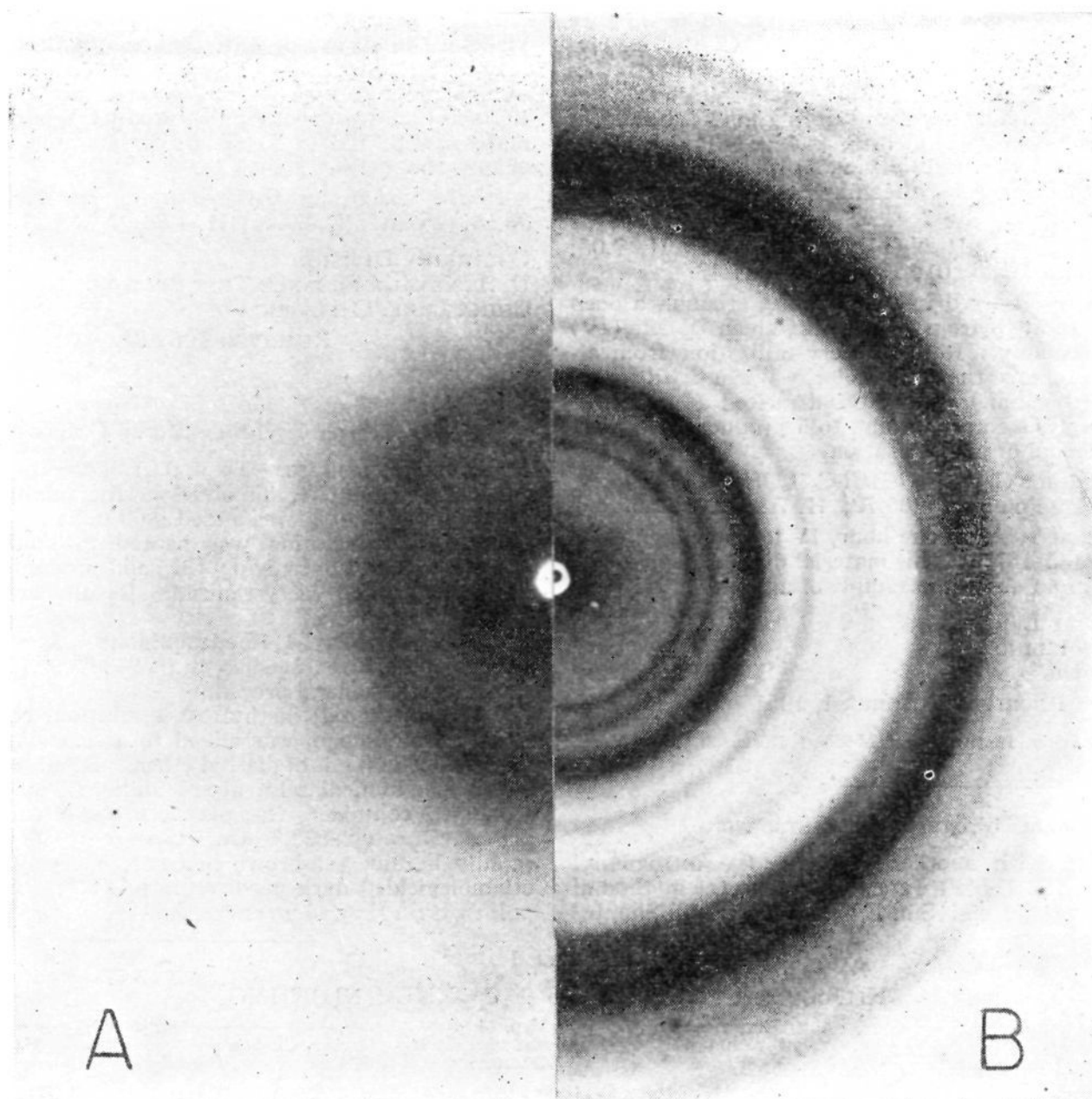


Fig. 3.—Effect of water vapor upon the X-ray diffraction pattern of a film of sublimated guanine: A, immediately after sublimation; B, after 2 days at 100% humidity at 25°.

From our results the influence of spatial order on the infrared absorption band width is also evident at room temperature.

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NEW COMPOUNDS

1,5-Diphenyl-3-(β -morpholinoethyl)-2-pyrazoline Hydrochloride

1,5-Diphenyl-3-(β -morpholinoethyl)-2-pyrazoline hydrochloride was prepared by an acid-catalyzed isomerization of the phenylhydrazone of 1-phenyl-5-morpholino-1-penten-3-one hydrochloride. The method employed was a modification of that described by Nisbet.¹

1-Phenyl-5-morpholino-1-penten-3-one Hydrochloride (I).—A mixture of 36.5 g. (0.25 mole) of benzalacetophenone, 31 g. (0.25 mole) of morpholine hydrochloride and 10 g. (0.3 mole) of paraformaldehyde in 25 ml. of absolute ethanol was heated quickly to the boiling temperature with frequent

stirring. One milliliter of concentrated hydrochloric acid was then added and the mixture boiled under reflux 30 minutes. Three more grams of paraformaldehyde was added gradually through the reflux condenser and the boiling continued another 30 minutes. After the contents had cooled to room temperature, 150 ml. of acetone was added and the mixture was allowed to stand overnight in the refrigerator. Thirty grams (44%) of pale yellow crystals, m.p. 175.5–176.6° dec.² was collected. The crude hydrochloride was dissolved in 200 ml. of boiling absolute ethanol, the solution treated with Norite and allowed to cool slowly. Twenty-seven grams of white crystals, m.p. 175.5–177° dec., was collected. Repeated crystallization furnished feathery white needles melting at 177–179° dec.

*Anal.*³ Calcd. for $C_{15}H_{19}NO_2 \cdot HCl$: C, 63.93; H, 7.15; N, 4.97. Found: C, 64.34, 64.40; H, 7.30, 7.22; N, 5.08, 5.17.

Phenylhydrazone (II).—When prepared in the usual manner (yield 89%) and recrystallized from absolute ethanol, this derivative melts at 175–179°, depending on the rate of heating.

Anal. Calcd. for $C_{21}H_{25}N_3O \cdot HCl$: C, 67.81; H, 7.05; N, 11.30. Found: C, 68.59, 68.61; H, 7.16, 7.24; N, 11.16, 11.07.

1,5-Diphenyl-3-(β -morpholinoethyl)-2-pyrazoline Hydrochloride (III).—A suspension of 10.3 g. (0.027 mole) of crude II in 150 ml. of 1 *N* hydrochloric acid was heated to boiling. While heating, the mixture gradually became thin and changed from yellow to chartreuse. At the boiling

(1) H. B. Nisbet, *J. Chem. Soc.*, 1237 (1938).

(2) All melting points are corrected.

(3) Analyses by Emily Davis, Jean Fortney and K. Pih.