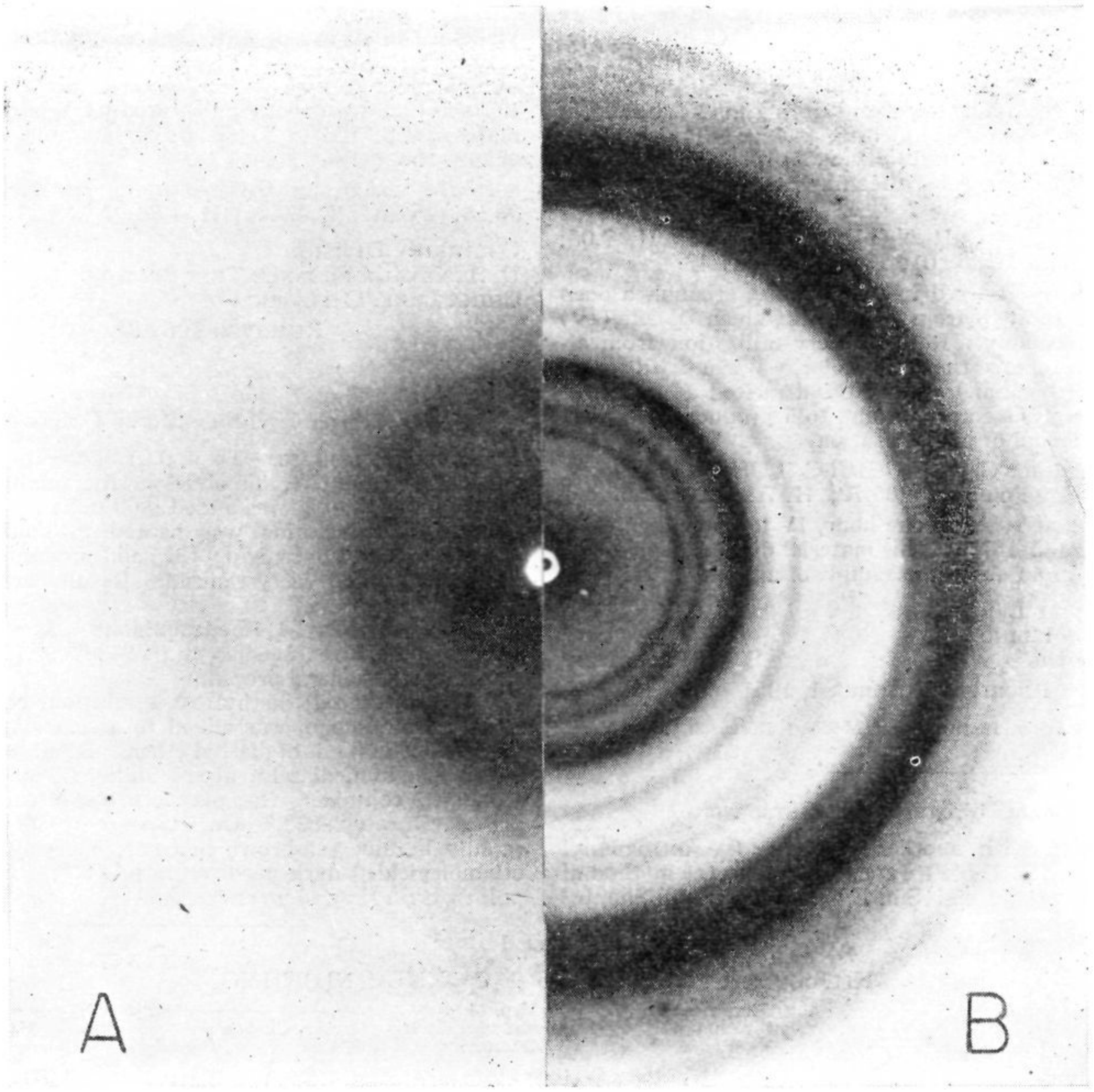

Fig. 3.—Effect of water vapor upon the X-ray diffraction pattern of a film of sublimate of guanine: A, immediately after sublimation; B, after 2 days at 100% humidity at 25°.

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

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RECEIVED JULY 18, 1951

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

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[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.

point the mixture was a pale yellow-green. The mixture was boiled ten minutes and then allowed to cool slowly. After standing at 10° for three hours, 10.0 g. of chartreuse-colored needles, m.p. 182.5–183.5°, was collected. Recrystallization from hot water and drying at 25° furnished 9.0 g. of hydrated product melting at 140–143° dec. The product lost water slowly on drying *in vacuo*. Drying for two hours at 100° furnished the anhydrous pyrazoline·HCl, m.p. 187.5–189° dec.

Anal. Calcd. for $C_{21}H_{25}N_3O \cdot HCl$: C, 67.81; H, 7.05; N, 11.30. Found: C, 68.01; H, 7.14; N, 11.17.

When III was dissolved in hot absolute ethanol, a deep green solution resulted from which light green leaflets (IV) separated on cooling. Repeated crystallization from alcohol failed to remove the green color. When dried for 40 hours at 25° (0.5 mm.), the material melted at 158–161° and had an analysis corresponding to a product containing one mole of alcohol of crystallization.

Anal. Calcd. for $C_{21}H_{25}N_3O \cdot HCl \cdot C_2H_5OH$: C, 66.09; H, 7.72; N, 10.08. Found: C, 65.72; H, 7.85; N, 9.85.

After drying at 100° for one hour, IV lost its green color and melted at 185–187°. This material did not depress the melting point of an authentic sample of anhydrous III.

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RECEIVED OCTOBER 1, 1951

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Some Nitroguanyl Hydrazones

In connection with another problem, the nitroguanyl hydrazones listed in Table I were prepared by the method of Whitmore, Revukas, and Smith,[1] or Smith and Shoub,[2] from the appropriate carbonyl compound and nitroaminoguanidine. The hydrazones were recrystallized from water, 95% ethanol, or suitable mixtures of these two solvents.

TABLE I

NITROGUANYL HYDRAZONES, $R_1R_2C{=}NNHC(NH)NHNO_2$

Carbonyl compound	Empirical formula of hydrazone	M.p. of hydrazone, °C. (cor.)	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Acetaldehyde	$C_3H_7O_2N_5$	144–145^a	24.83	24.98	4.86	4.78
Butyraldehyde	$C_5H_{11}O_2N_5$	103–104^b	...	...	..	..
Isobutyraldehyde	$C_5H_{11}O_2N_5$	129.5–130.5	34.67	34.48	6.40	6.38
Heptaldehyde	$C_8H_{17}O_2N_5$	103–103.5^c	...	...	..	..
Decylaldehyde	$C_{11}H_{23}O_2N_5$	112–113	51.34	51.48	9.01	9.22
d-Glucose	$C_7H_{17}O_8N_5$^{d}	143–144	28.09	28.19	5.73	5.81
Methyl *n*-amyl ketone	$C_8H_{17}O_2N_5$	112–113^e	...	...	..	..
Methyl *n*-undecyl ketone	$C_{14}H_{29}O_2N_5$	115–116	56.16	56.08	9.76	9.89
4-Methylcyclohexanone	$C_8H_{15}O_2N_5$	122–123	45.06	45.24	7.09	7.17
Glyoxal	$C_4H_8O_4N_{10}$	> 300	18.46	17.90	3.10	3.39
Diacetyl	$C_6H_{12}O_4N_{10}$	285–290	25.00	25.3	4.20	4.3
Furfural	$C_6H_7O_3N_5$	213–214	36.55	36.02	3.58	3.57
Phenylacetaldehyde	$C_9H_{11}O_2N_5$	151–151.5	48.86	48.80	5.01	5.16
Hydrocinnamaldehyde	$C_{10}H_{13}O_2N_5$	135	51.05	51.20	5.57	5.63
4-Hydroxbenzaldehyde	$C_8H_9O_3N_5$	253	43.05	43.09	4.06	4.44
2,4-Dihydroxybenzaldehyde	$C_8H_9O_4N_5$	> 300^f	40.17	40.85	3.79	3.93
2-Methoxybenzaldehyde	$C_9H_{11}O_3N_5$	185.5	45.57	45.77	4.67	4.70
4-Methylbenzaldehyde	$C_9H_{11}O_2N_5$	179–180	48.86	48.95	5.01	5.05
4-Isopropylbenzaldehyde	$C_{11}H_{15}O_2N_5$	187	53.00	53.47	6.07	6.18
2-Chlorobenzaldehyde	$C_8H_8O_2N_5Cl$	192	39.76	39.61	3.34	3.34
2,4-Dichlorobenzaldehyde	$C_8H_7O_2N_5Cl_2$	222–224	34.80	35.05	2.56	2.96
3,4-Dichlorobenzaldehyde	$C_8H_7O_2N_5Cl_2$	233–234	34.80	34.63	2.56	2.52
3-Nitrobenzaldehyde	$C_8H_8O_4N_6$	239–240	38.10	38.17	3.20	3.04

[a] 234° was reported in ref. 2. [b] 95° was reported in ref. 2. [c] 93° was reported in ref. 2. [d] This formula is for a monohydrate. Calcd.: N, 23.41. Found: N, 23.59. [e] 109.5° was reported in ref. 2. [f] Darkens about 215–225°; does not soften or melt up to 300°.

1-Nitroguanyl-3,4-dimethylpyrazole.—One gram of acetylacetone in 10 ml. of water was added dropwise with stirring to a solution consisting of 2.38 g. of nitroaminoguanidine, 3 ml. of acetic acid and 150 ml. of water at 80°. When the solution was cooled, the product separated as white plates; m.p. 126°. Recrystallization from water did not change the melting point.

Anal. Calcd. for $C_6H_9N_5O_2$: C, 39.34; H, 4.95; N, 38.24. Found: C, 39.66; H, 4.86; N, 38.24.

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RECEIVED JULY 31, 1951

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[1] W. F. Whitmore, A. J. Revukas and G. B. L. Smith, THIS JOURNAL, **57**, 706 (1935).

[2] G. B. L. Smith and E. P. Shoub, *ibid.*, **59**, 2077 (1937).

Morpholinyl Substituted Quinones[1]

General Procedure.—To a 0.01 molar quantity of the appropriate quinone, dissolved in the minimum quantity of hot 95% ethanol, was added 0.02 mole (1.74 g.) of morpholine. The solution was heated to boiling and then allowed to stand overnight; the solid product was removed by filtration and recrystallized. Results are summarized in Table I.

2,5-Dimorpholinyl-1,4-benzoquinone. A.—A 47% conversion to dark red needles, m.p. 248–249° (dec.), was obtained by the general procedure.

B.—A saturated, diethyl ether solution, containing 1.10 g. of hydroquinone, was added to a solution of 1.74 g. of morpholine in 5 ml. of diethyl ether. Small, colorless platelets formed immediately; after standing 36 hours in a tightly stoppered container, the platelets had changed to small prisms, m.p. 82–83°.[2] On exposure to air this product rapidly became red-brown in color; recrystallization from ethanol yielded dark needles; m.p. 247°, a mixed melting point with A showed no depression.

C.—A slow current of air was bubbled through a refluxing solution of 2.4 g. of *p*-hydroxybenzaldehyde (0.02 mole) and 5.2 g. of morpholine (0.06 mole) in 50 ml. of water for 24

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[1] The melting points are corrected.

[2] Because this compound decomposed rapidly in air, it was not analyzed; it is probably the di-(morpholinium) salt of hydroquinone.

TABLE I

MORPHOLINYL SUBSTITUTED QUINONES AND HYDROQUINONES

Compound (Mo = morpholinyl)	M.p., °C.	Recryst. solvent	Color and crystal habit	Formula	Analyses, N, % Calcd.	Analyses, N, % Found
2,5-Di-(Mo)-1,4-benzoquinone[a]	248–249 dec.	Ethanol	Red needles	$C_{14}H_{18}O_4N_2$	10.07	10.00
2,5-Di-(Mo)-3-methyl-1,4-benzoquinone	158–159	Ethanol	Red prisms	$C_{15}H_{20}O_4N_2$	9.59	9.61
2,5-Di-(Mo)-3,5-dimethyl-1,4-benzoquinone	166.5–168.5	Ethanol	Red needles	$C_{16}H_{22}O_4N_2$	9.15	9.16
2(or 5)-Mo-3-methyl-6-isopropyl-1,4-benzoquinone	238–239	.....	Violet needles	$C_{14}H_{19}O_3N$	5.62	5.65
2-Mo-5-ethoxy-1,4-benzoquinone[b]	200	Ethanol	Scarlet plates	$C_{12}H_{15}O_4N$	5.92	5.98
2,5-Di-(Mo)-3-chloro-1,4-benzoquinone	195–195.5	Ethanol	Brown red needles	$C_{14}H_{17}O_4N_2Cl$	8.96	8.89
2-Mo-1,4-naphthoquinone[c]	152.5–153.5	Water	Orange needles	$C_{14}H_{13}O_3N$	5.76	5.65
4-Mo-1,2-naphthoquinone[d]	199–200	Water	Red prisms	$C_{14}H_{13}O_3N$	5.76	5.68
2,5-Di-(Mo)-3-methyl-6-isopropylhydroquinone[e]	183.5–184.5	Ethanol	Colorless needles	$C_{18}H_{28}O_4N_2$	8.33	8.26

[a] Reductive acetylation yielded the diacetate of 2,5-dimorpholinyl hydroquinone, m.p. 226.5–229.5°. Calcd. for $C_{18}H_{24}O_6N_2$: N, 7.69. Found: N, 7 71. [b] When this reaction was performed in alcohol-free benzene, ethanol could be recovered and identified in the distillate as its 3,5-dinitrobenzoate. [c] Best prepared from equimolar quantities of morpholine and 1,4-naphthoquinone in hot acetone. Reductive acetylation yielded both a monoacetate, m.p. 169.5–170.5° (Calcd. for $C_{16}H_{17}O_4N$: N, 4.88. Found: N, 4.85), and a diacetate, m.p. 157–158° (Calcd. for $C_{18}H_{19}O_5N$: N, 4.25. Found: N, 4.19). [d] Best prepared from equimolar quantities in cold diethyl ether. [e] Acetylation with acetic anhydride and anhydrous sodium acetate gave a mono-acetate, m.p. 178–179°, after two recrystallizations from 95% ethanol (Calcd. for $C_{20}H_{28}O_5N_2$: N, 7.40. Found: N, 7.43); a mixed melting point with the starting hydroquinone was 145–150°.

hours. The red product was removed by filtration and melted at 248° (dec.) after one recrystallization from ethanol; a mixed melting point with A was the same. The yield of 2.5 g. represented a conversion of 45%.

D.—A solution of 3.0 g. of vanillin and 3.5 g. of morpholine in 4 ml. of 95% ethanol was allowed to stand for a month. The solvent was then evaporated and the residue recrystallized from a minimum of benzene; the red needles melted at 248° (dec.), and were identical with those made by method A.

By evaporating the mother liquors and extracting the residue with a cold 50–50 diethyl ether and 95% ethanol mixture there was recovered a small amount of **2-morpholinyl-5-methoxy-1,4-benzoquinone**, m.p. 194° (dec.). This latter product was also prepared by the partial demethoxylation of 2,5-dimethoxy-1,4-benzoquinone with morpholine in cold ethanol.

Anal. Calcd. for $C_{11}H_{13}O_4N$: N, 6.27. Found: N, 6.17.

E.—Morpholine (1.3 g.) was added all at once to a refluxing solution of 1.3 g. of 2,5-dichloro-1,4-benzoquinone in 30 ml. of 95% ethanol; a vigorous reaction ensued. After three minutes the red solid was removed by filtration. Recrystallization from ethanol gave a product which did not depress the melting point of a sample of dimorpholinylbenzoquinone made by method A. The yield was 0.8 g.

F.—Monoanilinobenzoquinone and morpholine also react in hot alcohol to yield 2,5-dimorpholinylbenzoquinone and aniline.

Monomorpholinylbenzoquinone.—A cold solution of morpholine (0.8 g.) in 10 ml. of diethyl ether was added slowly with vigorous stirring to a saturated ethereal solution which contained 2 g. of *p*-benzoquinone and which was cooled to 0°. A precipitate of 2,5-dimorpholinylbenzoquinone formed and was removed by filtration (0.3 g.). Dark purple crystals, decomposing about 135°, separated when the ethereal solution was evaporated. This material was purified by extracting it from less soluble impurities with small volumes of 2:1 mixture of diethyl ether and petroleum ether (b.p. 30–80°); purple, warty masses, with a greenish luster were deposited upon slow evaporation of the solvent; m.p. 139° (dec.). Attempted recrystallization from ligroin decomposed the substance.

Anal. Calcd. for $C_{10}H_{11}O_3N$: N, 7.25. Found: N, 7.15.

2,5-Dimorpholinyl-3,6-dichloro-1,4-benzoquinone.—To a suspension of 1.8 g. of 2,5-dichlorobenzoquinone in 90 ml. of 95% ethanol at 15° was added with stirring 1.7 g. of morpholine. After five minutes the solution was heated to boiling and filtered from 0.2 g. of 2,5-dimorpholinylbenzoquinone. Partial evaporation of the filtrate and cooling gave 0.9 g. of the product which was recrystallized from ethanol; reddish-brown plates; m.p. 202–204°.

Anal. Calcd. for $C_{14}H_{16}O_4N_2Cl_2$: N, 8.07. Found: N, 8.03.

The same product was obtained from one equivalent of 2,3,5,6-tetrachlorobenzoquinone and four equivalents of morpholine in boiling ethanol.

4,5-Dimorpholinylcatechol.—A solution of 2.2 g. of catechol and 3.5 g. of morpholine in 25 ml. of ethanol was refluxed for 11.5 hours while a slow stream of air was bubbled in. The reddish-brown solution was evaporated to 15 ml. and cooled; 0.5 g. of product separated. One recrystallization from ethanol gave rosettes of colorless, hexagonal prisms; m.p. 222°.

Anal. Calcd. for $C_{14}H_{20}O_4N_2$: N, 10.00. Found: N, 10.09.

The same compound was obtained in small yield by allowing a solution of 2.4 g. of salicylaldehyde, 3.5 g. of morpholine, and 5 ml. of dioxane to stand for three months.

2,5-Dimorpholinyl-3,6-dichlorohydroquinone.—A solution of 2,5-dimorpholinylbenzoquinone (0.3 g.) was refluxed for three hours with 15 ml. of absolute ethanol saturated with dry hydrogen chloride. The white **dihydrochloride, which** separated on cooling, was recrystallized from 95% ethanol; m.p. 239–240°.

Anal. Calcd. for $C_{14}H_{20}O_4N_2Cl_4$: N, 6.62. Found: N, 6.60.

The diacetate ester, made by the reductive acetylation of 2,5-dimorpholinyl-3,6-dichlorobenzoquinone, melted at 267–269°.

Anal. Calcd. for $C_{18}H_{22}O_6N_2Cl_2$: N, 6.47. Found: N, 6.56.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
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RECEIVED JULY 31, 1951

Esters of Hydantoin-5-propionic Acid

Phenacyl Hydantoin-5-propionate.—To 1 g. of hydantoin-5-propionic acid, neutralized with sodium hydroxide in 5 ml. of aqueous solution, was added 1 g. of phenacyl bromide and the mixture was refluxed for one hour. The crystalline product, which separated on cooling, was purified by recrystallization from ethanol, m.p. 145–146° (58%).

Anal. Calcd. for $C_{14}H_{14}O_5N_2$: N, 9.65. Found: N, 9.71.

***p*-Nitrobenzyl Hydantoin-5-propionate.**—This ester, prepared in like manner, was obtained in 59% yield; shiny plates, m.p. 66–67°.

Anal. Calcd. for $C_{13}H_{13}O_6N_3$: N, 13.68. Found: N, 13.52.

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