SOME N-METHYL-N-(4-CHLORO-1-PHTHALAZINYL)HYDRAZONES*

B. I. Buzykin, N. N. Bystrykh, A. P. Stolyarov,
S. A. Flegontov, and Yu. P. Pitaev

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N-Methyl-N-(4-chloro-1-phthalazinyl)-(E)-hydrazones of the corresponding carbonyl compounds were obtained by condensation of 1-methyl-1-(4-chloro-1-phthalazinyl)hydrazine with carbonyl compounds. The PMR spectra of the products in a number of solvents at various temperatures and the UV spectra in solution and in the solid form were recorded. It was established that a change in the nature of the substituents in the ylidene fragment leads to a change in the three-dimensional structure and the reaction center (C_{pht}—Cl, C_{pht}—N, C=N) in acid hydrolysis reactions.

In a continuation of our research on hydrazino derivatives of phthalazine and phthalazone [2, 3] in order to arrive at a synthesis of compounds with a fixed hydrazone structure, we obtained N-methyl-N-(4-chloro-1-phthalazinyl)hydrazones II-IX (Tables 1 and 2) by condensation of 1-methyl-1-(4-chloro-1-phthalazinyl)hydrazine (I) with a number of carbonyl compounds.

Like other 1-chlorophthalazines [4] with a substituent in the 4 position, hydrazine I and hydrazones III and V undergo exchange of a chlorine atom by an ethoxy group in alcoholic alkali to give, respectively, 1-methyl-1-(4-ethoxy-1-phthalazinyl)hydrazine (X), acetaldehyde N-methyl-N-(4-ethoxy-1-phthalazinyl)hydrazone (XI), and benzaldehyde N-methyl-N-(4-ethoxy-1-phthalazinyl)hydrazone (XII).

Replacement of chlorine also occurs when aromatic hydrazones V-VIII are treated with refluxing 90% AcOH. The presence in the IR spectra of hydrazones XIII-XVI of absorption bands at 1660-1670 and 3160-3200 cm^{-1} (C=O and NH), the position of the NH signal in the PMR spectra (Table 2), which is characteristic for phthalazones [2], and the UV spectral data (Table 1) constitute evidence that in solution and in crystalline form (see scheme top of following page), they exist primarily in the lactam form, i.e., they have N-methyl-N-(phthalaz-4-on-1-yl)hydrazone structures.

Under similar conditions aliphatic hydrazones II and III undergo hydrolysis with cleavage of the C_{pht}—N bond. Hydrolysis of acetophenone hydrazone IX in 90% AcOH leads to acetophenone and, partially, 4-chlorophthalazone. Thus the direction of the acid hydrolysis of N-methyl-N-(4-chloro-1-phthalazinyl)hydrazones is determined by the nature of the substituents in the ylidene fragment.

A shift in the position and a decrease in the intensity of the long-wave band as compared with the corresponding aldehyde hydrazones III and V are observed in the UV spectra of ketone hydrazones IV and IX (Table 1). The signal of the 8-H proton in the PMR spectra (Table 2) of aldehyde hydrazones II, III, V, VII, XI, and XII is found at considerably weaker field than the signals of the other protons of the phthalazine ring. This difference is absent in the spectra of the ketone hydrazones. This may be explained by the difference in the structures of the aldehyde and ketone derivatives and aliphatic and aromatic derivatives [5-9], which differ with respect to the angles of rotation about the C_{pht}—N and N—N bonds.

A comparative analysis of the UV spectra of phthalazine, 1-chloro- and 1,4-dichlorophthalazine [2], 1-dimethylamino-4-chlorophthalazine (XVII), naphthalene and 1-dimethylaminonaphthalene [10], and benzene and dimethylaniline [11] and the PMR spectral data (the temperature dependence in various solvents; Tables 1 and 3) attest to a low barrier to rotation of the $N(CH_3)_2$ group and to the nonplanar structure of amine XVII, the conformation of which

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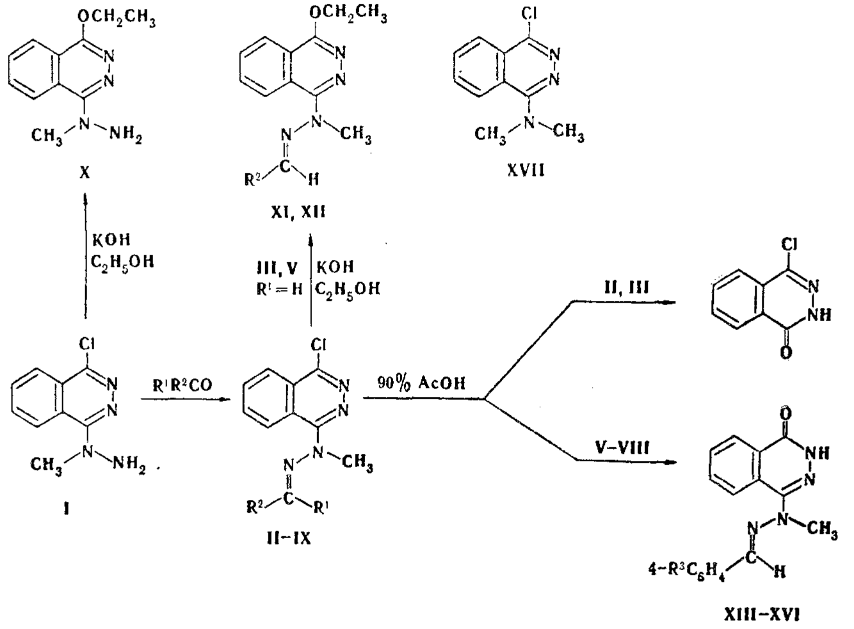

II $R^1=R^2=H$; III $R^1=H$, $R^2=CH_3$; IV $R^1=R^2=CH_3$; V—VIII $R^1=H$, $R^2=C_6H_4R^3$-4; V $R^3=H$; VI $R^3=Br$; VII $R^3=OH$; VIII $R^3=NO_2$; IX $R^1=CH_3$, $R^2=C_6H_5$; XI $R^2=CH_3$; XII $R^2=C_6H_5$; XIII $R^3=H$; XIV $R^3=Br$; XV $R^3=OH$; XVI $R^3=NO_2$

TABLE 1. UV Spectra of Hydrazines I and X, Hydrazones II-IX and XI-XVI, and Substituted Dimethylamine XVII

Compound	λ_{max}, nm (lg ε)		
	dioxane	acetonitrile	crystal
I	315 (3,90); 260 (3,72)*	316 (3,89); 259 (3,72)*; 213 (4,73)	325, 267, 213
II	325 (3,92); 245 (3,95)*	323 (3,92); 250 (3,95)*; 217 (4,56)	332, 265, 212
III	332 (4,02); 245 (4,13)*	333 (3,98); 241 (4,02)*; 217 (4,63)	355, 275, 208
IV	336 (3,88)	336 (3,93); — 215 (4,70)	338, 216
V	356 (4,26); 296 (4,11)	357 (4,19); 291 (4,09); 219 (4,63)	364, 298, 220
VI	359 (4,31); 299 (4,15)		
VII	364 (4,17); 284 (4,18)		
VIII	388† 256*		
IX	352 (3,95); 245 (4,20)*	351 (3,96); 240 (4,16)*; 215 (4,68)	357, 250, 214
X	303 (3,72); 250 (3,70)*		
XI	315 (3,93); 245 (4,15)*		
XII	345 (4,19); 295 (4,15)*		
XIII	320 (4,24)		
XIV	324 (4,28)		
XV	320 (4,11); 288 (4,18)		
XVI	374 (4,30); 255 (4,26)		
XVII	320 (3,76); 262 (3,56)*	322 (3,66); 262 (3,43)*; 214 (4,56)	322, 264, 212

*Shoulder.

†Does not dissolve completely.

is evidently similar to the conformation of 4-dimethylaminoquinazoline ($\Theta \sim 65°$, $\Delta G^{\neq} \leq 34.7$ kJ/mole) [12].

The NCH_3 signal in the spectrum of hydrazine I is found at weaker field* than in the spectrum of amine XVII, whereas the signal of the 8-H proton is shifted to weak field as compared with the signals of the 5-H—7-H protons. A similar pattern is also observed in the spectra of hydrazine X (Table 3). The observed effect may be due to deshielding of the 8-H proton by the CH_3 or NH_2 groups in the case of a more planar conformation of hydrazines X and I as compared with amine XVII. The closeness of the dipole moments of amine XVII (5.51 D in

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*Note the error in [2]: δ_{NH_3} in d_6-DMSO is 3.35 ppm.

TABLE 2. PMR Spectra of Hydrazones II-VII, IX, and XI-XIII

Compound	Solvent	δ, ppm			
		H-8[a]	C–H and (or) H_{av}	NCH_3[b]	other protons
II	$CDCl_3$	8,70	6,40d 6,63d (2H, CH)[c]	3,60	—
II	d_6-DMSO	8,70	6,59d 6,89d (2H, CH)[c]	3,58	—
III	CH_2Cl_2	8,97	7,32q (1H, CH) (J=5,2 Hz)	3,66	2,09d (3H, CH_3) (J=5,2 Hz)
III	$C_2H_2Br_4$	8,80	—	3,61	2,09d (3H, CH_3) (J=5,2 Hz)
III	$C_2H_2Br_4$ (+160°)	8,83	—	3,68	2,10d (3H, CH_3) (J=5,2 Hz)
III	d_6-DMSO	8,82	7,35q (1H, CH) (J=5,2 Hz)	3,54	2,00d (3H, CH_3) (J=5,2 Hz)
IV	CCl_4	8,18	—	3,28	2,15s (3H, CH_3), 2,23s (3H, CH_3)
IV	CH_2Cl_2	8,06	—	3,24	2,11s (3H, CH_3), 2,21s (3H, CH_3)
IV	CH_2Cl_2 (−80°)	—[d]	—	3,13 br m	2,10s (3H, CH_3), 2,13s (3H, CH_3)
IV	d_6-DMSO	—[d]	—	3,18	2,10s (3H, CH_3), 2,25s (3H, CH_3)
V	$CDCl_3$	8,77	7,78s (1H, CH); 7,18m (3H); 7,41m (2H)	3,78	—
V	$C_2H_2Br_4$	8,88	— 7,35m (3H); 7,55m (2H)	3,83	—
V	$C_2H_2Br_4$ (+170°)	8,98	— 7,39m (3H); 7,63m (2H)	3,91	—
V	d_6-DMSO	8,83	— 7,35m (3H); 7,60m (2H)	3,76	—
VII	DMSO	8,82	— 6,82d 7,42d (4H, AA′BB′)	—	9,84 (OH)
IX	$CDCl_3$	—[d]	7,33m (3H)	3,42	2,62s (3H, CH_3)
IX	CH_2Cl_2	—[d]	7,35m (3H)	3,40	2,63s (3H, CH_3)
IX	CH_2Cl_2 (−80°)	—[d]	7,39m (3H)	3,32	2,72s (3H, CH_3)
IX	$C_2H_2Br_4$	8,14	7,45m (3H)	3,46	2,66s (3H, CH_3)
IX	$C_2H_2Br_4$ (+150°)	—[d]	7,43m (3H)	3,56	2,59s (3H, CH_3)
IX	d_6-DMSO	8,16	7,44m (3H); 7,81m (2H)	3,33	2,65s (3H, CH_3)
XI	CH_2Cl_2	8,58	7,04q (1H, CH) (J=5,2 Hz)	3,46	2,00d (3H, CH_3) (J=5,2 Hz); 1,50t (3H, CH_3) 4,64q (2H, CH_2)
XI	d_6-DMSO	8,50	7,15q (1H, CH) (J=5,2 Hz)	3,43	2,28d (3H, CH_3) (J=5,2 Hz); 1,48t (3H, CH_3) 4,55q (2H, CH_2)
XII	$CDCl_3$	8,65	7,25m (3H); 7,50m (2H); 7,76s (1H, CH)	3,72	1,52t (3H, CH_3); 4,63q (2H, CH_2)
XII	d_6-DMSO	8,62	7,26m (3H); 7,56m (3H)	3,68	1,48t (3H, CH_3); 4,60q (2H, CH_2)
XIII	d_6-DMSO	—[d]	7,32m (3H); 7,55m (2H)	3,43	12,21s (1H, NH)

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[a] Multiplet; the multiplet of 5-H—7-H aromatic protons is found at 7.70-8.25 ppm. [b] Singlet. [c] An AB system with J_{AB} = 10 Hz, $\Delta\nu_{AB}$ = 13.7 Hz in $CDCl_3$ and 24 Hz in d_7-DMSO. [d] In the region of 5-H—7-H aromatic protons.

TABLE 3. PMR Spectra of Hydrazines I and X and Substituted Dimethylamine XVII

Compound	Solvent	ppm		
		multiplet	singlets	
		H-8	NH[a]	N—CH_3
I	$CDCl_3$	8,60	4,22 (2H)	3,37
I	$C_2H_2Br_4$	8,63	4,28 (2H)	3,39
I	$C_2H_2Br_4$ (+130°)	8,63	4,53 (2H)	3,41
I	d_6-DMSO	9,14	5,12 s (2H)	3,35
I	hexametapol	9,58	5,80 (2H)	—
I	hexametapol (+150°)	9,35	5,20 (2H)	—
X	$CDCl_3$	8,25	4,12 (2H)	3,22[b]
X	d_6-DMSO	8,65	4,73 (2H)	3,18[b]
XVII	CCl_4	c	—	3,18 (6H)
XVII	CH_2Cl_2	c	—	3,15 (6H)
XVII	CH_2Cl_2 (−100°)	c	—	2,99 (6H)
XVII	d_6-DMSO	c	—	3,15 (6H)
XVII	d_6-DMSO (+150°)	c	—	3,15 (6H)

[a] Broad singlet. [b] The protons of the CH_3CH_2O group of hydrazone X have chemical shifts at 1.50 t (3H, CH_3) and 4.60 q (2H, CH_2) in $CDCl_3$ and at 1.41 t (3H, CH_3) and 4.50 q (2H, CH_2) in d_6-DMSO. [c] In the region of 5-H—7-H aromatic protons.

dioxane at 25°C) and hydrazine I (5.38 D) confirms this conclusion* (compare with the μ_{exp} values of phthalazone hydrazones in [2]). The compressed conformation of the I and X molecules as compared with XVII may be due to intramolecular interaction of the p electrons of the ring 2-N atom with the hydrogen atoms of the NH_2 groups or to interaction of the p electrons of the NH_2 group with the 8-H proton.

An increase in the temperature of a solution of hydrazine I in tetrabromoethane to 150°C (at higher temperatures the compound undergoes chemical changes) leads only to a shift of the NH_2 signal to weak field (Table 3), i.e., the planar conformation of hydrazine I is extremely stable. The changes in the PMR spectrum are more substantial (Table 3) in the case of heating in hexametapol; this is evidently associated with a decrease in the intermolecular interaction with the solvent.

The lack of doubling of the signal in the PMR spectra of hydrazones II-V, VII, IX, and XI-XIII constitutes evidence for realization of one geometrical isomer (in analogy with [5-7, 15], the E isomer). The NCH_3 signal of the aldehyde hydrazones is found at weaker field than the same signal of ketone hydrazones, the position of which approaches the position of the NCH_3 signal in amine XVII. This fact and the difference in the relative position of the 8-H and 5-H—7-H multiplets in both groups of hydrazones is explained by rotation about the N—N bond in ketone hydrazones as compared with aldehyde hydrazones.

We were unable to obtain a clear answer regarding the three-dimensional structures of these compounds by comparison of the experimental (dioxane, 25°C: V 4.55 D, VI 4.14 D, and VIII 4.21 D) and calculated dipole moments or by Exner's graphical method [16].

The UV spectra of the aliphatic aldehyde hydrazones II, III, and XI contain an intense long-wave absorption band at 325-336 nm and a shoulder at 245-248 nm; with respect to their form, they are similar to the spectra of hydrazines I and X, although the maximum is shifted bathochromically. The transition to aromatic hydrazones V-VIII and XII is accompanied by a still greater bathochromic shift of the absorption maxima because of the realization of a common conjugation system. The shoulder at 245 nm for hydrazones II, III and IX and the band at 248-300 nm for V-VIII and XII are close to the absorption bands of the methylhydrazones of the corresponding aldehydes [6, 17], and this attests to the development of a quasiautonomous system and, consequently, to partial interaction of the electron systems of the hydrazone grouping and the phthalazine ring. This is also confirmed by the significant decrease in the intensity of the long-wave band in the spectra of hydrazones III and V as compared with the spectra of acetaldehyde and benzaldehyde N-methyl-N-phenylhydrazones [7, 8]. Conse-

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*For the phthalazine ring μ was estimated at 5.0 D on the basis of experimental data (in dioxane at 25°C) for phthalazine (5.04 D; 4.88 D in p-xylene [13]) and 1-chloro- (5.37 D) and 1,4-dichlorophthalazine (5.28 D). The values of the remaining bond moments are the usual ones [14].

TABLE 4. Ratios of the Integral Intensities* of the Short-Wave and Long-Wave Bands (J_{sw}/J_{lw}) in the UV spectra and Factor of Their Change in Acetonitrile and in the Crystalline State A = J_{sw}/J_{lw}(acetonitrile)/J_{sw}/J_{lw}(crystal)

Compound	J_{sw}/J_{lw}		A
	acetonitrile	crystal	
I	5,02	5,84	0,86
IV	4,28	2,46	1,74
V	2,85	3,66	0,80
XVII	5,36	6,70	0,80

*Determined with an accuracy of 15-20% by weighing the areas of the absorption bands.

quently, the ptahalazine ring in aldehyde hydrazones II, III, V-VIII, XI, and XII is also rotated partially about the N—C_{pht} bond, although to a lesser extent than in ketone hydrazones IV and IX, in which, as we stated above, rotation about the N—N bond also occurs. The disruption of the coplanarity of the IV and IX molecules should decrease as the temperature is lowered and should be minimal for the crystalline state; this is reflected in the UV and PMR spectra.

The PMR spectra of hydrazones III and V remain practically unchanged up to 170°C (Table 2). Heating hydrazones IX in tetrabromoethane to 150°C leads to a strong-field shift of the CCH_3 signals and to a low-field shift of the NCH_3 signals, while a decrease in the temperature of the solution in CH_2Cl_2 to —80°C leads to the opposite pattern. A strong-field shift of the NCH_3 signal is also observed in the spectrum of IV when the temperature is lowered, and it becomes a multiplet at —10°C. The nature of this effect is unclear, although the possibility that it is a consequence of the development of an interaction with the nitrogen atoms [18] is not excluded. Of the two CCH_3 signals, virtually only one undergoes a weak-field shift. In all cases the position of the signals of the protons of the phthalazine ring depends only slightly on the temperature. The temperature dependence of the CCH_3 signals in the spectra of III, IV, and IX confirms their E-isomer structure and makes it possible to assign the strong-field signal in the spectra of hydrazone IV to the CCH_3 group in the E position and the lower-field signal to the CCH_3 group in the Z position with respect to the amine nitrogen atom.

In addition to the long-wave bands, the UV spectra of hydrazines I and X, hydrazones II-V and IX, amine XVII, and phthalazine (260 and 214 nm) and 1-chlorophthalazine (266 and 217 nm) in acetonitrile contain an absorption band at ~215 nm, the position and high intensity of which remain practically constant for all of the compounds that have a phthalazine ring. This band is also retained in the UV spectra of crystalline samples of hydrazine I, hydrazones II-V and IX, and amine XVII. Since this band is virtually independent of the nature of the substituents in the phthalazine ring (at least in the 1 and 4 positions), it is logical to assume that it depends only slightly on the conformational changes in the crystals. From the ratio of the integral intensities of the short-wave (J_{sw}) and long-wave (J_{lw}) bands from the spectra of the solution and the crystals (Table 4) it may be assumed that appreciable changes in the conformations of I, V, and XVII do not occur on passing to the crystalline state, whereas the IV molecule takes on a conformation more favorable for conjugation; this is in agreement with data on the temperature dependence of the PMR spectra.

Thus, the dependence of the direction of the hydrolysis reaction and the UV and PMR spectra of N-methyl-N-(4-chloro-1-phthalazinyl)hydrazones on the nature of the ylidene fragment is apparently related to the difference in the angles of rotation about the N—N and C_{pht}—N bonds.

EXPERIMENTAL

See [2, 3] for the conditions for recording of the UV and IV (mineral oil suspensions) spectra and monitoring of the purity of the substances. The crystalline films for the UV spectra were obtained by applying a drop of a solution of the compound in dioxane or THF and

TABLE 5. Yields, Melting Points, and Results of Elementary Analysis of Hydrazones II-IX and XI-XVI

Compound	mp, °C	Crystallization solvent	Found, %				Empirical formula	Calc., %				Yield, %
			C	H	Cl	N		C	H	Cl	N	
II	148	CH_3OH	54,7	4,0	16,2	25,2	$C_{10}H_9ClN_4$	54,4	4,1	16,1	25,4	82
III	145,5—147,5	C_2H_5OH	56,6	4,6	15,0	24,1	$C_{11}H_{11}ClN_4$	56,3	4,7	15,1	23,9	90
IV	108—109	Hexane	58,3	5,3	14,3	22,6	$C_{12}H_{13}ClN_4$	58,0	5,2	14,3	22,5	90
V	174—175	CH_3OH	64,5	4,4	11,8	18,6	$C_{16}H_{13}ClN_4$	64,8	4,4	12,0	18,9	93
VI	235—237	DMF	51,4	3,3	9,6*	14,9	$C_{16}H_{12}BrClN_4$	51,1	3,2	9,5*	14,9	96
VII	201—202	C_2H_5OH	61,6	4,2	11,3	18,0	$C_{16}H_{13}ClN_4O$	61,4	4,2	11,4	17,9	88
VIII	304—305	DMF	56,3	3,8	10,5	20,8	$C_{16}H_{12}ClN_5O_2$	56,2	3,8	10,4	20,5	98
IX	148—149	Hexane	66,0	4,8	11,2	18,2	$C_{17}H_{15}ClN_4$	65,7	4,8	11,3	18,0	65
XI	94	50% C_2H_5OH	64,1	6,5	—	23,2	$C_{13}H_{16}N_4O$	63,9	6,6	—	23,0	80
XII	98—99	50% C_2H_5OH	70,9	5,8	—	18,1	$C_{18}H_{18}N_4O$	70,6	5,9	—	18,3	96
XIII	225—226,5	50% dioxane	69,8	5,1	—	20,3	$C_{16}H_{14}N_4O$	69,1	5,0	—	20,1	82
XIV	238—241	50% C_2H_5OH	53,4	3,8	22,6†	15,8	$C_{16}H_{13}BrN_4O$	53,8	3,6	22,4†	15,7	68
XV	165—167	CH_3OH	65,5	4,6	—	19,2	$C_{16}H_{14}N_4O_2$	65,3	4,8	—	19,1	65
XVI	298—300	DMF	59,3	4,2	—	21,8	$C_{16}H_{13}N_5O_3$	59,4	4,0	—	21,7	75

*Found, %: Br 21.3. Calculated, %: Br 21.3.

†Percentage of bromine.

removing the solvent. The PMR spectra were recorded* with a Varian T-60 spectrometer at 36°C, and the temperature dependences were recorded with a BS-467 spectrometer; the internal standard was hexamethyldisiloxane, and the chemical shifts are presented relative to tetramethylsilane. The dielectric permeabilities of dioxane solutions of I, V, VI, VIII, and XVII were measured by the zero-beat method at 1 MHz with an IDM-1 apparatus at 25°C, and the refractive indexes were measured with an IRF-23 refractometer.

Formaldehyde N-Methyl-N-(4-chloro-1-phthalazinyl)hydrazone (II). One to two drops of 98% H_2SO_4 were added to a solution of 2.08 g (10 mmole) of 1-methyl-1-(4-chloro-1-phthalazinyl)hydrazine (I) in 100 ml of absolute ethanol, after which excess gaseous CH_2O was bubbled through the mixture at 15-20°C for 30 min. Two-thirds of the volume of the solvent was then removed *in vacuo*, and the white needles of hydrazone II (Table 5) were removed by filtration.

Acetaldehyde N-Methyl-N-(4-chloro-1-phthalazinyl)hydrazone (III). One to two drops of 98% H_2SO_4 and two drops of freshly distilled acetaldehyde were added to a suspension of 2.08 g (10 mmole) of hydrazine I in 50 ml of ethanol, and the mixture was stirred at 20°C for 5 min and at 60-70°C for another 5 min. It was then cooled and worked up to give pale-green needles of III.

Acetone N-Methyl-N-(4-chloro-1-phthalazinyl)hydrazone (IV). One to two drops of 98% H_2SO_4 were added to a suspension of 2.08 g (10 mmole) of hydrazine I in 15 ml of acetone, and the mixture was stirred for 20 min. The acetone was removed, and the residue was recrystallized to give pale-green needles of IV with a $\nu_{C=N}$ band at 1648 cm^{-1} (w).

Benzladehyde (V), 4-Bromo- (VI), 4-Hydroxy- (VII), and 4-Nitrobenzaldehyde (VIII) and Acetophenone (IX) N-Methyl-N-(4-chloro-1-phthalazinyl)hydrazones. A 10-mmole sample of the appropriate aldehyde or ketone in 15-25 ml of alcohol was added to a solution of 10 mmole of hydrazine I in 60 ml of ethanol (methanol for V), and the mixture was refluxed for 30 min. It was then cooled and worked up to give small pale-yellow needles of V or VI, yellow-green needles of VII (ν_{OH} = 3137 cm^{-1}), yellow flakes of VIII, or lignt-green needles of IX.

1-Methyl-1-(4-ethoxy-1-phthalazinyl)hydrazine (X). A solution of 1.04 g (5 mmole) of hydrazine I and 0.3 g of KOH in 20 ml of ethanol was refluxed for 1 h, after which the alcohol was removed *in vacuo*, and the residue was treated with chloroform. The chloroform solution was separated from the sediment, the chloroform was removed *in vacuo*, and the residue was crystallized from alcohol to give 0.9 g (85%) of white needles of hydrazine IX with mp 123-124°C. IR spectrum: 3300, 3193, (ν_{NH_2}); 1634 cm^{-1} (δ_{NH_2}). Found: C 60.3; H 6.5; N 25.5 . $C_{11}H_{14}N_4O$. Calculated: C 60.6; H 6.4; N 25.7%.

Acetaldehyde (XI) and Benzaldehyde (XII) N-Methyl-N-(4-ethoxy-1-phthalazinyl)hydrazones. These compounds were obtained from hydrazones III and V (the latter was refluxed for 80 min) (see Tables 1, 2, and 5) by the method used to synthesize hydrazine X.

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Benzaldehyde (XIII), 4-Bromo- (XIV), 4-Hydroxy- (XV), and 4-Nitrobenzaldehyde (XVI) N-Methyl-N-(phthalaz-4-on-1-yl)hydrazones. A solution of 20 mmole of hydrazone V (or VI-VIII, respectively) in 30-50 ml of 90% AcOH was refluxed for 60-80 min, after which it was cooled and treated with 100 ml of water, and the precipitate was removed by filtration and washed with 5% sodium carbonate solution. This procedure gave pale-yellow needles of XIII, white flakes of XIV, light-green powdery XV, and fine yellow needles of XVI (Tables 1, 2, and 5). IR spectrum: XIII 3157 (NH) and 1662 (C=O); XIV 3166 (NH) and 1668 (C=O); XV 3200 (NH) and 1662 (C=O); XVI 3162 (NH) and 1664 cm^{-1} (C=O).

Saponification of Hydrazones II, III, and IX in 90% AcOH. A solution of 5 mmole of the appropriate hydrazone in 6 ml of 90% AcOH was refluxed for 45 min, after which it was cooled, and the precipitated white acicular crystals (in the case of hydrazones II and III) were removed by filtration and washed with water and 5% NaOH to give 4-chlorophthalazone, with mp 274°C (from alcohol), an additional amount of which was isolated from the mother liquor for an overall yield of 60-80%. In the case of hydrazone IX the solution was neutralized with saturated $NaHCO_3$ and extracted with $CHCl_3$. The chloroform layer was dried over Na_2SO_4, and the chloroform was removed *in vacuo*. Considerable amounts of acetophenone and traces of 4-chlorophthalazone were identified by thin-layer chromatography and UV spectroscopy.

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