SPECTRA AND STRUCTURE OF 1-AMINOPHTHALAZINES

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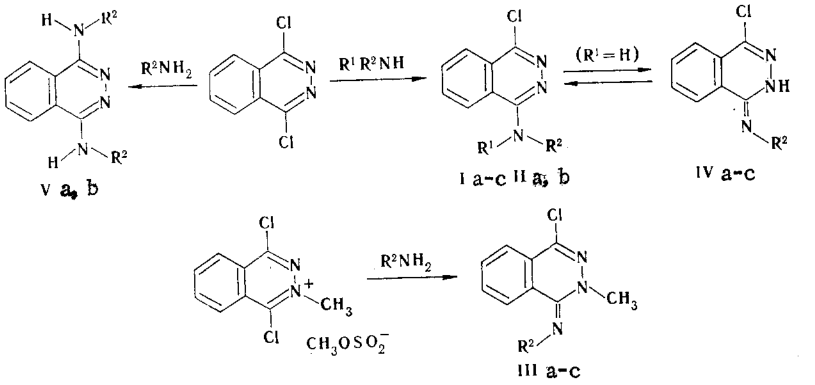
UDC 547.852.7.07:541.623:543.422

On the basis of VU and PMR spectroscopic data with the aid of the method of experimental structures and the method of dipole moments it was concluded that the products of the reaction of 1,4-dichlorophthalazine with ammonia, methylamine, and aniline in solutions and in the crystalline form exist primarily as Z conformers of the amino tautomeric form. Conversion to the tautomeric imino form was established for 1-phenylamino-4-chlorophthalazine in a number of solvents. The imines of 2-methyl-4-chlorophthalazine exist as the E isomers.

Amino—imino tautomerism in the amino heterocycle series has been studied quite extensively [1, 2]. This problem has not been discussed for 1-aminophthalazines, and the amino form has been assigned to them a priori [3-5]. The amino structure has been confirmed only for 1,4-diaminophthalazine on the basis of a comparison with the UV spectrum of 1,4-dimorpholinophthalazine [5]. Moreover, it is known that 1-hydroxyphthalazines [6-8] and unsubstituted [9] and aryl- [10] and aklyl(aryl)ylidenehydrazino derivatives of phthalazine [11-13] exist in solutions and in the crystalline form primarily in the tautomeric form with an exocyclic multiple bond. The questions of the three-dimensional structures of the imino (E, Z isomerism) and amino forms also have not been discussed.

In order to study these problems we used the reaction of ammonia, methylamine, and aniline with 1,4-dichlorophthalazine to obtain products of mono- (Ia-c) and disubstitution (Va, b) and the reaction with 1,4-dichloro-2-methylphthalazinium methylsulfate, viz., the imine and methyl- and phenylimine of 2-methyl-4-chlorophthalazone (IIIa-c) (fixed imino form III); we also used the reaction of 1,4-dichlorophthalazine with dimethylamine and methylaniline to obtain 1-dimethylamino- (IIa) and 1-(N-methyl-N-phenylamino)-4-chlorophthalazines (IIb) (fixed amino form II).



I $R^1=H$; I, III, IV a $R^2=H$, b $R^2=CH_3$, c $R^2=C_6H_5$; II $R^1=CH_3$; II, V a $R^2=CH_3$, b $R^2=C_6H_5$

The UV spectra of imines IIIa-c (Table 1 and Fig. 1) are similar to the UV spectra of the hydrazones of 4-substituted 2-methylphthalazones [9-13], but the long-wave band is shifted hypsochromically (Δλ 20-30 nm) as a result of shortening of the conjugation chain. The band at λ 260-275 nm contains a shoulder that is shifted hypsochromically 10 nm from its maximum (Figs. 1 and 2). The doublet character of this band is also peculiar to phthalazone hydrazones [9-13].

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TABLE 1. UV and IR Spectra of Amines Ia-c, IIa, b, and Va, b and Imines IIIa-c and Their Sulfates

Compound	ν, cm⁻¹ (mineral oil)		λ_{max}, nm (lg ε)	
	NH	C=N	acetonitrile	methanol
Ia	3313, 3205	1650	310 (3,75); 256 (3,48); 230 (3,85)[a]; 212 (4,56)	316 (3,88); 260 (3,63); 233 (4,00); 212 (4,68)
Ia · H_2SO_4	2400—3500	1652, 1684	294 (3,70); 267 (3,95); 244 (4,18)[a]; 220 (4,60)	295 (3,85); 265 (3,76); 213 (4,64)
Ib	3316	1584, 1614 w	325 (3,88); 260 (3,63); 235 (3,95)[a]; 210 (4,68)	324 (3,93); 270 (3,70); 233 (4,00); 212 (4,72)
Ib · H_2SO_4	2400—3300	1648	307 (3,78); 268 (4,14); 247 (4,14)[a]; 220 (4,62)	309 (3,83); 266 (4,00); 214 (4,54)
Ic	3100, 3200	1600, 1614 w	338 (4,06); 285 (3,84)[a]; 272 (3,90)[a]; 248 (4,20); 213 (4,72)	344 (4,02); 288 (3,81); 248 (4,16); 213 (4,72)
Ic · H_2SO_4	2500—3200	1570, 1600	312 (3,90); 277 (4,11); 248 (4,15)[a]; 221 (4,67)	319 (3,88); 277 (4,00); 248 (4,08)[a]; 218 (4,58)
IIa			322 (3,66) 262 (3,43)[a]; 214 (4,56)	330 (3,85); 260 (3,60)[a]; 217 (4,67)
IIa · H_2SO_4	2400—2800, 3400, 3530	1610, 1620	321 (3,82); 276 (3,93); 246 (3,88); 217 (4,52)	322 (3,88); 277 (3,95); 247 (4,00); 220 (4,54)
IIb		1596	333 (3,85); 285 (3,85)[a]; 253 (4,02); 215 (4,68)	340 (3,81); 285 (3,81); 253 (3,94); 215 (4,63)
IIb · H_2SO_4	2400—3100	1597, 1608	326 (3,95); 272 (4,02); 222 (4,63)	328 (3,92); 282 (3,97); 222 (4,54)
IIIa	3292	1607	330 (3,71); 273 (3,99); 235 (3,82)[a]; 210 (4,65)	322 (3,72); 274 (3,98); 242 (3,85)[a]; 211 (4,58)
IIIa · H_2SO_4	2400—3300	1606, 1692	288 (3,76); 264 (3,85); 243 (4,15); 222 (4,56)	293 (3,80); 267 (3,83); 245 (4,13); 212 (4,54)
IIIb	—	1604[a], 1622	335 (3,73); 271 (3,98); 228 (4,15); 212 (4,54)	325 (3,81); 273 (3,94); 228 (4,22)[a]; 212 (4,54)
IIIb · H_2SO_4	2500—3260	1615	307 (3,85); 272 (3,90); 246 (4,08)[a]; 222 (4,51)	305 (3,83); 272 (3,88); 247 (4,08)[a]; 222 (4,48)
IIIc	—	1622	340 (3,89); 275 (4,26); 242 (4,18)[a]; 212 (4,68)	338 (3,90); 275 (4,26); 238 (4,23); 211 (4,69)
IIIc · H_2SO_4	2400—2800, 3100—3200	1600	328 (3,88); 276 (4,00); 226 (4,51)	332 (3,88); 295 (3,88); 277 (3,94); 225 (4,52)
Va	3281[a], 3346	1609[a], 1623	348 (3,72); 222 (4,36)	344 (3,70); 222 (4,40); 204 (4,54)
Vb	3190, 3340	1610	370 (4,08); 267 (4,45); 210 (4,78)	372 (4,05); 266 (4,40); 210 (4,78)

[a] Shoulder.

The UV spectra of 1-dimethylamino-4-chlorophthalazine have long-wave (λ 320 nm) and short-wave (λ 215 nm) absorption bands. Thus, as one can see from Fig. 1 and Table 1, although the positions of the maxima of the absorption bands of amine IIa and imines IIIa-c are rather close, the morphology of the spectra indicates the different character of the chromophore systems in these molecules (π—n and π—π interactions). A comparison of the UV spectra of imine IIIa, amine IIa, and amination product Ia (Fig. 1 and Table 1) in various solvents and in the solid form* makes it possible to draw the rather debatable conclusion that Ia exists in amino form I under the investigated conditions.

A similar conclusion regarding the amino structure of amination product Ib was drawn upon comparison of its UV spectra with the spectra of methylimine IIIb and tertiary amine IIa (Table 1). In the case of amine Ib and diamine Va one observes in their PMR spectra spin-spin coupling of the protons of the H—N—CH_3 group (J = 4.6 Hz), which was proved by the use of proton double homonuclear resonance. In the case of suppression of the doublet at 3.05 for amine Ib and at 2.93 ppm for amine Va the broad quartet at 7.67 ppm for amine Ib and at 6.45 ppm for amine Va merges into a singlet signal, whereas, on the other hand, in the case of suppression of the broad quartets in the 7.67 and 6.45 ppm regions the doublet signals at, respectively, 3.05 and 2.93 ppm merge into a singlet signal. This is also weighty evidence in favor of the realization of amino form I for amines Ib and Va.

The UV spectra of IIb contain, in addition to long- and short-wave bands, a band with λ 253 nm (the chromophore system of the methylphenylamino group [14]) and weak absorption in the form of a shoulder at 285 nm. A comparison of the UV spectra of Ic with the spectra of amini IIb and imine IIIc (Table 1 and Fig. 2) makes it possible to conclude that primarily

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*For these and all remaining compounds the UV spectra were also recorded in DMSO, CCl_4, $CHCl_3$, dioxane, isooctane, mineral oil, and in crystalline films.

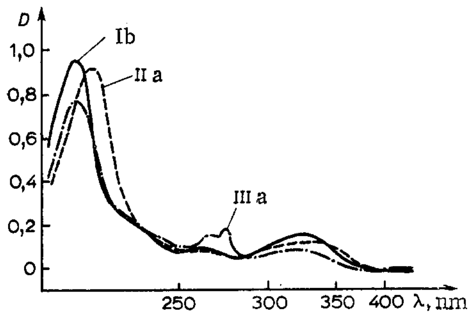


Fig. 1

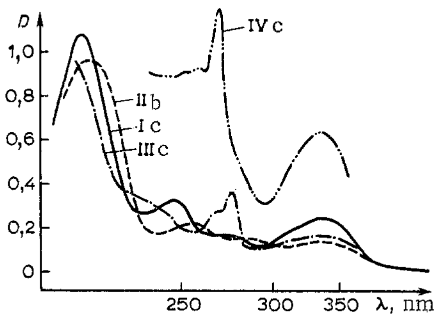


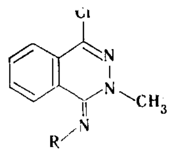
Fig. 2

Fig. 1. UV spectra of amines Ib and IIa and imine IIIa in methanol (c $2 \cdot 10^{-5}$ mole/liter).

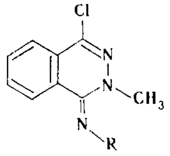
Fig. 2. UV spectra of amines Ic and IIb and phenylimine IIIc in acetonitrile (c $2 \cdot 10^{-5}$ mole/liter) and the Ic $\rightleftarrows$ IVc tautomeric mixture in isooctane (without determination of the concentration).

amino form I is realized for amination product Ic in polar, and low-polarity solvents and in solid form, whereas in nonpolar media one observes a tautomeric equilibrium that is shifted to favor imino form IVc in the case of its highest concentration in isooctane and CCl_4. The Ic $\rightleftarrows$ IVc tautomeric equilibrium is virtually independent of the temperature (15-70°C) in pure solvents and is shifted somewhat to favor imino form IVc in isooctane—isopropyl alcohol (20:1) as the temperature is raised.

Imines IIIa-c can exist in the Z or E geometrical form relative to the exocyclic C=N bond. It has been previously shown [9-13] that 2-methylphthalazone hydrazones (III, $R^2 = NR^3R^4$) exist in the E form in all cases. The 2-CH_3 chemical shifts of imine IIIa and phenylimine IIIc in the PMR spectra are virtually identical. Hence it follows that the spatial environment of the N—CH_3 group remains unchanged. The 8-H signal of imine IIIc is shifted to strong field as compared with the analogous signal of imine IIIa and is found in the region of the aromatic 5-, 6-, and 7-H protons (Table 2). It is known that the phenyl ring in phenylimines of various heterocyclic ketones is turned with respect to the C_{ar}—N bond (~60°) [15]. The strong-field shift of the 8-N proton can be explained by realization in phenylimine IIIc of the E form and by rotation of the phenyl ring about the C—N bond. In this case the 8-H proton falls under the influence of the anisotropy of the phenyl ring, which, as is well known [16], leads to a shift of its signal to strong field. This conclusion is in agreement with the UV sepctral data and the method of dipole moments. The position and intensity of the band of phenylimine IIIc as compared with the spectra of imines IIIa, b (Table 1) constitute evidence for the absence of interaction of the π system of the phenyl ring with the π system of the phthalazineimine fragment.



E form



Z form

A comparison of μ_{exp} and μ_{calc} for the E and Z forms of phenylimine IIIc confirms the realization of the E form for it (Table 3).

Introduction of a methyl group at the imine nitrogen atom on passing from imine IIIa to methylimine IIIb does not lead to an appreciable change in the 2-CH_3 and 8-H δ values, and it is difficult to give preference to the E or Z form for them from the PMR spectral data. However, from a comparative analysis of μ_{exp} and μ_{calc} for imines IIIa,b (Table 3) we concluded that the E form is also preferable for them.

In crystals of amine IIa the dimetnylamino group has a trigonal-pyramidal conformation (the sum of the angles at the nitrogen atom is 346.9°, and $C_{\pi}^{N} = 0.327$) and is rotated 33° about the C—N bond [17]. The data from UV and PMR spectroscopy are in agreement with these results [18] and constitute evidence for the low degree of conjugation of the unshared elec-

TABLE 2. PMR Spectra of Amines Ia-c, IIa, b, and Va, b and Imines IIIa-c

Compound	Solvent	δ, ppm					
		5-, 6- and 7-H	8-H[b]	H_{arom}[b]	2-R[c]	N—R	other protons
Ia	A	7,98	8,32	—	—	—	7,28 br. s (2H, NH_2)
Ia	B	7,80	8,25	—	—	—	6,38 br. s (2H, NH_2)
Ib	A	7,93	8,20	—	—	3,05 d (CH_3, J=4,6 Hz)	7,67 br. q (1H, NH, J=4,6 Hz)
Ic	A	7,95 (5H+2H arom)	8,62	7,28 (3H)	—	9,22	—
IIb	A	8,32—6,95 (9H)			—	3,58 (CH_3)	—
IIIa	C	7,55	7,88	—	3,59	—	5,32 br.s (1H, NH)
IIIa	A	7,70	8,27	—	3,57	—	3,33 br.s (1H, NH)
IIIb	A	7,68	8,17	—	3,52	—	3,42 s (3H, NCH_3)
IIIb	C	7,52	8,05	—	3,52	—	3,46 s (3H, NCH_3)
IIIc	A	7,88—6,71 (9H)			3,58	—	—
IIIc	C	7,67—6,20 (9H)			3,57	—	—
Va	A	7,68 (2H); 7,98 (2H)		—	—	2,93 d (6H, J=4,6 Hz)	6,45 br.q.(2H, J=4,6 Hz)
Vb	A	8,08 (2H); 8,98 (2H)		7,43 (10H)	—	10,55	—

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[a] Solvents: A is d_6-DMSO, B is dioxane, and C is $CDCl_3$. [b] Multiplet. [c] Singlet.

TABLE 3. Experimental (dioxane, 25°C) and Calculated (by the vector activity method) Values of the Dipole Moments for Amines Ia-c, IIa, b, and Va, b and Imines IIIa-c

Compound	μ_{exp}, D	μ_{calc}, D			
		amino form		imino form	
		E	Z	E	Z
Ia	6,01±0,01	5,35		1,76	0,53
Ib	6,34±0,04	4,39	5,82	2,34	0,95
Ic	5,14±0,01	4,82	5,33	2,79	0,75
IIa	5,51±0,01	—		—	
IIb	5,15±0,02	4,76	5,44	—	
IIIa	2,67±0,03	—		3,55	0,95
IIIb	3,00±0,01	—		2,57	1,68
IIIc	2,60±0,01	—		3,41	1,22
Va	5,10±0,04	6,21 (Z, Z); 5,00 (Z, E); 3,89 (E, E)		—[a]	
Vb	5,15±0,01	5,52 (Z, Z); 5,00 (Z, E); 4,48 (E, E)		—[b]	

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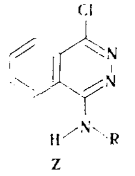
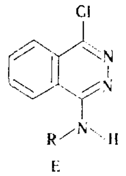
[a] Amino—imino form; 2.29 (E, E), 1.54 (E, Z), 2.29 (Z, Z), and 3.30 (Z, E); diimino form: 0.87 (E, E), 0.52 (E, Z), 1.73 (Z, Z). [b] Amino—imino form: 2.85 (E, E), 1.54 (E, Z), 1.73 (Z, Z), and 3.30 (Z, E).

tron pair of the dimethylamino group with the π system of the heteroring and the low barrier to rotation about the C—N bond [18].



Z



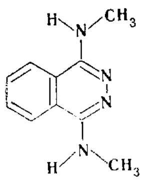
E

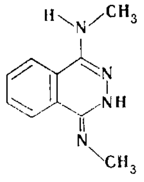
Replacement of one methyl group in IIa by a hydrogen atom on passing to amine Ib leads to a significant increase in the intensity of the long-wave and medium-wave bands in the UV spectra (Δε 3000 and 1600), i.e., the methylamino group has a more planar conformation. The presence of a weak-field 8-H signal (Table 2) indicates the absence, under ordinary conditions, of free rotation about the C—N bond. From a comparison of μ_{exp} and the calculated values of the dipole moments by the vector additivity method for the two conformations of amine Ib (Table 3) we concluded that the Z form, which is preferable to the E conformation according to the steric parameters, is realized. The increase in the intensities of the long-wave ($\Delta\varepsilon$ 4000) and medium-wave ($\Delta\varepsilon$ 2600) bands in the UV spectra of passing from amine Ib to phenylamine Ic (the effect of participation of the π system of the phenyl ring in interaction with the π system of the phthalazine ring) and the presence in its PMR spectra of a weak-field 8-H signal (Table 2) also indicate the high degree of conjugation of the electron systems of the heteroring and the aniline fragment.

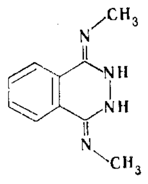
An examination of the μ_{exp} and μ_{calc} values of the E and Z conformations of amine Ic did not make it possible to choose between one or another conformation. However, in the case of the E form, by virtue of steric hindrance (compare with phenylamine IIIc), the phenyl ring would be turned about the C-N bond, and in this case the 8-H proton would undergo a strong-field shift. On the basis of this, preference was given to the Z conformer for phenylamine Ic.

1,4-Bis(methylamino)- (Va) and 1,4-bis(phenylamino) phthalazines (Vb) can exist in one of three tautomeric forms (V, VI, or VII) or can even exist in the form of a tautomeric mixture of two or three forms.

The signal of the 6-, 7-, and 8-H protons in the PMR spectra of amines Va, b (d_6-DMSO*) is a symmetrical multiplet (Table 2). This as well as the UV spectral data, and a comparison of the μ_{exp} and μ_{calc} values for the possible conformers of diamino form V, amino imino form VI, and diimino form VII (Table 3) indicate unambiguously that primarily diamino form V is realized for the investigated Va, b in solutions in DMSO and dioxane; of the three possible conformers, preference is given to the Z, Z form.

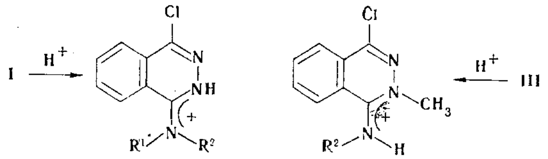

V


VI


VII

Amines Ia-c and IIa, b and imines IIIa-c are quite strong multicenter bases and readily form stable salts (for example, sulfates), from which they are isolated unchanged by the action of alkalis.

A comparison of the UV spectra of the cationic forms of amines Ia-c and IIa, b and imines IIIa-c shows that they have similar spectra both with respect to form and with respect to the positions of the absorption bands (Table 1 and Fig. 3). This indicates that they have similar electron structures. Hence it may be concluded that aminophthalazines Ia-c and IIa, b are protonated at the $N_{(2)}$ atom of the phthalazine ring, whereas phthalazone imines IIIa-c are protonated at the exocyclic imine nitrogen atom. A similar conclusion was also previously drawn for hydrazino derivatives of phthalazines [19].



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*The insufficient solubilities of Va, b made it impossible to use less polar solvents.

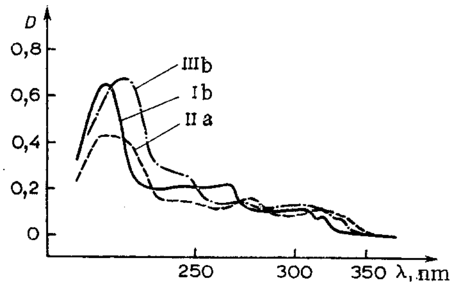

Fig. 3. UV spectra of the cationic forms of amines Ib and IIa and imine IIIb in acetonitrile (c $2 \cdot 10^{-5}$ mole/liter).

One's attention should be directed to the fact that in the case of protonation of amines Ia-c and IIa,b the intensity of the medium band (λ 260-280 nm, ε 2000-7000) in the UV spectra increases significantly (Δε 6000-9000); its doublet character, which is characteristic for the UV spectra of phthalazone derivatives [9-13], is manifested distinctly. This may constitute evidence for an increase in the degree of conjugation of the amino group with the phthalazine ring in salts of aminophthalazines that are protonated at the $N_{(2)}$ atom.

In a study of the UV spectra of imine IIIa in methanol* we observed an interesting peculiarity. The spectrum of the substance depends on its concentration in solution. This dependence bears the same character as the dependence on the pH of the medium. Methanol is possibly capable of protonating imine IIIa and of forming a very strong intermolecular hydrogen bond at the imino nitrogen atom or of adding to the C=N bond to form a geminal amino alcohol. This effect is manifested very slightly in ethanol and propanol.

EXPERIMENTAL

See [12, 18] for details concerning the conditions of the spectral measurements, monitoring of the purity, and other physicochemical measurements. The acetonitrile, chloroform, and CCl_4 were distilled twice over P_2O_5 in an argon atmosphere, and the DMSO was distilled over NaOH; the purification of the dioxane and the removal of oxygen from the solvents were carried out by the method in [20] with subsequent rectification with a column (17 theoretical plates).

1-Amino- and 1-Methylamino-4-chlorophthalazine (Ia,b, Table 4). An aqueous solution of ammonia or methylamine (150-200 ml) was added dropwise in the course of 2 h to a hot solution of 5 g (25 mmole) of 1,4-dichlorophthalazine in 40-60 ml of DMF in such a way that the reaction mixture boiled uniformly. Water (150-200 ml) was then added, and the mixture was allowed to stand in a refrigerator overnight. The precipitate was removed by filtration, washed repeatedly with water, and dried. A 5-10% solution of H_2SO_4 in dioxane was added dropwise with vigorous stirring to a saturated solution of this product in a mixture of 300 ml dry dioxane and 50 ml of DMF until a copious precipitate formed. This precipitate was removed by filtration, washed successively with dioxane and diethyl ether, and dried. The sulfates of amines Ia,b were obtained correspondingly. Treatment of saturated aqueous solutions of the latter with 5-10% KOH solution converted them to the bases.

1-Phenylamino-4-chlorophthalazine (Ic) and 1,4-Bis(phenylamino)phthalazine (Vb). These compounds were obtained by the method in [4]. The sulfate of amine Ic was obtained by the addition of a 5% solution of H_2SO_4 in diglyme to a saturated solution of the amine in diglyme with the subsequent addition of a fivefold excess of dry diethyl ether.

1-Dimethylamino-4-chlorophthalazine (IIa). This compound was obtained by the method in [9]. Its sulfate was obtained in a solution of dry diethyl ether.

1-(N-Methyl-N-phenylamino)-4-chlorophthalazine (IIb). A 3.3-g sample of N-methylaniline was added dropwise to a hot mixture of 6 g (30 mmole) of 1,4-dichlorophthalazine in 60-70 ml of ethanol, and the mixture was refluxed for 35 min. It was then cooled and treated with 500 ml of 1% KOH solution and allowed to stand for 3-5 h. The precipitated amine IIb was removed by filtration, washed with water, and dried. The sulfate of amine IIb was obtained by the method used to prepare the salt of amine IIa.

Imine (IIIa), Methylimine (IIIb), and Phenylimine (IIIc) 2-Methyl-4-chlorophthalazone. A freshly prepared solution of 1,4-dichloro-2-methylphthalazinium methylsulfate [9] (from 5 g of 1,4-dichlorophthalazine) was added dropwise with vigorous stirring in an argon atmosphere to dry liquefied, respectively, ammonia (50 ml) or methylamine (25 ml) at −20 to −40°C or to aniline (8 ml) at room temperature, after which stirring was continued for 30 min, and the excess gaseous amines were removed by raising the temperature to room temperature. The mass was treated with 20-30 ml of 10% KOH solution, and the mixture was extracted with chloroform. The organic layer was separated and dried with Na_2SO_4, and the solvent was removed to dryness in the vacuum created by a water aspirator and then at 50-60°C for 5-7 h in the vacuum created by an oil pump. A 5% solution of H_2SO_4 in ether was added dropwise with stirring to

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*In order to exclude possible traces of ions (distillation over sodium or magnesium methoxide) we used another method to purify the methanol. Traces of carbonyl compounds were removed by means of 2,4-dinitrophenylhydrazine, after which the methanol was distilled twice with a fractionating column in an argon atmosphere, maintained over 3 Å molecular sieves for 15-20 days, and once again distilled with a rectification column (17 theoretical plates).

TABLE 4. Characteristics of Ia–c, IIa,b, and IIIa–c and Their Sulfates

Compound	mp, °C	Found, %					Empirical formula	Calc., %					Yield,[a] %
		C	H	Cl	N	S		C	H	Cl	N	S	
Ia	221—223[b, c]	53,4	3,2	19,8	23,5	—	$C_8H_6ClN_3$	53,5	3,3	19,8	23,4	—	40
Ia · H_2SO_4	222[d]	35,4	2,9	12,7	15,0	11,4	$C_8H_6ClN_3 \cdot H_2SO_4$	35,3	2,9	12,8	15,1	11,5	54
Ib	223—224[e]	55,8	4,1	18,3	21,4	—	$C_9H_8ClN_3$	55,8	4,1	18,4	21,7	—	60
Ib · H_2SO_4	296—298,5[f]	37,0	3,5	12,3	14,5	11,0	$C_9H_8ClN_3 \cdot H_2SO_4$	37,1	3,4	12,2	14,4	10,8	65
Ic	205—206[g, h]	66,0	3,9	14,2	16,5	—	$C_{14}H_{10}ClN_3$	65,8	3,9	13,9	16,5	—	80
Ic · H_2SO_4	204—206[i]	47,8	3,4	10,2	11,8	9,2	$C_{14}H_{10}ClN_3 \cdot H_2SO_4$	47,5	3,4	10,0	11,9	9,1	91[j]
IIa · H_2SO_4	144—147[k]	39,0	4,0	11,6	13,6	10,5	$C_{10}H_{10}ClN_3 \cdot H_2SO_4$	39,3	3,9	11,6	13,7	10,5	80[j]
IIb	136,5—137,5[c]	66,5	4,5	13,3	15,6	—	$C_{15}H_{12}ClN_3$	66,8	4,5	13,2	15,6	—	67
IIb · H_2SO_4	203—205[c]	49,1	3,7	9,9	11,4	8,6	$C_{15}H_{12}ClN_3 \cdot H_2SO_4$	49,0	3,8	9,7	11,4	8,7	75[j]
IIIa	116—119[c]	55,6	4,1	18,5	21,7	—	$C_9H_8ClN_3$	55,8	4,1	18,4	21,7	—	40
IIIa · H_2SO_4	291[c]	37,0	3,4	12,3	14,5	10,9	$C_9H_8ClN_3 \cdot H_2SO_4$	37,1	3,4	12,2	14,4	10,8	50
IIIb	80—81[c]	57,7	4,8	17,0	20,3	—	$C_{10}H_{10}ClN_3$	57,8	4,8	17,1	20,2	—	38
IIIb · H_2SO_4	230—233[c]	39,2	3,9	11,8	13,8	10,5	$C_{10}H_{10}ClN_3 \cdot H_2SO_4$	39,3	3,9	11,6	13,7	10,5	45
IIIb · CF_3COOH	137—140[l]	45,0	3,6	11,1	13,1	—	$C_{10}H_{10}ClN_3 \cdot CF_3COOH$	44,8	3,4	11,0	13,1	—	95[j]
IIIc	113—114[m]	66,6	4,5	13,3	15,6	—	$C_{15}H_{12}ClN_3$	66,8	4,5	13,2	15,6		20
IIIc · H_2SO_4	207—212[c]	49,1	3,7	9,8	11,5	8,8	$C_{15}H_{12}ClN_3 \cdot H_2SO_4$	49,0	3,8	9,7	11,4	8,7	34
Va	215—216[h]	63,6	6,5	—	29,5	—	$C_{10}H_{12}N_4$	63,8	6,4	—	29,8	—	19
Vb	230—231[h, n]	76,8	5,0	—	17,8	—	$C_{20}H_{16}N_4$	76,9	5,1	—	17,9	—	71

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[a] Except for the specially stipulated cases, the yields are based on the 1,4-dichlorophthalazine. [b] Literature data: mp 202°C [3], 201-202°C [21], and 221-222°C [22]. [c] From ethanol. [d] From DMSO. [e] From methanol. [f] From DMF. [g] According to [4], this compound has mp 200°C. [h] From acetone. [i] From ethanol–ether (5:1). [j] Based on the base. [k] From ethanol–ether (3:1). [l] From acetone–ether. [m] From petroleum ether. [n] According to [4], this compound has mp 223°C.

a saturated solution of the resulting residue in anhydrous diethyl ether until copious precipitates of the sulfates of imines IIIa-c formed.

The resulting salts were converted to bases IIIa-c in aqueous solutions.

1,4-Bis(methylamino)phthalazine (Va). Dry methylamine was bubbled for 30-45 min at 170-180°C in an argon atmosphere into a solution of 4 g (20 mmole) of 1,4-dichlorophthalazine in 5 ml of hexametapol, after which the mixture was cooled and treated with 100 ml of water, and the aqueous mixture was allowed to stand overnight in a refrigerator. Two crystallizations of the precipitate from acetone gave yellow prisms of amine Va.

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