Protonation of 1,4-Bis(alkylamino)benzo[*g*]phthalazine. Crystal Structure of Di-{1,4-bis-(3-methoxypropylamino)-3(2)*H*-benzo[*g*]phthalazinium} Tetrachlorocobaltate Monohydrate

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Reaction of the monohydrochloride of 1,4-bis-(3-methoxypropylamino)benzo[*g*]phthalazine (**3'a**) with cobalt(II) dichloride in neutral medium afforded a new salt of di-{1,4-bis-(3-methoxypropylamino)-3(2)*H*-benzo[*g*]phthalazinium}$^{2+}$ $CoCl_4^{2-}$ H_2O (**4**), the structure of which has been determined by *X*-ray methods. It crystallizes in the space group $P\bar{1}$ with a = 15.0008(10), b = 13.0621(8), c = 12.1465(8) Å, α = 100.515(6), β = 107.268(4), and γ = 92.687(7), Z = 2. The structure was solved by Patterson methods and refined by least-squares to R 0.074. The structure consists of dimeric (3-methoxypropylamino)-3(2)*H*-benzo[*g*]phthalazinium cations held one with each other and both with the anions and the water molecule by a network of hydrogen bonds and piling up along the *a* axis in a group of four molecules. The u.v., i.r., ^1H, and ^{13}C n.m.r. spectroscopic data of the parent monohydrochloride (**3'a**) which are now reported for the first time, compared with those corresponding to the free base (**3a**), are also in agreement with the protonation of the heteroaromatic ring of 1,4-bis(alkylamino)benzo[*g*]phthalazine.

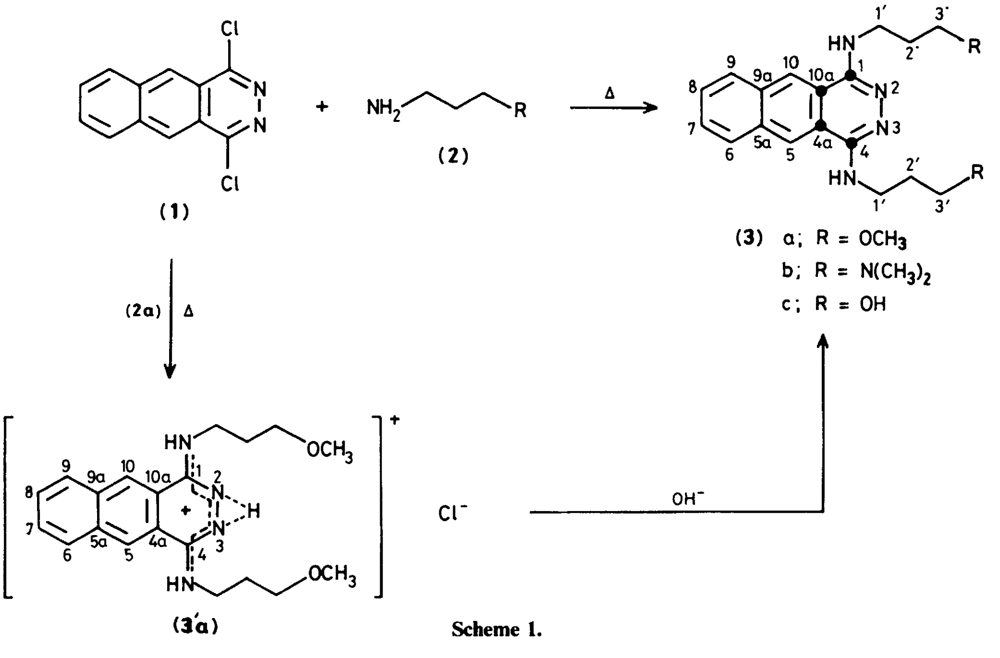
It is known that many kinds of organic cations are more biologically active than their neutral species. Thus, antibacterial action (*e.g.* aminoacridines) is linked with ionization and many effective biocides selective against protozoas are the salts of strong organic bases.[1] Recently, we have described the synthesis of 1,4-bis(alkylamino)benzo[*g*]phthalazines[2] whose intercalation with DNA is now being investigated.[3] We are also interested in the protonation of these new types of aromatic systems containing two of the four conjugated nitrogen atoms as part of the ring with the other two in an exocyclic amino group.

Some years ago it was reported that 1,4-diaminophthalazine forms a hydrochloride salt.[4] In a similar way, we had observed that nucleophilic substitution of 1,4-dichlorobenzo[*g*]phthalazine (**1**) with 3-methoxypropylamine (**2a**) afforded the monohydrochloride of 1,4-bis-(3-methoxypropylamino)benzo[*g*]phthalazine (**3'a**) which, in a basic medium, gave the corresponding free base (**3a**) (See Scheme 1).

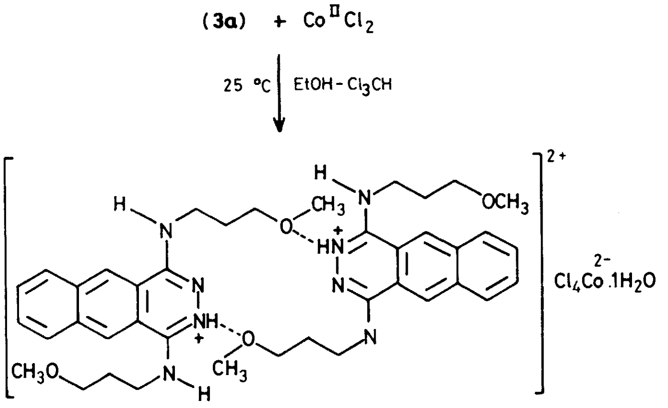
We now report the crystalline structure of a new tetrachlorocobaltate salt (**4**) obtained from the monohydrochloride (**3'a**) by treatment with cobalt(II) dichloride in neutral medium (see Scheme 2). We also report here the u.v., i.r., ^1H, and ^{13}C n.m.r. spectroscopic parameters of the parent hydrochloride (**3'a**).

Experimental

M.p.s are uncorrected. I.r. and u.v. spectra were recorded on 257 and 550 Perkin-Elmer spectrometers, respectively. ^1H and ^{13}C



Scheme 1.



(4)

Scheme 2.

n.m.r. spectra were recorded on Varian XL-300 and Bruker WP-spectrometers, respectively, using Me_4Si as internal standard. Analytical t.l.c. was performed on aluminium sheets coated with a 0.2 mm layer of silica gel 60 F_{254} (Merck). Flash chromatography was performed on a column using silica gel 60 (Merck), with u.v. light (254 nm), and/or an iodine chamber. Compound (**3′a**) was obtained following the procedure reported for (**3a**).[2]

1,4-*Bis-*(3-*propylamino*)*benzo*[g]*phthalazine Monohydrochloride* (**3′a**).—A mixture of 1,4-dichlorobenzo[*g*]phthalazine (13 mmol) and 3-methoxypropylamine (25 ml) was heated in an autoclave at 130 °C for 12 h. After cooling to room temperature, the excess of 3-methoxypropylamine was evaporated to dryness under vacuum. The residue was dissolved in ethanol (5 ml) and purified by flash chromatography using benzene–ethyl acetate–ethanol (v/v), (2:1:0.06) as eluent. The appropriate fractions monitored by t.l.c. were combined. The removal of solvents from the fraction with R_f 0.12 afforded a yellow solid (1.7 g, 38%) (**3′a**), m.p. 186–187 °C (Found: C, 61.1; H, 6.7; N, 14.35; Cl, 9.1. $C_{20}H_{26}N_4O_2\cdot 1HCl$ requires C, 61.45; H, 7.0; N, 14.3; Cl, 9.1%).

Di-{1,4-*bis-*(3-*methoxypropylamino*)-3(2)H-*benzo*[g]*phthalazinium*} *Tetrachlorocobaltate Monohydrate* (**4**).—A solution of the metal salt $CoCl_2\cdot 6H_2O$ (0.38 mmol) in EtOH (5 ml) was refluxed for 5 min with triethyl orthoformate (0.25 ml) as dehydration agent,[5] and cooled to room temperature. Then, (**3′a**) (0.38 mmol) dissolved in chloroform (7 ml) was added. With vigorous stirring the blue cobalt(II) dichloride solution changed to green. By addition of n-hexane (*ca.* 5 ml) a precipitate was formed, filtered off, and crystallized in an anhydrous mixture of acetonitrile–diglyme (v/v 1:1). No precautions were taken to exclude the atmospheric oxygen. After two weeks at room temperature dark green prismatic crystals of (**4**) appeared. Since these crystals are very unstable out the solvent they were carefully separated and dried under nitrogen, m.p. 190—193 °C [Found: C, 51.8; H, 6.0; N, 12.0. $(C_{40}H_{54}N_8O_4)^{2+}Cl_4Co^{2-}\cdot 1H_2O$ requires C, 51.8; H, 6.1; N, 12.05%].

Table 1. Final atomic co-ordinates

Atom	*x*	*y*	*z*
Co(1)	0.215 4(1)	−0.071 3(1)	0.320 4(1)
Cl(1)	0.110 0(2)	−0.171 8(2)	0.156 7(2)
Cl(2)	0.232 8(2)	0.098 9(2)	0.301 7(2)
Cl(3)	0.360 1(2)	−0.129 8(3)	0.357 1(4)
Cl(4)	0.166 7(2)	−0.083 0(3)	0.474 9(2)
C(1)	0.123 5(6)	0.501 9(6)	0.021 6(7)
N(2)	0.129 4(5)	0.432 5(5)	−0.066 0(6)
N(3)	0.140 7(5)	0.330 7(5)	−0.046 2(6)
C(4)	0.145 8(6)	0.297 8(6)	0.051 2(7)
C(5)	0.139 9(5)	0.374 3(6)	0.151 5(7)
C(6)	0.143 6(6)	0.348 2(6)	0.257 2(8)
C(6A)	0.136 9(5)	0.422 6(6)	0.351 5(7)
C(7)	0.139 0(6)	0.396 0(7)	0.461 1(8)
C(8)	0.130 2(7)	0.471 2(9)	0.550 8(8)
C(9)	0.121 0(7)	0.574 2(9)	0.536 4(8)
C(10)	0.119 0(7)	0.603 8(7)	0.435 0(9)
C(10A)	0.126 4(5)	0.526 9(7)	0.337 4(7)
C(11)	0.122 6(6)	0.554 1(6)	0.230 1(8)
C(12)	0.128 6(5)	0.478 6(6)	0.136 3(7)
N(13)	0.111 1(5)	0.599 6(5)	0.003 8(6)
C(14)	0.106 3(7)	0.628 9(7)	−0.107 8(8)
C(15)	0.198 4(7)	0.643 6(8)	−0.125 2(8)
C(16)	0.265 9(7)	0.728 1(10)	−0.033 2(9)
O(17)	0.351 7(5)	0.735 5(6)	−0.057 4(6)
C(18)	0.429 4(9)	0.773 4(14)	0.030 5(12)
N(19)	0.153 8(5)	0.197 5(5)	0.054 7(6)
C(20)	0.139 1(7)	0.117 3(7)	−0.053 4(8)
C(21)	0.120 6(8)	0.010 2(7)	−0.027 1(9)
C(22)	0.057 3(9)	−0.065 3(9)	−0.138 9(12)
O(23)	0.108 7(6)	−0.084 6(7)	−0.215 3(8)
C(24)	0.043 9(11)	−0.143 4(11)	−0.325 4(11)
C(1′)	0.369 5(6)	0.462 1(7)	−0.344 3(8)
N(2′)	0.363 8(5)	0.534 7(6)	−0.259 1(7)
N(3′)	0.358 9(5)	0.634 5(6)	−0.278 5(6)
C(4′)	0.359 5(6)	0.666 0(7)	−0.377 2(8)
C(5′)	0.366 9(5)	0.587 3(7)	−0.474 6(7)
C(6′)	0.367 6(6)	0.613 1(7)	−0.580 3(8)
C(6A′)	0.376 2(6)	0.534 6(8)	−0.671 3(8)
C(7′)	0.376 9(8)	0.559 7(9)	−0.780 0(10)
C(8′)	0.384 6(8)	0.481 4(12)	−0.869 0(9)
C(9′)	0.391 9(8)	0.379 6(12)	−0.850 0(11)
C(10′)	0.391 0(7)	0.352 4(9)	−0.749 0(11)
C(10A′)	0.383 5(6)	0.431 2(7)	−0.654 0(9)
C(11′)	0.381 5(6)	0.407 4(7)	−0.546 3(9)
C(12′)	0.372 8(6)	0.484 0(6)	−0.457 1(7)
N(13′)	0.367 0(6)	0.362 9(6)	−0.327 5(7)
C(14′)	0.351 7(12)	0.340 5(9)	−0.214 1(9)
C(15′)	0.325 9(9)	0.231 8(10)	−0.223 5(11)
C(16′)	0.231 9(8)	0.193 9(9)	−0.304 2(9)
O(17′)	0.158 0(5)	0.231 2(5)	−0.266 2(5)
C(18′)	0.070 6(8)	0.185 5(12)	−0.346 4(10)
N(19′)	0.351 8(5)	0.765 5(6)	−0.385 0(6)
C(20′)	0.342 8(8)	0.850 5(7)	−0.291 7(9)
C(21′)	0.397 9(11)	0.948 4(8)	−0.288 7(10)
C(22′)	0.499 5(12)	0.944 0(11)	−0.249 9(11)
O(23′)	0.525 5(7)	0.923 2(11)	−0.135 2(9)
C(24′)	0.615 1(14)	0.934 8(17)	−0.075 0(18)
O(W)	0.420 5(6)	0.172 4(6)	−0.463 5(8)

Crystal Structure Determination of (**4**).—*Crystal data.* $[C_{40}H_{54}N_8O_4]^{2+}[CoCl_4]^{2-}\cdot H_2O$, triclinic, $M = 929.68$, $a = 15.0008(10)$, $b = 13.0621(8)$, $c = 12.1465(8)$ Å, $\alpha = 100.515(6)$, $\beta = 107.268(4)$, $\gamma = 92.687(7)°$, $U = 2221.6(3)$ Å^3, space group $P\bar{1}$. The compound incorporates two molecules of solvent per unit cell. A green prism-like sample of 0.50 × 0.40 × 0.10 mm inside a capillary was used for the analysis on a Philips PW 1100 diffractometer, with Cu-K_α radiation, graphite monochromator, ω–2θ scans, bisecting geometry, 1 × 1° detector apertures, 1.5° scan width and using 0.5 min per reflexion. The stability was checked every 90 min, with an observed decay of 17% in 2.5 days of recording. The cell parameters were obtained from a least-squares fit of the angular position of 88 reflexions with $\theta \leqslant 45°$.

The solution was given from the Patterson function, completed through the Mithril system[6] and refined by least-squares methods[7,8] on F_{obs}. All hydrogen atoms, except those of

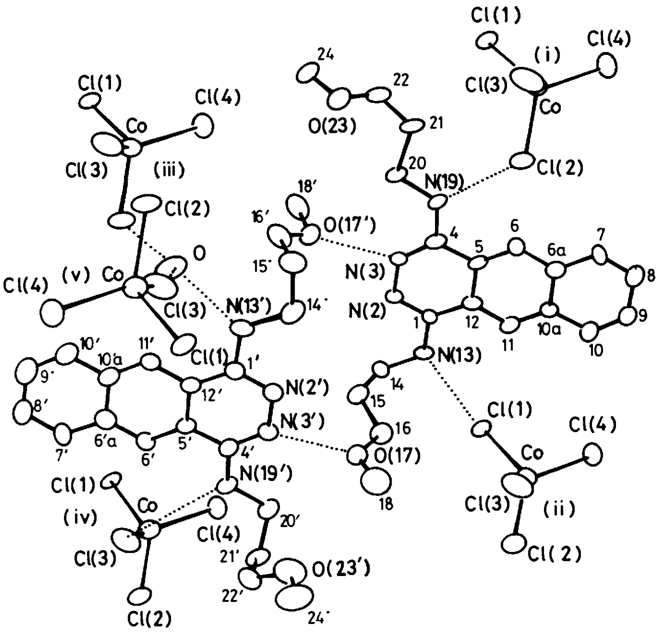


Figure 1. An ORTEP[10] view of the compound as seen along the *a* axis and showing the hydrogen-bonding network. Roman numbering indicates the symmetry operations described in Table 3

the water molecule, were unambigously obtained in a difference synthesis and included isotropically in the final cycles of refinement. Of the 6 610 independent data, up to 60° in θ, 3 502 were considered observed [$I > 4\sigma(I)$]. Refinement converged at $R = 0.074$ and $R_w = 0.083$. The weight were choosen to give no trends in $<w\Delta F>$ *versus* $<F_{obs}>$ and $<\sin\theta/\lambda>$, by the use of functions of $w = K/[f(F_{obs})]\cdot[g(\sin\theta/\lambda)]$ type, K being a scale factor to ensure that $<w\Delta^2F>$ *ca.* 1. The final shift error was 0.10 for the 743 variables, with a maximum thermal factor of 0.22(1) Å^2 for U_{22}[C(23')]. The highest final residual electron density was 0.49 e Å^{-3}. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 1. After isotropic refinement, an empirical absorption correction was performed,[9] which gave 0.663—1.768, for the maximum and minimum absorption corrections.

Results and Discussion

Molecular Geometry of (**4**).—The structure of compound (**4**) is shown in Figure 1 together with the atomic numbering used in the crystallographic work. The main geometrical parameters are given in Tables 2 and 3. The dimeric protonated cation has three ring systems, which are quite planar within experimental error and at *ca.* 3° with each other. The double character of the bonds in the pyridazine rings is maintained at C(1)–N(2) and C(1')–N(2'), while the other formal double bond seems to be redistributed between C(4)–N(3) and C(4)–N(19) and analogously in the dashed section in Figure 1. The proton was clearly located at N(3) and N(3'), which remain planar and support the formal charge. It is noteworthy that the angle distribution in these rings is equal for both moieties except at the point of attachment of the substituents. The substituent chains behave differently (see Table 3) because of the hydrogen bonds present in the crystal, which join the two moieties in one dimer. The whole crystal is built by repeating units of the four dimers along the *a* axis (see Figure 2) and held together through the hydrogen bonding network, which involves the dimers with tetrachlorocobaltate dianions and the water molecule (see Table 3).

Table 2. Selected bond distances (Å) and angles (°)

Molecule	Undashed	Dashed
C(1)–C(12)	1.460(13)	1.464(14)
C(4)–C(5)	1.456(12)	1.453(12)
C(1)–N(2)	1.294(11)	1.295(12)
C(4)–N(3)	1.313(12)	1.339(13)
N(2)–N(3)	1.403(10)	1.369(11)
C(5)–C(12)	1.420(12)	1.407(12)
C(1)–N(13)	1.345(11)	1.349(13)
C(4)–N(19)	1.328(11)	1.328(12)
N(13)–N(14)	1.457(13)	1.538(16)
N(19)–C(20)	1.474(11)	1.477(13)
C(14)–C(15)	1.467(16)	1.429(18)
C(20)–C(21)	1.521(14)	1.479(16)
C(15)–C(16)	1.505(13)	1.460(15)
C(21)–C(22)	1.521(14)	1.463(23)
C(16)–O(17)	1.406(15)	1.398(15)
C(22)–O(23)	1.371(19)	1.412(18)
O(17)–C(18)	1.326(13)	1.407(12)
O(23)–C(24)	1.452(13)	1.312(20)
C(12)–C(1)–N(2)	123.2(8)	122.5(8)
C(5)–C(4)–N(3)	117.5(7)	117.6(8)
C(1)–N(2)–N(3)	116.4(7)	117.5(8)
C(4)–N(3)–N(2)	127.4(7)	126.8(8)
C(1)–C(12)–C(5)	118.1(7)	118.6(8)
C(4)–C(5)–C(12)	117.4(7)	117.1(8)
N(2)–C(1)–N(13)	117.3(7)	117.0(8)
N(3)–C(4)–N(19)	120.0(7)	120.4(8)
C(12)–C(1)–N(13)	119.5(7)	120.4(8)
C(5)–C(4)–N(19)	122.5(7)	122.0(8)
C(1)–N(13)–C(14)	122.6(7)	119.4(8)
C(4)–N(19)–C(20)	121.6(7)	125.9(8)
N(13)–C(14)–C(15)	113.4(8)	112.1(9)
N(19)–C(20)–C(21)	108.7(7)	110.5(9)
C(14)–C(15)–C(16)	114.1(9)	113.5(11)
C(20)–C(21)–C(22)	110.6(9)	113.8(10)
C(15)–C(16)–O(17)	109.6(9)	115.4(10)
C(21)–C(22)–O(23)	107.0(11)	108.1(13)
C(16)–O(17)–C(18)	118.9(9)	111.1(8)
C(22)–O(23)–C(24)	106.0(11)	118.1(14)

Table 3. Selected torsion angles (°) and main interactions (Å,°) (symmetry code: i, *x*, *y*, *z*; ii, *x*, 1 + *y*, *z*; iii, *x*, *y*, *z* − 1; iv, *x*, *y* + 1, *z* − 1; v, 1 − *x*, −*y*, −*z*)

Molecule	Undashed	Dashed
N(3)–N(2)–C(1)–N(13)	−178.9(7)	−175.1(8)
N(2)–N(3)–C(4)–N(19)	178.0(8)	178.2(8)
N(2)–C(1)–N(13)–C(14)	−1.3(12)	3.7(14)
N(3)–C(4)–N(19)–C(20)	−11.9(12)	0.4(14)
C(1)–N(13)–C(14)–C(15)	−77.3(11)	164.3(10)
C(4)–N(19)–C(20)–C(21)	−161.2(8)	140.9(10)
N(13)–C(14)–C(15)–C(16)	−60.4(11)	−69.7(14)
N(19)–C(20)–C(21)–C(22)	150.7(9)	−67.9(13)
C(14)–C(15)–C(16)–O(17)	179.7(9)	−69.6(14)
C(20)–C(21)–C(22)–O(23)	68.0(12)	−59.7(15)
C(15)–C(16)–O(17)–C(18)	−154.7(11)	−176.4(10)
C(21)–C(22)–O(23)–C(24)	−172.1(10)	−167.8(15)

X–H ··· Y	X–H	X ··· Y	H ··· Y	X–H ··· Y
N(3)–H(3) ··· O(17')	0.95(9)	2.842(10)	1.92(10)	165(9)
N(3')–H(3') ··· O(17)	0.87(10)	2.803(10)	2.01(10)	152(9)
N(13')–H(13') ··· O(Wi)	0.87(9)	3.006(11)	2.15(8)	166(9)
N(19)–H(19) ··· Cl(2i)	0.85(9)	3.393(8)	2.55(9)	171(8)
N(13)–H(13) ··· Cl(1ii)	0.96(10)	3.219(7)	2.37(10)	147(9)
O(W) ··· Cl(2iii)		3.311(8)		
N(19')–H(19') ··· Cl(3iv)	0.96(10)	3.671(10)	2.74(11)	164(7)
O(W) ··· Cl(3v)		3.274(9)		

The ranges of bond lengths and angles are 2.234(4)—2.286(3) Å and 106.9(1)—111.8(1)°.

Spectroscopic Data of (**3′a**).—The structure of the starting monohydrochloride (**3′a**) has been investigated on the basis of the analytical and spectroscopical parameters which have been compared with those corresponding to the parent base. From the u.v. spectra of (**3a**) and (**3′a**) taken in chloroform (Table 4) it is observed that protonation of the base (**3a**) [→(**3′a**)] produces an hypsochromic shift in the long wavelength bands (364 → 352 and 415 → 380 nm) which on salt formation usually indicates the participation of the cation $>C=\overset{+}{N}H$.[11] The longer wavelength inflection (at 461 nm) which may correspond to an ($n \rightarrow \pi^*$) transition in (**3a**) disappears in (**3′a**) probably due to the fact that the lone pair of electrons on the nitrogen is more localized by the presence of the proton. Furthermore, a marked hyperchromic effect on the ($\pi \rightarrow \pi^*$) bands (249 → 263 and 255 → 271 nm) also occurs. The last effect seems to be in agreement with the large hyperchromic shift observed for some nitrogen heterocycles with amino groups α or β to the protonated nitrogen atoms.[12]

Comparison of the i.r. spectra (Table 4) also confirms the protonated structure of (**3′a**). In the 3 500—3 000 cm^{-1} region in which the hydrogen bonding has a marked effect on absorption the 1,4-bis(alkylamino)benzo[*g*]phthalazinium salt shows four bands corresponding to γ(NH) and $\gamma(=\overset{+}{N}H)$ modes, while in (**3a**) only a sharp γ(NH) exocyclic band appears at 1 410 cm^{-1}. It is interesting to note that according to Witkop's hypothesis,[11] in salt (**3′a**) the presence of the other basic nitrogen atom leads to the complete disappearance of the immonium bands which usually appear at 2 500—1 900 cm^{-1}. Furthermore, as expected, the absorption of the C=N and C=C aromatic groups at 1 600—1 500 cm^{-1} moves to higher frequencies (1 650—1 560 cm^{-1}) in (**3′a**).[13,14]

^{13}C and ^{1}H n.m.r. spectroscopic data for (**3a**) and (**3′a**) are shown in Tables 5 and 6, respectively. The ^{13}C chemical shifts of (**3a**) have been assigned on the basis of ^{13}C parameters previously reported for naphthalene, anthracene, and phthal-

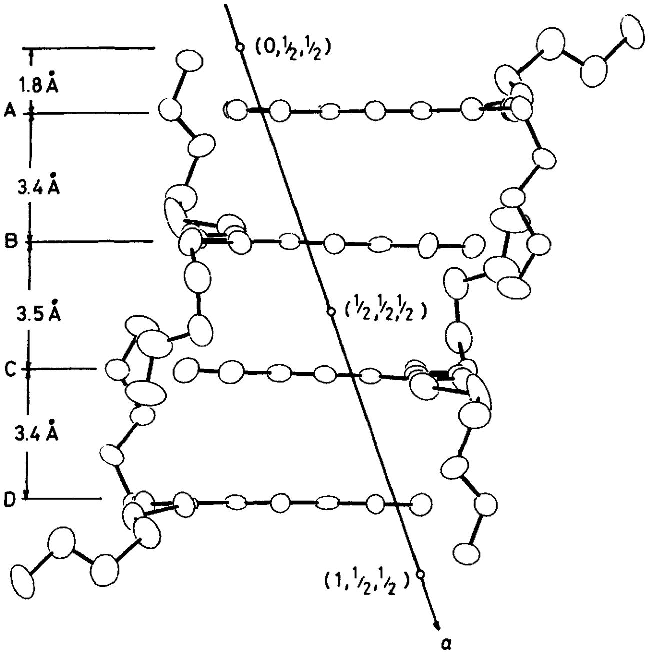


Figure 2. A view of the crystal piled along the a axis. Circles stand for inversion centres with the corresponding co-ordinates. A and D stand for the original undashed moiety and for the corresponding symmetry related by (1 − *x*, 1 − *y*, 1 − *z*), while B and C are for the (*x*, *y*, 1 + *z*) dashed moiety and the corresponding (1 − *x*, 1 − *y*, 1 − *z*) one

Table 4. U.v. and i.r. spectroscopic data of (**3a**) and (**3′a**)

Compound	$\lambda_{max.}$/nm (log ε) (CHCl$_3$)	$\nu_{max.}$/cm^{-1} (CHCl$_3$)
(**3a**)	249 (4.55), 255infl. (4.49)	3 410
	300 (3.94), 306infl. (3.92)	1 605
	364 (3.52), 415 (3.56)	1 545, 1 495vs
	461infl. (3.27)	
(**3′a**)	263 (4.75), 271 (4.79)	3 400, 3 320, 3 250, 3 200
	300 (3.69), 308infl. (3.69)	1 655, 1 640s
	352 (3.65), 380 (3.73)	1 590, 1 560vs

Table 5. ^{13}C N.m.r. (CDCl$_3$) spectroscopic data of (**3a**) and (**3′a**)

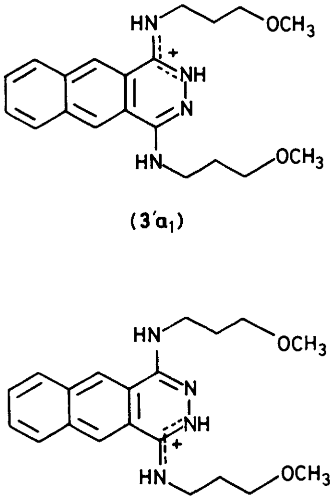
	δ (p.p.m.)									
Compound	C(1), C(4)	C(4a), C(10a)	C(5), C(10)	C(5a), C(9a)	C(6), C(9)	C(7), C(8)	C(1′)	C(2′)	C(3′)	OCH$_3$
(**3a**)	149.41	118.71	121.28	133.72	128.64	127.55	40.99	29.09	72.50	58.78
(**3′a**)	148.93	117.14	126.17	134.05	129.04	129.04	39.75	28.64	70.57	58.74
δ[(**3′a**)—(**3a**)]	−0.48	−1.6	+4.89	+0.33	+0.40	+1.49	−1.24	−0.45	−1.93	−0.04

Table 6. ^{1}H N.m.r. {[^{2}H$_6$]DMSO, δ(p.p.m.)} spectroscopic data for (**3a**) and (**3′a**)

	Aromatic protons			Alkylamino chain					*J*/Hz		
Compound	H(5), H(10)	H(6), H(9)	H(7), H(8)	H(1′)	H(2′)	H(3′)	OCH$_3$	NH	$J_{1',2'}$	$J_{2',3'}$	$J_{1'NH}$
(**3a**)	8.80	8.11	7.70	3.47	1.95	3.48	3.28	6.72[a]	7.0	6.3	5.0
	(s, 2 H)	(m, 2 H)	(m, 2 H)	(m, 4 H)	(m, 4 H)	(t, 4 H)	(s, 6 H)	(t, 2 H)			
(**3a**)	8.80	8.13	7.71	3.50	1.91	3.48	3.28		7.0	6.3	
in (OH$^-$)[b]	(s, 2 H)	(m, 2 H)	(m, 2 H)	(t, 4 H)	(m, 4 H)	(t, 4 H)	(s, 6 H)				
(**3a**)	9.17	8.23	7.84	3.51	1.99	3.49	3.28		7.2	6.1	
in (H$^+$)[c]	(s, 2 H)	(m, 2 H)	(m, 2 H)	(t, 4 H)	(m, 4 H)	(t, 4 H)	(s, 6 H)				
(**3′a**)	9.42	8.14	7.82	3.52	2.00	3.50	3.28	8.76[a]	6.9	6.1	
	(s, 2 H)	(m, 2 H)	(m, 2 H)	(t, 4 H)	(m, 4 H)	(t, 4 H)	(s, 6 H)	(m, br)			

[a] This signal disappears by treatment with D$_2$O. [b] Taken after adding of a drop of concentrated sodium hydroxide. [c] Taken after adding of a drop of concentrated sulphuric acid.

azine.[15] Negative and positive signs are used for upfield and downfield-induced shift on salt formation. In (**3′a**) the nitrogen protonation results in chemical shifts of −0.45, −1.6, and +4.89 p.p.m. for the α, β, and γ aromatic carbons respectively, which seems to be in agreement with the protonation of the heterocyclic nitrogens.[16] The ^{1}H n.m.r. spectrum of (**3a**) shows coupling between the NH exocyclic protons and the vicinal 1′-methylene group (*J* 5.0 Hz), which is consistent with the amino tautomer as occurs in other aminodiazines.[17] Since the free pairs of electrons of a nitrogen heterocycle, on protonation, increase the value of the ^{1}H chemical shifts with respect to the non-protonated species, the ^{1}H n.m.r. spectrum of (**3a**) has also been compared in neutral basic and acidic media using hexadeuteriated dimethyl sulphoxide as solvent. There are few differences in chemical shifts from (**3a**) in neutral or alkaline media. However, in acidic medium, as expected, all the aromatic proton signals experience a downfield shift which is higher for H(5) and H(10) at the position α to the ring nitrogen atom (Δδ 0.37 p.p.m.).[18] Similar shifts can be observed for the hydrochloride salt (**3′a**) where the deshielding undergone by H(5) and H(10) is much bigger (Δδ 0.62 p.p.m.) than that on partial protonation of (**3a**). Furthermore, the NH protons in (**3a**) undergo a deshielding of *ca.* 2.0 p.p.m. In addition to the spectroscopic observations, the assumption that protonation of (**3a**) [→(**3′a**)] occurs at the ring nitrogen atoms with the positive charge being shared between the four endocyclic and exocyclic nitrogen atoms is also consistent with the protonated structure assigned by Cookson *et al.* to some dimethylaminopyridazine derivatives.[19] The presumed contribution to structure (**3′a**) of the 2*H*- and 3*H*-tautomeric cations (**3′a**$_1$) and (**3′a**$_2$) (Scheme 3), which in solution may exist in fast equilibrium,[20] could explain the formation of the crystalline tetrachlorocobaltate salt (**4**). Its cationic moiety has been formed by trapping two identical 1,4-bis-(3-methoxypropylamino)-3(2)*H*-benzo[*g*]phthalazinium ions to form a new dimeric protonated cation in which the two ions are chiefly stabilized by means of two intermolecular bonds between $=\overset{+}{N}H$ of one cation and a methoxy group of the alkylamino chain of the other.



(**3′a**$_1$)

(**3′a**$_2$)

Scheme 3.

For the anionic moiety of (**4**), it is well known that the tetrahedral complex $[CoCl_4]^{2-}$ responsible for the blue colour is usually formed by reaction of a neutral cobalt(II) dichloride molecule with two chloride anions trapped as ligands, in this case from two molecules of the parent hydrochloride (**3′a**).[21]

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