Pyrrolidinoindoline Alkaloids from *Psychotria colorata*[1]

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Fractionation of an alkaloid extract of *Psychotria colorata* flowers led to the isolation of six alkaloids, identified by UV, 1D and 2D NMR, and MS as (−)-calycanthine, isocalycanthine, (+)-chimonanthine, hodgkinsine, quadrigemine C, and a new alkaloid (**1**), whose structure was deduced by X-ray analysis to be (8-8a),(8′-8′a)-tetradehydroisocalycanthine 3a(*R*), 3′a(*R*).

Psychotria colorata (Willd., ex R & S.) Muell. Arg. belongs to a plant genus commonly used medicinally to alleviate pain. The most reported therapeutical uses of different parts of *P. colorata* among the Amazon caboclos are in the treatment of earache (flowers) and abdominal pain (roots and fruits).[2]

Flowers and leaves of *P. colorata* showed positive tests for alkaloids and a similar qualitative composition.[3,4] Phytochemical investigation of leaves led to the identification of calycanthine, isocalycanthine, and quadrigemine C.[5]

An alkaloid extract of *P. colorata* flowers showed a marked dose-dependent naloxone-reversible analgesic activity, suggesting an opioid-like pharmacological profile.[3,5] The data suggest the involvement of both μ and κ opioid receptors in the analgesic activity, inasmuch as *P. colorata* alkaloids have proved to exert analgesic effects in behavioral tests (thermal and nonthermal nociceptive tests) involving activation of these subtypes of opioid receptors.

The tail-flick test was chosen to follow the fractionation of the flower extract from which five known and one new alkaloid (**1**) were isolated. The purpose of this paper is to detail the isolation of these alkaloids and the structure elucidation of **1**.

The total alkaloid extract was fractionated by size-exclusion chromatography (SEC) on Sephadex LH20, and the fractions were submitted to an analgesic activity test (tail flick) (data not shown). Repeated purifications by Si gel, alumina, and medium-pressure reversed-phase chromatography of the active fractions led to the isolation of six alkaloids.

The CIMS of compound **1** showed a MH^+ peak at *m*/*z* 343, which suggested a molecular composition of $C_{22}H_{22}N_4$, which was confirmed by the M^+ ion in the EIMS spectrum at *m*/*z* 342. A low fragment at *m*/*z* 171 is also present in the EIMS spectrum. The UV spectrum of compound **1** showed absorption maxima at 274, 280, and 300 nm (sh), and the ^{1}H NMR spectrum of **1** (Table 1) showed the presence of 11 protons: an *o*-disubstituted aromatic system; two methylene groups, and an *N*-methyl group. Its ^{13}C NMR spectrum (Table 2) also showed the presence of 11 resonances. A ^{1}H−^{15}N GHMBC spectrum (gradient-enhanced heteronuclear multiple bond correlation)[6] was also recorded, showing the presence of two nitrogen atoms, one resonating at δ 202, long-range correlated with the protons at δ 7.03, and one at δ 98, which is long-range correlated with the protons at δ 3.57, 3.28, and 1.70 (Table 2). A 1D NOE experiment[7] indicated a linking of the *N*-methyl group to an aliphatic methylene. Proton and carbon resonances were assigned based on E-COSY, GHSQC, and GHMBC experiments. From these data compound **1** appears to have a dimeric unsaturated indoline structure, endowed with a C_2 symmetry.

Table 1. ^{1}H NMR Chemical Shifts of **1** as Determined by E-COSY and ROESY Experiments (600 MHz, $CDCl_3$, δ in ppm from Internal TMS)

H	δ (ppm)	m	*J* (Hz)	significant cross-peak correlations in the ROESY spectrum[a]
2β	3.43	t	9.2	N-CH_3 (m), 3β (m), 3α (s)
2α	3.57	ddd	9.5, 9.2, 6.5	N-CH_3 (w), 3β (s), 3α (m)
3β	2.43	ddd	12.4, 9.5, 6.5	2β (m), 2α (s)
3α	1.70	ddd	12.4, 6.3, 1.0	2β (s), 2α (m)
4	6.66	dd	7.3, 1.0	2α (w), 2β (w)
5	6.70	ddd	7.8, 6.8, 2.6	
6	7.03	m		5 (s)
7	7.03	m		4 (s)
N−CH_3	3.28	s		

[a] Intensities of the cross peaks are defined as weak (w), medium (m) and strong (s).

A dihydrobromide derivative of compound **1** was prepared for the X-ray diffraction, which determined its primary structure and absolute configuration as depicted in Figure 1, along with its atomic numbering scheme. Thus, compound **1** is (8-8a), (8′-8′a)-tetradehydroisocalycanthine 3a(*R*),3′a(*R*).

The other isolates were identified as (−)-calycanthine, isocalycanthine, (+)-chimonanthine, hodgkinsine, and quadrigemine C, respectively, by comparison of their spectroscopic and physicochemical characteristics with

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Table 2. ^{13}C NMR Assignments for 1, and $^{B}C-H$ Connectivities as Determined by the GHMBC Experiments

C	δ (ppm)	m	connected protons
2	48.5	t	3.28 (N−CH_3)
3	29.9	t	3.57 (2α), 3.43 (2β)
3a	48.9	s	6.66 (4), 3.43 (2β), 2.43 (3β), 1.70 (3α)
4	123.0	d	7.03
4a	125.6	s	7.03, 6.70 (5), 2.43 (3β), 1.70 (3α)
5	121.9	d	7.03
6	128.2	d	6.66 (4)
7	123.9	d	6.70 (5)
7a	145.8	s	7.03, 6.66 (4)
8a	165.0	s	3.43 (2β), 3.28 (N−CH_3), 1.70 (3α)
N−CH_3	31.1	q	3.43 (2β)

^{15}N NMR Assignments for **1**, as determined from the $^{1}H-^{15}N$ GHMB experiment

N	δ (ppm)	connected protons[a]
1	98	3.57 (2α, s), 3.28 (N−CH_3, s), 1.70 (3α, s)
8	202	7.03 (s), 3.57 (2α, w)

[a] Intensities of the cross peaks are defined as weak (w), medium (m), and strong (s).

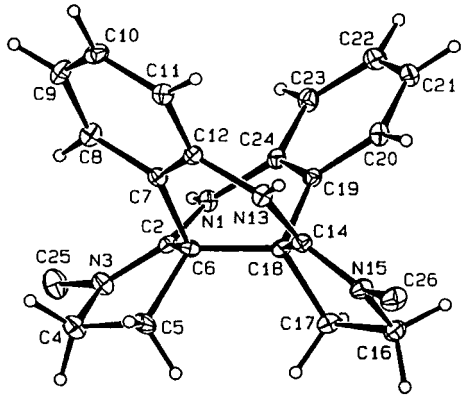
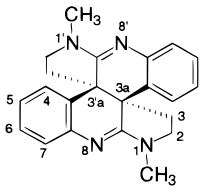


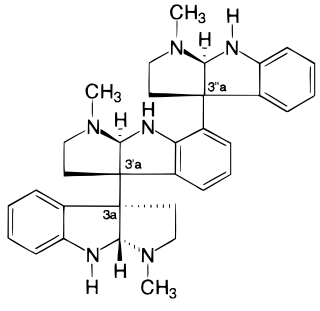
Figure 1. ORTEP plot of **1** dihydrobromide dihydrate with numbering scheme. H atoms of methyl groups are omitted for clarity.

literature data.[8−12] We report for the first time the full NMR assignments for hodgkinsine (**2**) (Tables 3 and 4). ^{1}H NMR data not previously detailed in the literature for (+)-chimonanthine and (−)-calycanthine, as well as their CD values, are presented.



(**1**)

(8-8a),(8'-8'a)-tetradehydroisocalycanthine 3a(*R*), 3a'(*R*)



(**2**) hodgkinsine

Experimental Section

General Experimental Procedures. Melting points have been measured on a Buchi 510 mp apparatus and are reported uncorrected. Optical rotations have been measured on a Perkin−Elmer 241 polarimeter. UV spectra have been recorded on a Hewlett−Packard 8452A spectrophotometer (average concentrations 10^{-4} M); CD spectra have been measured on a JASCO J-500 dicrograph (*c* 10^{-4} M). TLC (Si gel 60 F_{254}) were eluted with $CHCl_3$−MeOH−NH_4OH. Spots were revealed by spraying with Dragendorff reagent or 10% H_2SO_4−MeOH, followed by heating, or by absorption of the UV light (254 nm). Column chromatography was performed with Si gel 60 (63−200 μm or 40−63 μm) or with neutral alumina (activity I) (art 1.0177, Merck). HPLC analyses were carried out on a Waters 600-MS liquid−liquid chromatograph, connected with a Waters PDA 991 detector and a NEC 386/25 personal computer. A symmetry C18 column (5 μm, 4.6 × 250 mm, Waters) was used, eluted with MeOH−H_2O−Et_2NH 80:20:0.1 at a flow rate of 1 mL/min. Samples were filtered prior to each injection through Millex FH_{13} filters (5 μm, Millipore). Preparative HPLC was carried out on a Varian 5000 liquid−liquid chromatograph, connected to a L-4200 UV/vis detector (Merck−Hitachi) and a HP 3396A integrator (Hewlett−Packard). A Symmetryprep C18 column was used (7 μm, 7.8 × 150 mm, Waters), eluted with the same mixture of the analytical conditions, at a flow rate of 1.8 mL/min. Samples (400 μL, 4 mg each) were filtered before each injection. EIMS (70 eV) and CIMS (isobutane) were recorded on a VG 7070 EQ mass spectrometer; 200-MHz NMR spectra were recorded on a Bruker AC 200 spectrometer. Samples were dissolved in $CDCl_3$ and TMS was used as reference. 600-MHz NMR spectra were registered in phase-sensitive mode at 301 K (243 K for hodgkinsine) on a three-channel Varian Unity−600 spectrometer, operating at 599.919 MHz for ^{1}H, at 150.858 for ^{13}C, and at 60.798 MHz for ^{15}N, employing an actively shielded *z* gradient and a pulsed field gradient (pfg) accessory, equipped with a pfg triple-resonance indirect detection probe ($^{1}H\{^{13}C,^{15}N\}$), a waveform generator on all three channels, and running the Varian Software Vnmr 5.1B. The ^{1}H and ^{13}C spectra were referencered to TMS. The ^{15}N spectra were referencered with an external reference of pure $CH_3-^{15}NO_2$ taken as +380.2 ppm from pure liquid ammonia. Experimental conditions for DQF−

Table 3. ^{1}H NMR Chemical Shifts of the Two Stable Conformers at 243 K of **2** as Determined by E-COSY and ROESY Experiments (600 MHz, $CDCl_3$, δ in ppm from Internal TMS)

H	minor conformer δ (ppm)	major conformer δ (ppm)	mult	J (Hz)	significant cross-peak correlations in the ROESY spectrum
2β	2.86	2.86	m		
2α	2.36	2.37	m		
3β	2.44	2.43	m		
3α	2.11	2.13	m		
4	7.17	7.22	d	7.8	6.79, 6.84 (5)
5	6.79	6.84	t	7.2	7.17 (4), 7.08, 7.10 (6)
6	7.08	7.10	t	7.3	6.79, 6.84 (5), 6.62 (7),
7	6.62	6.65	d	7.7	7.08, 7.10 (6), 4.04 (N−H)
8a	4.52 (6.5)[a]	4.97	br s	4.8[a]	2.20 (N−CH_3), 4.13 (N−H)
N−H	4.04 (5.7)[a]	4.12	br s	6.5[a]	
N−CH_3	2.20	2.42	s		4.52 (8a), 2.86 (2β)
2′β	2.92	2.86	m		
2′α	2.32	2.36	m		
3′β	2.59 (11.4)	2.53	m	12.6	7.37 (4″), 2.92 (2′β)
3′α	2.07	2.01	dd	12.6, 5.5	
4′	5.57	7.23	d	7.7	6.16, 6.70 (5′), 2.53, 2.59 (3′β), 2.07 (3′α)
5′	6.16	6.70	t	7.4	6.98, 7.13 (6′), 5.57, 7.23 (4′)
6′	6.98	7.13	d	7.9	6.16, 6.70 (5′)
8a′	4.23	5.08	br s	6.7[a]	
N−H	3.72	4.25	br s	5.0	
N−CH_3	2.31	2.45	s		2.92 (2′β)
2″β	3.01	2.89	m		
2″α	2.56	2.51	m		
3″β	3.01 (11.0)	3.04	dd	12.6	
3″α	1.91	1.87	dd	12.6, 5.5	
4″	7.37	5.44	d	7.9	6.80, 6.20 (5″), 2.56 (2″α)
5″	6.81	6.20	t	7.3	7.11 (6″)
6″	7.11	6.89	t	7.3	6.81 (5″), 6.46 (7″), 3.01 (3″β)
7″	6.46	6.51	d	7.9	7.11 (6″)
8a″	5.08	5.08	br s		2.46 (N−CH_3)
N−H	4.15	4.20	br s		
N−CH_3	2.46	2.38	s		

[a] The coupling constant has been extracted from the E-COSY experiment.

COSY, NOESY, ROESY, E-COSY, HMQC, HMBC, GHSQC, and GHMBC experiments are reported by Verotta et al.[13]

Plant Material. *P. colorata* flowers were collected in several places around the city of Belém (Pará, Brazil) during the dry season (March to August) of 1993. Identification was confirmed by Dr. Brian Boom of the New York Botanical Garden, and a voucher specimen is deposited there (ZC 23, NYBG).

Extraction and Isolation. Dried *P. colorata* flowers (1.4 kg) were extracted with MeOH. The crude extract (78.1 g) was taken up with 5% HCl (280 mL) and extracted with Et_2O (3 × 280 mL). The organic phases were pooled and washed with H_2O. The combined aqueous phases were treated with 6 N NaOH (84 mL) to pH 10 and extracted with $CHCl_3$ (3 × 280 mL). The organic phases were pooled, washed with H_2O, dried (Na_2SO_4), and evaporated to dryness under vacuum, yielding 7.1 g of alkaloid extract (0.51% of dried starting material), which was chromatographed on a column (4.5 × 85 cm) of Sephadex LH20 (360.5 g), eluting with CH_2Cl_2 (2 L), at a flow rate of 0.5 mL/min. Fractions (10 mL) were pooled: 1−49 (fraction A, 1.97 g), 50−85 (fraction B, 2.48 g), 86−120 (fraction C, 1.34 g), 121−181 (fraction D, 1.30 g).

Fraction A (1.97) was chromatographed on Si gel (flash chromatography, 4.5 × 20 cm), eluting with cyclohexane−EtOAc−Et_2NH (10:10:1) (2 L). Fractions of 14 mL each were collected and combined according to their TLC and HPLC patterns. Combined fractions 73−117 (211 mg) were further purified by preparative HPLC to yield 20 mg of quadrigemine C: amorphous white powder; $[\alpha]^{20}_D$ −64° (*c* 1, $CHCl_3$), $[\alpha]^{20}_D$ +40° (*c* 0.2, MeOH); R_f 0.19 (SiO_2; $CHCl_3$−MeOH−NH_4OH 9:1:0.15); t_R 31.29 min.

Fraction B (2.48 g) was purified on Si gel (flash, 4 × 20 cm) eluting with cyclohexane−EtOAc−Et_2NH (10:10:1) (4 L). Fractions of 14 mL each were collected and combined according to their TLC and HPLC patterns. Fractions 131−214 (310 mg) were purified through preparative HPLC, obtaining 41 mg of hodgkinsine (2): colorless needles from hexane−$CHCl_3$ 4:1; mp 128 °C; $[\alpha]^{20}_D$ −33.6° (*c* 1, $CHCl_3$); CD (MeOH), λ_{max} ($\Delta\epsilon$) = 241 (−5.6), 257 (+5.4), 310 (+6.5) L mol^{-1} cm^{-1}; ^{1}H and ^{13}C NMR (600 MHz, and 150.9 MHz, $CDCl_3$) see Tables 3 and 4. R_f 0.23 (SiO_2; $CHCl_3$−MeOH−NH_4OH 9:1:0.15); t_R = 13.53 min.

Fraction C (1.34 g) was purified on neutral alumina (activity I, 100 g on a 3 × 24 cm column), eluting with CH_2Cl_2−EtOAc−MeOH (5:5:0.5). Fractions were combined according to their TLC and HPLC patterns. Fractions 22−27 (385 mg) and 28−44 (315 mg) were submitted to further purifications. Fractions 22−27 (385 mg) were chromatographed twice on neutral alumina (eluting with CH_2Cl_2−$CHCl_3$ 7:3) and then on Si gel (12 g eluting with $CHCl_3$−*i*PrOH−NH_4OH 12:3:0.1) obtaining 107.5 mg of compound **1**.

Fractions 28−44 (315 mg) were purified through preparative HPLC, to yield 24 mg of (+)-chimonanthine: white powder from diisopropyl ether−$CHCl_3$ 3:1; mp 171−172 °C; $[\alpha]^{20}_D$ +264.5° (*c* 1, EtOH); CD (MeOH), λ_{max} ($\Delta\epsilon$) 246 (+ 9.78), 300 (+ 3.69) L mol^{-1} cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 7.20 (1H, d, J = 7.4 Hz, H-4), 7.00 (1H, t, J = 7.6 Hz, H-6), 6.67 (1H, t, J =

Table 4. ^{13}C NMR Assignments for the Two Stable Conformers at 243 K of **2**, and $^{B}C-H$ Connectivities as Determined by the HMBC Experiments

C	minor conformer δ (ppm)	major conformer δ (ppm)	mult	connected protons
2	51.9	5.17	t	
3	35.7	37.6	t	
3a	63.0	62.8	s	7.22 (4)
4	126.3	126.4	d	7.08, 7.10 (6)
4a	131.6	131.7	s	6.79, 6.84 (5), 6.62, 6.65 (7)
5	118.2	118.5	t	6.62, 6.65 (7), 7.10 (6)
6	127.8	127.9	t	7.17, 7.22 (4)
7	109.0	109.0	d	4.97 (8a), 6.84 (5)
7a	150.8	150.8	s	7.08, 7.10 (6), 7.22 (4)
8a	87.0	86.4	s	2.20 (CH_3) 2.86 (2β), 4.04 (N−H)
N−CH_3	34.9	35.2	q	
2′	51.7	51.9	t	
3′	37.6	36.7	t	
3a′	62.9	63.0	s	5.57 (4′)
4′	122.4	121.9	d	6.98 (6′)
4a′	132.3	132.3	s	6.16 (5′), 2.59 (3′β)
5′	115.3	116.8	d	
6′	125.0	126.0	s	5.57, 7.23 (4′)
7′	nd	nd		
7a′	149.5	150.8	s	6.98, 7.13 (6′), 5.57, 7.23 (4′)
8a′	82.6	81.7	s	2.31 (CH_3)
N−CH_3	34.9	35.0	q	
2″	52.2	51.9	t	
3″	38.4	38.0	t	
3a″	60.3	60.0	s	
4″	124.0	124.2	d	6.20 (5″), 6.89 (6″), 6.46 (7″)
4a″	132.7	131.7	s	6.81, 6.20 (5″), 6.46, 6.51 (7″)
5″	118.2	117.5	d	6.46 (7″)
6″	127.9	127.4	d	6.20 (5″), 7.37 (4″)
7″	108.4	108.1	d	6.81, 6.20 (5″)
7a″	152.1	151.1	s	7.37 (4″), 6.89, 7.11 (6″)
8a″	82.3	82.3	s	2.46 (CH_3)
N−CH_3	34.9	35.1	q	

7.3, H-5), 6.55 (1H, d, J = 7.7 Hz, H-7), 4.35 (1H, br s, H-8a), 2.50 (3H, m, H-2+H-3β), 2.31 (3H, s, N−CH_3), 2.07 (1H, dt, J = 12.0, 6.4, H-3α); ^{13}C NMR (50.2 MHz, $CDCl_3$), identical to the literature;[12] R_f 0.32 (SiO_2; $CHCl_3$−MeOH−NH_3 9:1:0.15); t_R = 5.00 min.

Fraction D (1.30 g) was purified on Si gel (65 g, 3 × 24 cm column), eluted with $CHCl_3$−*i*PrOH−NH_4OH (12:3:0.1) (500 mL). Fractions were combined according to their composition yielding 28 mg of (−)-calycanthine and 4 mg of a compound that was identified as isocalycanthine by TLC and HPLC comparison with a pure sample [R_f 0.84 (SiO_2; $CHCl_3$−MeOH−NH_3 9:1:0.15; t_R 2.39 min)].

(−)-Calycanthine: pale yellow powder from EtOH; mp 251−252 °C; $[\alpha]^{20}_D$ −463° (*c* 1, EtOH); CD (MeOH), λ_{max} ($\Delta\epsilon$) 239 (+3.33), 255 (−16.67), 310 (−27.5) L mol^{-1} cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 7.02 (1H, dd, J = 8.0,1.0 Hz, H-7), 6.83 (1H, dt, J = 7.5,1.0 Hz, H-6), 6.55 (1H, td, J = 7.5,1.0, H-5), 6.28 (1H, dd, J = 8.0, 1.0 Hz, H-4), 4.33 (1H, s, H-8a), 3.15 (1H, dt, J = 13.2, 5.5 Hz, H-3β), 2.63 (1H, ddd, J = 12.0, 5.6, 1.4 Hz, H-2β), 2.42 (3H, s, N−CH_3), 2.26 (1H, ddd, J = 12.0, 4.1, 1.4 Hz, H-2α), 1.63 (1H, br s, N−H), 1.30 (1H, ddd, J = 13.2, 4.1, 1.4 Hz, H-3α); ^{13}C NMR (50.2 MHz, $CDCl_3$) identical to the literature;[12] R_f 0.74 (SiO_2, $CHCl_3$−MeOH−NH_3 9:1:0.15); t_R 4.21 min.

(8−8a),(8′-8′a)-Tetradehydroisocalycanthine (3a-(*R*),3′a(*R*)-(1): $C_{22}H_{22}N_4$ (MW 342), colorless needles from diisopropyl ether−$CHCl_3$ 3:1. mp= 253 °C. $[\alpha]^{20}_D$ −449° (*c* 1.0, EtOH); UV (MeOH), λ_{max} (log ϵ) 274 (4.377), 280 (4.371), 300 sh (4.035) nm; CD (MeOH), λ_{max} ($\Delta\epsilon$) 259 (+11.33), 286 (−12.15), 299 (−11.15) L mol^{-1} cm^{-1}; EIMS *m/z* $[M]^+$ 342 (100), 327 (6), 313 (18), 298 (12), 284 (19), 270 (7), 209 (12), 171 (33), 149 (21), 129 (12); CIMS *m/z* $[M]^+$ 342 (100), $[M + H]^+$ 343 (58), 91 (5), 79 (7), 67 (12); ^1H, ^{13}C and ^{15}N NMR ($CDCl_3$) see Tables 1 and 2; R_f 0.78 (SiO_2; $CHCl_3$−MeOH−NH_4OH 9:1:0,15); t_R = 3.34.

Preparation of 1 Dihydrobromide. To a solution of **1** (10 mg, dissolved in 0.5 mL of $CHCl_3$) is added a stoichiometric amount of HBr (33% solution in AcOH) (10.2 μL) at 0°. The mixture was left at 4 °C in the dark for 24 h, and the precipitate formed was dissolved in H_2O and extracted with $CHCl_3$. The aqueous phase was evaporated to dryness and crystallized from EtOH: $C_{22}H_{24}Br_2N_4$ (MW 504) mp 315−316 °C (dec); $[\alpha]^{20}_D$ −212.4° (*c* 1, EtOH); ^1H NMR (CD_3OD, 200 MHz) 7.33 (2H, m, H-6 + H-7), 7.17 (1H, dt, J = 6.8, 1.3 Hz, H-5), 7.09 (1H, dd, J = 7.8, 1.3 Hz, H-4), 4.08 (2H, ddd, J = 9.5, 5.2, 3.0 Hz, H-2), 3.62 (3H, s, N−CH_3), 3.03 (1H, dt, J = 13.5, 9.5 Hz, H-3β), 2.08 (1H, ddd, J = 13.5, 5.2, 3.1 Hz, H-3α).

X-ray Crystallography of 1 Dihydrobromide Dihydrate.[14] For diffractometry, a colorless prismatic crystal measuring 0.62 × 0.36 × 0.29 mm^3 was mounted on a four-circle Syntex P4 diffractometer equipped with graphite monochromator and Mo Kα radiation. Lattice parameters were determined by least-squares fits to the setting parameters of 46 reflections in the range 13.18° < 2θ < 27.98°; 5497 intensity data were collected in the range 4.8° < 2θ < 55.0° with limits *h* 0, 9; *k* −13, 13; *l* −19, 19. Data reduction and application of Lorentz, polarization, absorption (empirical ψ scans, T_{max} = 0.961, T_{min} = 0.682) and decay correction (4.9% at the

end of data collection) were carried out using the XSCANS[15] system software. The structure was solved by direct methods [SIR92[16]] and refined by SHELX93.[17] Hydrogen atoms were derived from Fourier difference synthesis and refined with constraints on X−H distances (DFIX in SHELX93) and on isotropic displacement parameters. Disordered H atoms of the two methyl groups were included in structure factors calculations but not refined. One of the two H_2O molecules is disordered on two positions with the ratio 0.76:0.24; the H atoms of the minor part of this disordered H_2O molecule were not localized. All non-H atoms were refined anisotropically by full-matrix least-squares based on F^2. Neutral atomic scattering factors and anomalous dispersion effects were those included in SHELX93. The absolute configuration of the molecule was determined without ambiguity by the Flack[18] method. The plot was drawn by ORTEP II[19] with thermal ellipsoids at 20% of probability level.

Formula $(C_{22}H_{24}N_4)^{2+}.2\ Br^-\cdot 2\ H_2O$, F_w 540.30, monoclinic, space group $P2_1$, a 7.421 (1), b 10.220 (1), c 14.808 (1) Å, β 94.927 (6)°; V 1118.9 (2) Å^3, Z 2, D_c 1.604 g cm^{-3}, μ(Mo Kα) 3.649 mm^{-1}, λ (Mo Kα) 0.71073 Å, F (000) 548 electrons, merging R 0.0146, total number of reflections 5114, observed [$I > 2\sigma(I)$] 4076, final agreement indices on observed reflections R 0.0286, R_w (based on F^2) 0.0586.

The molecule presents about C_2 symmetry, and it is doubly protonated on N1 and N13. The distances C24−N1, N1−C2, C2−N3, C12−N13, N13−C14, and C14−N15 are 1.419 (3), 1.319 (3), 1.307 (4), 1.422 (4), 1.312 (4), and 1.297 (3) Å long, respectively, showing a complete delocalization of the double bonds N1−C2 and N13−C14 present in the neutral molecule. Despite the number of linked rings, the molecule does not show any particularly strained bond.

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References and Notes

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