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# Structure of 4,10-Dibenzyl-4,10-diazabicyclo[5.5.0]dodec-1(7)-ene Dihydrochloride, $C_{24}H_{32}N_2^{2+}.2Cl^-$

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Abstract. $M_r = 419.44$, orthorhombic, Pcab, $a = 12.737$ (2), $b = 16.796$ (2), $c = 10.364$ (1) Å, $V = 2217.2$ (5) Å^3, $Z = 4$, $D_x = 1.257$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 2.75$ mm^{-1}, m.p. 503–508 K decomposed, $F(000) = 896$, $T = 295$ K, final $R = 0.040$ for 1618 non-zero reflections. The molecule has $\bar{1}$ symmetry. The N atoms are protonated, and hydrogen-bonded to the Cl$^-$ ions [N$^+ \cdots$Cl$^-$ 3.064 (1), H$\cdots$Cl$^-$ 2.06 (2) Å, $\angle$N$^+$–H$\cdots$Cl$^-$ 172 (2)°]. The seven-membered ring takes a chair-like conformation. The benzyl group is bonded equatorially to the ring.

Introduction. The title compound was assumed to take one of the conformations, (1), (2) or (3). The last two conformations would display a nonclassical interaction between the proton bonded to the N atom and the double bond. To ascertain whether or not such an interaction was present, the compound was synthesized (Kimura, 1984, unpublished). The structure (1) has been confirmed by the present X-ray crystallographic study.

(1)

(2)   (3)

R = CH₂Ph

$C_{24}H_{32}N_2^{2+}.2Cl^-$
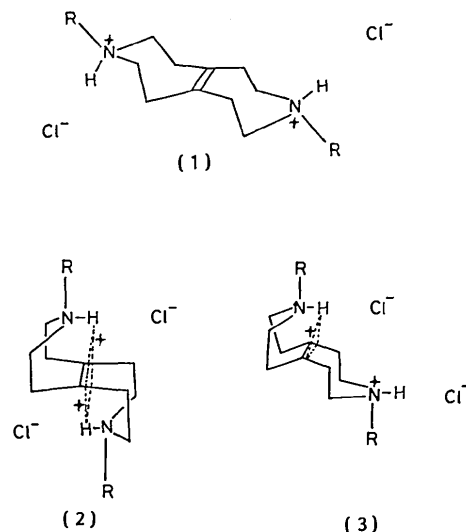
Experimental. Crystalline diammonium dichloride–(1) was deposited when a solution of the [5.5.0]amine in CCl_4 saturated with HCl gas was allowed to stand for 4 months at room temperature. Colorless prisms (slow evaporation from ethanol) with developed {010}. Systematic absences $0kl$ for l odd, $h0l$ for h odd, $hk0$ for k odd, space group $Pcab$. Crystal $0.35 \times 0.23 \times 0.28$ mm. Rigaku AFC-5 four-circle diffractometer. Lattice parameters determined with 19 reflections in the range $12° < 2\theta < 54°$ by least-squares method. Intensities measured up to $2\theta = 120°$, $\omega-2\theta$ scan method [scan speed $4°$ min^{-1} in 2θ; scan range (2θ): $1.5°$ + $0.30°\tan\theta$], Ni-filtered Cu $K\alpha$, 40 kV, 200 mA (rotating anode), background measured for 4 s on either side of the peak. Three reference reflections showed no intensity deterioration. Lorentz and polarization corrections; no absorption correction. All the 1649 unique data (ranging over $h = 0$ to 14, $k = 0$ to 18, $l = 0$ to 11) used in the refinement. Number of non-zero reflections 1618. Structure solved by $MULTAN78$, and refined (non-H atoms anisotropic) by block-diagonal least squares; $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1.0/[\sigma(F)^2 - 0.1034|F_o| + 0.0047|F_o|^2]$ for $|F_o| > 0$ and 1.7502 for $|F_o| = 0$. H-atom positions determined from a difference Fourier map, and refined isotropically in the least squares. Extinction correction for the seven strongest reflections (200, 231, 040, 132, 203, 121 and 331) $[I_{corr} = I_o/(1 - 1.02 \times 10^{-5}I_o)]$. $R = 0.041$ for 1649 reflections, $wR = 0.049$, $S = 1.92$, $(\Delta/\sigma)_{max}$ in the final refinement cycle for non-H and H atoms 0.2 and 1.2 respectively, max. and min. $\Delta\rho$ in the final difference Fourier map $+0.17$ and -0.34 e Å^{-3}, respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computations carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center. Programs $MULTAN78$ (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), $HBLS$-V (Ashida, 1973), $MOLCON$ (Fujii, 1979) and $ORTEP$ (Johnson, 1965).

Discussion. Final atomic parameters are listed in Table 1.* The thermal ellipsoids of the molecule with the atomic numbering are shown in Fig. 1. Bond lengths and angles are listed in Table 2, and torsion angles concerning the conformation of the seven-membered ring in Table 3.

The molecule has $\bar{1}$ symmetry (the atoms related by the center are denoted with a prime hereafter). The N atoms are protonated [N$^+$–H 1.02 (2) Å, C–N$^+$–H

109 (1), 106 (1)°]. The cation is linked to the chloride ions *via* a hydrogen bond. Two seven-membered rings are fused through the double bond C(10)=C(10') whose center lies on $\bar{1}$. χ_4 in Table 3 is -1.2 (3)°, being close to 0° as expected from the sp^2 hybridization of C(10). The endocyclic torsion angles χ_{4-i} ($i = 1$ to 3) are nearly equal to $-\chi_{4+i}$, indicating that the ring takes

Table 1. *Final atomic parameters (positional $\times 10^4$) with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i \beta_{ii}/a_i^{*2}.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Cl	6512.7 (3)	4733.8 (3)	4055.0 (4)	3.52 (2)
N	5014.1 (9)	5906.3 (7)	2736 (1)	2.33 (5)
C(1)	5525 (1)	7025.3 (9)	4230 (1)	2.74 (6)
C(2)	5944 (1)	6731.5 (9)	5375 (2)	3.35 (7)
C(3)	6746 (2)	7140.0 (9)	5994 (2)	4.15 (9)
C(4)	7136 (1)	7831.5 (9)	5482 (2)	4.76 (9)
C(5)	6729 (2)	8130.3 (9)	4350 (2)	4.62 (9)
C(6)	5920 (1)	7731.0 (9)	3727 (2)	3.68 (8)
C(7)	4642 (1)	6579.0 (9)	3593 (2)	2.89 (6)
C(8)	4066 (1)	5414.7 (9)	2352 (1)	2.69 (6)
C(9)	4337 (1)	4668.5 (9)	1603 (2)	3.03 (7)
C(10)	4580 (1)	4792.8 (8)	186 (1)	2.69 (6)
C(11)	6147 (1)	5581 (1)	791 (2)	3.19 (7)
C(12)	5639 (1)	6222.1 (9)	1624 (1)	2.97 (7)

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

Atoms translated by a center of symmetry in the molecule are shown with a prime.

|			
C(1)–C(2)	1.392 (3)	N–C(7)	1.513 (2)
C(1)–C(6)	1.389 (3)	N–C(8)	1.516 (2)
C(1)–C(7)	1.504 (3)	N–C(12)	1.498 (2)
C(2)–C(3)	1.388 (3)	C(9)–C(10)	1.515 (3)
C(3)–C(4)	1.370 (3)	C(11)–C(12)	1.524 (3)
C(4)–C(5)	1.377 (3)	C(10')–C(11)	1.509 (3)
C(5)–C(6)	1.389 (3)	C(10)–C(10')	1.333 (4)
C(8)–C(9)	1.514 (3)		
C(2)–C(1)–C(6)	118.9 (2)	C(8)–N–C(12)	114.5 (1)
C(2)–C(1)–C(7)	119.0 (2)	N–C(7)–C(1)	113.3 (2)
C(6)–C(1)–C(7)	122.1 (2)	N–C(8)–C(9)	113.8 (2)
C(1)–C(2)–C(3)	120.1 (2)	N–C(12)–C(11)	114.3 (2)
C(2)–C(3)–C(4)	120.5 (2)	C(8)–C(9)–C(10)	115.4 (2)
C(3)–C(4)–C(5)	120.2 (2)	C(9)–C(10)–C(10')	121.1 (2)
C(4)–C(5)–C(6)	120.0 (2)	C(10')–C(11)–C(12)	114.4 (2)
C(1)–C(6)–C(5)	120.4 (2)	C(9)–C(10)–C(11')	117.9 (2)
C(7)–N–C(8)	108.1 (1)	C(10)–C(10')–C(11)	121.0 (2)
C(7)–N–C(12)	110.7 (1)		
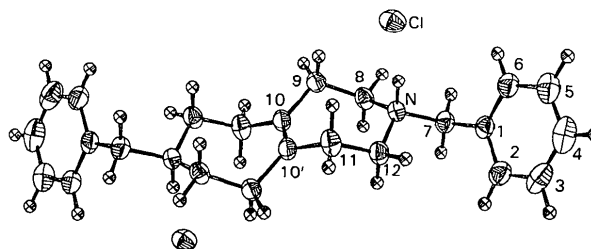
Fig. 1. View of the molecule with numbering of non-H atoms. Ellipsoids of 50% probability are used for the non-H atoms; the H atoms are represented as spheres equivalent to $B = 1.0$ Å^2.

Table 3. *Torsion angles* (°) *concerning the confor-
mation of the seven-membered ring*

Endocyclic

χ_1	C(12)–N–C(8)–C(9)	62·1 (2)
χ_2	N–C(8)–C(9)–C(10)	−79·1 (2)
χ_3	C(8)–C(9)–C(10)–C(10′)	65·4 (3)
χ_4	C(9)–C(10)–C(10′)–C(11)	−1·2 (3)
χ_5	C(10)–C(10′)–C(11)–C(12)	−63·4 (3)
χ_6	C(10′)–C(11)–C(12)–N	81·2 (2)
χ_7	C(11)–C(12)–N–C(8)	−63·9 (2)

Exocyclic

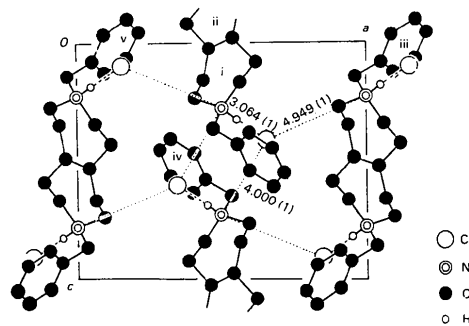|		
χ_8	C(9)–C(8)–N–C(7)	−174·0 (2)
χ_9	C(8)–N–C(7)–C(1)	169·8 (2)
χ_{10}	C(11)–C(12)–N–C(7)	173·6 (2)
χ_{11}	C(12)–N–C(7)–C(1)	−64·1 (2)
χ_{12}	N–C(7)–C(1)–C(2)	−84·6 (2)

Fig. 2. Molecular arrangement in a sheet parallel to (010). Interionic interactions are shown by dotted lines with the distances in Å. H atoms attached to C are omitted. Symmetry code: (i) x, y, z; (ii) $1 - x, 1 - y, -z$; (iii) $\frac{1}{2} + x, 1 - y, \frac{1}{2} - z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $-\frac{1}{2} + x, 1 - y, \frac{1}{2} - z$.

a chair-like conformation (Bocian & Strauss, 1977*a,b*) with a pseudo mirror plane passing through the N and the midpoint of the C(10)=C(10′) bond. Such a conformation has recently been found in some cyclo-heptene rings (Weeks, Duax, Finnegan, Delecki & Kojić-Prodić, 1984).

The benzyl group is bonded equatorially to N: $\chi_8 = -174\cdot0$ (2)°. The exocyclic and endocyclic torsion angles in Table 3 are in agreement within 12° with the corresponding angles of the azacycloheptanone ring in 1-benzyl-5-phenyl-1-azacycloheptan-4-one hydrochloride (Fukuyama, Shimizu, Kashino & Haisa, 1974). The endocyclic C–N and C(sp^3)–C(sp^2) bond lengths and bond angles are in agreement within the experimental errors with those found in the aza-cycloheptanone ring.

The molecular arrangement in a sheet parallel to (010) is shown in Fig. 2. It is seen that the sheet is formed by Coulombic interactions and hydrogen bonding, each ion being coordinated by three counter ions with N···Cl distances of 3·064 (1) (hydrogen bond), 4·000 (1) and 4·949 (1) Å. The short contacts in the sheet are: Cl···C(8^{iii}) 3·573 (2) and Cl···H(7^{iv}) 2·63 (2) Å. The sheets are stacked along **b** by van der Waals interactions.

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3,5-Diamino-2,4,6-trinitrobenzoic Acid, C₇H₅N₅O₈

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Abstract. $M_r = 287\cdot1$, monoclinic, $P2_1/c$, $a = 7\cdot2461$ (5), $b = 10\cdot3097$ (7), $c = 13\cdot962$ (1) Å, $\beta = 101\cdot023$ (6)°, $V = 1023\cdot8$ (2) Å³, $Z = 4$, $D_x = 1\cdot862$ g cm⁻³, $\lambda(\mathrm{Cu}\,K\bar{\alpha}) = 1\cdot5418$ Å, $\mu = 15\cdot48$ cm⁻¹, $F(000) = 584$, $T = 294$ K, final $R = 0\cdot039$ for 1574 unique observed reflections. The results are compared