Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°), *with e.s.d.'s in parentheses*

S(1)—C(2)	1·726 (3)	C(6)—O(14)	1·223 (3)
S(1)—C(13)	1·738 (3)	C(7)—C(8)	1·435 (3)
C(2)—N(3)	1·365 (4)	C(8)—C(9)	1·496 (3)
C(2)—C(7)	1·389 (3)	C(8)—C(13)	1·360 (4)
N(3)—C(4)	1·287 (4)	C(9)—C(10)	1·512 (5)
C(4)—N(5)	1·362 (3)	C(10)—C(11)	1·509 (6)
N(5)—C(6)	1·394 (4)	C(11)—C(12)	1·543 (5)
C(6)—C(7)	1·433 (3)	C(12)—C(13)	1·493 (4)
C(2)—S(1)—C(13)	91·6 (1)	C(6)—C(7)—C(8)	128·7 (2)
S(1)—C(2)—N(3)	122·4 (2)	C(9)—C(8)—C(13)	121·7 (2)
S(1)—C(2)—C(7)	111·0 (2)	C(7)—C(8)—C(13)	111·6 (2)
N(3)—C(2)—C(7)	126·7 (2)	C(7)—C(8)—C(9)	126·6 (2)
C(2)—N(3)—C(4)	113·4 (2)	C(8)—C(9)—C(10)	111·9 (2)
N(3)—C(4)—N(5)	125·3 (3)	C(9)—C(10)—C(11)	112·3 (3)
C(4)—N(5)—C(6)	123·9 (2)	C(10)—C(11)—C(12)	113·0 (3)
N(5)—C(6)—C(7)	112·5 (2)	C(11)—C(12)—C(13)	109·9 (3)
N(5)—C(6)—O(14)	120·0 (2)	C(12)—C(13)—C(8)	126·1 (2)
C(7)—C(6)—O(14)	127·4 (2)	C(12)—C(13)—S(1)	121·3 (2)
C(6)—C(7)—C(2)	118·1 (2)	C(8)—C(13)—S(1)	112·6 (2)
C(8)—C(7)—C(2)	113·2 (2)		
C(8)—C(9)—C(10)—C(11)	45·2 (4)	C(11)—C(12)—C(13)—C(8)	−12·1 (4)
C(9)—C(10)—C(11)—C(12)	−59·3 (4)	C(13)—C(8)—C(9)—C(10)	−16·7 (4)
C(10)—C(11)—C(12)—C(13)	40·5 (4)	C(12)—C(13)—C(8)—C(9)	−0·1 (5)

atoms refined by full-matrix least-squares refinement using *SHELX*76 (Sheldrick, 1976). The hydrogen atoms, located from a difference Fourier map, were refined isotropically. At the final stage of refinement, weights were introduced resulting in $R = 0{\cdot}06$, $wR = 0{\cdot}07$. $w = 1/(\sigma^2|F_o| + 0{\cdot}00219|F_o|^2)$, $S = 1{\cdot}9$. Shift/e.s.d. < 0·1. Final difference Fourier map was featureless with $\Delta\rho$ within ± 16 e Å^{-3}. The atomic scattering factors used for all the atoms were as provided in the *SHELX*76 program. Computer programs: *PARST* (Nardelli, 1983) for geometrical calculations. Table 1 lists the final atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms.* The numbering scheme and molecular connectivity are given in the perspective view of Fig. 1. The bond lengths, bond angles and selected torsion angles are shown in Table 2.

Related literature. Biological activities of 2-aminothiophene and thieno[2,3-*d*]pyrimidine have attracted the attention of medicinal chemists (Nakanishi, Imamura & Maruyama, 1970; Wellings, 1972; Manhas, Sharma & Amin, 1972).

* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates, bond lengths and angles involving hydrogen atoms, torsion angles and least-squares-planes equations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52134 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 1,4,7,10-Tetraazacyclododecane Tetrahydrochloride

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Abstract. $[C_8H_{24}N_4]Cl_4$, $M_r = 318{\cdot}1$, orthorhombic, *Pbcn*, $a = 13{\cdot}788$ (3), $b = 9{\cdot}511$ (2), $c = 10{\cdot}643$ (2) Å, $V = 1395{\cdot}7$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}51$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 8{\cdot}35$ cm^{-1}, $F(000) = 672$, $T = 150$ K, $R = 0{\cdot}033$, $wR = 0{\cdot}045$ for 1136 unique observed reflections. The cations exhibit crystallographic twofold rotation symmetry and [3333] quadrangular conformation, with protonated N atoms occupying corner positions. Chloride counterions connect adjacent cations through hydrogen bonding.

Experimental. The title compound (also known as cyclen tetrahydrochloride, $[H_4cyclen]Cl_4$) was obtained by a literature method (Hay & Norman, 1979),

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and recrystallized by slow cooling from a supersaturated aqueous solution. Crystal size [0·14(001→00$\bar{1}$) × 0·40(110→$\bar{1}\bar{1}$0) × 0·48(1$\bar{1}$0→$\bar{1}$10)mm]. Nicolet *R*3*m* diffractometer, cell constants from a least-squares fit of setting angles for 24 reflections ($2\theta_{av}$ = 21·2°). Data collected for $3{\cdot}5 < 2\theta < 50°$, $0 \le h \le 12$, $-12 \le k \le 0$, $0 \le l \le 17$, utilizing ω (Wyckoff) scans. Control reflections (200, 0$\bar{2}$0, 002) monitored every 100 reflections, no significant variation. Data corrected for Lorentz and polarization factors, analytical absorption correction (T_{max} = 0·838, T_{min} = 0·688). Of 1444 measured reflections, 1136 [$F_o > 2{\cdot}5\sigma(F_o)$] used in calculations. Structure solved by Patterson map interpretation; full-matrix (91 parameters, data/parameters = 12·5) weighted $\{w = [\sigma^2(F) + g(F)^2]^{-1}$, $g = 8 \times 10^{-4}\}$ least-squares refinement on *F*. Non-H atoms refined anisotropically, C-bound H atoms in idealized positions [C—H = 0·96 Å, U(H) = 1·2 × U_{iso}(C)], N-bound H atoms located in a ΔF map and included in refinement. At convergence {mean Δ/σ = 0·001, max. Δ/σ = 0·003 [for *y*/*b*, Cl(2)] over last 2 cycles} R = 0·033, wR = 0·045, S = 1·32, slope of normal probability plot = 1·149, max. $\Delta\rho$ = +0·6 e Å^{-3} [near Cl(1), min. $\Delta\rho$ = −0·4 e Å^{-3}]. Neutral-atom scattering factors used (*International Tables for X-ray Crystallography*, 1974); software for diffractometer provided with Nicolet *R*3*m*; *SHELXTL* programs (Sheldrick, 1983) used for data reduction, structure solution, refinement and plotting. The structure of the cyclenH$_4^{4+}$ cation and the numbering scheme used are depicted in Fig. 1. Atomic coordinates are given in Table 1, and bond distances, bond angles and torsional angles are given in Table 2.*

* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52088 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

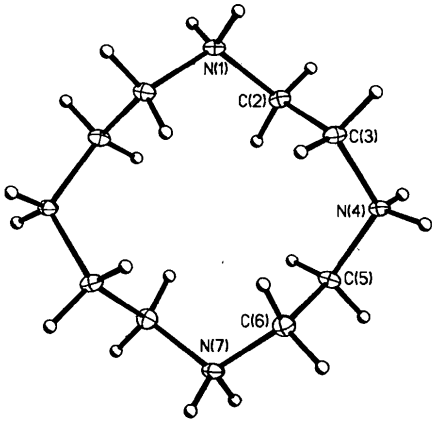

Fig. 1. Thermal ellipsoid plot (50% probability) of the cyclenH$_4^{4+}$ cation. H atoms have been drawn as spheres, with arbitrary radii.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

Estimated standard deviations in the least significant digits are given in parentheses.

	x	*y*	*z*	U_{iso}
N(1)	0·0000	0·5100 (2)	0·2500	0·0094 (7)
C(2)	0·0609 (1)	0·4265 (2)	0·1606 (2)	0·0111 (6)
C(3)	0·1446 (1)	0·3565 (2)	0·2304 (2)	0·0116 (6)
N(4)	0·1854 (1)	0·2333 (2)	0·1599 (2)	0·0098 (5)
C(5)	0·1203 (1)	0·1088 (2)	0·1413 (2)	0·0106 (6)
C(6)	0·0915 (1)	0·0395 (2)	0·2652 (2)	0·0119 (6)
N(7)	0·0000	−0·0429 (2)	0·2500	0·0108 (7)
Cl(1)	0·67214 (4)	0·17220 (5)	0·12050 (5)	0·0157 (2)
Cl(2)	0·40798 (4)	0·26748 (5)	0·05180 (4)	0·0115 (2)
H(1)	−0·042 (2)	0·563 (2)	0·204 (2)	0·012 (6)
H(7)	0·011 (2)	−0·102 (3)	0·190 (2)	0·021 (6)
H(4*a*)	0·201 (2)	0·258 (3)	0·084 (3)	0·016 (6)
H(4*b*)	0·246 (2)	0·207 (3)	0·204 (2)	0·027 (7)

* U_{iso} is defined as $\frac{1}{3}$ of the trace of the U tensor. H atoms listed were refined isotropically.

Table 2. *Bond lengths* (Å), *bond angles* (°), *hydrogen-bonding distances* (Å), *and torsion angles* (°)

Estimated standard deviations in the least significant digits are given in parentheses.

N(1)—C(2)	1·497 (2)	C(2)—C(3)	1·526 (3)
C(3)—N(4)	1·501 (3)	N(4)—C(5)	1·499 (3)
C(5)—C(6)	1·527 (3)	C(6)—N(7)	1·493 (2)
N(1)—H(1)	0·91 (2)	N(7)—H(7)	0·87 (3)
N(4)—H(4*a*)	0·87 (3)	N(4)—H(4*b*)	0·99 (2)
C(2)—N(1)—C(2′)	115·9 (2)	N(1)—C(2)—C(3)	110·3 (1)
C(2)—C(3)—N(4)	112·4 (2)	C(3)—N(4)—C(5)	117·3 (2)
N(4)—C(5)—C(6)	112·5 (2)	C(5)—C(6)—N(7)	110·6 (1)
C(6)—N(7)—C(6′)	116·8 (2)		
C(2′)—N(1)—C(2)—C(3)	−71·5 (1)	N(1)—C(2)—C(3)—N(4)	159·1 (2)
C(2)—C(3)—N(4)—C(5)	−65·0 (2)	C(3)—N(4)—C(5)—C(6)	−63·3 (2)
N(4)—C(5)—C(6)—N(7)	157·6 (2)	C(5)—C(6)—N(7)—C(6′)	−72·0 (1)
Cl(1)—H(4*a*)	2·31 (3)	Cl(1)—H(4*b*)	2·20 (3)
Cl(1)—H(1)	2·25 (2)	Cl(2)—H(7)	2·23 (2)
Cl(2)—H(4*a*)	2·87 (2)	Cl(2)—H(4*b*)	2·82 (2)

Related literature. The 'hole' sizes and conformations exhibited by tetraaza ring systems have been of considerable interest (Anichini, Fabbrizzi, Paoletti & Clay, 1977; Martin, DeHayes, Zompa & Busch, 1974; Hancock & McDougall, 1980; Thöm, Fox, Boeyens & Hancock, 1984; Hannongbua & Rode, 1985; Thöm, Hosken & Hancock, 1985). In cyclododecane (Dunitz & Shearer, 1960), azacyclododecane hydrochloride (Dunitz & Weber, 1964) and 2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane (Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978), the twelve-membered ring folds to form four repeating units, each containing two adjacent bonds with a *gauche* configuration and one bond with an *anti* configuration. This conformation, which establishes four 'corner' atoms, has been labeled a quadrangular [3333] conformation (Dale, 1980). The cyclenH$_4^{4+}$ ring also exists in the [3333]

quadrangular conformation, with the protonated N atoms located in corner positions (see Fig. 1).

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Structure of a Melanin Precursor: 1-Methylindole-5,6-diol

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Abstract. $C_9H_9NO_2$, $M_r = 163{\cdot}18$, rhombohedral, *R3c*, $a = 12{\cdot}814\ (4)$ Å, $\alpha = 114{\cdot}59\ (2)°$, $V = 1220{\cdot}4$ Å^3, $Z = 6$, $D_x = 1{\cdot}332$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}089$ mm^{-1}, $F(000) = 516$, $T = 293\ (1)$ K. $R = 0{\cdot}027$ for 410 observed reflections with $I > 3\sigma(I)$. The C—O distances in the catechol [1·396 (4) and 1·388 (5) Å] are identical. The indole moiety is planar with O(1) 0·139 (2) Å out of the plane of the indole moiety. The structure is stabilized by two short intermolecular distances O(1)···H(O1) 1·80 and O(1)···H(O2) 1·73 Å and there is a short intramolecular contact O(2)···H(O1) of 2·03 Å.

Experimental. A small crystal of approximate dimensions 0·16 × 0·17 × 0·32 mm was obtained by cutting a long needle. Accurate cell dimensions and a crystal orientation matrix were determined on an Enraf–Nonius CAD-4 diffractometer by a least-squares refinement of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data were collected by the $\omega/2\theta$ scan method and variable scan speed (0·55–3·5° min^{-1}) using graphite-monochromatized radiation in the range $2 < \theta < 25°$. The intensities of three standard reflections, monitored at regular intervals, did not decrease over the course of the data collection. Intensities of 790 reflections were measured, of which 410 had $I > 3\sigma(I)$, and were used in the structure solution and refinement. Data were corrected for Lorentz and polarization factors; absorption correction was deemed unnecessary.

The structure was solved by direct methods using *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Delcercq & Woolfson, 1982). Refinement of the structure was by full-matrix least-squares calculations on *F*'s, initially with isotropic and finally with anisotropic temperature factors for the non-H atoms. At an intermediate stage in the refinement, a difference map revealed all H atoms which were included in the subsequent cycles at fixed positions and with an overall isotropic thermal parameter. Refinement converged with $R = 0{\cdot}027$ and $wR = 0{\cdot}030$; maximum shift/e.s.d. < 0·02, $S = 1{\cdot}008$, and $w = 1/(\sigma^2F + 0{\cdot}040F^2)$. Scattering factors were those of Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). A difference map calculated at the conclusion of the refinement had no chemically significant features with electron density $\pm 0{\cdot}10$ e Å^{-3}. All computer programs used are part of the Enraf–

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