

Orthorhombic  
 $P2_12_12_1$   
 $a = 9.3972 (1) \text{ \AA}$   
 $b = 12.3917 (1) \text{ \AA}$   
 $c = 13.7857 (2) \text{ \AA}$   
 $V = 1605.31 (3) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.615 \text{ Mg m}^{-3}$   
 $D_m$  not measured

#### Data collection

Siemens CCD three-circle diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996a)  
 $T_{\min} = 0.383$ ,  $T_{\max} = 0.600$   
 17 926 measured reflections  
 2950 independent reflections

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.024$   
 $wR(F^2) = 0.043$   
 $S = 1.001$   
 2950 reflections  
 169 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0135P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

Cell parameters from 5772 reflections  
 $\theta = 1\text{--}25^\circ$   
 $\mu = 5.111 \text{ mm}^{-1}$   
 $T = 173 \text{ K}$   
 Block  
 $0.30 \times 0.10 \times 0.10 \text{ mm}$   
 Colourless, transparent

2576 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.055$   
 $\theta_{\max} = 26.02^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -14 \rightarrow 14$   
 $l = -16 \rightarrow 16$   
 305 standard reflections  
 frequency: 840 min  
 intensity decay: none

$\Delta\rho_{\max} = 0.266 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.399 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute structure: Flack (1983)  
 Flack parameter =  $-0.003 (8)$

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Si1—H1	1.37 (3)	Si1—N11	2.021 (2)
Si1—C1	1.870 (3)	Si1—Br1	2.2797 (9)
Si1—N1	2.018 (3)		
H1—Si1—C1	133.6 (11)	N1—Si1—N11	171.27 (11)
H1—Si1—N1	85.7 (11)	H1—Si1—Br1	112.9 (11)
C1—Si1—N1	92.81 (12)	C1—Si1—Br1	113.44 (10)
H1—Si1—N11	85.6 (11)	N1—Si1—Br1	92.35 (8)
C1—Si1—N11	93.35 (12)	N11—Si1—Br1	90.87 (8)

The data collection nominally covered a sphere of reciprocal space, by a combination of eight sets of exposures; each set had a different  $\varphi$  angle for the crystal and each exposure covered  $0.3^\circ$  in  $\omega$ . The crystal-to-detector distance was  $6.0 \text{ cm}$ . Coverage of the unique set was over 99% complete to at least  $25^\circ$  in  $\theta$ . Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. All H atoms could be located by difference Fourier synthesis. Whereas the H atom bonded to silicon was refined isotropically, the others were refined with fixed individual displacement parameters [ $U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$  or  $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ] using a riding model with  $\text{C—H}_{\text{methyl}} = 0.98$  or  $\text{C—H}_{\text{aromatic}} = 0.95 \text{ \AA}$ . The methyl groups were allowed to rotate about their local threefold axis.

Data collection: SMART (Siemens, 1995). Cell refinement: SMART. Data reduction: SAINT (Siemens, 1995). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL96 (Sheldrick, 1996b). Molecular graphics: XP in SHELXTL-Plus (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1258). Services for accessing these data are described at the back of the journal.

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### 1,10-Phenanthroline-1-ium Chloride Bis(1,10-phenanthroline) Solvate at 143 K

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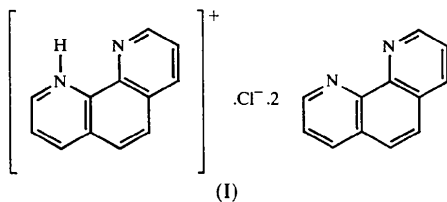
#### Abstract

The crystal and molecular structure of the title compound,  $\text{C}_{12}\text{H}_9\text{N}_2^+\text{Cl}^- \cdot 2\text{C}_{12}\text{H}_8\text{N}_2$ , has been determined at 143 K. It consists of three phenanthroline units and one

$Cl^-$  ion. One of the phenanthroline molecules is protonated at an N atom. In agreement with other authors, the protonated phenanthroline forms a hydrogen bond to another phenanthroline molecule. The third phenanthroline is not involved in any hydrogen bond at all. The C—N—C angle at the protonated N atom is significantly larger than the corresponding angle at the non-protonated N atom. Comparing the structure of the title compound with four similar structures, it was found that the angle between the phenanthroline molecules forming the hydrogen bond correlates with the distance between the two N atoms: with an increasing angle between the aromatic ring systems, the N...N distance decreases. For the  $Cl^-$  ion, six contacts less than 3 Å to H atoms (bound to C atoms) are observed.

### Comment

In the course of our work on Lewis acid–base reactions between silicon compounds and aromatic nitrogen heterocycles, we obtained single crystals of the title compound, (I). The reaction of 1,1-dichlorosilacyclopentane with 1,10-phenanthroline in benzene yields a white powder which precipitates from the solution. Hydrolysis by small amounts of humidity seems to be the cause of formation of compound (I).



The crystal structure of (I) consists of three discrete phenanthroline molecules of which one is protonated at one of the N atoms, and a  $Cl^-$  ion. Bond lengths are very similar in the three molecules, but the angle C50—N6—C51 [121.7(2)°] is significantly different from corresponding values, which range from 116.8(2)° at N5 to 117.6(2)° at N4. This result is in agreement with four similar structures, retrieved from the Cambridge Structural Database (Version 5.12, April 1997; Allen & Kennard, 1993) in which a hydrogen bond between a phenanthroline and a protonated phenanthroline is found:  $C_{24}H_{17}N_4^+.ClO_4^-$  (Maresca *et al.*, 1989),  $C_{12}H_9N_2^+.NO_3^- \cdot C_{12}H_8N_2 \cdot H_2O$  (Thevenet & Rodier, 1981), and  $C_{12}H_9N_2^+.C_5H_{10}I_2NS_2Te^- \cdot C_{12}H_8N_2$  and  $C_{12}H_9N_2^+.C_5H_{10}Br_2NS_2Te^- \cdot C_{12}H_8N_2$  (Krishnakumar *et al.*, 1996). The C—N—C angle at the protonated N atom in these four structures has a mean value of 118(2)°, whereas at the non-protonated N atom, the mean value is 122.8(9)°. Comparing the geometry of the corresponding hydrogen bonds with the angle between the phenanthroline molecules, which the hydrogen bond is formed between, reveals an interest-

ing correlation: when the angle between the two aromatic ring systems increases [38.9/42.6° in  $C_{24}H_{17}N_4^+.ClO_4^-$ ; 43.9° in  $C_{12}H_9N_2^+.NO_3^- \cdot C_{12}H_8N_2 \cdot H_2O$ ; 55.8° in  $C_{12}H_9N_2^+.C_5H_{10}I_2NS_2Te^- \cdot C_{12}H_8N_2$ ; 57.7° in  $C_{12}H_9N_2^+.C_5H_{10}Br_2NS_2Te^- \cdot C_{12}H_8N_2$  and 71.06(3)° in (I)], the distance between the two N atoms, connected by the hydrogen bond, decreases [3.01(3), 3.00(3), 2.967, 2.839, 2.842 and 2.784(3) Å, respectively].

An explanation for this effect may be that with an increasing angle between the aromatic planes, the repulsion between these planes is reduced and the two N atoms can form a shorter and stronger hydrogen bond.

The  $Cl^-$  ion does not form a hydrogen bond, but six contacts less than 3 Å to H atoms (bound to carbon) have been found:  $Cl1 \cdots H49$  2.716(3),  $Cl1 \cdots H9^i$  2.723(3),  $Cl1 \cdots H6^{ii}$  2.725(3),  $Cl1 \cdots H29^{ii}$  2.765(2),  $Cl1 \cdots H25^{iii}$  2.784(3) and  $Cl1 \cdots H28^{iv}$  2.822(3) Å [symmetry codes: (i) 2 - x, 2 - y, 1 - z; (ii) x,  $\frac{3}{2} - y$ , z -  $\frac{1}{2}$ ; (iii) x, 1 + y, z; (iv) 2 - x, 1 - y, 1 - z].

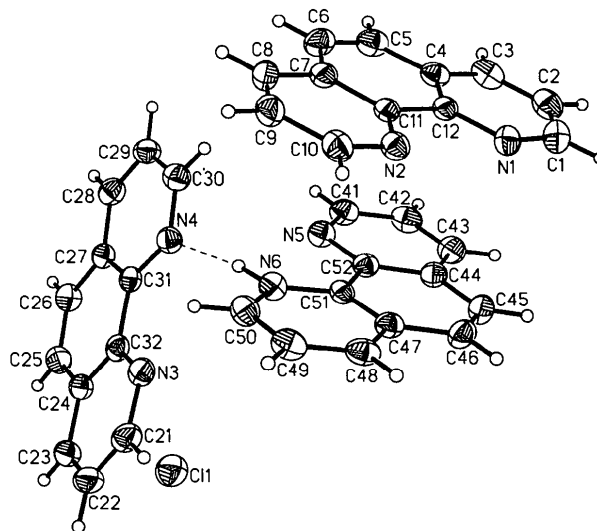


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

### Experimental

1,1-Dichlorosilacyclopentane (1.26 mmol) was dissolved in benzene (20 ml). During continuous stirring, a solution of 1,10-phenanthroline (1.2 mmol) in benzene (20 ml) was added. Immediately, a white powder began to precipitate. After removing benzene and drying *in vacuo* (2–3 mbar for 5 h; 1 mbar = 100 Pa), the powder was transferred into a glove box under argon. Crystals of the title compound were obtained by sublimation at  $10^{-4}$  mbar and 363 K.

#### Crystal data

$C_{12}H_9N_2^+.Cl^- \cdot 2C_{12}H_8N_2$   
 $M_r = 577.07$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å

Monoclinic	Cell parameters from 6993 reflections
$P2_1/c$	$\theta = 1-25^\circ$
$a = 12.9274 (1) \text{ \AA}$	$\mu = 0.176 \text{ mm}^{-1}$
$b = 10.7353 (1) \text{ \AA}$	$T = 143 \text{ K}$
$c = 20.1194 (2) \text{ \AA}$	Cube
$\beta = 92.849 (1)^\circ$	$0.20 \times 0.20 \times 0.20 \text{ mm}$
$V = 2788.71 (4) \text{ \AA}^3$	Colourless
$Z = 4$	
$D_x = 1.374 \text{ Mg m}^{-3}$	
$D_m$ not measured	

**Data collection**

Siemens CCD three-circle diffractometer	5723 independent reflections
$\omega$ scans	3841 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996a)	$R_{\text{int}} = 0.105$
$T_{\text{min}} = 0.733, T_{\text{max}} = 1.000$	$\theta_{\text{max}} = 26.52^\circ$
41 669 measured reflections	$h = -16 \rightarrow 16$
	$k = -13 \rightarrow 13$
	$l = -25 \rightarrow 25$

**Refinement**

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.054$	$\Delta\rho_{\text{max}} = 0.269 \text{ e \AA}^{-3}$
$wR(F^2) = 0.121$	$\Delta\rho_{\text{min}} = -0.281 \text{ e \AA}^{-3}$
$S = 1.063$	Extinction correction: <i>SHELXL96</i>
5723 reflections	Extinction coefficient: 0.0059 (7)
393 parameters	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
H atoms: see below	
$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 0.9665P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected bond angles ( $^\circ$ )

C1—N1—C12	117.3 (2)	C30—N4—C31	117.6 (2)
C10—N2—C11	117.3 (2)	C41—N5—C52	116.8 (2)
C21—N3—C32	117.2 (2)	C50—N6—C51	121.7 (2)

The data collection nominally covered a sphere of reciprocal space, by a combination of seven sets of exposures; each set had a different  $\varphi$  angle for the crystal and each exposure covered  $0.3^\circ$  in  $\omega$ . The crystal-to-detector distance was 5.95 cm. Coverage of the unique set is over 99% complete to at least  $26^\circ$  in  $\theta$ . Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. The data were corrected for Lorentz and polarization effects. All H atoms were located by difference Fourier synthesis and the H atoms bonded to carbon were refined with fixed individual displacement parameters [ $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ] using a riding model with C—H = 0.95 Å. The H6N atom was refined isotropically without any constraints or restraints.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS96* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996b). Molecular graphics: *XP* (Siemens, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1259). Services for accessing these data are described at the back of the journal.

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**6-Acetyl-3,4-dihydro-2,2-dimethyl-2H-benzopyran-3,7-diyl Diacetate**

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**Abstract**

The title compound,  $\text{C}_{17}\text{H}_{20}\text{O}_6$ , is an important precursor in the synthesis of a biologically active chalcone. It contains the dihydropyran unit in a distorted chair conformation, with the 3-acetoxy group arranged in an axial position.

**Comment**

3-Methyl-2-butenylated (prenylated) phenolics and their cyclic analogues are known to possess a variety of biological activities, *viz* antibacterial (Ahluwalia *et al.*, 1989), antifungal (Bhakuni & Chaturvedi, 1984),