

# 1-Aminoadamantane as Guest Molecule in Dodecasil 1H: an X-ray Crystallographic Study

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**Abstract.** Dodecasil 1H,  $34\text{SiO}_2 \cdot 3\text{M}^{12} \cdot 2\text{M}^{12'} \cdot 1\text{M}^{20}$  with  $\text{M}^{12}, \text{M}^{12'} = \text{N}_2$  and  $\text{M}^{20} = 1\text{-aminoadamantane}$ , is hexagonal with  $a = 13.825(2) \text{ \AA}$ ,  $c = 11.189(2) \text{ \AA}$  and crystallizes in space group  $P6/mmm$ . With 767 unique reflexions the structure has been refined to a weighted reliability factor  $R_w = 0.054$ . The three-dimensional four-connected host framework is built by corner sharing  $[\text{SiO}_4]$  tetrahedra and shows three types of cagelike voids,  $[5^{12}]$  cages,  $[4^3 5^6 6^3]$  cages and  $[5^{12} 6^8]$  cages, the latter housing the 1-aminoadamantane guest molecule. Difference Fourier synthesis  $\rho(\text{obs}) - \rho(\text{calc}(\text{Si}, \text{O}))$  delineate the guest molecules within the different types of cage. Residual electron densities reveal positional disorder of the 1-aminoadamantane guest molecule. Four crystallographically different preferred orientations for the 1-aminoadamantane guest molecule are found.

**Key words:** clathrasil, tectosilicate, 1-aminoadamantane, crystal structure.

## 1. Introduction

Clathrasils are clathrate compounds with silica frameworks. They represent a new class of porous tectosilicates with no exchange capacities for guest species and are, therefore, different from zeolites [1]. The polytypic series of dodecasils contains clathrasils which are built by linking hexagonal layers of face sharing pentagonal dodecahedra in various stacking sequences [2]. Dodecasil 1H is the simplest member of that polytypic series with  $\bar{A}\bar{A}$  stacking sequence. We report here on a crystallographic study of the orientational ordering of the 1-aminoadamantane guest species within the silica host framework.

## 2. Experimental

Crystals were synthesized under hydrothermal conditions. A 1M aqueous solution of ethylenediamine tetramethoxysilane was hydrolysed to give a 0.5 M homogeneous solution of silicic acid. The methanol formed through hydrolysis was not removed. 1-Aminoadamantane was added to the solution which was then sealed under nitrogen in silica tubes and kept at  $200^\circ\text{C}$  for about two weeks.

For X-ray data collection on a Philips PW1100 automatic four circle diffractometer a colourless prismatic hexagonal plate (edge:  $140 \mu\text{m}$ ; thickness:  $40 \mu\text{m}$ ) was selected. The intensities of 7680 reflexions were recorded in  $\omega$ - $2\theta$  scan mode ( $\theta \text{ max} = 50^\circ$ ) using graphite monochromatized  $\text{MoK}\alpha$  radiation. By averaging symmetrically equivalent intensities 2018 unique reflexions were obtained, 767 of which had  $|F_0| \geq 6 \sigma |F_0|$ . No corrections for absorption ( $\mu = 6.13 \text{ cm}^{-1}$ ) were applied. The SHELX-76 system was used for structure refinement [3] and the refined cell parameters were determined with the program LAT [4].

Table I. Atomic and thermal parameters  $U_{ij}$  [ $\text{\AA}^2$ ] with standard deviations. Temperature factors of the form

$$\exp[-2\pi^2(U_{11} \cdot h^2 \cdot a^{*2} \dots 2U_{12}hka^*b^*)], \quad B = 8\pi^2 \left[ \frac{(U_{11} + U_{22} + U_{33})}{3} \right]$$

Atom	No. of positions	x	y	z
Si(1)	12	0.4186(2)	0.2093(1)	0.2252(2)
Si(2)	12	0.3876(2)	0.0(0)	0.3618(2)
Si(3)	6	0.2625(3)	0.1313(2)	0.0(0)
Si(4)	4	0.3333(0)	0.6667(0)	0.1386(4)
O(1)	24	0.1048(5)	0.3934(6)	0.3028(5)
O(2)	12	0.5440(5)	0.2720(3)	0.8169(8)
O(3)	12	0.3386(6)	0.1693(3)	0.1142(7)
O(4)	6	0.3612(7)	0.0(0)	0.5(0)
O(5)	6	0.1860(7)	0.0(0)	0.0(0)
O(6)	6	0.5(0)	0.0(0)	0.3411(9)
O(7)	2	0.3333(0)	0.6667(0)	0.0(0)
N		0.0(0)	0.0(0)	0.2095(43)
C(1)		0.0(0)	0.0(0)	0.3410(41)
C(2)		0.1214(0)	0.0607(0)	0.3870(35)
C(3)		0.1214(0)	0.0607(0)	0.5248(37)
C(4)		0.0607(0)	0.1214(0)	0.5706(49)
[5 <sup>12</sup> ]-cage		0.5(0)	0.0(0)	0.0(0)
[4 <sup>3</sup> 5 <sup>5</sup> 6 <sup>3</sup> ]-cage		0.3333(0)	0.6667(0)	0.5(0)

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$B_{\text{eq}}$
Si(1)	0.0183(15)	0.0192(26)	0.0185(13)	-0.0059(26)	-0.0030(13)	0.0096(13)	1.474
Si(2)	0.0180(10)	0.0244(16)	0.0141(13)	0	-0.0055(10)	0.0122(8)	1.487
Si(3)	0.0100(20)	0.0238(17)	0.0204(21)	0	0	0.0050(10)	1.426
Si(4)	0.0230(17)	0.0230(17)	0.0142(26)	0	0	0.0115(8)	1.584
O(1)	0.0524(37)	0.1077(53)	0.0692(40)	0.0201(44)	0.0432(34)	0.0559(39)	6.035
O(2)	0.0156(40)	0.0771(52)	0.0845(72)	-0.0065(22)	-0.0129(45)	0.0078(20)	4.663
O(3)	0.0383(48)	0.0832(49)	0.0308(45)	0	0	0.0192(24)	4.116
O(4)	0.0452(47)	0.0873(96)	0.0168(50)	0	0	0.0437(48)	3.929
O(5)	0.0317(48)	0.0167(54)	0.0744(84)	0	0	0.0083(27)	3.232
O(6)	0.0449(44)	0.1243(114)	0.0309(67)	0	0	0.0662(57)	5.266
O(7)	0.2211(238)	0.2211(238)	0.0242(145)	0	0	0.1106(119)	12.275

Table II. (a) Interatomic distances of the 1-aminoadamantane guest molecule as obtained after refining a theoretical model using soft constraints on the guest molecule geometry. (b) Selected angles and distances of the silica host framework

(a)			(b)
Atoms	$d_{\text{obs}}$ [ $\text{\AA}$ ]	$d_{\text{calc}}$ [ $\text{\AA}$ ]	
N-C(1)	1.4715	1.4710	Si-O distances in the range of 1.543 $\text{\AA}$ - 1.589 $\text{\AA}$ ; $\bar{d}$ (Si-O) = 1.568 $\text{\AA}$
C(1)-C(2)	1.5417	1.5410	
C(2)-C(3)	1.5415	1.5410	Si-O-Si angles in the range of 166.9° - 180.0°; $\bar{\alpha}$ (Si-O-Si) = 170.52°
C(3)-C(4)	1.5412	1.5410	

### 3. Results of the Structure Refinement

The crystal structure of dodecasil 1H was first described with piperidine as guest molecule [5]. The title compound crystallizes with an isotypical  $\text{SiO}_2$  host framework in the hexagonal space group  $P6/mmm$  and  $a = 13.825(2)$  and  $c = 11.189(2)$  Å. Anisotropic refinement of the host framework with a data set up to  $\theta = 30^\circ$  converged at  $R = 0.204$ ,  $R_w = 0.127^*$  using all reflexions; the smaller data set with  $|F_0| \geq 6\sigma|F_0|$  and intensities up to  $\theta = 50^\circ$  led to  $R' = 0.138$ ,  $R'_w = 0.135$ . Considering the guest molecules within the cages as described later the residuals improved to  $R = 0.183$ ,  $R_w = 0.057$ ,  $R' = 0.114$ ,  $R'_w = 0.054$ . Final results, atomic parameters and selected bond angles and distances are listed in Tables I and II.

### 4. Description of the Structure

The  $\text{SiO}_2$  host framework (Figure 1) is isotopological with the one already described [5]; Si–O–Si angles,  $\angle(\text{Si–O–Si}) = 170.52^\circ$ , and Si–O distances,  $\bar{d}(\text{Si–O}) = 1.568$  Å, show remarkable deviations from the mean values of those from known  $\text{SiO}_2$  polymorphs ( $144^\circ$  for  $\angle(\text{Si–O–Si})$  [6];  $1.608$  Å for  $\bar{d}(\text{Si–O})$  [7]). This is in excellent agreement with the results obtained for dodecasil 1H with piperidine as guest molecule ( $\angle(\text{Si–O–Si}) = 170.6^\circ$ ;  $\bar{d}(\text{Si–O}) = 1.565$  Å) [5]. Although the difference in size of the guest species piperidine,  $\text{C}_6\text{NH}_{11}$ , and 1-aminoadamantane,  $\text{C}_{10}\text{NH}_{17}$ , is remarkable, no influence on angles and distances of the  $\text{SiO}_2$  host lattice could be detected. The geometry of the host lattice of the two phases is identical within the limits of experimental error. The unusually high temperature factors of the oxygen atoms indicate that these extreme values are strongly affected by static or dynamic disorder as described by Liebau [8].

Analysis of residual electron density maxima obtained from difference Fourier synthesis ( $\rho(\text{obs}) - \rho(\text{calc}(\text{Si}, \text{O}))$ ) shows that the  $\text{N}_2$  molecules present as guest species in the smaller dodecahedral [ $5^{12}$ ] and [ $4^3 5^6 6^3$ ] cages, are not randomly oriented but show preferred orientations similar to that already reported for dodecasil 1H synthesized with piperidine as

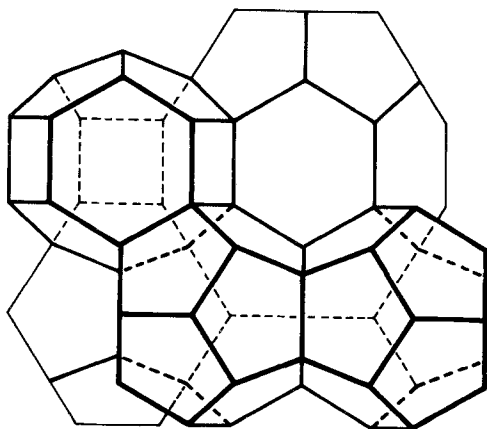


Fig. 1. Linkage of [ $5^{12}$ ], [ $4^3 5^6 6^3$ ] and [ $5^{12} 6^8$ ] cages in dodecasil 1H. Si atoms occupy the corners of the frame, O atoms are located near the middle of each Si–Si bond.

$$* R_w = \frac{\sum(|F_0| - |F_i|) \cdot \sqrt{w}}{\sum(|F_0|) \cdot \sqrt{w}}$$

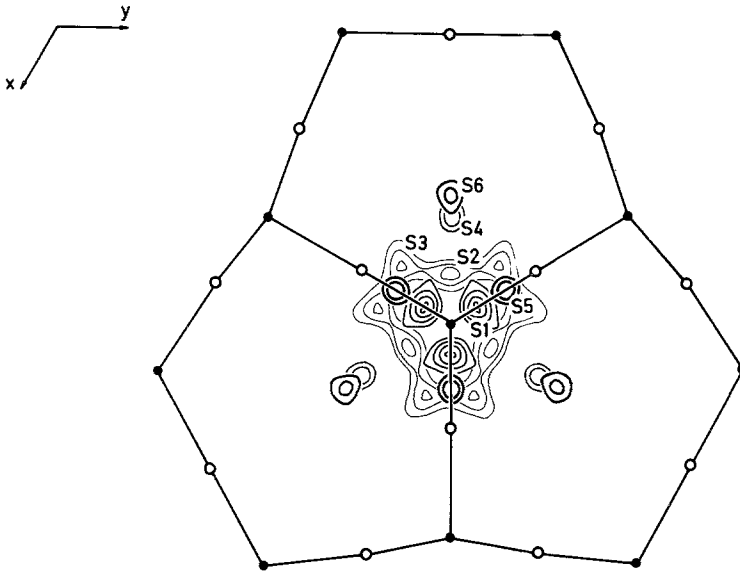


Fig. 2. Composite map of the residual electron density maxima in the  $[4^3 5^6 6^3]$  cage ( $\Delta_{\text{isoline}} = 0.37 e/\text{\AA}^3$ ; first line:  $0.75 e/\text{\AA}^3$ ). The cage is shown as a projection parallel to  $z$  with Si atoms as full circles and O atoms as open circles.

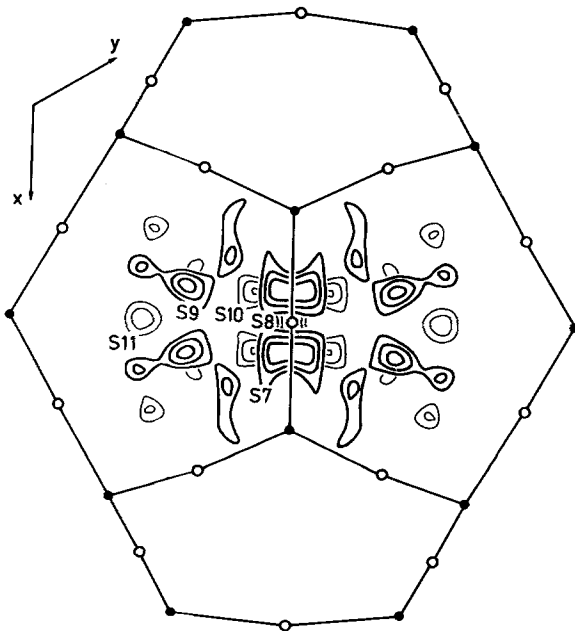


Fig. 3. Composite map of the residual electron density maxima in the  $[5^{12}]$  cage ( $\Delta_{\text{isoline}} = 0.37 e/\text{\AA}^3$ ; first line:  $0.75 e/\text{\AA}^3$ ). Only maxima exceeding  $1.25 e/\text{\AA}^3$  are marked. The cage is shown as a projection parallel to  $z$ ; Si atoms full circles, O atoms open circles.

$M^{20}$  [5] (Figures 2 and 3, Tables III and IV). No detailed discussions will be given. For structure refinement a single nitrogen atom in the centres of the cages has been used. To obtain the best least-squares fit temperature factors and site occupation factors have been refined

Table III. Positions and heights of the residual electron density maxima found in the  $[4^3 5^6 6^3]$  cage

Maximum	x	y	z	Height [ $e/\text{\AA}^3$ ]
S(1)	0.3161	0.6839	0.4530	1.80
S(2)	0.3629	0.6371	0.5000	1.57
S(3)	0.2653	0.5847	0.5000	1.53
S(4)	0.2144	0.6072	0.4519	1.38
S(5)	0.2964	0.5928	0.4203	1.35
S(6)	0.1860	0.5930	0.4105	1.23

to give an average in occupation of the cage with random orientation of the guest molecule (Table I).

In contrast to the 18-fold disordered piperidine guest molecule in [5], the 1-aminoadamantane guest molecule within the  $[5^{12}6^8]$  cage (point symmetry  $6/mmm$ ) clearly shows up from difference Fourier synthesis. The high symmetry of the guest molecule (point group  $3m$ ), the good fit in size, and the fact that the tricyclic carbon frame of the guest molecule remains more or less undistorted inside the cage enables us to analyze the orientational disorder of the 1-aminoadamantane guest molecule by means of X-ray crystallography.

The cubic point symmetry  $m\bar{3}$  of adamantane  $C_{10}H_{16}$  is reduced to trigonal  $3m$  by substitution of hydrogen in position 1 of the hydrocarbon molecule by  $-NH_2$ , assuming free rotation of the  $-NH_2$  group along the C–N bond. From geometric considerations the guest molecule should occupy the cage such that the threefold rotation axis of the guest molecule is parallel to the long axis of the cage. So the sixfold axis of the  $[5^{12}6^8]$  cage and the threefold axis of the guest molecule coincide. Since the point group  $3m$  of the guest molecule is a subgroup of point group  $6/mmm$  of the  $[5^{12}6^8]$  cage it is possible to obtain an undistorted representation of the guest in a difference Fourier synthesis calculated in space group  $6/mmm$ . Rotation of the guest along the threefold axis by  $60^\circ$  yields a set of two orientations with the threefold axis transformed to a six fold axis. Introducing a mirror plane perpendicular to the sixfold axis another set of two orientations of the guest molecule arises (Figures 4 and 5). So there are two possible guest molecule orientations with the amino group in an up position and two with the amino group in a down position. Assuming these four crystallographically different orientations for the 1-aminoadamantane guest, its average symmetry will become

Table IV. Positions and heights of the residual electron density maxima found in the  $[5^{12}]$  cage

Maximum	x	y	z	Maximum height [ $e/\text{\AA}^3$ ]
S(7)	0.4652	0	0	1.65
S(8)	0.5000	0	0.0472	1.61
S(9)	0.4734	0.8754	0	1.54
S(10)	0.4904	0.0422	0.0387	1.42
S(11)	0.4117	0.8233	0.0412	1.27

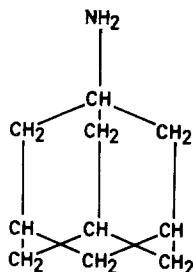


Fig. 4. 1-aminoadamantane guest molecule shown as isolated molecule.

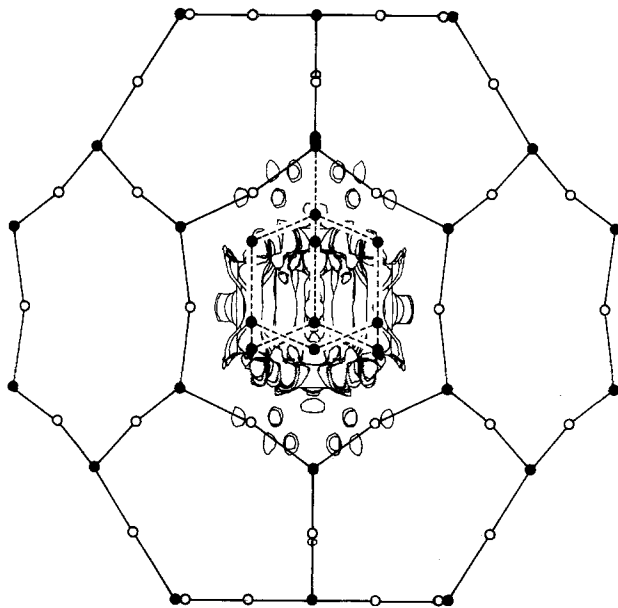


Fig. 5. Composite map of difference Fourier sections showing the residual electron density bigger than  $1.12 e/\text{\AA}^3$  in the  $[5^{12}6^8]$  cage. A series of sections representing one half of the cage starting from the cage centre is mapped. The 1-aminoadamantane guest molecule is included in one orientation as obtained from structure refinement. The cage is shown as a projection parallel to  $x$ ; Si atoms full circles, O atoms open circles.

$6/mmm$ , which is in agreement with the  $[5^{12}6^8]$  cage symmetry and the inherent symmetry of the data set.

The residual electron density obtained from difference Fourier synthesis clearly supports the model described above. Structure refinement with an 1-aminoadamantane model applying soft constraints (weight factor  $1/\sigma^2$ ;  $\sigma = 0.01$ ) on C—C and C—N bonds with  $d(\text{C—C}) = 1.541 \text{ \AA}$ ;  $d(\text{C—N}) = 1.471 \text{ \AA}$ , and  $\sigma(d) = 0.01 \text{ \AA}$  yields an ideal fit onto the diffraction data. Deviation of observed distances from those of the model were less than  $0.001 \text{ \AA}$  (Table II), the  $R_w$  value improved from 0.146 to 0.054.

The interpretation of the orientational disorder of 1-aminoadamantane is in good agreement with the rule proposed by Jewess [9] that only 'like' symmetry elements are significant for the interpretation of disorder from diffraction experiments, i.e., that the threefold axis of the guest

coincides with the sixfold axis of the host framework. To decide whether 1-aminoadamantane is statically or dynamically disordered, a series of experiments at different temperatures has to be performed.

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