3·43 Å, involving C(2)···C(7), C(7)···C(2), and C(8*a*)···C(8*a*) in both types of cation. In one level of the stacks the unlike cations are base-paired; in the other level their hydrophobic C(71) sides are juxtaposed.

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2,4-Diaminoquinazoline Monohydrate: A Redetermination

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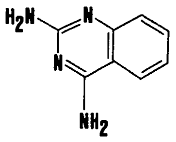
Abstract. $C_8H_8N_4.H_2O$, $M_r = 178{\cdot}20$, tetragonal, $I4_1/a$, $a = b = 21{\cdot}587\,(2)$, $c = 7{\cdot}622\,(2)$ Å, $U = 3551{\cdot}8$ Å^3, $Z = 16$, $D_x = 1{\cdot}333$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}792$ mm^{-1}, $F(000) = 1504$, $T = 291\,(2)$ K, final $R = 0{\cdot}045$ for 1697 observed reflections. Bond distances within the rings alternate as in naphthalene and exocyclic C—N bonds show considerable double-bond character. Neighboring diaminoquinazoline molecules are hydrogen bonded to water and to each other, stacked, and perpendicularly juxtaposed.

Introduction. 2,4-Diaminoquinazoline (I) is the parent compound of an interesting series of antifolate drugs (Hansch, Fukunaga, Jow & Hynes, 1977). Its structure was determined by Hunt, Schwalbe, Bird & Mallinson (1980), although the data suffered from inaccuracies attributed to the Renninger effect (Hunt, 1979). Two other structures in the 2,4-diaminoquinazoline (DAQ) series have also been determined: 2,4,6-triamino-5-chloroquinazoline (II) shows interesting $NH_2\cdots NH_2$ hydrogen bonding with partially pyramidal amino group geometry (Rogan & Williams, 1980), and diethyl *N*-[*p*-(2,4-diamino-6-quinazolinylmethyl)amino]benzoyl-aspartate is a powerful antifolate drug with similarities to methotrexate (Mastropaolo, Smith, Camerman & Camerman, 1981). To aid the discussion of substituent effects it appeared desirable to undertake a higher-precision structure determination of DAQ monohydrate.



(I)

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Experimental. Shiny octagonal prism grown from aqueous ethanol and bounded by faces at the following distances (mm) from an arbitrary origin within the crystal: (100), 0·001; (110), 0·001; (010), 0·11; $(\bar{1}10)$, 0·19; $(\bar{1}00)$, 0·26; $(\bar{1}\bar{1}0)$, 0·23; $(0\bar{1}0)$, 0·17; $(1\bar{1}0)$, 0·057; (001), 0·001; $(00\bar{1})$, 0·80. Unit-cell dimensions by least-squares analysis of setting angles of 25 reflections with θ values 16·20–72·23° measured with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å) or, where resolved, Cu $K\alpha_1$ ($\lambda = 1{\cdot}54051$ Å) on an Enraf–Nonius CAD-4 diffractometer. Data collection by means of ω–2θ scans, scan rate variable with intensity (0·84–3·35° min^{-1}), ω scan interval $(1{\cdot}50 + 0{\cdot}14\tan\theta)°$, background counts taken over the first and final sixths of the scan range. Intensity and orientation control reflections every 1 h and 100 reflections, respectively, remained steady throughout. Data corrected for Lorentz–polarization effects assuming an ideally mosaic monochromator, and for absorption by a Gaussian integration procedure (Busing & Levy, 1957) (range of transmission factors 0·717–0·851). During the late stages of refinement, correction for extinction by an empirical equation (Sheldrick, 1976). 4422 reflections measured between limits $-27 \leq h \leq 27$, $0 \leq k \leq 27$, $0 \leq l \leq 9$, $\theta \leq 78°$ were merged ($R_{\rm int} = \{\sum_{hkl}[N\sum_{\rm eq}w(\bar{F}-F)^2]/\sum_{hkl}[(N-1) \times \sum_{\rm eq}wF^2]\}^{1/2} = 0{\cdot}0086$) to give 1833 unique reflections; 1697 deemed observed ($F > 3\sigma$) and used in structure refinement. E.s.d.'s based on counting statistics as well as experimental instability of 0·02 times the net count.

The structure was independently solved by the *EEES* procedure in *SHELX76* (Sheldrick, 1976). All non-H atoms were located in an E map and refined with isotropic temperature factors. All H atoms then appeared in a difference electron density map. Final refinement adjusted positional parameters for all atoms, anisotropic thermal parameters for non-H atoms, and isotropic temperature factors for H atoms. Scattering factors were taken from Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H atoms. In the last cycle the highest ratio of shift to e.s.d. was 0·06. The function minimized was $\sum w(|F_o| - |F_c|)^2$, in which reflections were weighted by $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$, where k converged to 5·3487 and g converged to 0·000188, suggesting no unexpected instability. The final discrepancy indices for observed data were $R = 0{\cdot}045$ and $wR = 0{\cdot}058$. A final difference Fourier synthesis showed no feature larger than $\pm 0{\cdot}08$ e Å^{-3}.

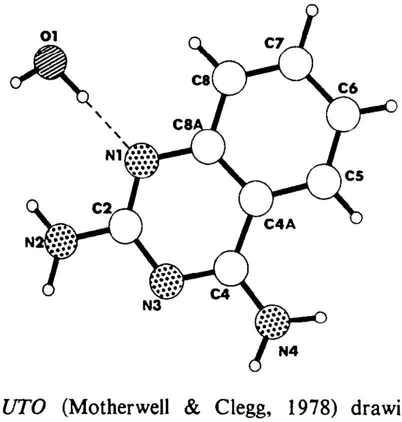

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule and solvent projected onto their least-squares plane. N atoms are stippled and the O atom is hatched.

Discussion. The molecule with its numbering scheme is depicted in Fig. 1. Final atomic coordinates are given in Table 1, with bond distances and angles in Table 2 and hydrogen-bond geometry in Table 3.*

The agreement between this study and its less precise predecessor (Hunt, Schwalbe, Bird & Mallinson, 1980) is reasonable: for bond distances between non-H atoms, the average difference is 0·008 Å (1σ) and the worst discrepancy [for N(1)—C(2)] is 4σ; for bond angles the average difference is 0·5° (1σ) and the worst case is C(6)—C(7)—C(8) ($3{\cdot}5\sigma$). The shortening of the 1–2, 3–4, 5–6, and 7–8 bonds relative to others in naphthalene and its derivatives is evident in this bicyclic system too. The C—N bonds N(1)—C(2) and N(3)—C(4) are almost equal in length and about 0·03 Å shorter than the intervening C(2)—N(3) bond; a similar statement can be made about the C—C bonds C(5)—C(6) and C(7)—C(8) relative to C(6)—C(7). The N(4) amino group appears to donate more electron density to the ring than N(2) as judged from the shorter C(4)—N(4) bond which has more double-bond character than C(2)—N(2). Bond angles at the unsubstituted ring N atoms N(1) and N(3) are less than 120° in accord with valence-shell electron-pair repulsion effects. The distortion thus introduced is compensated mainly at C(2) with an internal ring angle of 127·3 (1)°. The internal ring angle directly opposite, C(4)—C(4*a*)—C(8*a*), is considerably less than 120°; other angles within both rings are fairly near the ideal 120°. The amino groups of each molecule are bent slightly toward each other.

It is now possible to ascertain the effect of 5-chloro-6-amino substitution [structure (II)] on the 2,4-diaminoquinazoline system (Rogan & Williams, 1980). Introduction of a third amino group slightly reduces the demand for electrons from the other two: for (II) the distances C(2)—N(2) and C(4)—N(4) are lengthened by 0·009 (4) and 0·007 (4) Å, respectively,

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* Lists of structure factors, anisotropic thermal parameters, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42924 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic vibration terms*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}*(Å^2)
O(1)	1989 (1)	4542 (1)	4158 (1)	484 (3)
N(1)	2022 (1)	3477 (1)	2256 (2)	383 (3)
C(2)	2256 (1)	3473 (1)	652 (2)	361 (3)
N(2)	2523 (1)	4007 (1)	69 (2)	526 (4)
N(3)	2247 (1)	2999 (1)	−515 (1)	373 (3)
C(4)	1977 (1)	2478 (1)	−3 (2)	367 (3)
N(4)	1986 (1)	2000 (1)	−1123 (2)	537 (4)
C(4*a*)	1679 (1)	2427 (1)	1687 (2)	363 (4)
C(5)	1357 (1)	1901 (1)	2266 (2)	548 (5)
C(6)	1081 (1)	1894 (1)	3887 (3)	632 (6)
C(7)	1123 (1)	2413 (1)	4972 (2)	557 (5)
C(8)	1437 (1)	2930 (1)	4442 (2)	460 (4)
C(8*a*)	1720 (1)	2948 (1)	2775 (2)	345 (3)
H(11)	198 (1)	417 (1)	345 (3)	85 (7)
H(12)	202 (1)	486 (1)	333 (3)	93 (8)
H(21)	265 (1)	430 (1)	96 (4)	116 (10)
H(22)	277 (1)	399 (1)	−103 (3)	71 (6)
H(41)	222 (1)	203 (1)	−215 (4)	86 (8)
H(42)	184 (1)	159 (1)	−81 (3)	77 (7)
H(5)	130 (1)	156 (1)	148 (3)	68 (6)
H(6)	89 (1)	151 (1)	424 (3)	77 (7)
H(7)	93 (1)	239 (1)	631 (3)	75 (6)
H(8)	148 (8)	330 (1)	521 (3)	60 (6)

* Isotropic temperature factors for H atoms. All parameters have been multiplied by 10^4 for non-H atoms and by 10^3 for H atoms.

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

N(1)–C(2)	1·323 (2)	C(5)–C(6)	1·372 (2)
C(2)–N(2)	1·363 (2)	C(6)–C(7)	1·395 (3)
C(2)–N(3)	1·356 (2)	C(7)–C(8)	1·367 (2)
N(3)–C(4)	1·325 (2)	C(8)–C(8*a*)	1·410 (2)
C(4)–N(4)	1·339 (2)	C(4*a*)–C(8*a*)	1·400 (2)
C(4)–C(4*a*)	1·444 (2)	N(1)–C(8*a*)	1·373 (2)
C(4*a*)–C(5)	1·403 (2)		
C(2)–N(1)–C(8*a*)	116·2 (1)	C(8*a*)–C(4*a*)–C(4)	116·0 (1)
N(3)–C(2)–N(1)	127·3 (1)	C(8*a*)–C(4*a*)–C(5)	119·7 (1)
N(2)–C(2)–N(1)	117·2 (1)	C(6)–C(5)–C(4*a*)	120·5 (2)
N(2)–C(2)–N(3)	115·5 (1)	C(7)–C(6)–C(5)	119·8 (2)
C(4)–N(3)–C(2)	117·0 (1)	C(8)–C(7)–C(6)	120·8 (2)
C(4*a*)–C(4)–N(3)	121·5 (1)	C(8*a*)–C(8)–C(7)	120·2 (1)
N(4)–C(4)–N(3)	117·4 (1)	N(1)–C(8*a*)–C(8)	119·2 (1)
N(4)–C(4)–C(4*a*)	121·1 (1)	N(1)–C(8*a*)–C(4*a*)	121·8 (1)
C(5)–C(4*a*)–C(4)	124·3 (1)	C(8)–C(8*a*)–C(4*a*)	119·0 (1)

Table 3. *Hydrogen-bond angles and contact distances with e.s.d.'s in parentheses*

	Angle at H (°)	N···O (Å)
O(1)–H(11)···N(1^{i})	177 (2)	2·719 (2)
O(1)–H(12)···O(1^{ii})	177 (2)	2·832 (2)
N(2)–H(22)···O(1^{iii})	142 (2)	2·954 (2)
N(4)–H(41)···N(3^{iv})	174 (2)	3·051 (2)
N(4)–H(42)···O(1^{v})	138 (2)	3·242 (2)

Symmetry code: (i) x, y, z; (ii) $-0{\cdot}25+y, 0{\cdot}75-x, -0{\cdot}25+z$; (iii) $0{\cdot}75-y, 0{\cdot}25+x, -0{\cdot}75+z$; (iv) $0{\cdot}5-x, 0{\cdot}5-y, -0{\cdot}5-z$; (v) $-0{\cdot}25+y, 0{\cdot}25-x, 0{\cdot}25-z$.

relative to their values in the present structure. Steric hindrance involving the extra substituents is probably responsible for the lengthening of C(4*a*)–C(5) and C(5)–C(6) in (II), and also for additional bending of the N(4) amino group toward N(2).

Packing of DAQ molecules in the unit cell is controlled by hydrogen bonding (Table 3), in which water plays a key role (Fig. 2), and by stacking. The water molecules are hydrogen bonded to form infinite spirals along the 4_1 and 4_3 axes. Successive O···O distances are 2·832 (2) Å. Each DAQ molecule is attached to the spiral at two points: by acceptance at N(1) of water proton H(11) and by donation of proton H(22) from amino N(2) to a water O atom three-quarters of a turn down the spiral. The N···O distances of 2·719 (2) and 2·954 (2) Å, respectively, show that the former interaction is quite strong; its N···H distance is only 1·75 (2) Å. DAQ molecules are clustered around the spirals with a 67·1 (4)° angle between the screw axis and the normal to the quinazoline least-squares plane. DAQ molecules are linked in pairs by the usual N(4)–H(41)···N(3′) hydrogen bonds about a center of symmetry (Koetzle & Williams, 1976). The N···N distance of 3·051 (2) Å is typical for such systems. This mode of packing places N(4) 3·242 (2) Å from a water O atom and permits H(42) to be weakly hydrogen bonded. On each amino group the N–H distance to the one strongly hydrogen-bonded atom is 0·02–0·04 Å (1–2σ) longer than to the other H atom. This effect of hydrogen bonding was observed with great precision in a neutron diffraction study of trimethoprim (Koetzle & Williams, 1976).

DAQ molecules form stacked pairs across centers of symmetry at the Wyckoff *c* positions. The benzene ring of one molecule covers the pyrimidine ring of another. Packing of the molecules is completed by edge-on contact between the benzene ring of one molecule and a pyrimidine moiety from a different stack.

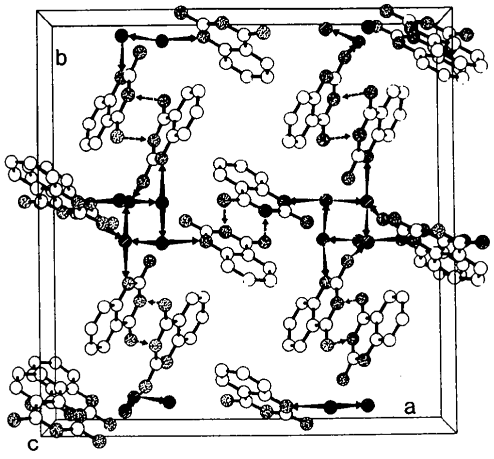

Fig. 2. The unit-cell contents viewed down **c**. Hydrogen bonds are shown as arrows from proton donor to proton acceptor; those to molecules in an adjacent unit cell are depicted by dashed lines.

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3-[(*Z*)-*p*-Chlorophenylthio-(*E*)-trimethylsilylmethylidene]-1,4-dimethyl-4-trimethylsilylazetidin-2-one: an α-Alkylidene-*β*-lactam

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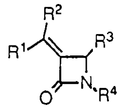
Abstract. $C_{18}H_{28}ClNOSSi_2$, $M_r = 398{\cdot}12$, triclinic, $P\bar{1}$, $a = 10{\cdot}943\ (3)$, $b = 13{\cdot}018\ (3)$, $c = 8{\cdot}074\ (1)$ Å, $\alpha = 76{\cdot}74\ (1)$, $\beta = 99{\cdot}04\ (2)$, $\gamma = 90{\cdot}27\ (2)°$, $V = 1105{\cdot}0\ (4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}196$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 3{\cdot}34$ cm^{-1}, $F(000) = 424$, $T = 295$ K, final $R = 0{\cdot}044$ for 2908 observed reflections. The *β*-lactam ring is approximately planar with none of its four atoms deviating by more than 0·018 (3) Å from their least-squares plane. The structure shows that 3-[(*Z*)-*p*-chlorophenylthio-(*E*)-trimethylsilylmethylidene]-4-methyl-4-trimethylsilylazetidin-2-one, which is formed by addition of chlorosulfonylisocyanate (CSI) to the allene (Me)(Me$_3$Si)-$C^3{=}C^2{=}C^1(SiMe_3)(SC_6H_4Cl)$, results from CSI addition to the $C^2{=}C^3$ bond and not to the $C^1{=}C^2$ bond as found for several other closely related allenes.



(1)

Introduction. Several potent *β*-lactamase inhibitors possess the α-alkylidene-*β*-lactam subunit (1). Included in this class are the asparenomycins (Kawamura, Yasuda, Mayama & Tanaka, 1982), Ro15-1903 (Arisawa & Then, 1982) and 6-[(*Z*)-methoxymethylene]-penicillanic acid (Brenner, 1985). We have recently developed a strategy to prepare synthetically versatile members of this class *via* the addition of chlorosulfonylisocyanate, CSI, to functionalized allenes (Buynak, Pajouhesh, Lively & Ramalakshmi, 1984; Buynak, Rao, Pajouhesh, Chandrasekaran, Finn, de Meester & Chu, 1985; Buynak, Rao, Chandrasekaran, Haley, de Meester & Chu, 1985). The reaction of CSI with olefins is well documented (Rasmussen & Hassner, 1976). The 2 + 2 addition occurs in a stereo- and regiospecific fashion with the N atom bonding to that C atom bearing the highest degree of carbocation-

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