# Structure of a Pentaazabicyclononane

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**Abstract.** 4-Benzamido-2,7-dibenzoyl-1,2,4,6,7-penta-azabicyclo[4.2.1]nonane, $C_{25}H_{24}N_6O_3$, $M_r = 456 \cdot 51$, triclinic, $P\bar{1}$, $a = 9 \cdot 195$ (1), $b = 11 \cdot 457$ (2), $c = 12 \cdot 139$ (2) Å, $\alpha = 89 \cdot 77$ (2), $\beta = 72 \cdot 79$ (1), $\gamma = 76 \cdot 52$ (1)°, $V = 1184 \cdot 9$ (4) Å$^3$, $Z = 2$, $D_x = 1 \cdot 279$ g cm$^{-3}$, $\lambda$(Cu $K\alpha$) = $1 \cdot 54178$ Å, $\mu = 6 \cdot 74$ cm$^{-1}$, $F(000) = 480$, $T = 295$ K, final $R = 0 \cdot 056$ for 2421 independent observed reflections. In this molecule the bicyclononane cage is slightly 'twisted' about an axis through the bridgehead N atoms. The bonds from the bridgehead N atoms to the neighboring cage atoms are nearly eclipsed; the Newman projection down this axis has angles of N—N = $0 \cdot 0$ and N—C = $8 \cdot 4°$ for the four-atom bridge, N—C = $109 \cdot 1$ and N—N = $115 \cdot 3°$ for the two-atom bridge, and N—C = $255 \cdot 3°$ for the single-atom bridge.

**Experimental.** Clear $0 \cdot 32 \times 0 \cdot 21 \times 0 \cdot 08$ mm crystal, recrystallized from ethanol. Synthesized by G. Kumar and J. Boyer of the University of Illinois at Chicago. Automated Nicolet $R3m$ diffractometer with incident-beam graphite monochromator (Cu $K\alpha$), 25 centered reflections within $39 \leq 2\theta \leq 60°$ used for determining lattice parameters. Data corrected for Lorentz, polarization, but not for absorption effects, $(\sin\theta/\lambda)_{max} = 0 \cdot 57$ Å$^{-1}$, range of $hkl$: $-10 \leq h \leq 6$, $-12 \leq k \leq 11$, $-13 \leq l \leq 8$. Standards 005, 060, 520, monitored every 60 reflections with linear variation of $5 \cdot 4\%$ over data collection, $\theta$–$2\theta$ mode, scan width $(1 \cdot 8 +$

Table 1. *Atom coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$)

| | $x$ | $y$ | $z$ | $U_{eq}$* |
|---|---|---|---|---|
| N(1) | 11097 (3) | 2273 (2) | 2142 (2) | 52 (1) |
| N(2) | 9636 (3) | 2549 (2) | 3018 (2) | 54 (1) |
| C(3) | 9000 (4) | 1595 (3) | 3681 (3) | 53 (1) |
| N(4) | 9366 (3) | 545 (2) | 2903 (2) | 48 (1) |
| C(5) | 10910 (4) | −267 (3) | 2758 (3) | 53 (1) |
| N(6) | 12201 (3) | 174 (2) | 1998 (2) | 51 (1) |
| N(7) | 11863 (3) | 509 (2) | 950 (2) | 51 (1) |
| C(8) | 11032 (4) | 1795 (3) | 1051 (3) | 59 (1) |
| C(9) | 12304 (4) | 1346 (3) | 2420 (2) | 54 (1) |
| C(10) | 9200 (4) | 3669 (3) | 3526 (3) | 68 (2) |
| O(11) | 8270 (3) | 3899 (2) | 4509 (2) | 98 (1) |
| C(12) | 9840 (4) | 4637 (3) | 2861 (3) | 63 (2) |
| C(13) | 9466 (5) | 4974 (4) | 1895 (3) | 104 (2) |
| C(14) | 9976 (7) | 5923 (4) | 1303 (4) | 131 (3) |
| C(15) | 10846 (6) | 6522 (3) | 1698 (4) | 110 (3) |
| C(16) | 11237 (5) | 6174 (4) | 2661 (4) | 96 (2) |
| C(17) | 10718 (4) | 5242 (3) | 3259 (3) | 81 (2) |
| N(18) | 8160 (3) | −67 (2) | 3119 (2) | 54 (1) |
| C(19) | 7832 (4) | −724 (3) | 4048 (3) | 53 (1) |
| O(20) | 8428 (3) | −703 (2) | 4820 (2) | 71 (1) |
| C(21) | 6729 (4) | −1494 (3) | 4052 (2) | 50 (1) |
| C(22) | 6882 (4) | −2530 (3) | 4620 (3) | 72 (2) |
| C(23) | 5929 (5) | −3304 (3) | 4617 (4) | 85 (2) |
| C(24) | 4812 (4) | −3040 (4) | 4066 (4) | 83 (2) |
| C(25) | 4633 (4) | −2002 (4) | 3524 (4) | 90 (2) |
| C(26) | 5593 (4) | −1230 (3) | 3504 (3) | 73 (2) |
| C(27) | 12488 (4) | −112 (3) | −78 (3) | 54 (1) |
| O(28) | 12137 (3) | 373 (2) | −909 (2) | 77 (1) |
| C(29) | 13515 (4) | −1349 (3) | −223 (3) | 61 (1) |
| C(30) | 14510 (4) | −1776 (3) | 422 (3) | 75 (2) |
| C(31) | 15473 (5) | −2936 (4) | 176 (4) | 107 (2) |
| C(32) | 15453 (6) | −3660 (4) | −716 (4) | 124 (3) |
| C(33) | 14485 (5) | −3232 (3) | −1362 (4) | 117 (2) |
| C(34) | 13526 (4) | −2088 (3) | −1134 (3) | 83 (2) |

\* Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

| | | | | |
|---|---|---|---|---|
| N(1)–N(2) | 1·412 (3) | N(1)–C(8) | 1·458 (4) | |
| N(1)–C(9) | 1·464 (4) | N(2)–C(3) | 1·482 (4) | |
| N(2)–C(10) | 1·345 (4) | C(3)–N(4) | 1·445 (4) | |
| N(4)–C(5) | 1·466 (4) | N(4)–N(18) | 1·406 (4) | |
| C(5)–N(6) | 1·464 (4) | N(6)–N(7) | 1·426 (4) | |
| N(6)–C(9) | 1·473 (4) | N(7)–C(8) | 1·481 (4) | |
| N(7)–C(27) | 1·337 (3) | C(10)–O(11) | 1·232 (4) | |
| C(10)–C(12) | 1·498 (5) | C(12)–C(13) | 1·347 (6) | |
| C(12)–C(17) | 1·364 (6) | C(13)–C(14) | 1·396 (6) | |
| C(14)–C(15) | 1·352 (8) | C(15)–C(16) | 1·354 (7) | |
| C(16)–C(17) | 1·386 (6) | N(18)–C(19) | 1·351 (4) | |
| C(19)–O(20) | 1·219 (4) | C(19)–C(21) | 1·490 (5) | |
| C(21)–C(22) | 1·370 (5) | C(21)–C(26) | 1·374 (5) | |
| C(22)–C(23) | 1·386 (6) | C(23)–C(24) | 1·361 (7) | |
| C(24)–C(25) | 1·357 (6) | C(25)–C(26) | 1·383 (6) | |
| C(27)–O(28) | 1·239 (4) | C(27)–C(29) | 1·487 (4) | |
| C(29)–C(30) | 1·379 (5) | C(29)–C(34) | 1·391 (5) | |
| C(30)–C(31) | 1·392 (5) | C(31)–C(32) | 1·373 (8) | |
| C(32)–C(33) | 1·361 (8) | C(33)–C(34) | 1·375 (5) | |
| | | | | |
| N(2)–N(1)–C(8) | 113·8 (3) | N(2)–N(1)–C(9) | 114·0 (2) | |
| C(8)–N(1)–C(9) | 103·4 (2) | N(1)–N(2)–C(3) | 121·3 (2) | |
| N(1)–N(2)–C(10) | 115·0 (2) | C(3)–N(2)–C(10) | 118·3 (2) | |
| N(2)–C(3)–N(4) | 108·5 (2) | C(3)–N(4)–C(5) | 114·6 (3) | |
| C(3)–N(4)–N(18) | 113·7 (2) | C(5)–N(4)–N(18) | 112·6 (2) | |
| N(4)–C(5)–N(6) | 113·1 (2) | C(5)–N(6)–N(7) | 109·7 (3) | |
| C(5)–N(6)–C(9) | 113·2 (2) | N(7)–N(6)–C(9) | 99·4 (2) | |
| N(6)–N(7)–C(8) | 110·6 (2) | N(6)–N(7)–C(27) | 126·7 (2) | |
| C(8)–N(7)–C(27) | 121·0 (2) | N(1)–C(8)–N(7) | 104·9 (2) | |
| N(1)–C(9)–N(6) | 107·4 (3) | N(2)–C(10)–O(11) | 120·7 (3) | |
| N(2)–C(10)–C(12) | 118·6 (3) | O(11)–C(10)–C(12) | 120·7 (3) | |
| C(10)–C(12)–C(13) | 120·0 (4) | C(10)–C(12)–C(17) | 120·9 (3) | |
| C(13)–C(12)–C(17) | 119·0 (4) | C(12)–C(13)–C(14) | 120·7 (5) | |
| C(13)–C(14)–C(15) | 120·2 (5) | C(14)–C(15)–C(16) | 119·0 (4) | |
| C(15)–C(16)–C(17) | 120·9 (5) | C(12)–C(17)–C(16) | 120·1 (4) | |
| N(4)–N(18)–C(19) | 121·9 (3) | N(18)–C(19)–O(20) | 122·0 (3) | |
| N(18)–C(19)–C(21) | 115·6 (3) | O(20)–C(19)–C(21) | 122·4 (3) | |
| C(19)–C(21)–C(22) | 117·7 (3) | C(19)–C(21)–C(26) | 123·6 (3) | |
| C(22)–C(21)–C(26) | 118·6 (4) | C(21)–C(22)–C(23) | 120·3 (4) | |
| C(22)–C(23)–C(24) | 120·6 (4) | C(23)–C(24)–C(25) | 119·2 (4) | |
| C(24)–C(25)–C(26) | 120·8 (4) | C(21)–C(26)–C(25) | 120·4 (3) | |
| N(7)–C(27)–O(28) | 117·1 (3) | N(7)–C(27)–C(29) | 122·0 (3) | |
| O(28)–C(27)–C(29) | 120·9 (3) | C(27)–C(29)–C(30) | 125·0 (3) | |
| C(27)–C(29)–C(34) | 116·2 (3) | C(30)–C(29)–C(34) | 118·7 (3) | |
| C(29)–C(30)–C(31) | 120·1 (4) | C(30)–C(31)–C(32) | 120·5 (5) | |
| C(31)–C(32)–C(33) | 119·4 (4) | C(32)–C(33)–C(34) | 121·0 (4) | |
| C(29)–C(34)–C(33) | 120·3 (4) | | | |

$\Delta_{\alpha 1\alpha 2})°$, scan rate a function of count rate ($8°$ min$^{-1}$ minimum, $30°$ min$^{-1}$ maximum), 3448 reflections measured, 3131 unique, $R_{int} = 0.018$, 2421 observed with $F_o > 3\sigma(F_o)$. Structure solved by direct methods. The least-squares refinement used program SHELXTL (Sheldrick, 1980). $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$, $g = 0.00023$, isotropic secondary-extinction value, $p = 0.0026$ (5), in $F_c^* = F_c/[1.0 + 0.002(p)F_o^2/\sin 2\theta]^{0.25}$. 344 parameters refined: atom coordinates, anisotropic temperature factors for all non-H atoms, isotropic temperature factors for H, benzene-ring H atoms included using riding model, C–H = 0.96 Å, C–C–H = 120.0°, $1.1 U_{eq}(C)$. $(\Delta/\sigma)_{max} = -0.008$, $R = 0.056$, $wR = 0.057$, $S = 1.512$. Final difference Fourier map excursions 0.40 and $-0.23$ e Å$^{-3}$. Atomic scattering factors from International Tables for X-ray Crystallography (1974).† Atom numbering for Tables 1 and 2 (atom parameters, bond distances and bond angles) follows that shown in Fig. 1. The hydrogen-bond parameters are: $H(18)\cdots O(28)' = 1.98$ (3), $N(18)\cdots O(28)' = 2.808$ (5) Å, and N–H$\cdots$O = $168.9$ $(1.8)°$.

**Related literature.** The title compound and a closely related pentaazabicyclo[3.2.2]nonane are products of a benzoylhydrazine/formaldehyde/orthoformate conden-
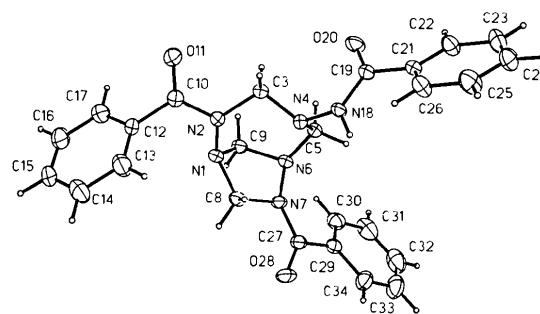


Fig. 1. Thermal-ellipsoid plot of 4-benzamido-2,7-dibenzoyl-1,2,4,6,7-pentaazabicyclo[4.2.1]nonane, drawn at 20% probability level.

sation reaction which proceeds through the intermediate compound 1,3,5-tribenzamido-1,3,5-hexahydrotriazine. For the structure of the pentaazabicyclo[3.2.2]-nonane see George (1987). For the structure of the hexahydrotriazine see George & Gilardi (1987).

† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43455 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**References**

George, C. (1987). Acta Cryst. Submitted.
George, C. & Gilardi, R. (1987). Acta Cryst. C43, 1003–1005.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Sheldrick, G. M. (1980). SHELXTL. Minicomputer programs for structure determination. Univ. of Gottingen.

# Structure of a Substituted Hexahydrotriazine

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**Abstract.** 1,3,5-Tribenzamido-1,3,5-hexahydrotriazine monohydrate, $C_{24}H_{24}N_6O_3.H_2O$, $M_r = 462.51$, monoclinic, $P2_1/c$, $a = 12.655$ (1), $b = 14.721$ (2), $c = 13.339$ (2) Å, $\beta = 107.25$ (1)°, $V = 2373.2$ (5) Å$^3$, $Z = 4$, $D_x = 1.294$ Mg m$^{-3}$, $\lambda$(Cu K$\alpha$) = $1.54178$ Å, $\mu = 0.709$ mm$^{-1}$, $F(000) = 976$, $T = 295$ K, final $R = 0.042$, $wR = 0.045$ for 3054 independent observed reflections. In this molecule the hexahydrotriazine ring is chair-shaped and bond distances and bond angles are normal. There are four hydrogen bonds between the water molecule and the primary molecule and its symmetry equivalents. There is an additional inter-molecular hydrogen bond between an amide nitrogen and a carbonyl oxygen.

**Experimental.** Colorless $0.08 \times 0.25 \times 0.30$ mm crystal, crystallized from methanol/water. Synthesized by G. Kumar and J. Boyer of the Univ. of Illinois at Chicago. Automated Nicolet $R3m$ diffractometer with incident-beam graphite monochromator, $\lambda = 1.54178$ Å (Cu K$\alpha$), 25 centered reflections within $37 \leq 2\theta \leq 90°$ used for determining lattice parameters.