# Structure of 6,8-Diacetyl-2,4-dinitro-2,4,6,8-tetraazabicyclo[3.3.0]octane

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**Abstract.** $C_8H_{12}N_6O_6$, $M_r = 288.22$, orthorhombic, $P2_12_12_1$, $a = 8.482$ (1), $b = 11.844$ (2), $c = 11.943$ (2) Å, $V = 1199.8$ (4) Å$^3$, $Z = 4$, $D_x = 1.596$ Mg m$^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 1.15$ mm$^{-1}$, $F(000) = 600$, $T = 295$ K, final $R = 0.035$, $wR = 0.046$ for 1092 independent observed reflections. This bicyclic heterocycle has a *cis* ring junction, and ring torsions centered about the shared bond are nearly eclipsed (17.0 and 18.8°). The acetyl groups are disposed asymmetrically across the pseudo-mirror plane of the molecule, with the carbonyl of one pointing towards, and that of the other pointing away from the ring junction. The amino N atoms vary in hybridization. The two acetylated amines are nearly trigonal planar, with the N—C(keto) bonds bent only 6.9 and 7.6° from the adjacent C—N—C planes, while the two nitroamines are nearly tetrahedral, with their N—N bonds bent 31.0 and 31.9° from adjacent C—N—C planes.

**Experimental.** A clear colorless $0.20 \times 0.24 \times 0.27$ mm data crystal was provided by Dr Clifford L. Coon of the Livermore National Laboratory, California. An automated Siemens $R3m/V$ diffractometer with incident beam monochromator was used for data collection. 25 centered reflections within $39 \leq 2\theta \leq 77°$ were used for determining lattice parameters. $[\sin(\theta)/\lambda]_{max} = 0.570$ Å$^{-1}$; range of $hkl$: $0 \leq h \leq 9$, $-13 \leq k \leq 0$, $0 \leq l \leq 13$. Standards 400, 333 and 006, monitored every 97 reflections, showed random variation of 2.0% over data collection: $\theta/2\theta$ mode, scan width $[2\theta(K\alpha_1) - 1.0]$ to $[2\theta(K\alpha_2) + 1.0]°$, $\omega$-scan rate a function of count rate ($2.5°$ min$^{-1}$ minimum, $15.0°$ min$^{-1}$ maximum), 1149 reflections measured, 1130 unique, 1092 observed with $F_o > 3\sigma(F_o)$. Data were corrected for Lorentz and polarization effects.

The structure solution, by direct methods, and the least-squares refinement used programs in *SHELXTL*80 (Sheldrick, 1980). $\Sigma w(|F_o| - |F_c|)^2$ was minimized where $w^{-1} = \sigma^2(|F_o|) + g(F_o)^2$, $g = 0.000225$. Secondary-extinction parameter $p = 0.005$ (1) in $F_c^* = F_c/[1.0 + 0.002(p)F_o^2/\sin(2\theta)]^{0.25}$. There were 212 parameters refined: atom coordinates, anisotropic thermal parameters for all non-H atoms, coordinates and isotropic thermal parameters

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* (Å$^2 \times 10^3$)

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

|        | $x$        | $y$       | $z$       | $U_{eq}$ |
|--------|-----------|-----------|-----------|----------|
| C(1)   | 7326 (3)  | 2537 (2)  | 3635 (3)  | 35 (1)   |
| N(2)   | 8669 (3)  | 2012 (2)  | 3087 (2)  | 43 (1)   |
| C(3)   | 8539 (4)  | 2000 (3)  | 1885 (3)  | 51 (1)   |
| N(4)   | 6905 (3)  | 2375 (2)  | 1713 (2)  | 40 (1)   |
| C(5)   | 6001 (3)  | 2536 (2)  | 2750 (3)  | 35 (1)   |
| N(6)   | 5334 (3)  | 3650 (2)  | 2820 (2)  | 38 (1)   |
| C(7)   | 6528 (3)  | 4452 (3)  | 3186 (3)  | 42 (1)   |
| N(8)   | 7572 (3)  | 3734 (2)  | 3846 (2)  | 39 (1)   |
| N(2')  | 9393 (3)  | 1090 (2)  | 3573 (3)  | 57 (1)   |
| O(2a)  | 9125 (4)  | 908 (2)   | 4555 (3)  | 80 (1)   |
| O(2b)  | 10326 (3) | 575 (2)   | 2977 (3)  | 80 (1)   |
| N(4')  | 6153 (3)  | 1944 (2)  | 802 (2)   | 47 (1)   |
| O(4a)  | 6979 (4)  | 1576 (2)  | 48 (2)    | 71 (1)   |
| O(4b)  | 4728 (3)  | 2016 (2)  | 787 (2)   | 59 (1)   |
| C(6')  | 3791 (3)  | 3988 (3)  | 2730 (3)  | 41 (1)   |
| O(6)   | 3508 (2)  | 5002 (2)  | 2737 (2)  | 55 (1)   |
| C(9)   | 2531 (4)  | 3113 (3)  | 2653 (3)  | 53 (1)   |
| C(8')  | 8525 (4)  | 4085 (3)  | 4696 (3)  | 44 (1)   |
| O(8)   | 9268 (3)  | 3407 (2)  | 5242 (2)  | 67 (1)   |
| C(10)  | 8576 (4)  | 5335 (3)  | 4907 (3)  | 57 (1)   |

for all non-methyl H atoms, methyl H atoms included using riding model [coordinate shifts of C applied to attached H atoms, torsion of methyl group allowed, C—H set to 0.96 Å, H angles idealized, $U(\text{H}) = 1.1 U_{eq}(\text{C})$]. $(\Delta/\sigma)_{max} = 0.003$, ratio of observations to parameters = 5.5:1, $R = 0.035$, $wR = 0.046$, $S = 2.25$ ($R = 0.036$ for all data). Final difference Fourier excursions were 0.19 and $-0.19$ e Å$^{-3}$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atom numbering for Tables 1 (atom coordinates) and 2 (bond distances and angles) follows that shown in Fig. 1.*

**Related literature.** This ring system (saturated 2,4,6,8-tetraazabicyclo[3.3.0]octane) occurs in five crystal structures reported by Koppes, Chaykovsky, Adolph, Gilardi & George (1987); one is very similar, being the same as the title compound except that the two nitro groups are replaced by acetyl groups. The structural statistics of nitramine groups were

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

| | | | | |
|---|---|---|---|---|
| C(1)—N(2) | 1.453 (4) | C(1)—C(5) | 1.543 (4) |
| C(1)—N(8) | 1.455 (4) | N(2)—C(3) | 1.440 (4) |
| N(2)—N(2') | 1.380 (4) | C(3)—N(4) | 1.470 (4) |
| N(4)—C(5) | 1.470 (4) | N(4)—N(4') | 1.360 (4) |
| C(5)—N(6) | 1.438 (3) | N(6)—C(7) | 1.456 (4) |
| N(6)—C(6') | 1.373 (4) | C(7)—N(8) | 1.459 (4) |
| N(8)—C(8') | 1.364 (4) | N(2')—O(2a) | 1.214 (5) |
| N(2')—O(2b) | 1.226 (4) | N(4')—O(4a) | 1.222 (4) |
| N(4')—O(4b) | 1.212 (4) | C(6')—O(6) | 1.225 (4) |
| C(6')—C(9) | 1.492 (4) | C(8')—O(8) | 1.211 (4) |
| C(8')—C(10) | 1.502 (5) | | |
| | | | |
| N(2)—C(1)—C(5) | 105.2 (2) | N(2)—C(1)—N(8) | 112.5 (2) |
| C(5)—C(1)—N(8) | 102.9 (2) | C(1)—N(2)—C(3) | 113.2 (2) |
| C(1)—N(2)—N(2') | 119.9 (2) | C(3)—N(2)—N(2') | 116.5 (3) |
| N(2)—C(3)—N(4) | 102.0 (2) | C(3)—N(4)—C(5) | 114.4 (2) |
| C(3)—N(4)—N(4') | 116.1 (2) | C(5)—N(4)—N(4') | 118.5 (2) |
| C(1)—C(5)—N(4) | 101.4 (2) | C(1)—C(5)—N(6) | 104.3 (2) |
| N(4)—C(5)—N(6) | 111.9 (2) | C(5)—N(6)—C(7) | 110.0 (2) |
| C(5)—N(6)—C(6') | 129.7 (2) | C(7)—N(6)—C(6') | 119.8 (2) |
| N(6)—C(7)—N(8) | 101.8 (2) | C(1)—N(8)—C(7) | 112.8 (2) |
| C(1)—N(8)—C(8') | 120.7 (2) | C(7)—N(8)—C(8') | 125.8 (2) |
| N(2)—N(2')—O(2a) | 117.6 (3) | N(2)—N(2')—O(2b) | 115.9 (3) |
| O(2a)—N(2')—O(2b) | 126.3 (3) | N(4)—N(4')—O(4a) | 117.0 (3) |
| N(4)—N(4')—O(4b) | 117.0 (3) | O(4a)—N(4')—O(4b) | 125.9 (3) |
| N(6)—C(6')—O(6) | 118.2 (3) | N(6)—C(6')—C(9) | 119.0 (3) |
| O(6)—C(6')—C(9) | 122.8 (3) | N(8)—C(8')—O(8) | 120.5 (3) |
| N(8)—C(8')—C(10) | 116.2 (3) | O(8)—C(8')—C(10) | 123.3 (3) |

discussed briefly by Archibald, Gilardi, Baum & George (1990).

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Fig. 1. A thermal ellipsoid plot of the title compound with ellipsoids drawn at the 20% probability level.

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# Structure of a Chiral Bicyclic β-Hydroxyphosphonamide – an Asymmetric Olefination Intermediate, C25H41N2O2P

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**Abstract.** (3a*R*,7a*R*)-2,3,3a,4,5,6,7,7a-Octahydro-2-[(*R*)-α-(1-hydroxy-4-*tert*-butylcyclohexyl)phenyl-methyl]-1,3-dimethyl-1*H*-1,3,2-benzodiazaphosphole 2-oxide, $C_{25}H_{41}N_2O_2P$, $M_r = 432.59$, orthorhombic, $P2_12_12_1$, $a = 10.636$ (2), $b = 12.759$ (1), $c = 18.185$ (2) Å, $V = 2467.8$ (5) Å$^3$, $Z = 4$, $D_x = 1.164$ Mg m$^{-3}$, $\lambda$(Cu $K\bar{\alpha}$) = 1.54178 Å, $\mu = 1.138$ mm$^{-1}$, $F(000) = 944$, $T = 293$ K, $R = 0.047$, $wR = 0.039$ for 1884 observed reflections. The title compound is constituted of a (1*R*,2*R*)-*N*,*N*'-dimethyl-1,2-diaminocyclohexane attached to a tetrahedrally coordinated phosphoryl group. A phenylmethyl group with an *R* configuration bridges the P atom and the 4-*tert*-butylcyclohexanol ring. The tertiary alcohol is in the axial position and the

4-*tert*-butyl is in the equatorial position. The molecules are held in the crystal through intermolecular hydrogen bonds of the O—H···O type and by van der Waals interactions.

**Experimental.** The reaction of the anion formed from the chiral non-racemic bicyclic phosphonamide (I) (Hanessian & Beaudoin, 1992) with 4-*tert*-butyl-cyclohexanone gave a crystalline adduct (II) in which the orientations of the substituents at the bond forming sites were elucidated by single-crystal X-ray-diffraction studies.



(I)          (II)
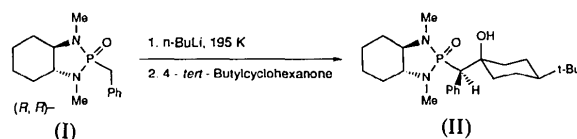
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