organic compounds

(3,5-Dinitro-1,3,5-triazinan-1-yl)-methanone

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In the title compound, $C_5H_9N_5O_5$, prepared from hexamine by acetylation and nitration, the triazine ring adopts a chair conformation with all three substituent groups lying on the same side of the ring.

Related literature

For the Bachmann process, see: Bachmann & Sheehan (1949). For the synthesis, see: Warman et al. (1973). For a related structure, see: Choi et al. (1975).

$$COCH_3$$
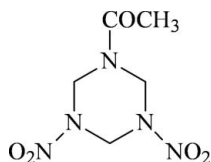
Experimental

Crystal data

$C_5H_9N_5O_5$	M_r = 219.17

Monoclinic, $P2_1/n$
a = 8.8972 (18) Å
b = 10.061 (2) Å
c = 9.890 (2) Å
β = 100.42 (3)°
V = 870.7 (3) Å^3

Z = 4
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 293 K
0.50 × 0.50 × 0.40 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.929, T_{max} = 0.943

3599 measured reflections
1988 independent reflections
1419 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.142
S = 1.03
1988 reflections

138 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Data collection: RAPID-AUTO (Rigaku, 2000); cell refinement: RAPID-AUTO; data reduction: CrystalStructure (Rigaku/MSC, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

References

Bachmann, W. E. & Sheehan, J. C. (1949). J. Am. Chem. Soc. **71**, 1482–1485.
Choi, C. S., Santoro, A. & Marinkas, P. L. (1975). Acta Cryst. B**31**, 2934–2937.
Higashi, T. (1995). ABSCOR. Rigaku Corporation, Tokyo, Japan.
Rigaku (2000). RAPID-AUTO. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2000). CrystalStructure. Molecular Structure Corporation, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). Acta Cryst. A**64**, 112–122.
Warman, M., Siele, V. I. & Gilbert, E. E. (1973). J. Heterocycl. Chem. **10**, 97–98.

supporting information

(3,5-Dinitro-1,3,5-triazinan-1-yl)methanone

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S1. Comment

1-Acetyl-3,5-dinitro-1,3,5-triazinane (1-acetylhexahydro-3,5-dinitro-1,3,5-triazine) (I) is obtained as a by-product in the synthesis of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) from 1,3,5,7 -tetraazaadamantane (hexamine) by the Bachmann process (Bachmann & Sheehan, 1949). As part of our search for the reaction mechanism involved in the nitro-lysis of hexamine, we synthesized the title compound, and describe its structure here.

  In (I), the hexahydrotriazine ring adopts a chair conformation with all three substituent groups lying on the same side of the triazine ring.The ring bond distances and angles are almost identical (the maximum deviation from the average C—N bond distance [1.44 (8) Å] is 0.01Å and the maximum deviation from the average bond angle [112 (3)°] is 3°). The three ring N atoms are equally distant from the plane through the C atoms (C1, C2 and C3) (0.40±0.06 (2) Å). This deviation is slightly larger than that found in hexahydro-1,3,5-triacetyl-1,3,5-triazine (TRAT) (Choi *et al.*, 1975), due to the three different substituent groups on the hexahydrotriazine ring in (I), whereas in TRAT, the three groups are the same. In (I) the three substituent groups are essentially planar with maximum deviations from the mean plane of these groups for atoms N1, N2 and N3 of 0.02 (4), 0.09 (6) and 0.10 (3) Å respectively.

S2. Experimental

The title compound was prepared from hexamine according to a literature method (Warman *et al.*, 1973). Crystals suitable for X-ray analysis were obtained by slow evaporation of an nitromethane solution at room temperature.

S3. Refinement

All H atoms were positioned geometrically and treated as riding, with C—H bond lengths constrained to 0.97 Å (alicyclic CH), 0.96 Å (methyl CH), and with $U_{iso}(H)$ = 1.2 (1.5 for methyl groups) times $U_{eq}(C)$.
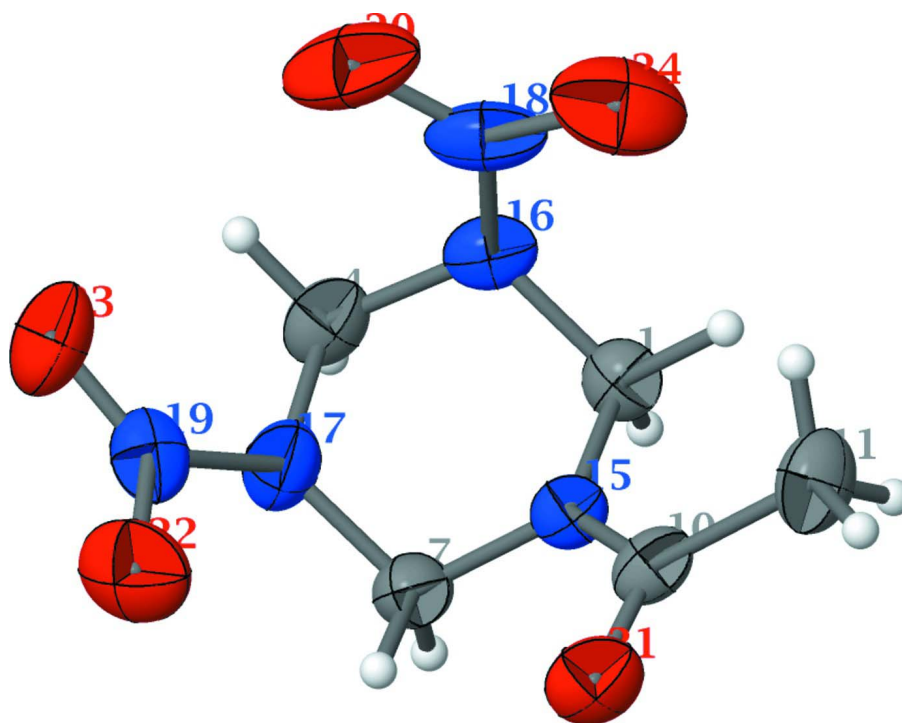
Figure 1

The molecular structure and atom numbering scheme for the title compound (I). Non-H atoms are shown as 50% probability displacement ellipsoids.
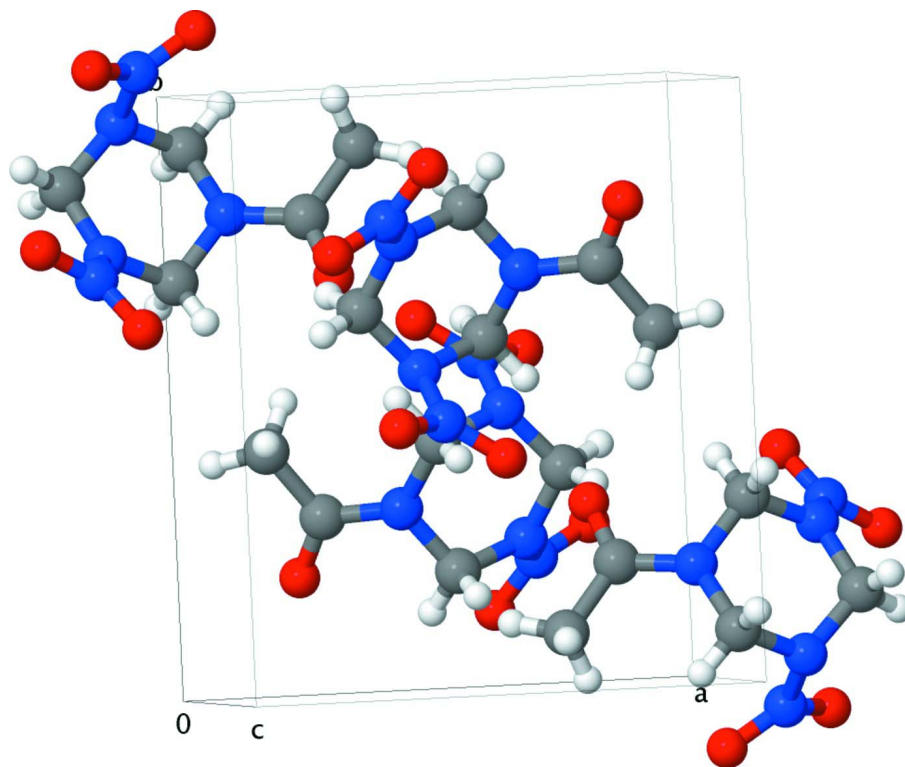
Figure 2

The packing of the title compound, viewed down the *c* axis of the unit cell.

(3,5-Dinitro-1,3,5-triazinan-1-yl)methanone

Crystal data

$C_5H_9N_5O_5$	$F(000) = 456$
$M_r = 219.17$	$D_x = 1.672$ Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 431 (2) K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.8972$ (18) Å	Cell parameters from 3599 reflections
$b = 10.061$ (2) Å	$\theta = 2.8–27.5°$
$c = 9.890$ (2) Å	$\mu = 0.15$ mm^{-1}
$\beta = 100.42$ (3)°	$T = 293$ K
$V = 870.7$ (3) Å^3	Block, colorless
$Z = 4$	$0.50 \times 0.50 \times 0.40$ mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer	3599 measured reflections
Radiation source: fine-focus sealed tube	1988 independent reflections
Graphite monochromator	1419 reflections with $I > 2\sigma(I)$
Detector resolution: 10.00 pixels mm^{-1}	$R_{int} = 0.028$
ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 2.8°$
Absorption correction: multi-scan	$h = -11\rightarrow11$
(*ABSCOR*; Higashi, 1995)	$k = -13\rightarrow13$
$T_{min} = 0.929$, $T_{max} = 0.943$	$l = -12\rightarrow12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from
Least-squares matrix: full	neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.051$	H-atom parameters constrained
$wR(F^2) = 0.142$	$w = 1/[\sigma^2(F_o^2) + (0.09P)^2]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
1988 reflections	$(\Delta/\sigma)_{max} = 0.002$
138 parameters	$\Delta\rho_{max} = 0.28$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.26$ e Å^{-3}
Primary atom site location: structure-invariant	Extinction correction: *SHELXL97* (Sheldrick,
direct methods	2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier	Extinction coefficient: 0.242 (16)
map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.47469 (19)	0.41301 (16)	0.32195 (16)	0.0389 (4)
H1A	0.5005	0.3837	0.4168	0.047*
H1B	0.4000	0.4839	0.3170	0.047*
C2	0.72467 (19)	0.35894 (19)	0.26987 (18)	0.0456 (4)
H2A	0.8044	0.3941	0.2248	0.055*
H2B	0.7713	0.3329	0.3624	0.055*
C3	0.51659 (19)	0.19589 (16)	0.23350 (19)	0.0429 (4)
H3A	0.4708	0.1292	0.1680	0.052*
H3B	0.5392	0.1547	0.3236	0.052*
C4	0.26587 (18)	0.29469 (17)	0.16314 (15)	0.0385 (4)
C5	0.1604 (2)	0.4079 (2)	0.1715 (2)	0.0531 (5)
H5A	0.0627	0.3892	0.1158	0.080*
H5B	0.2020	0.4873	0.1390	0.080*
H5C	0.1485	0.4201	0.2653	0.080*
N1	0.41055 (15)	0.30361 (13)	0.23592 (13)	0.0357 (3)
N2	0.61111 (16)	0.46206 (14)	0.27642 (13)	0.0405 (4)
N3	0.65682 (16)	0.24375 (17)	0.19558 (16)	0.0491 (4)
N4	0.5835 (2)	0.54679 (16)	0.16262 (16)	0.0550 (5)
N5	0.69287 (18)	0.21008 (15)	0.07159 (15)	0.0468 (4)
O1	0.6820 (2)	0.55437 (17)	0.09159 (16)	0.0839 (6)
O2	0.22571 (14)	0.19538 (13)	0.09572 (13)	0.0525 (4)
O3	0.6163 (2)	0.12455 (17)	0.00671 (15)	0.0723 (5)
O4	0.80447 (17)	0.26203 (18)	0.03929 (15)	0.0685 (5)
O5	0.4676 (2)	0.61206 (16)	0.14783 (19)	0.0819 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0417 (9)	0.0443 (9)	0.0292 (7)	−0.0021 (7)	0.0023 (6)	−0.0039 (6)
C2	0.0363 (9)	0.0593 (11)	0.0390 (9)	−0.0075 (8)	0.0013 (7)	−0.0027 (8)
C3	0.0415 (9)	0.0399 (9)	0.0479 (9)	−0.0033 (7)	0.0094 (7)	0.0018 (7)
C4	0.0371 (8)	0.0507 (9)	0.0274 (7)	−0.0073 (7)	0.0055 (6)	0.0032 (7)
C5	0.0363 (9)	0.0751 (13)	0.0465 (10)	0.0059 (9)	0.0041 (7)	0.0011 (9)
N1	0.0341 (7)	0.0390 (7)	0.0327 (7)	−0.0025 (5)	0.0024 (5)	−0.0012 (5)
N2	0.0441 (8)	0.0439 (8)	0.0297 (7)	−0.0106 (6)	−0.0034 (6)	0.0009 (6)
N3	0.0420 (8)	0.0595 (9)	0.0480 (9)	−0.0067 (7)	0.0141 (6)	−0.0122 (7)
N4	0.0761 (11)	0.0453 (9)	0.0368 (8)	−0.0260 (8)	−0.0076 (8)	0.0032 (7)
N5	0.0487 (9)	0.0542 (9)	0.0368 (8)	0.0130 (7)	0.0059 (7)	0.0037 (7)
O1	0.1182 (14)	0.0832 (12)	0.0533 (9)	−0.0413 (11)	0.0236 (10)	0.0118 (8)
O2	0.0479 (7)	0.0615 (8)	0.0450 (7)	−0.0159 (6)	0.0006 (6)	−0.0099 (6)
O3	0.1003 (13)	0.0668 (9)	0.0496 (8)	−0.0102 (9)	0.0129 (8)	−0.0185 (7)
O4	0.0577 (9)	0.0945 (11)	0.0598 (9)	0.0010 (9)	0.0281 (7)	−0.0005 (8)
O5	0.0946 (13)	0.0625 (10)	0.0768 (12)	0.0044 (9)	−0.0163 (9)	0.0260 (9)

Geometric parameters (Å, º)

C1—N1	1.4440 (19)	C4—O2	1.2184 (19)
C1—N2	1.455 (2)	C4—N1	1.359 (2)
C1—H1A	0.9700	C4—C5	1.487 (2)
C1—H1B	0.9700	C5—H5A	0.9600
C2—N3	1.445 (2)	C5—H5B	0.9600
C2—N2	1.458 (2)	C5—H5C	0.9600
C2—H2A	0.9700	N2—N4	1.398 (2)
C2—H2B	0.9700	N3—N5	1.365 (2)
C3—N1	1.440 (2)	N4—O5	1.209 (2)
C3—N3	1.449 (2)	N4—O1	1.220 (2)
C3—H3A	0.9700	N5—O3	1.208 (2)
C3—H3B	0.9700	N5—O4	1.215 (2)
N1—C1—N2	109.82 (13)	C4—C5—H5A	109.5
N1—C1—H1A	109.7	C4—C5—H5B	109.5
N2—C1—H1A	109.7	H5A—C5—H5B	109.5
N1—C1—H1B	109.7	C4—C5—H5C	109.5
N2—C1—H1B	109.7	H5A—C5—H5C	109.5
H1A—C1—H1B	108.2	H5B—C5—H5C	109.5
N3—C2—N2	111.37 (13)	C4—N1—C3	120.14 (13)
N3—C2—H2A	109.4	C4—N1—C1	126.71 (14)
N2—C2—H2A	109.4	C3—N1—C1	113.15 (13)
N3—C2—H2B	109.4	N4—N2—C1	114.91 (14)
N2—C2—H2B	109.4	N4—N2—C2	114.86 (15)
H2A—C2—H2B	108.0	C1—N2—C2	113.33 (13)
N1—C3—N3	110.59 (14)	N5—N3—C2	120.76 (15)
N1—C3—H3A	109.5	N5—N3—C3	120.23 (15)

N3—C3—H3A	109.5	C2—N3—C3	115.80 (14)
N1—C3—H3B	109.5	O5—N4—O1	125.60 (18)
N3—C3—H3B	109.5	O5—N4—N2	116.75 (17)
H3A—C3—H3B	108.1	O1—N4—N2	117.51 (19)
O2—C4—N1	119.99 (16)	O3—N5—O4	125.20 (17)
O2—C4—C5	122.20 (16)	O3—N5—N3	116.89 (16)
N1—C4—C5	117.81 (15)	O4—N5—N3	117.74 (16)
O2—C4—N1—C3	0.0 (2)	N2—C2—N3—N5	112.60 (17)
C5—C4—N1—C3	178.88 (14)	N2—C2—N3—C3	−47.2 (2)
O2—C4—N1—C1	−179.01 (15)	N1—C3—N3—N5	−110.68 (18)
C5—C4—N1—C1	−0.2 (2)	N1—C3—N3—C2	49.2 (2)
N3—C3—N1—C4	126.86 (15)	C1—N2—N4—O5	28.9 (2)
N3—C3—N1—C1	−53.98 (18)	C2—N2—N4—O5	163.00 (15)
N2—C1—N1—C4	−123.74 (16)	C1—N2—N4—O1	−155.26 (16)
N2—C1—N1—C3	57.17 (17)	C2—N2—N4—O1	−21.1 (2)
N1—C1—N2—N4	80.18 (16)	C2—N3—N5—O3	−169.79 (16)
N1—C1—N2—C2	−54.65 (17)	C3—N3—N5—O3	−10.9 (2)
N3—C2—N2—N4	−85.27 (16)	C2—N3—N5—O4	14.7 (2)
N3—C2—N2—C1	49.60 (18)	C3—N3—N5—O4	173.59 (16)