Absorption correction:
ψ scan (Sheldrick, 1993)
$T_{min} = 0.899$, $T_{max} = 0.985$
14322 measured reflections
3711 independent reflections
2890 reflections with
$I > 2\sigma(I)$

$h = -7 \rightarrow 7$
$k = -17 \rightarrow 10$
$l = -28 \rightarrow 20$
2 standard reflections
every 58 reflections
intensity decay: 6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.072$
$S = 1.373$
3711 reflections
272 parameters
H atoms riding
$w = \exp[5.00(\sin\theta/\lambda)^2]/$
$\quad [\sigma^2(F_o^2) + (0.0349P)^2]$
$\quad$ where $P = (0.333F_o^2$
$\quad\quad + 0.667F_c^2)$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.132$ e Å^{-3}
$\Delta\rho_{min} = -0.116$ e Å^{-3}
Extinction correction:
SHELXL93
Extinction coefficient:
0.0115 (12)
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C7	1.263 (2)	C1—C6	1.529 (2)
N1—C6	1.461 (2)	C7—C16	1.473 (2)
N3—C17	1.264 (2)	C17—C26	1.482 (3)
N3—C1	1.460 (2)		
C7—N1—C6	117.5 (2)	N1—C6—C1	108.86 (15)
C17—N3—C1	119.2 (2)	N1—C7—C16	122.2 (2)
N3—C1—C6	109.30 (14)	N3—C17—C26	121.0 (2)

The intensity data were corrected for Lorentz and polarization effects and for absorption. A decay correction was also applied. All non-H atoms were refined anisotropically.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991a). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

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2,4,6,8-Tetraazabicyclo[3.3.1]nonane-3,7-dione and 2,4,6,8-Tetraacetyl-2,4,6,8-tetra-azabicyclo[3.3.1]nonane-3,7-dione

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Abstract

The title compounds, 2,4,6,8-tetraazabicyclo[3.3.1]-nonane-3,7-dione, (I) ($C_5H_8N_4O_2$), and 2,4,6,8-tetra-acetyl-2,4,6,8-tetraazabicyclo[3.3.1]nonane-3,7-dione, (II) ($C_{13}H_{16}N_4O_6$), display similar conformations, each with the cyclic urea moieties and bridgehead atoms forming two mean planes having a dihedral angle of approximately 110°. The CO of each acetyl group is *anti* to the CO of the cyclic urea to which it is attached.

Comment

The stereochemistry of bicyclo[3.3.1]nonane and hetero analogues has been studied by a variety of physical and theoretical methods (Zefirov & Palyulin, 1991; Eliel & Wilen, 1994) because their structures are related to those of natural products (alkaloids) and adamantanoid compounds (Eres'ko *et al.*, 1979; Peters, 1979; Vogtle, 1992). While exploring predictive structure–property relationships of new molecules (Piacenza, Legsaï, Blaive & Gallo, 1996), it was found that no structural data were

available for tetraazadione derivatives in this series. Therefore, the crystal structures of (I) and (II) were determined and the results are presented below.

(I)   (II)
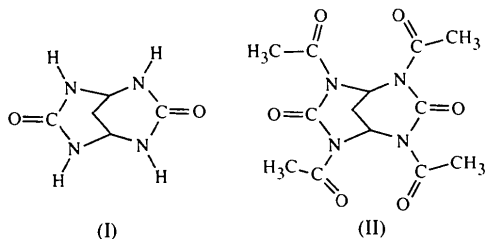
Both compounds have similar conformations of the skeletal framework, with each cyclic urea group and adjacent bridgehead C atoms defining a nearly planar moiety [none of the five atoms deviates by more than about 0.035 Å from the least-squares plane in (I)]; the two mean planes intersect along a line defined by the bridgehead C atoms, with dihedral angles of 109.57 (4) and 111.88 (11)° for (I) and (II), respectively.

This conformation, which was predicted by molecular-mechanics calculations (Akyev, Lebedev, Pivina & Khmel'nitskii, 1989), is different from that which is observed in azabicyclo[3.3.1]nonanone (with no cyclic urea moiety): this exists with two possible conformations, chair and boat, for each six-membered ring (Arias et al., 1994; Eliel & Wilen, 1994). In this case, the absence of a cyclic urea prevents the planarity, reported here, of five atoms in the six-membered rings. On the other hand, the roof-shaped conformation of 2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (gly-coluril) (Li et al., 1994; Xu, Gantzel & Clark, 1994) and derivatives (Boileau, Wimmer, Pierrot, Baldy & Gallo, 1985; Boileau, Wimmer, Gilardi et al., 1988; Delpeyroux, Blaive, Gallo, Graindorge & Lescop, 1994) is very similar to that reported here. Note, however, that compound (I) crystallizes in an orthorhombic Pbca form, whereas glycoluril has two crystalline forms (orthorhombic Pnma or Cmcm).

In (II), each CO of the four acetyl groups is anti to the CO of the cyclic urea to which it is attached; this conformation, which originates from the best accommodation of dipole moments, has been observed in tetraacetyl-glycoluril (Pierrot, Baldy, Wimmer, Gallo & Boileau, 1985) and dinitrodiacetylglycoluril (Boileau, Wimmer, Pierrot, Baldy & Gallo, 1985). All bond lengths and angles in (I) and (II) are in the expected ranges. The introduction of the four acetyl groups has almost no effect on the two CH_2—$C_{bridgehead}$ bonds and on the four $C_{bridgehead}$—N bonds. However, it increases the length of each of the four urea N—C bonds (by about 0.035 Å) and reduces the length of each urea CO bond (by about 0.044 Å) due to the extended conjugation between two acetyls and a cyclic urea (Tables 1 and 2); for the same reason the urea NCN angle is reduced by 3.5°.

There is a molecular twofold symmetry axis in compounds (I) (through C9) and (II) (through C7) which does not match the space groups for these structures. For (I), this may be due to the intermolecular hydrogen-bonding scheme which clearly lacks a twofold axis [O2···N6^i 2.859 (1), O2···N4^{ii} 2.863 (1), O5···N1^{iii} 2.900 (1) Å; symmetry codes: (i) $-\frac{3}{2} + x$, y, $\frac{1}{2} - z$; (ii) x, $-\frac{1}{2} - y$, $-\frac{3}{2} + z$; (iii) x, $-\frac{1}{2} - y$, $-\frac{1}{2} + z$]. For (II), no explanation is found, but all the procedures we used (CAD-4 Software; Enraf–Nonius, 1989) for evaluating higher symmetry gave no space group other than monoclinic $P2_1/c$.
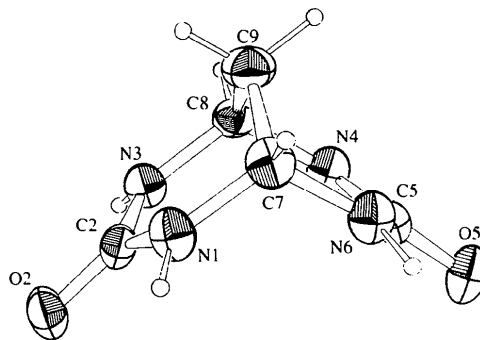

Fig. 1. An ORTEPII (Johnson, 1976) view of compound (I). Displacement ellipsoids are shown at the 50% probability level.
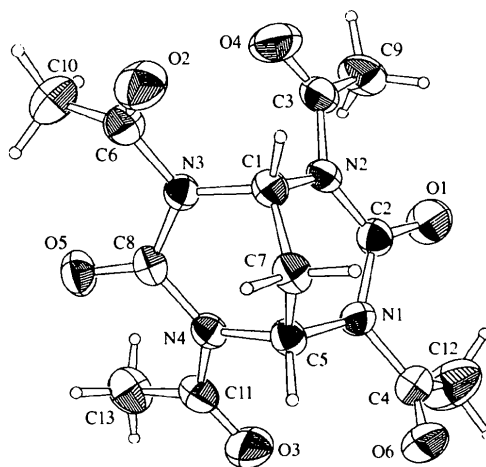
Fig. 2. An ORTEPII (Johnson, 1976) view of compound (II). Displacement ellipsoids are shown at the 50% probability level.

Experimental

1,1,3,3-Tetraethoxypropane was reacted with urea by cyclocondensation for 10 h at 363 K in the presence of HCl in water (pH 1) to give compound (I). Compound (II) was prepared by acetylating the two cyclic unsubstituted urea groups in (I) with sodium acetate in acetic anhydride for 5 h at 413 K. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated chloroform solution for (II) and water for (I).

Compound (I)

Crystal data

$C_5H_8N_4O_2$
$M_r = 156.15$
Orthorhombic
Pbca
$a = 11.388\,(2)$ Å
$b = 10.171\,(2)$ Å
$c = 11.767\,(5)$ Å
$V = 1363\,(1)$ Å^3
$Z = 8$
$D_x = 1.52$ Mg m^{-3}
$D_m = 1.500$ Mg m^{-3}
D_m measured by flotation in chloroform

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15$–$18°$
$\mu = 0.113$ mm^{-1}
$T = 294$ K
Prism
$0.60 \times 0.50 \times 0.40$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2655 measured reflections
1192 independent reflections
1005 reflections with
$I > 3\sigma(I)$

$R_{int} = 0.026$
$\theta_{max} = 25°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 13$
2 standard reflections
frequency: 60 min
intensity decay: 0.28%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.052$
$S = 1.835$
1005 reflections
100 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.257$ e Å^{-3}
$\Delta\rho_{min} = -0.291$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (I)*

O2—C2	1.243 (2)	N1—C2	1.352 (2)
N1—C7	1.454 (2)	C7—C9	1.509 (2)
C7—N1—C2	122.5 (1)	O2—C2—N1	121.2 (1)
N6—C7—N1	112.1 (1)	N3—C2—N1	117.9 (1)
N1—C7—C9	108.3 (1)	C7—C9—C8	105.2 (1)

Compound (II)

Crystal data

$C_{13}H_{16}N_4O_6$
$M_r = 324.30$
Monoclinic
$P2_1/c$
$a = 8.979\,(2)$ Å
$b = 16.265\,(6)$ Å
$c = 10.342\,(1)$ Å
$\beta = 99.63\,(2)°$
$V = 1489\,(1)$ Å^3
$Z = 4$
$D_x = 1.45$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12$–$16°$
$\mu = 0.109$ mm^{-1}
$T = 294$ K
Cubic
$0.40 \times 0.40 \times 0.40$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

$R_{int} = 0.024$
$\theta_{max} = 24°$

$\omega/2\theta$ scans
Absorption correction: none
2570 measured reflections
2321 independent reflections
2058 reflections with
$I > 0.5\sigma(I)$

$h = -10 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 11$
2 standard reflections
frequency: 60 min
intensity decay: 0.32%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.062$
$S = 2.165$
2058 reflections
208 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.272$ e Å^{-3}
$\Delta\rho_{min} = -0.192$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 2. *Selected geometric parameters (Å, °) for (II)*

O1—C2	1.208 (3)	C1—C7	1.497 (3)
N2—C1	1.464 (3)	C3—O4	1.200 (3)
N2—C2	1.381 (2)	C3—C9	1.480 (4)
N2—C3	1.432 (3)		
C1—N2—C2	120.3 (2)	O1—C2—N2	123.0 (2)
C1—N2—C3	116.3 (2)	N2—C3—O4	118.5 (2)
C2—N2—C3	121.6 (2)	N2—C3—C9	118.9 (2)
N2—C1—N3	109.6 (2)	O4—C3—C9	122.5 (2)
N2—C1—C7	108.0 (1)	C1—C7—C5	105.0 (2)
N1—C2—N2	115.0 (2)		

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *BEGIN* in *SDP* (Frenz, 1985); program(s) used to solve structures: direct methods (*MULTAN80*; Main *et al.*, 1980); program(s) used to refine structures: *LSFM* in *SDP*; molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990) for (II).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1467). Services for accessing these data are described at the back of the journal.

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Dimethyl 2-Iodobenzoylphosphonate, an Unusual Example of a Crystalline α-Keto-phosphonate

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Abstract

The crystal structure analysis of the title compound, $C_9H_{10}IO_4P$, is a rare example of a full structural determination of an α-ketophosphonate ester, a type of compound which normally forms an oil. The P—C(carbonyl) bond is long, there is evidence that steric repulsion between the I and O(carbonyl) atoms is unexpectedly weak and there is a short intermolecular I···O contact linking the molecules in chains. The structure is compared with 2-iodobenzoyl compounds and with a nickel complex of an α-ketophosphonate.

Comment

Acylphosphonates are a particularly interesting group of phosphonates. The proximity of the carbonyl and phosphoryl groups confers special physical, chemical and biological properties on these compounds, while the electron-withdrawing nature of the functional groups results in increased reactivity of both groups and of the bond linking them; for these reasons they are normally considered to be a separate class of phosphonate. Acylphosphonates and their derivatives have been reviewed recently (Breuer, 1996). As these substances normally form oils, dimethyl 2-iodobenzoyl-phosphonate, (I), represents an unusual example of a crystalline acylphosphonate ester suitable for X-ray structural analysis.

(I)
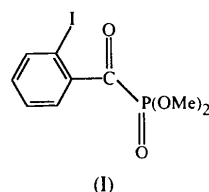
The molecular structure shows some features of special interest. The P—C7 bond distance is long; the Cambridge Structural Database (Allen & Kennard, 1993; Fletcher, McMeeking & Parkin, 1996) revealed 50 structures with 55 fragments containing phosphonate esters attached to trigonal planar C_{sp^2} atoms. Mean P=O, P—O and P—C distances were 1.461 (2), 1.567 (2) and 1.791 (3) Å, respectively; the P=O and P—O distances of the title compound correspond well with those in the database, but the P—C7 distance is close to the maximum previously found, *i.e.* 1.856 Å in menthylmethyl (R_P)-phenylphosphonate (Donohue & Mandel, 1981), and would be considered somewhat long even for a P—C_{sp^3} bond (Allen, Kennard, Watson, Brammer & Orpen, 1987).
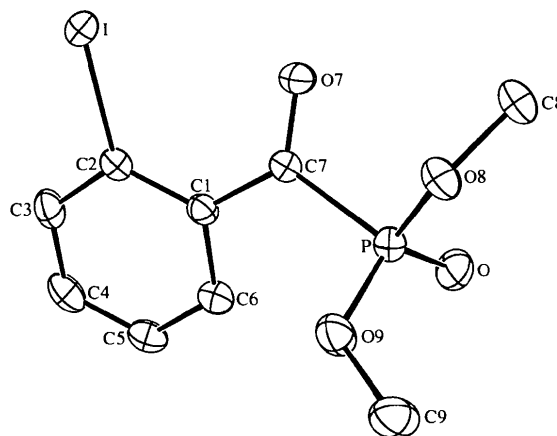

Fig. 1. Molecular structure of (I) showing 25% probability ellipsoids. H atoms are omitted for clarity.

The intramolecular I···O7 distance [3.094 (4) Å] is distinctly less than the sum of van der Waals radii (3.50 Å; Bondi, 1964); allied to this the dihedral angle of the ketophosphorus plane against the benzenoid plane