

## Refinement

Refinement on <i>F</i>	$(\Delta/\sigma)_{\max} = 0.001$
<i>R</i> = 0.038	$\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$
<i>wR</i> = 0.054	$\Delta\rho_{\min} = -0.43 \text{ e } \text{Å}^{-3}$
<i>S</i> = 1.972	Extinction correction: none
3238 reflections	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
268 parameters	
Only H-atom <i>U</i> 's refined	
<i>w</i> = $1/\sigma^2(F)$	

Table 3. Selected geometric parameters (Å, °) for (V)

S1—O1	1.431 (2)	S2—N3	1.629 (2)
S1—O2	1.427 (2)	S2—C6	1.782 (3)
S1—N1	1.657 (2)	S3—O5	1.435 (2)
S1—C1	1.769 (3)	S3—O6	1.432 (2)
S2—O3	1.433 (2)	S3—N6	1.654 (2)
S2—O4	1.431 (2)	S3—C12	1.770 (3)
O1—S1—O2	118.3 (1)	O4—S2—N3	106.7 (1)
O1—S1—N1	105.4 (1)	O4—S2—C6	107.4 (1)
O1—S1—C1	109.0 (1)	N3—S2—C6	109.5 (1)
O2—S1—N1	107.8 (1)	O5—S3—O6	119.2 (1)
O2—S1—C1	110.9 (1)	O5—S3—N6	107.4 (1)
N1—S1—C1	104.4 (1)	O5—S3—C12	109.9 (1)
O3—S2—O4	120.0 (1)	O6—S3—N6	106.7 (1)
O3—S2—N3	105.9 (1)	O6—S3—C12	108.0 (1)
O3—S2—C6	107.1 (1)	N6—S3—C12	104.7 (1)
C4—N3—S2—C6	77.9 (2)	S2—C6—C7—N4	102.0 (2)
N3—S2—C6—C7	-69.7 (2)	C6—C7—N4—C8	79.4 (4)

Table 4. Hydrogen-bonding geometry (Å, °) for (V)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C1—H2...N5 <sup>i</sup>	0.941	2.585	3.305 (5)	133.7
C3—H5...O3 <sup>ii</sup>	0.987	2.349	3.227 (4)	147.7
C10—H19...O6 <sup>iii</sup>	0.986	2.573	3.440 (5)	146.7
C10—H20...O4 <sup>iv</sup>	0.941	2.493	3.154 (5)	127.3
C11—H22...O1 <sup>v</sup>	0.942	2.518	3.342 (5)	146.1
C12—H23...O2 <sup>vi</sup>	0.903	2.551	3.427 (5)	163.5

Symmetry codes: (i)  $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$ ; (ii)  $x, y - 1, z$ ; (iii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (iv)  $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$ ; (v)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (vi)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

The structures were solved by direct methods and Fourier techniques, with all atoms (including H atoms) observed after a series of difference syntheses. All non-H atoms were treated anisotropically. For (IV), all H atoms were treated isotropically, while for (V), H atoms were placed as found and only their *U*<sub>iso</sub> parameters were refined. Final refinement to convergence was by full-matrix least squares. All calculations were performed on a Silicon Graphics Indy R4600 workstation.

For both compounds, data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1985); cell refinement: *MSCIAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1993); program(s) used to solve structures: *SIR* (Burla *et al.*, 1989); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

The IUPAC names of compounds (IV) and (V) were obtained using the ACD/ILAB Web service version 2.6 at <http://www.acdlabs.com/ilab>

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1255). Services for accessing these data are described at the back of the journal.

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*para*-Acetoxyacetanilide†

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## Abstract

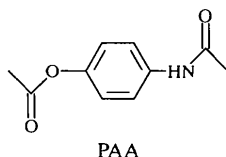
*para*-Acetoxyacetanilide, C<sub>10</sub>H<sub>11</sub>NO<sub>3</sub>, is a habit modifier of the analgesic *para*-hydroxyacetanilide. Its structure is compared to that of *para*-hydroxyacetanilide and other simple biologically active acetanilides. The main difference is found to be its non-planar nature; the dihedral angle between the planes of the aryl ring and the acetoxy group is 83.5 (6)°

## Comment

Interest in the crystal growth properties of pharmaceutical compounds led us to investigate the use of

† Alternative name: methyl 4-acetamidobenzoate.

*para*-acetoxyacetanilide (PAA) as an additive to modify the crystal properties of *para*-hydroxyacetanilide (PHA), commonly known as paracetamol or as acetaminophen. PAA is a known synthetic impurity found during the industrial production of PHA (Fairbrother, 1973) and is known to modify the crystal habit, strain content and dissolution rate of PHA, and to be a nucleation and growth inhibitor (Chow *et al.*, 1985, Prasad *et al.*, 1998). PAA is also of interest as a prodrug of PHA (Ditert, 1968). The crystal structure of PAA was obtained to further our attempts to model its incorporation into crystalline PHA.



Comparison of the molecular structure of PAA to those of the two known polymorphs of PHA (Haisa *et al.*, 1974, 1976) reveals that the equivalent geometric parameters are generally in good agreement. The most significant variations in bond length occur at N1. The N1—C6 and N1—C9 distances of 1.414 (2) and 1.358 (3) Å are respectively slightly shorter and slightly longer than those found at ambient temperature for PHA [1.422 (5)/1.425 (3) and 1.341 (6)/1.340 (3) Å]. There is closer agreement with values for the neutron structure of unsubstituted acetanilide (Johnson *et al.*, 1995).

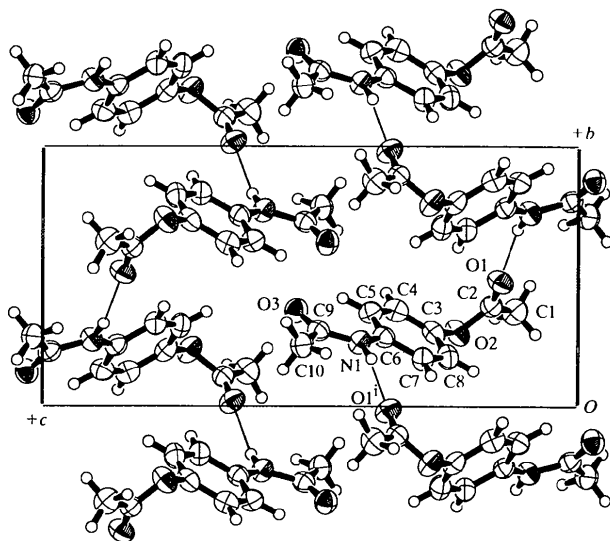


Fig. 1. ORTEP (Johnson, 1976) packing diagram of PAA viewed along the *a* axis. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms as small spheres of an arbitrary size. Atom H1N is bonded to N1. [Symmetry code: (i)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ .]

The structures of two other simple *para*-substituted acetanilides are known (Haisa *et al.*, 1980; Patel *et al.*, 1983) and these are also in good agreement with that of PAA.

The dihedral angle between the plane of the aryl ring and the amide plane defined by O3, C9, C10 and N1 is 10.2 (1)°. This is flatter than in any of the above related compounds [range 17.7 to 29°] and brings the amide oxygen O3 into closer contact with an aryl proton [O3...H5 = 2.25 Å] than in the PHA structures [2.34 and 2.38 Å]. The plane of the acetoxy group as defined by O1, C2, C1 and O2 is twisted to approach the normal to the ring plane [dihedral angle 83.5 (6)°]. This contrast with the comparatively planar PHA molecules may have significant packing consequences for PAA incorporation into PHA crystals. The twist may be due to the amide and acetoxy functions of adjacent molecules being connected by hydrogen bonding (Table 2), forming chains of molecules related by a  $2_1$  screw axis. The dihedral angle between the ring planes of adjacent molecules is 44.14 (6)°.

## Experimental

PAA was synthesized by the method of Chattaway (1931). Crystals (m.p. 429 K) were obtained by slow evaporation of an ethanol solution.

### Crystal data

C<sub>10</sub>H<sub>11</sub>NO<sub>3</sub>  
*M<sub>r</sub>* = 193.20  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 7.2264 (9) Å  
*b* = 8.0250 (18) Å  
*c* = 16.5902 (12) Å  
 $\beta$  = 92.052 (8)°  
*V* = 961.5 (3) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.335 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 24 reflections  
 $\theta$  = 17.75–20.40°  
 $\mu$  = 0.099 mm<sup>-1</sup>  
*T* = 295 K  
 Plate  
 0.65 × 0.45 × 0.08 mm  
 Colourless

### Data collection

Rigaku AFC-7S diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 2508 measured reflections  
 2331 independent reflections  
 1235 reflections with  $I > 2\sigma(I)$

$R_{\text{int}}$  = 0.012  
 $\theta_{\text{max}}$  = 28.01°  
 $h = 0 \rightarrow 9$   
 $k = 0 \rightarrow 10$   
 $l = -21 \rightarrow 21$   
 3 standard reflections every 150 reflections  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.147$

$(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$

$S = 0.997$   
 2331 reflections  
 150 parameters  
 H atoms treated by a  
 mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0739P)^2 + 0.0414P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Extinction correction:  
*SHELXL97* (Sheldrick,  
 1997)  
 Extinction coefficient:  
 0.029 (5)  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)

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Table 1. Selected geometric parameters (Å, °)

O1—C2	1.195 (2)	N1—C9	1.358 (3)
O2—C2	1.342 (2)	N1—C6	1.414 (2)
O2—C3	1.415 (2)	C1—C2	1.487 (3)
O3—C9	1.222 (2)	C9—C10	1.503 (3)
C2—O2—C3	117.09 (14)	C8—C3—O2	119.17 (18)
C9—N1—C6	129.25 (17)	C7—C6—N1	117.21 (17)
O1—C2—O2	122.39 (17)	C5—C6—N1	123.69 (17)
O1—C2—C1	126.34 (18)	O3—C9—N1	123.43 (17)
O2—C2—C1	111.26 (16)	O3—C9—C10	122.37 (17)
C4—C3—O2	119.12 (17)	N1—C9—C10	114.19 (17)
C3—O2—C2—O1	−2.7 (3)	C9—N1—C6—C7	−168.3 (2)
C2—O2—C3—C4	99.8 (2)	C9—N1—C6—C5	10.3 (3)
C2—O2—C3—C8	−84.1 (2)	C6—N1—C9—O3	−4.8 (3)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1N...O1 <sup>†</sup>	0.86 (2)	2.09 (2)	2.934 (2)	166 (1)

Symmetry code: (i)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ .

Methyl-H atoms were modelled in a riding mode and their orientations were found by refining rotation about the C—Me bonds. All other H atoms were treated isotropically. All calculations were performed on a Silicon Graphics Indy R4600.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SAPI* (Fan, 1988). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Software used to prepare material for publication: *SHELXL97*; *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1270). Services for accessing these data are described at the back of the journal.

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## [2,3:5,6]Dibenzo[2.2.2]octa-2,5,7-triene (C<sub>2</sub>/c) and [2,3:5,6]dibenzo[2.2.2]octa-2,5-diene†

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## Abstract

Two barrelene homologs are reported. Strain in the bicyclic framework of [2,3:5,6]dibenzo[2.2.2]octa-2,5,7-triene, (I) (C<sub>16</sub>H<sub>12</sub>), which is manifest in the deviations from ideality of the bond angles in the central bicyclic ring system and compression of the double bond [1.312 (3) Å], is reduced in the more saturated derivative, [2,3:5,6]dibenzo[2.2.2]octa-2,5-diene, (II) (C<sub>16</sub>H<sub>14</sub>), with the corresponding single bond being 1.5380 (19) Å. The formation of isomorphs of (I) in both chiral (C<sub>2</sub>) and achiral (C<sub>2</sub>/c) space groups has implications for asymmetric syntheses involving solid (I) which rely on a non-centrosymmetric space group.

## Comment

Recent controversy concerns the origin of elongated interannular C—C single bonds in anthracene and related cycloadducts (Baldrige *et al.*, 1997). We prepared the title compounds, (I) and (II), as the first in a series of compounds designed to investigate features responsible for the anomalous bond properties in these systems. Bond distances and angles within the aromatic rings

† Alternative names: 9,10-dihydro-9,10-ethenoanthracene and 9,10-dihydro-9,10-ethanoanthracene.