

## Diels–Alder adducts of medium-ring carbocyclic dienes prepared by rearrangement of catalytically generated cyclic oxonium ylides

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Received 28 June 2001

Accepted 13 August 2001

The novel bicyclic and tricyclic systems dimethyl (4*aS*\*,6*S*\*)-6-methoxy-7-oxo-4*a*,5,6,7,8,9-hexahydro-2*H*-benzocycloheptene-3,4-dicarboxylate, C<sub>16</sub>H<sub>20</sub>O<sub>6</sub>, (I), dimethyl (4*aS*\*,6*R*\*)-6-methoxy-7-oxo-4*a*,5,6,7,8,9-hexahydro-2*H*-benzocycloheptene-3,4-dicarboxylate, C<sub>16</sub>H<sub>20</sub>O<sub>6</sub>, (II), (3*aS*\*,9*R*\*,10*aS*\*,-10*bR*\*)-9-methoxy-2-oxa-1,3*a*,4,6,7,8,9,10,10*a*,10*b*-decahydro-3*H*-cyclohepta[*e*]indene-1,3,8-trione, C<sub>14</sub>H<sub>16</sub>O<sub>5</sub>, (III), and (1*S*\*,2*R*\*,9*S*\*,10*aR*\*)-9-methoxy-8-oxo-1,2,3,5,6,7,8,9,10,10*a*-decahydrobenzocyclooctene-1,2-dicarboxylic acid, C<sub>15</sub>H<sub>20</sub>O<sub>6</sub>, (IV), have been crystallographically characterized, allowing the determination of the relative configuration of the stereogenic centres. The poor quality of the dicarboxylic acid crystals necessitated the use of synchrotron radiation.

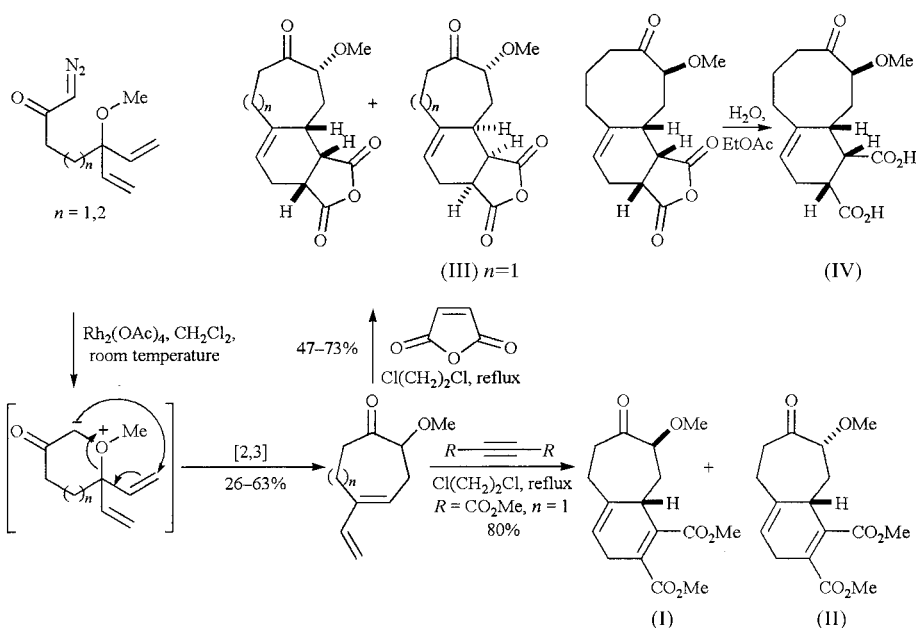
### Comment

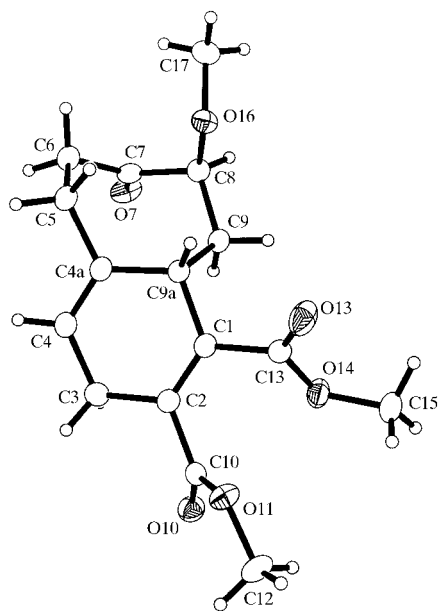
As part of a broad programme concerning the rapid construction of medium-ring polycyclic units found in natural products, we explored the Diels–Alder reactions of vinyl-substituted cycloheptene and cyclooctene systems generated by formal [2,3]-rearrangement of carbenoid-derived oxonium ylides. The novel bicyclic and tricyclic systems containing a seven-membered carbocycle, compounds (I), (II) and (III), were prepared by the reaction of dimethylacetylene dicarboxylate or maleic anhydride with 2-methoxy-5-vinyl-cyclohept-4-enone, itself prepared by [2,3]-sigmatropic ring-expansion of catalytically generated cyclic divinyl-substituted oxonium

ylides (see Scheme). Similarly, a bicyclic compound containing an eight-membered carbocycle, (IV), was prepared by reaction of maleic anhydride with 2-methoxy-5-vinyl-cyclooct-4-enone and hydrolysis of the resulting anhydride.

Crystallographic characterization has been an effective method of unambiguously establishing the stereochemical outcome of these Diels–Alder reactions, permitting the relative configuration of the stereogenic centres in each diastereoisomer to be determined. Compounds (I) and (II) form a pair of diastereomers, in which the relative configuration at C8 and C9*a* has been determined as *S*\*,*S*\* and *R*\*,*S*\*, respectively. Apart from this difference in configuration, the other significant differences in molecular structure are in the orientation of the ester side arms attached at C1 and C2. These differences can be seen in Figs. 1 and 2, and are illustrated by the following interplanar angles, where plane *A* contains atoms C13/O13/C15/O14, plane *B* C10/O10/O11/C12 and plane *C* C13/C1/C2/C10: *AB* angles are 135.7 and 13.5°, *AC* 41.2 and 81.6°, and *BC* 130.7 and 86.5° for (I) and (II), respectively. The differences are also shown by the C2–C1–C13–O13 and O10–C10–C2–C1 torsion angles (Tables 2 and 3). The different orientations have different intramolecular contact distances between the ester arms; the separation between O11 and O14 of 2.835 Å in (I), compared with 4.845 Å in (II), may be due to the formation of dimers in (I) through a weak C–H···O interaction between C4 and O13. In (II), where the two ester groups are almost orthogonal to one another, the closest contact is between O13 and C10 (2.65 Å).

The conformations of the two rings in this pair of structures are almost identical. In both cases, the six-membered ring adopts a nearly ideal boat conformation, with C3 and C9*a* displaced in the same direction from the plane of the remaining four atoms by 0.165 (2) and 0.205 (2) Å, respectively, for (I), and by –0.203 (3) and –0.235 (3) Å, respectively,

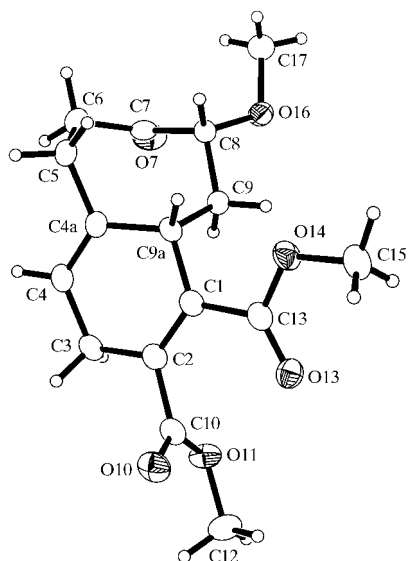




**Figure 1**  
A view of the molecule of (I) showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

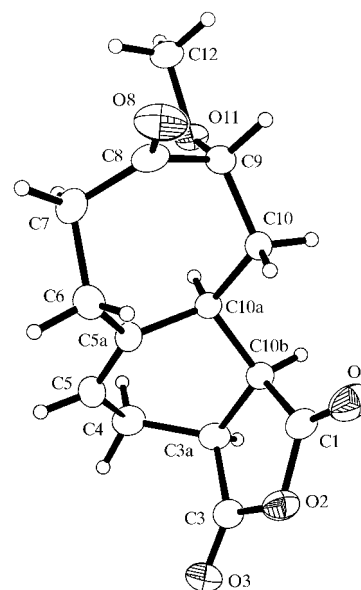
tively, for (II). The overall ring plane has an r.m.s. deviation of 0.087 Å for (I) and 0.103 Å for (II). The planes through the two half-rings defined by C9a/C1/C2/C3 and C9a/C4a/C4/C3 have deviations of only 0.007 and 0.004 Å, respectively, in (I), and 0.002 and 0.006 Å, respectively, in (II), with a hinge angle about C9a···C3 of 16.79 (9)° in (I) and 19.79 (11)° in (II). The puckering parameters (Cremer & Pople, 1975) for both the six-membered and the irregular seven-membered ring are given in Table 1.

Adduct (III) is a tricyclic compound with four stereogenic centres at C3a, C9, C10a and C10b, the relative configurations

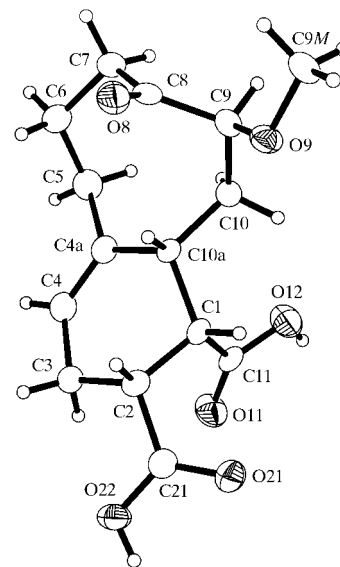


**Figure 2**  
A view of the molecule of (II) showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

of which have been determined as *S*\*, *R*\*, *S*\* and *R*\*, respectively (Fig. 3). As in the previous compounds, the six-membered ring adopts a nearly ideal boat conformation, with C4 and C10a displaced in the same direction from the plane of the other four ring atoms by 0.515 (2) and 0.565 (2) Å, respectively. The overall ring plane has an r.m.s. deviation of 0.087 Å, while the planes through the two half-rings, defined by C4/C3a/C10b/C10a and C4/C5/C5a/C10a, have deviations of only 0.004 and 0.008 Å, respectively, with a hinge angle of 46.75 (7)° about C4···C10a. The five-membered ring is planar to within 0.009 Å, but with O1 and O3 displaced in opposite



**Figure 3**  
A view of the molecule of (III) showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.



**Figure 4**  
A view of the molecule of (IV) showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

directions from the ring plane by 0.021 (2) and  $-0.042$  (2) Å, respectively.

Compound (IV) is again a bicyclic compound, but in this case containing an eight-membered carbocycle and a six-membered ring (Fig. 4). In this case, the six-membered ring adopts an envelope conformation, with C1 displaced by  $-0.703$  (7) Å from the plane of the other five atoms, which define a plane with an r.m.s. deviation of only 0.003 Å. The

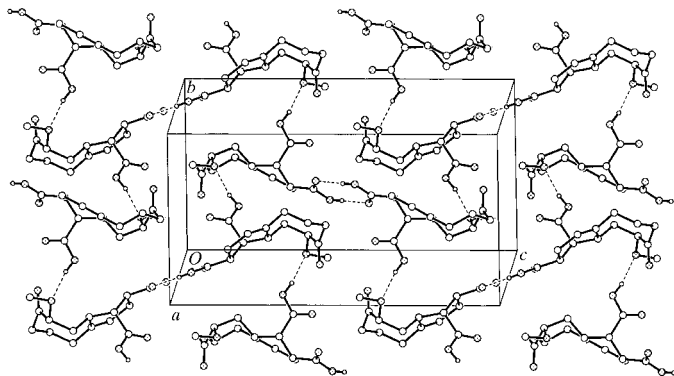


Figure 5

A view showing the two-dimensional network structure of (IV). C atoms are drawn as open circles, O atoms as dotted circles and H atoms as smaller open circles.

puckering parameters for the six-membered and irregular eight-membered ring are given in Table 1. The hydrogen bonding links molecules to form centrosymmetric dimers by inversion through  $(0, 1, \frac{1}{2})$ . These dimers are each linked to four neighbouring dimers related by  $2_1$  screw-axis operations (Fig. 5). These interactions result in a two-dimensional network structure which is infinite in the *bc* plane but does not propagate along the *a* axis.

## Experimental

The syntheses of (I), (II) and (III) have been described elsewhere (Clark *et al.*, 2001). Compound (IV) was produced by hydrolysis of (III) ( $n = 2$ ) as a result of adventitious water present in the solvent used for recrystallization. The Diels–Alder adducts (I) and (II) were each dissolved in the minimum quantity of warm diethyl ether, while adducts (III) and (IV) were each dissolved in the minimum quantity of warm ethyl acetate. In each case, the solution was allowed to cool to room temperature and then hexane was added until slight turbidity was observed. The solutions of the Diels–Alder adducts were allowed to evaporate slowly at room temperature over several days to afford crystals suitable for X-ray analysis.

Table 1  
Ring-puckering parameters (Å, °) for compounds (I)–(IV).

	Ring size	$q_2$	$q_3$	$q_4$	$\psi_2$	$\psi_3$	$Q_T$	$\theta$
(I)	6	0.253 (2)	0.012 (2)		298.6 (4)		0.253 (2)	87.3 (5)
(I)	7	0.515 (2)	0.675 (2)		253.6 (2)	144.2 (2)	0.849 (2)	
(II)	6	0.214 (1)	0.015 (1)		300.7 (3)		0.214 (1)	86.0 (3)
(II)	7	0.538 (1)	0.652 (1)		241.6 (1)	139.4 (1)	0.845 (1)	
(III)	6	0.624 (1)	$-0.021$ (1)		59.0 (1)		0.624 (1)	92.0 (1)
(III)	7	0.382 (1)	0.699 (1)		250.1 (2)	259.3 (1)	0.797 (1)	
(IV)	6	0.404 (4)	$-0.309$ (4)		180.6 (5)		0.509 (4)	127.5 (5)
(IV)	8	0.869 (4)	0.739 (4)	0.272 (4)	33.3 (3)	110.7 (3)	1.173 (4)	

## Compound (I)

### Crystal data

$C_{16}H_{20}O_6$   
 $M_r = 308.32$   
 Triclinic,  $P\bar{1}$   
 $a = 7.4878$  (9) Å  
 $b = 10.1793$  (12) Å  
 $c = 11.0220$  (13) Å  
 $\alpha = 69.955$  (2)°  
 $\beta = 83.957$  (2)°  
 $\gamma = 79.806$  (2)°  
 $V = 775.85$  (16) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.320$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5947 reflections  
 $\theta = 2.4$ – $28.7^\circ$   
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Block, colourless  
 $0.5 \times 0.3 \times 0.3$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\omega$  scans  
 9181 measured reflections  
 3597 independent reflections  
 3148 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.024$   
 $\theta_{max} = 28.7^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -13 \rightarrow 13$   
 $l = -14 \rightarrow 14$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.100$   
 $S = 1.06$   
 3597 reflections  
 202 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.1526P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.34$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.20$  e Å<sup>-3</sup>

Table 2

Selected torsion angles (°) for (I).

C1–C2–C10–O10	$-130.12$ (11)	C2–C1–C13–O13	$-134.76$ (12)
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## Compound (II)

### Crystal data

$C_{16}H_{20}O_6$   
 $M_r = 308.32$   
 Monoclinic,  $C2/c$   
 $a = 27.666$  (9) Å  
 $b = 5.066$  (2) Å  
 $c = 22.793$  (7) Å  
 $\beta = 105.149$  (5)°  
 $V = 3084$  (2) Å<sup>3</sup>  
 $Z = 8$

$D_x = 1.328$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 885 reflections  
 $\theta = 3.1$ – $18.1^\circ$   
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Block, colourless  
 $0.50 \times 0.45 \times 0.25$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\omega$  scans  
 10 535 measured reflections  
 3584 independent reflections  
 2967 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.058$   
 $\theta_{max} = 28.7^\circ$   
 $h = -37 \rightarrow 35$   
 $k = -4 \rightarrow 6$   
 $l = -27 \rightarrow 29$   
 Intensity decay: 3%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.126$   
 $S = 0.98$   
 3584 reflections  
 199 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 8.3P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.37$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.19$  e Å<sup>-3</sup>

Table 3

Selected torsion angles (°) for (II).

C1–C2–C10–O10	87.2 (2)	C2–C1–C13–O13	11.8 (3)
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## Compound (III)

## Crystal data

$C_{14}H_{16}O_5$	$D_x = 1.418 \text{ Mg m}^{-3}$
$M_r = 264.27$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5832 reflections
$a = 14.1076 (19) \text{ \AA}$	$\theta = 2.3\text{--}28.6^\circ$
$b = 11.3501 (15) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 7.7762 (10) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 96.280 (2)^\circ$	Block, colourless
$V = 1237.7 (3) \text{ \AA}^3$	$0.42 \times 0.40 \times 0.31 \text{ mm}$
$Z = 4$	

## Data collection

Bruker SMART1000 CCD area-detector diffractometer	$R_{\text{int}} = 0.033$
$\omega$ scans	$\theta_{\text{max}} = 28.6^\circ$
10 858 measured reflections	$h = -18 \rightarrow 18$
3047 independent reflections	$k = -14 \rightarrow 14$
2437 reflections with $I > 2\sigma(I)$	$l = -10 \rightarrow 10$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 0.2015P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
2896 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
173 parameters	
H-atom parameters constrained	

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.123P)^2 + 1.776P]$
$R[F^2 > 2\sigma(F^2)] = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.231$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
2715 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
192 parameters	
H-atom parameters constrained	

Due to very weak diffraction at high angles, data above  $\theta = 26^\circ$  for (IV) were excluded from the final cycles of refinement. In all cases, H atoms were placed geometrically, except for hydroxy and methyl H atoms, which were located from circular difference Fourier syntheses. Geometrically placed H atoms were refined riding on their carrier atoms, while those from the difference Fourier syntheses were refined as part of rigid groups allowed to rotate about the local C—O or C—C vector. The methine, methylene and methyl C—H distances were constrained to 1.00, 0.99 and 0.98 Å, respectively, and the O—H distance to 0.84 Å. H-atom displacement parameters were related to those of their carrier atoms by  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C}, \text{O})$ , where  $x = 1.5$  for OH and methyl H atoms, and 1.2 for all other CH. The Daresbury Laboratory SRS (Cernik *et al.*, 1997) was the radiation source for compound (IV); *SADABS* (Sheldrick, 1996) was used to correct for the beam decay at the synchrotron.

For compounds (I), (II) and (III), data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE* and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*. For compound (IV), data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE* and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2001).

Table 4

Hydrogen-bonding geometry (Å, °) for (III).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
$C6\text{—}H6B\cdots O3^i$	0.99	2.42	3.3900 (16)	168

Symmetry code: (i)  $1 - x, 1 - y, -z$ .

## Compound (IV)

## Crystal data

$C_{15}H_{20}O_6$	Synchrotron radiation
$M_r = 296.31$	$\lambda = 0.6892 \text{ \AA}$
Orthorhombic, $Pbca$	Cell parameters from 5549 reflections
$a = 14.676 (2) \text{ \AA}$	$\theta = 3.2\text{--}29.1^\circ$
$b = 9.967 (2) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 18.937 (3) \text{ \AA}$	$T = 150 (2) \text{ K}$
$V = 2770.0 (8) \text{ \AA}^3$	Tablet, colourless
$Z = 8$	$0.06 \times 0.05 \times 0.01 \text{ mm}$
$D_x = 1.421 \text{ Mg m}^{-3}$	

## Data collection

Bruker SMART CCD area-detector diffractometer on SRS Station 9.8	$R_{\text{int}} = 0.136$
$0.15^\circ \omega$ scans	$\theta_{\text{max}} = 26^\circ$
18 905 measured reflections	$h = -20 \rightarrow 17$
2715 independent reflections	$k = -14 \rightarrow 12$
1769 reflections with $I > 2\sigma(I)$	$l = -25 \rightarrow 24$

Table 5

Hydrogen-bonding geometry (Å, °) for (IV).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
$O12\text{—}H12\cdots O9^j$	0.84	1.89	2.716 (4)	168
$O22\text{—}H22\cdots O21^ii$	0.84	1.78	2.621 (4)	174

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

We would like to acknowledge EPSRC for a studentship (ALB) and the award of a diffractometer, CLRC for access to Station 9.8 and Mr A. N. Khlobystov for experimental assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1070). An additional figure is also available. Services for accessing these data are described at the back of the journal.

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