

Data collection

Enraf–Nonius CAD-4
diffractometer
2 θ/ω scans
Absorption correction: none
3850 measured reflections
2033 independent reflections
(plus 1259 Friedel-related reflections)
3120 reflections with
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 76.47^\circ$
 $h = -11 \rightarrow 11$
 $k = -12 \rightarrow 12$
 $l = -22 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.103$
 $S = 1.075$
3292 reflections
234 parameters
H atoms treated by a
mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.1628P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.089$

$\Delta\rho_{\text{max}} = 0.141 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.148 \text{ e } \text{\AA}^{-3}$
Extinction correction:
SHELXL97
Extinction coefficient:
0.0053 (5)
Scattering factors from
International Tables for Crystallography (Vol. C)
Absolute structure:
Flack (1983)
Flack parameter = 0.02 (18)

Table 1. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
C2—H2...O21 ⁱ	0.98	2.34	3.199 (2)	146
C22—H22...O5 ⁱⁱ	0.98	2.58	3.516 (2)	160
C22—H22...O11	0.98	2.51	2.848 (2)	100
C13—H133...O11 ⁱⁱⁱ	0.96	2.49	3.424 (2)	164
C24—H242...O23 ^{iv}	0.97	2.59	3.543 (2)	170
C25—H252...O4 ^{iv}	0.96	2.58	3.410 (2)	145

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

Friedel opposites were collected, were regarded as symmetry independent and were thus not merged. The absolute structure was also determined by refinement of the Flack enantiomorph parameter (χ) which refined to 0.02 (18) (Flack, 1983). H atoms were included using a riding model (*SHELXL97*; Sheldrick, 1997), but their displacement parameters were refined freely; rigid methyl groups were allowed to rotate but not tip, thus contributing one additional parameter each.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *CAD-SHEL* (Kopf, 1987). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (Burnett & Johnson, 1996). Software used to prepare material for publication: *PLATON96* (Spek, 1990).

Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1359). Services for accessing these data are described at the back of the journal.

References

- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP* III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1. Enraf–Nonius, Delft, The Netherlands.
Evans, D. A., Takacs, J. M., McGee, L. M., Ennis, M. D. & Mathre, D. J. (1981). *Pure Appl. Chem.* **53**, 1109–1127.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Jeffrey, G. A., Maluszynska, H. & Mitra, J. (1985). *Int. J. Biol. Macromol.* **7**, 336–348.
Köll, P. & Lützen, A. (1996). *Tetrahedron Asymmetry*, **7**, 637–640.
Köll, P. & Lützen, A. (1997). *Tetrahedron Asymmetry*, **8**, 29–32.
Kopf, J. (1987). *CAD-SHEL. Program for Data Reduction of Enraf–Nonius CAD-4 Data*. University of Hamburg, Germany.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
Steiner, T. (1996). *Crystallogr. Rev.* **6**, 1–57.

Acta Cryst. (1999). **C55**, 1542–1545

1,4,7,10-Tetraoxacyclododecane–acetone thiosemicarbazone (1/2)

OLIVER MOERS, KARNA WUJAYA, PETER G. JONES AND ARMAND BLASCHETTE

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

(Received 22 March 1999; accepted 6 May 1999)

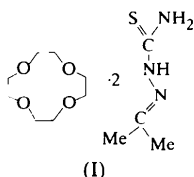
Abstract

In the centrosymmetric formula unit of the title complex, C₈H₁₆O₄·2C₄H₉N₃S, the 1,4,7,10-tetraoxacyclododecane molecule adopts the biangular [66] conformation and the thiosemicarbazone molecules are linked to the macrocycle *via* a long and appreciably bent N—N—H...O hydrogen bond [N...O 2.992 (2) Å and N—H...O 158 (2)°]. These units are associated into sheets by two additional hydrogen bonds, N—H...O and N—H...S, originating from the NH₂ group and utilizing the thioureido S atom or the second crystallographically independent ether O atom as acceptors.

Comment

According to a search of the October 1998 version of the Cambridge Structural Database (Allen & Kennard, 1993), the number of metal-free crystal structures in which 1,4,7,10-tetraoxacyclododecane (12-crown-4) has been found to interact directly with uncharged mol-

ecules is small. Apart from a ternary clathrate involving γ -cyclodextrin and water (Kamitori *et al.*, 1986), and a binary adduct with the zwitterion $^+H_3N-SO_3^-$ (Simonov *et al.*, 1993), only three adducts with uncharged molecules have been characterized by X-ray diffraction. These binary compounds, of general formula 12-crown-4·2*D*, where *D* is Ph_3SiOH (Babaian *et al.*, 1990), $(PhSO_2)_2NH$ (Wijaya *et al.*, 1998) or $(EtSO_2)_2CH_2$ (Michalides *et al.*, 1995), form a series displaying $O-H\cdots O$, $N-H\cdots O$ or $C-H\cdots O$ interactions between the respective substrate and the macrocyclic polyether. We now describe the solid-state structure of the title complex, (I), which was discovered adventitiously (see *Experimental*) and which represents only the second example of a binary adduct between 12-crown-4 and uncharged molecules connected by $N-H\cdots O$ interactions.



The centrosymmetric formula unit of (I) is shown in Fig. 1 and selected intramolecular geometric data are listed in Table 1. The macrocycle in (I) adopts the C_i symmetric and biangular [66] conformation, which also occurs in pure 12-crown-4 (Groth, 1978), in the aforementioned molecular 1:2 complexes and in a number of structures containing metal cations [for systematic conformational analyses of 12-crown-4 complexes see Raithby *et al.* (1997) and Hay *et al.* (1995)]. For the bond lengths and angles of the twelve-membered ring, the following normal ranges and mean values were observed: C—O 1.424 (2)–1.429 (2) Å [mean 1.427 (2) Å], C—C 1.499 (3)–1.501 (3) Å [mean 1.500 (3) Å], C—O—C 112.33 (14)–114.89 (14)° [mean 113.6 (1)°] and O—C—C 107.58 (14)–112.06 (16)° [mean 110.3 (2)°]. The torsion angles of the ring are given in Table 1.

The bond distances and angles of the acetone thiosemicarbazone molecule (Table 1) are in reasonable

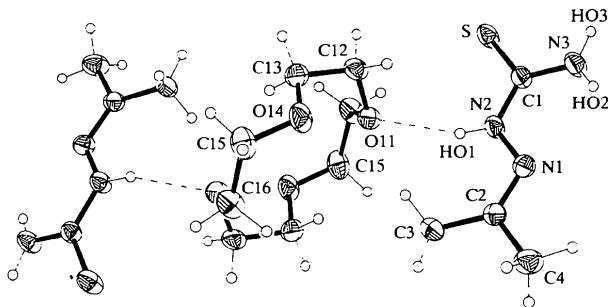


Fig. 1. The structure of (I) in the crystal. Displacement ellipsoids represent 50% probability levels and H-atom radii are arbitrary. Only the asymmetric unit is numbered. One H atom at C3 and one at C15' are obscured. [Symmetry code: (i) $1 - x, 2 - y, 1 - z$.]

agreement with less precise data obtained for the pure compound by X-ray diffraction at room temperature (final *R*1 value = 0.070; Palenik *et al.*, 1974); for convenience, the original atom-numbering scheme of the thiosemicarbazone moiety has been retained in Fig. 1. The molecules adopt identical conformations in the two structures, and relevant torsion angles for (I) are listed in Table 1.

The three independent H atoms bonded to N are well ordered and all of them are involved in hydrogen bonds, leading to the formation of sheets perpendicular to $[10\bar{1}]$ (Fig. 2 and Table 2). Within the centrosymmetric formula unit, the long and appreciably bent $N2-H\cdots O11$ bond (and its symmetry equivalent) links the hydrazine NH donors to the crown ether. Translation-related formula units are then associated into chains by weak $N3-H\cdots O14$ bonds originating from the amide functions and utilizing the second pair of equivalent ether O atoms as acceptors. Finally, interchain cross-linking is achieved *via* pairs of resonance-induced $N-H\cdots S$ hydrogen bonds (Allen *et al.*, 1997). The centrosymmetric $R_2^2(8)$ motif (Bernstein *et al.*, 1995) created by the latter interactions is also present in the structure of pure acetone thiosemicarbazone.

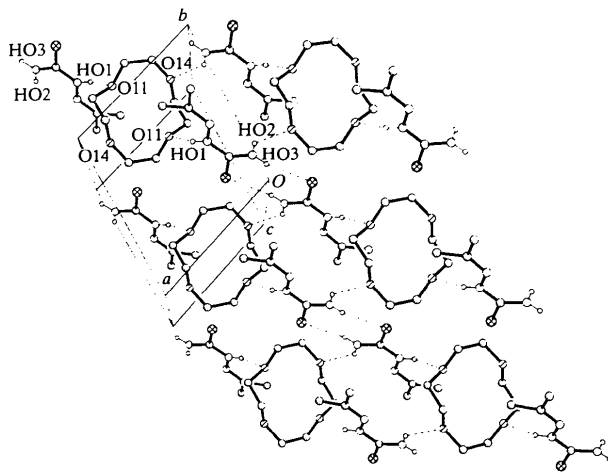


Fig. 2. The packing diagram for (I). H atoms not involved in hydrogen bonding have been omitted for clarity (see text). Hydrogen bonds are indicated by dashed lines.

Some additional features occurring in the hydrogen-bond network are noteworthy. First, the $N2-H\cdots O11$ bond in (I) is far less pronounced than the corresponding hydrogen bond in the 1:2 complex between 12-crown-4 and the stronger NH acid $(PhSO_2)_2NH$ (Wijaya *et al.*, 1998), where the relevant geometric parameters are $H\cdots O$ 1.98 (2), $N\cdots O$ 2.771 (2) Å and $N-H\cdots O$ 170 (2)°. Secondly, the $N2-H\cdots O11$ bond appears to be assisted by a $C3-H\cdots O11$ interaction that might be classified as a hydrogen bond (Desiraju, 1996). Thirdly, the catenating $N3-H\cdots O14$ contact probably belongs to a three-centre hydrogen bond, the second branch of

which forms an intramolecular N3—H···N1 motif of graph-set *S*(5). For clarity, the C3—H···O11 and N3—H···N1 contacts are not indicated in Figs. 1 and 2, but their geometric data have been included in Table 2.

Experimental

The crystal used for X-ray diffraction was obtained fortuitously during an attempt to cocrystallize [Na(12-crown-4)₂](MeSO₂)₂N with thiosemicarbazide, when acetone was used inadvertently as a solvent component. Bulk quantities of (I) are readily prepared by dissolving 12-crown-4 (0.22 g, 1.25 mmol) and thiosemicarbazide (0.23 g, 2.5 mmol) in anhydrous acetone (5 ml) and storing the solution at 243 K for several days [typical yield: 66%, 0.36 g; m.p. 416–418 K; for comparison, the m.p. of pure 12-crown-4 is *ca* 273 K (Groth, 1978) and of acetone thiosemicarbazone is 454 K (Gingras *et al.*, 1960)]. A satisfactory elemental analysis was obtained. ¹H NMR (CDCl₃, 200 MHz; δ, p.p.m.): 1.91 (*s*, 6H, *cis*-Me), 2.02 (*s*, 6H, *trans*-Me), 3.71 (*s*, 16H, 12-crown-4); δ(NH) not detected. For ¹H NMR resonances of acetone thiosemicarbazone, see Karabatsos *et al.* (1964).

Crystal data

C₈H₁₆O₄·2C₄H₉N₃S

M_r = 438.61

Triclinic

P $\bar{1}$

a = 7.847 (3) Å

b = 8.594 (3) Å

c = 9.867 (3) Å

α = 115.612 (14)°

β = 98.079 (15)°

γ = 104.033 (16)°

V = 558.8 (3) Å³

Z = 1

D_x = 1.303 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 48 reflections

θ = 10.0–11.5°

μ = 0.271 mm⁻¹

T = 143 (2) K

Block

0.4 × 0.3 × 0.3 mm

Colourless

Data collection

Stoe Stadi-4 diffractometer

ω/θ-scans

Absorption correction: none

3225 measured reflections

1975 independent reflections

1780 reflections with

I > 2σ(*I*)

R_{int} = 0.041

θ_{max} = 25.02°

h = -9 → 9

k = -10 → 10

l = -11 → 11

3 standard reflections

frequency: 90 min

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.036

wR(*F*²) = 0.093

S = 1.059

1975 reflections

141 parameters

H atoms: see below

w = 1/[σ²(*F_o*²) + (0.0361*P*)² + 0.2808*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.24 e Å⁻³

Δρ_{min} = -0.28 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S—C1	1.6958 (18)	N3—C1	1.326 (2)
N1—C2	1.280 (2)	C2—C4	1.493 (2)
N1—N2	1.388 (2)	C2—C3	1.497 (3)
N2—C1	1.342 (2)		
C2—N1—N2	117.30 (14)	N2—C1—S	119.36 (13)
C1—N2—N1	119.28 (15)	N1—C2—C4	117.14 (16)
N3—C1—N2	118.15 (16)	N1—C2—C3	126.07 (16)
N3—C1—S	122.48 (14)	C4—C2—C3	116.79 (16)
C2—N1—N2—C1	176.18 (16)		
N1—N2—C1—N3	-1.2 (3)		
N1—N2—C1—S	177.90 (12)		
N2—N1—C2—C4	178.24 (15)		
N2—N1—C2—C3	-1.2 (3)		
O11—C12—C13—O14	75.21 (17)		
C12—C13—O14—C15	-164.26 (15)		
C13—O14—C15—C16	96.55 (19)		
O14—C15—C16—O11 ⁱ	-73.6 (2)		
C15—C16—O11 ⁱ —C12 ⁱ	150.52 (15)		
C16—O11 ⁱ —C12 ⁱ —C13 ⁱ	-90.90 (17)		

Symmetry code: (i) 1 - *x*, 2 - *y*, 1 - *z*.

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

<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>
N2—HO1···O11	0.86 (2)	2.18 (2)	2.992 (2)	158 (2)
N3—HO2···O14 ⁱ	0.87 (2)	2.35 (2)	3.036 (2)	136 (2)
N3—HO2···N1	0.87 (2)	2.31 (2)	2.647 (2)	103 (2)
N3—HO3···S ⁱⁱ	0.85 (2)	2.54 (2)	3.380 (2)	169 (2)
C3—H3A···O11	0.98	2.54	3.238 (2)	128

Symmetry codes: (i) -*x*, 1 - *y*, -*z*; (ii) -*x*, -*y*, -*z*.

Hydrazine H atoms were freely refined. Methyl H atoms were located from difference syntheses, and were idealized and refined as rigid groups allowed to rotate but not tip. All other H atoms were treated as riding.

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL97*.

KW gratefully acknowledges a Doctoral Scholarship from the Deutscher Akademischer Austauschdienst (DAAD). The authors thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauff for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1332). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Bird, C. M., Rowland, R. S. & Raithby, P. R. (1997). *Acta Cryst.* **B53**, 680–695.
- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Babaian, E. A., Huff, M., Tibbals, F. A. & Hrcir, D. C. (1990). *J. Chem. Soc. Chem. Commun.* pp. 306–307.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.
- Gingras, B. A., Homal, R. W. & Bayley, C. H. (1960). *Can. J. Chem.* **38**, 712–719.
- Groth, P. (1978). *Acta Chem. Scand. Ser. A*, **32**, 279–280.

- Hay, B. P., Rustad, J. R., Zipperer, J. P. & Wester, D. W. (1995). *J. Mol. Struct.* **337**, 39–47.
- Kamitori, S., Hirotsu, K. & Higuchi, T. (1986). *J. Chem. Soc. Chem. Commun.* pp. 690–691.
- Karabatsos, G. J., Vane, F. M., Taller, R. A. & Hsi, N. (1964). *J. Am. Chem. Soc.* **86**, 3351–3357.
- Michalides, A., Henschel, D., Blaschette, A. & Jones, P. G. (1995). *Z. Naturforsch. Teil B*, **50**, 1018–1024.
- Palenik, G. J., Rendle, D. F. & Carter, W. S. (1974). *Acta Cryst.* **B30**, 2390–2395.
- Raithby, P. R., Shields, G. P. & Allen, F. H. (1997). *Acta Cryst.* **B53**, 241–251.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.
- Simonov, Yu. A., Fonari, M. S., Dvorkin, A. A., Malinovski, T. I., Lipkowski, J. & Ganin, E. V. (1993). *J. Incl. Phenom. Mol. Recognit. Chem.* **16**, 315–327.
- Stoe & Cie (1992a). *DIF4. Diffractometer Control Program*. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1992b). *REDU4. Data Reduction Program*. Stoe & Cie, Darmstadt, Germany.
- Wijaya, K., Moers, O., Jones, P. G. & Blaschette, A. (1998). *Acta Cryst.* **C54**, 818–820.

Acta Cryst. (1999). **C55**, 1545–1547

N,N'-Bis(2-tosylaminobenzylidene)-1,3-propanediamine†

JOSÉ MAHÍA,^a MIGUEL A. MAESTRO,^a MIGUEL VÁZQUEZ,^b
MANUEL R. BERMEJO,^b JESÚS SANMARTÍN^b AND
MARCELINO MANEIRO^b

^a*Servicios Xerais de Apoio á Investigación, Universidade da Coruña, Campus da Zapateira s/n, E-15071 A Coruña, Spain, and* ^b*Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, Av. das Ciencias s/n, E-15706 Santiago de Compostela (A Coruña), Spain. E-mail: sxaixs@udc.es*

(Received 3 February 1999; accepted 17 May 1999)

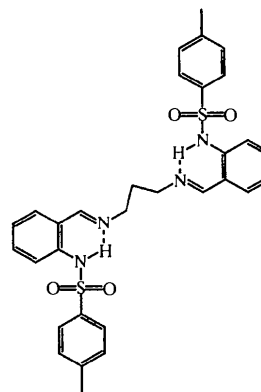
Abstract

The conformation of the title molecule, C₃₁H₃₂N₄O₄S₂, in the solid state is strongly influenced by intramolecular hydrogen-bond interactions (N—H···N), which probably minimize the steric hindrance of the tosyl groups. The molecule is not planar and with long distances between aminic N atoms [7.724 (3) Å], a major change in conformation will be required for it to act as a tetradentate ligand *via* its four N atoms.

† Alternative name: *N,N'*-{1,3-propanediylbis[2-(nitrobenzylidene)-*p*-phenylene]}bis(tolueno-4-sulfonamide).

Comment

In recent years, it has been recognized that Schiff base ligands derived from 1,3-diaminopropan-2-ol and salicylaldehyde, pyridine, pyrrole or imidazole (Butcher *et al.*, 1986*a,b*; Borer & Sinn, 1988; Mazurek *et al.*, 1985; Nishida & Kida, 1986) play an important role in the synthesis of model complexes for copper-containing metalloproteins. We are interested in obtaining secondary amides, in particular dianionic N₄ ligands like the title compound, H₂L, derived from the condensation of 1,3-propanediamine and 2-tosylaminobenzaldehyde. These could act as polydentate ligands through their N and O atoms. The molecular structure of the mononuclear complex [*N,N'*-bis(2-aminobenzylidene)-1,3-propanediamine]nickel(II), which contains a similar ligand without tosyl groups, has been reported previously (Bailey & McKenzie, 1974).



H₂L

To our knowledge, no X-ray crystal structure of either the uncoordinated or the coordinated H₂L ligand has been reported previously. Therefore, we have determined the crystal structure of H₂L so that subsequent changes upon the coordinated form may be investigated.

In this molecule, the N2=C14 and N3=C18 distances of 1.266 (3) and 1.271 (3) Å, respectively, are consistent with C=N double bonding. Both bond angles of 117.8 (2)° around the N2 and N3 atoms confirm their *sp*² character.

The disposition adopted by the 2-tosylaminobenzylidene groups in the solid state is conditioned by two strong N—H···N interactions. The distance between the N atoms are 2.666 (2) and 2.674 (3) Å for N1···N2 and N3···N4, respectively (H1A···N2 = 2.05 and H4A···N3 = 2.11 Å). As expected, these intramolecular hydrogen-bond interactions strongly influence the conformation of the molecule, forming N1—C8—C13—C14—N2—H1A and N4—C24—C19—C18—N3—H4A six-membered rings, with almost perfect plane deviations of 0.0936 and 0.1119 Å, respectively. There is also an intermolecular C—H···O interaction with C12···O2ⁱ = 3.362 (3), H12A···O2ⁱ = 2.57 Å and