

Two isomeric butadiene–N-(acetoxyphenyl)maleimide Diels–Alder adducts: supramolecular structure directed by C—H···X ($X = O$ and π) hydrogen bonds and perpendicular dipole carbonyl–carbonyl interactions

Jose G. Trujillo-Ferrara,^a Rosa Luisa Santillán-Baca,^b Norberto Farfán-García,^b Itzia I. Padilla-Martínez^c and Efrén V. García-Báez^{c*}

^aSección de Graduados y Departamento de Bioquímica, Escuela Superior de Medicina, Instituto Politécnico Nacional, México DF 11340, Mexico, ^bCentro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional, Avenida IPN 2508, México DF 07330, Mexico, and ^cUnidad Profesional Interdisciplinaria de Biotecnología, Instituto Politécnico Nacional, Avenida Acueducto s/n, Barrio La Laguna Ticomán, México DF 07340, Mexico

Correspondence e-mail: vgarcia@acei.upibi.ipn.mx

Received 1 September 2005

Accepted 18 January 2006

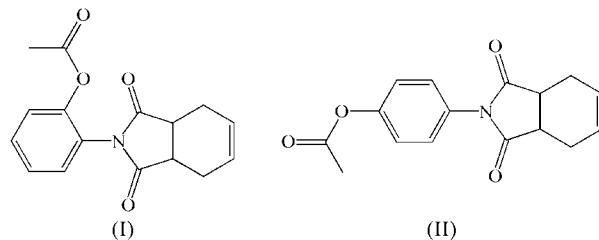
Online 11 February 2006

The molecular and supramolecular structures of 2-(1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-2-yl)phenyl acetate, $C_{16}H_{15}NO_4$, (I), and its *para* isomer, 4-(1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-2-yl)phenyl acetate, (II), are reported. The torsion angle between the succinimide and benzene rings depends on the position of the acetoxy substitution [89.7 (1) and 61.9 (1) $^\circ$ for (I) and (II), respectively]. The twist of the acetoxy group relative to the mean plane of the benzene ring is almost independent of the acetoxy position [66.0 (1) and 70.0 (1) $^\circ$]. Packing interactions for both compounds include soft C—H··· X ($X = O$ and Ph) interactions, forming chains of centrosymmetric dimers and interlinked chains for (I) and (II), respectively. In addition, three perpendicular dipole C=O···C=O interactions contribute to the supramolecular structure of (II).

Comment

Substituted *N*-arylmaleimides have been used to control the stereochemistry of Diels–Alder cycloadditions (Kitagawa *et al.*, 1998). Depending on the appropriate selection of the *ortho* substituent, the *N*—Ar torsion angle and the barrier to rotation are increased in comparison to those in the unsubstituted *N*-arylmaleimides (Curran *et al.*, 1994). More recently, molecular induced recognition between the diene and the maleimide have been used to control the stereochemistry of cycloaddition reactions (Bennes *et al.*, 2001). However, the X-ray structures of only five Diels–Alder adducts derived

from butadiene and substituted *N*-arylmaleimides have been reported, in contrast to almost 40 unsubstituted adducts (Cambridge Structural Database; Version of May 2005; Allen, 2002). Previously, the molecular and supramolecular structures of two Diels–Alder adducts between *ortho*- and *para*-*N*-acetoxyphenylmaleimides and -furan were reported (Trujillo-Ferrara *et al.*, 2004). The molecular and supramolecular structures of the Diels–Alder adducts 2-(1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-2-yl)phenyl acetate, (I), and its *para* isomer (II), are analyzed here.



Compounds (I) and (II) crystallize in the monoclinic space groups $P2_1/n$ and $P2_1/c$, respectively. Their molecular structures are shown in Figs. 1 and 2, and selected bond lengths and angles are listed in Tables 1 and 3, respectively. In both compounds, the succinimide group (C1/O1/N2/C3/O3/C3A/C7A) has an r.m.s. deviation from the mean plane of 0.002 Å, and the cyclohexene ring exhibits a boat-like conformation. The benzene ring is twisted relative to the succinimide ring by 89.7 (1) $^\circ$ in (I), the *ortho* isomer, and by 61.9 (1) $^\circ$ in (II), the *para* isomer. These results are in agreement with the expected values for the twist necessary to relieve unfavorable steric interactions between the *o*-acetoxy group, on the benzene ring, and the succinimide carbonyl groups. The twist exhibited by (I) is equivalent to the value found in other *ortho*-*tert*-butyl (Curran *et al.*, 1994) or F-substituted Diels–Alder adducts (Li *et al.*, 2005), but in this last compound and in (I), the *ortho* substituent points to the folded face of the cyclohexene ring. The acetoxy group is twisted by 66.0 (1) and 70.0 (1) $^\circ$ from the mean plane of the benzene ring in (I) and (II), respectively. These values contrast with the broad range found for Diels–

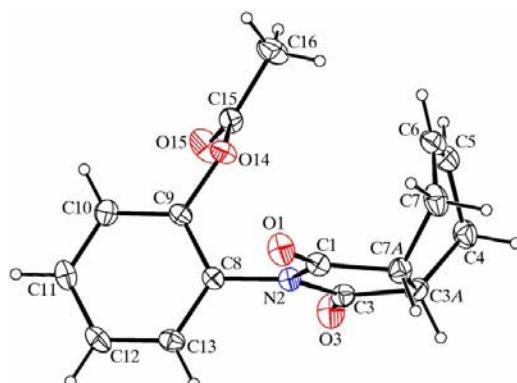


Figure 1

The molecular structure of the title *ortho* Diels–Alder adduct, (I), with displacement ellipsoids at the 30% probability level.

Alder adducts derived from *o*- and *p*-*N*-acetoxyphenyl-maleimides and -furan (Trujillo-Ferrara *et al.*, 2004).

The supramolecular structure is determined by soft C—H···X ($X = O$ and Ph) interactions in both compounds (Steiner, 2002; Umezawa *et al.*, 1998) and by carbonyl–carbonyl interactions in (II). The hydrogen-bonding geometry (including all symmetry codes) is listed in Tables 2 and 4 for (I) and (II), respectively. In (I), a centrosymmetric ring motif having graph set $R_2^2(18)$ (Bernstein *et al.*, 1995) is formed by C16—H16A···O3ⁱ interactions, involving a methyl H-atom donor and a succinimide carbonyl group as the acceptor. Although weak, the geometry of this Csp^3 —H···O interaction (Table 2) falls within the accepted ranges (Steiner & Desiraju, 1998). These dimers are interlinked by C12—H12···O15ⁱⁱ interactions between an aromatic H atom and the acetoxy carbonyl group (Table 2). Thus, chains of rings developing along the [3,9,13] direction, are formed (Fig. 3). In (II), anti-parallel chains having graph-set notation $C(6)$ are formed by C13—H13···O3ⁱⁱⁱ interactions, and these develop along the *b* axis (Table 4). The chains are interlinked by C7A—

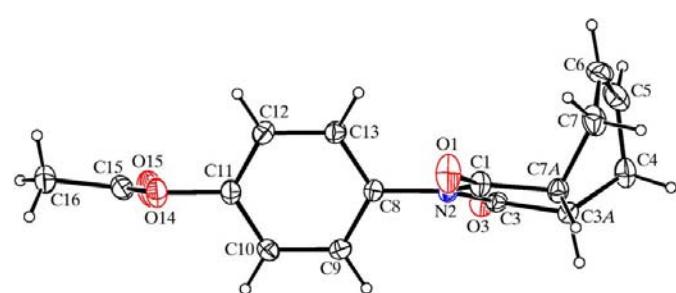


Figure 2

The molecular structure of the title *para* Diels–Alder adduct, (II), with displacement ellipsoids at the 30% probability level.

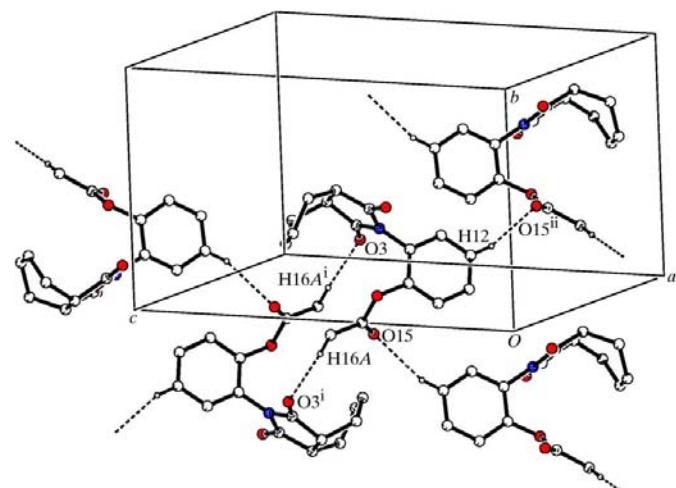


Figure 3

The supramolecular structure of the title *ortho* Diels–Alder adduct, (I), viewed along the *c* axis. [Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$]

H7A···Cg3^{iv} interactions between an axial H atom at the ring fusion and the benzene ring of a neighboring molecule (Table 4; Cg3 is the centroid of the C8–C13 ring) along the [504] direction (Fig. 4). Besides C—H···X ($X = O$ and Ph) hydrogen bonding, two carbonyl–carbonyl interactions contribute to the overall molecular architecture. Both imide carbonyl groups, C1=O1 and C3=O3, are simultaneously involved in perpendicular dipole interactions with the acetoxy carbonyl group C15=O15 [O15···C3^v = 3.152 (2) Å and C15=O5···C3^v = 139.3 (2)°; O15···C1 = 3.314 (2) Å and C15=O15···C1^v = 155.2 (2)°; symmetry code: (v) $x, -y + \frac{3}{2}, z - \frac{1}{2}$]. The O atom of the acetoxy carbonyl group C15=O15 donates electron density to the C atoms of both imide carbonyl groups C1=O1 and C3=O3. The donor–acceptor roles of the C1=O1 and C15=O15 carbonyl groups are exchanged in the third carbonyl interaction, C1=O1···C15^{vi} [O1···C15 = 3.160 (2) Å and C1=O1···C15^{vi} = 152.1 (2)°; symmetry code: (vi) $x, -y + \frac{5}{2}, z - \frac{1}{2}$]. Consequently, four-membered infinite antiparallel chains of rings zigzagging along the [010] direction are formed (Fig. 4). It is worthy of mention that the C···O distances fall below the cut-off at 3.6 Å and the C=O···C angles are in agreement with the average value of 159.7 (7)° characteristic of this dipole–dipole interaction (Allen *et al.*, 1998). Theoretical calculations have shown that this motif is frequently found in structures containing weak hydrogen-bonding donors and its strength is comparable to a C—H···O hydrogen bond (Allen *et al.*, 1998).

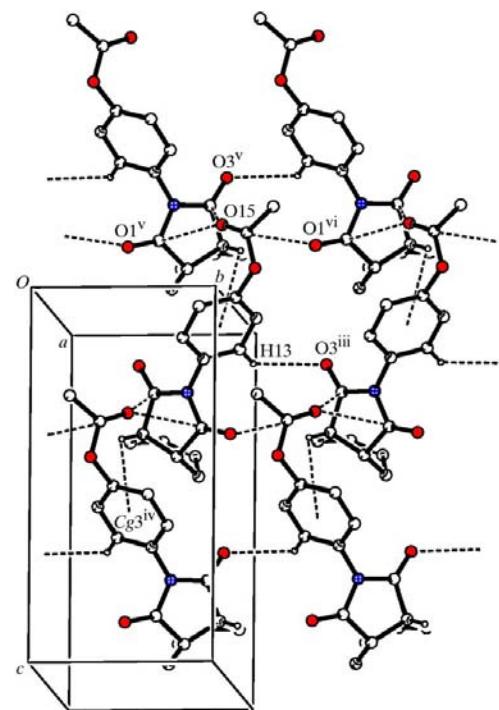


Figure 4

The supramolecular structure of the title *para* Diels–Alder adduct, (II), viewed along the *b* axis. [Symmetry codes: (iii) $x, y + 1, z$; (iv) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (vi) $x, -y + \frac{5}{2}, z - \frac{1}{2}$]

A brief comparison with the analogous Diels–Alder adducts from furan (Trujillo-Ferrara *et al.*, 2004) shows that the carbonyl group from the acetoxy group, at least one carbonyl group from the succinimide ring and the benzene ring are always engaged as acceptors in hydrogen bonding, whereas the OCH₃, Csp³H (axial) and Csp²H (aryl) H atoms always participate as hydrogen-bonding donors. However, instead of the tetrameric aggregates present in the supramolecular structure of furan derivatives, butadiene derivatives (I) and (II) are arranged in chains.

Experimental

Diels–Alder adducts (I) and (II) were obtained by the reaction between 1-(2-acetoxyphenyl)-1*H*-pyrrole-2,5-dione or 1-(4-acetoxyphenyl)-1*H*-pyrrole-2,5-dione (0.25 g, 1.8 mmol) and sulfolene (0.52 g, 2.2 mmol) dissolved in xylene (1.5 ml) in a sealed ampoule at 413 K for 10 h. The products crystallized as white solids in 82 and 85% yields, respectively. In both cases, crystals suitable for X-ray analysis were obtained from chloroform solutions by slow hexane diffusion. For (I) (m.p. 706–709 K), IR (KBr, cm^{−1}): ν 1770, 1704 (C=O), 1596 (C=C), 1366 (OAc), 1344, 1318 (C—N); ¹H NMR (p.p.m.): δ 7.43 (*td*, 1H, H_p), 7.32 and 7.29 (*m*, 1H each, H_m), 7.26 (*m*, 1H, H_b), 6.00 (*t*, 2H, H_{5,6}), 3.26 (*dd*, 2H, H_{3A,7A}), 2.71 and 2.73 (*ddd*, 4H, H_{4,7}), 2.19 (*s*, 3H, Me); ¹³C NMR (p.p.m.): δ 178.2 (C1,3), 167.6 (COO), 145.8 and 129.1 (C_o), 129.7 (C_i), 128.6 (C_p), 127.5 (C5,6), 126.0 and 123.6 (C_m), 39.2 (C3a,7a), 23.3 (C4,7), 20.8 (Me); MS *m/z* (%): 285 (6) (*M*⁺), 243 (100), 181 (1), 110 (95), 80 (34). For (II) (m.p. 688–691 K), IR (KBr, cm^{−1}): ν 1752, 1716 (C=O), 1598 (C=C), 1344 (OAc), 1344 (C—N); ¹H NMR (p.p.m.): δ 7.29 (*d*, 2H, H_o), 7.26 (*d*, 2H, H_m), 5.95 (*t*, 2H, H_{5,6}), 3.20 (*dt*, 2H, H_{3A,7A}), 2.67 and 2.28 (*m*, 4H, H_{4,7}), 2.27 (*s*, 3H, CH₃); ¹³C NMR (p.p.m.): δ 179.1 (C1,3), 169.0 (COO), 150.2 (C_p), 129.5 (C_i), 127.8 (C_o), 127.4 (C5,6), 122.2 (C_m), 39.2 (C3a,7a), 23.7 (C4,7), 21.1 (Me); MS *m/z* (%): 285 (6) (*M*⁺), 243 (100), 189 (4), 135 (15), 110 (3), 80 (46).

Compound (I)

Crystal data

C ₁₆ H ₁₅ NO ₄	<i>D</i> _x = 1.360 Mg m ^{−3}
<i>M</i> _r = 285.30	Mo <i>Kα</i> radiation
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Cell parameters from 24 reflections
<i>a</i> = 9.6673 (7) Å	<i>θ</i> = 10–11°
<i>b</i> = 9.6787 (7) Å	<i>μ</i> = 0.10 mm ^{−1}
<i>c</i> = 15.5880 (18) Å	<i>T</i> = 293 (2) K
β = 107.131 (2)°	Block, colorless
<i>V</i> = 1393.8 (2) Å ³	<i>Z</i> = 4
<i>Z</i> = 4	<i>D</i> _x = 1.314 Mg m ^{−3}

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>θ</i> _{max} = 28.0°
ω/2θ scans	<i>h</i> = −12 → 0
3470 measured reflections	<i>k</i> = 0 → 12
3291 independent reflections	<i>l</i> = −19 → 20
1861 reflections with <i>I</i> > 2σ(<i>I</i>)	3 standard reflections every 200 reflections intensity decay: 2.5%
<i>R</i> _{int} = 0.018	

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0644 <i>P</i>) ² + 0.0798 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.041	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.145	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.07	Δρ _{max} = 0.19 e Å ^{−3}
3291 reflections	Δρ _{min} = −0.19 e Å ^{−3}
190 parameters	
H-atom parameters constrained	

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

O14—C9	1.391 (2)	N2—C3	1.391 (2)
O14—C15	1.368 (2)	N2—C8	1.434 (2)
N2—C1	1.390 (2)		
C9—O14—C15	117.97 (13)	O3—C3—C3A	127.19 (17)
C1—N2—C3	112.73 (14)	N2—C8—C13	120.34 (15)
O1—C1—N2	123.52 (17)	O14—C9—C8	118.20 (15)
O1—C1—C7A	127.90 (17)	O14—C9—C10	121.41 (15)
O3—C3—N2	124.08 (17)	O14—C15—O15	122.45 (17)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

<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>
C16—H16A···O3 ⁱ	0.96	2.56	3.517 (3)	176
C12—H12···O15 ⁱⁱ	0.93	2.58	3.480 (3)	162

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

Compound (II)

Crystal data

C ₁₆ H ₁₅ NO ₄	Mo <i>Kα</i> radiation
<i>M</i> _r = 285.17	Cell parameters from 24 reflections
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	<i>θ</i> = 10–11°
<i>a</i> = 16.1630 (10) Å	<i>μ</i> = 0.10 mm ^{−1}
<i>b</i> = 6.5780 (10) Å	<i>T</i> = 293 (2) K
<i>c</i> = 13.5830 (10) Å	Block, colorless
β = 93.73 (2)°	<i>Z</i> = 4
<i>V</i> = 1441.1 (3) Å ³	0.20 × 0.15 × 0.09 mm
<i>Z</i> = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>h</i> = 0 → 21
ω/2θ scans	<i>k</i> = −8 → 0
3879 measured reflections	<i>l</i> = −17 → 17
3450 independent reflections	3 standard reflections every 200 reflections intensity decay: 2.5%
2056 reflections with <i>I</i> > 2σ(<i>I</i>)	
<i>R</i> _{int} = 0.020	
<i>θ</i> _{max} = 28.0°	

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0946 <i>P</i>) ² + 0.0607 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.051	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.182	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.14	Δρ _{max} = 0.43 e Å ^{−3}
3450 reflections	Δρ _{min} = −0.20 e Å ^{−3}
191 parameters	
H-atom parameters constrained	

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

O14—C11	1.415 (2)	N2—C3	1.394 (2)
O14—C15	1.341 (2)	N2—C8	1.434 (2)
N2—C1	1.390 (2)		
C11—O14—C15	118.19 (16)	O3—C3—C3A	128.12 (18)
C1—N2—C3	112.17 (14)	O14—C11—C10	121.18 (16)
O1—C1—N2	123.60 (17)	O14—C11—C12	116.95 (17)
O1—C1—C7A	127.50 (16)	O14—C15—O15	123.2 (2)
O3—C3—N2	123.76 (17)		

Table 4

 Hydrogen-bond geometry (\AA , $^\circ$) for (II).

Cg3 is the centroid of the C8–C13 ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C13—H13 \cdots O3 ⁱⁱⁱ	0.93	2.50	3.131 (2)	125
C7A—H7A \cdots Cg3 ^{iv}	0.98	2.65	3.611 (2)	167

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

All H atoms were refined as riding on their parent atoms, with C—H distances in the range 0.93–0.98 \AA , and $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for the other H atoms. The centroid of a set of atoms was calculated using the program *MERCURY* (Bruno *et al.*, 2002).

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1995); cell refinement: *CAD-4 EXPRESS*; data reduction: *JANA98* (Vaclav, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

This work was supported by CGPI–IPN (Coordinación General de Posgrado e Investigación del Instituto Politécnico Nacional).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM1003). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Baalham, C. A., Lommersse, J. P. M. & Raithby, P. R. (1998). *Acta Cryst.* **B54**, 320–329.
- Bennes, R., Sapró-Babiloni, M., Hayes, W. & Philip, D. (2001). *Tetrahedron Lett.* **42**, 2377–2380.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M. K., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Curran, D. P., Qui, H., Geib, S. J. & Demello, N. C. (1994). *J. Am. Chem. Soc.* **116**, 3131–3132.
- Enraf–Nonius (1995). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Kitagawa, O., Izawa, H., Sato, K., Dobashi, A., Taguchi, T. & Shiro, M. (1998). *J. Org. Chem.* **63**, 2634–2640.
- Li, B., Song, H.-B., Hsu, C.-T., Zhang, K.-L., Wu, C. & Yang, H.-Z. (2005). *Acta Cryst.* **C61**, o114–o117.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.
- Steiner, T. & Desiraju, G. R. (1998). *Chem. Commun.* pp. 891–892.
- Trujillo-Ferrara, J. G., García-Báez, E. V., Padilla-Martínez, I. I., Martínez-Martínez, F. J. & Farfan-García, N. (2004). *Acta Cryst.* **C60**, o427–o430.
- Umezawa, Y., Tsuboyama, S., Honda, K., Uzawa, J. & Nishio, M. (1998). *Bull. Chem. Soc. Jpn.* **71**, 1207–1213.
- Vaclav, P. (1998). *JANA98*. Institute of Physics AVCR, Cukravarnicka, 10 162 53, Prague, Czech Republic.