

Methoxy-ether and crown-ether
derivatives of tetrahomodioxo- and
octahomotetraoxacalix[4]arenesBernardo Masci,^a Stefano Saccheo,^a Massimiliano Fonsi,^a
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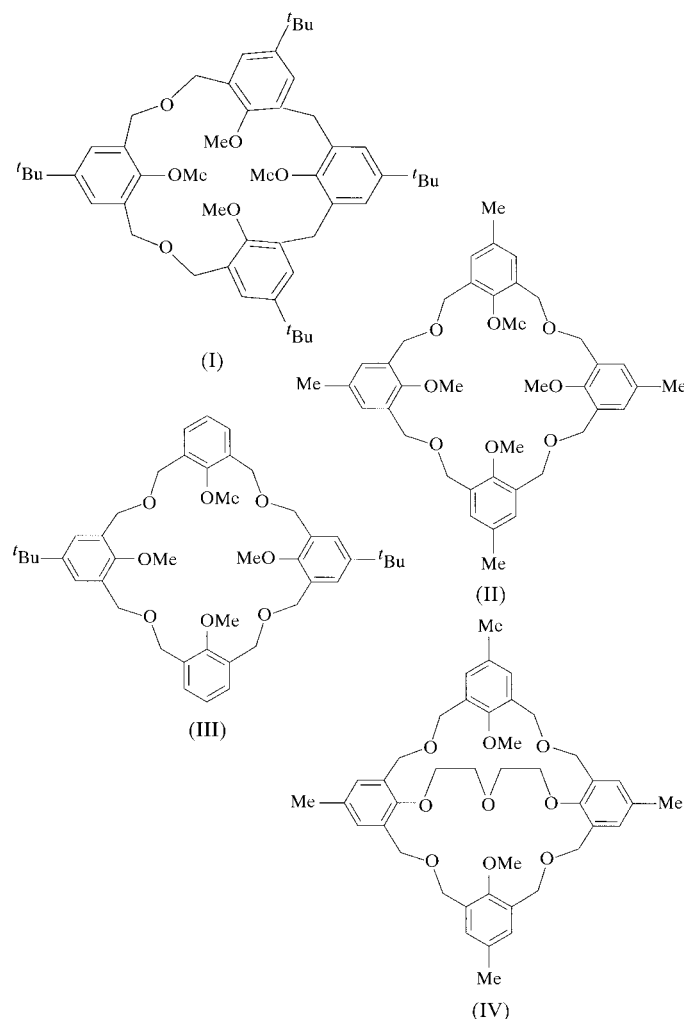
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Three methoxy-ether and one methoxy-ether/crown-ether derivatives of *p*-*tert*-butyltetrahomodioxo- and *p*-*R*-octahomotetraoxacalix[4]arenes (*R* = methyl, *tert*-butyl, H) have been investigated. The first three compounds, 7,15,21,27-tetra-*tert*-butyl-29,30,31,32-tetramethoxy-3,11-dioxapentacyclo[23.3.1.-1^{5,9}.1^{13,17}.1^{19,23}]ditriaconta-1(29),5,7,9(30),13,15,-17(31),19,21,-23(32),25,27-dodecaene, C₅₀H₆₈O₆, 33,34,35,36-tetramethoxy-7,15,23,31-tetramethyl-3,11,19,27-tetraoxapentacyclo[27.3.1.-1^{5,9}.1^{13,17}.1^{21,25}]hexatriaconta-1(33),5,7,9(34),13,15,17(35),21,-23,25(36),29,31-dodecaene, C₄₀H₄₈O₈, and 7,23-di-*tert*-butyl-33,34,35,36-tetramethoxy-3,11,19,27-tetraoxapentacyclo[27.3.-1.1^{5,9}.1^{13,17}.1^{21,25}]hexatriaconta-1(33),5,7,9(34),13,15,17(35),-21,23,25(36),29,31-dodecaene, C₄₄H₅₆O₈, in the partial-cone or 1,2-alternate conformations, present the common feature of methoxy-ether self-inclusion, while the fourth, 42,43-dimethoxy-7,15,23,31-tetramethyl-3,11,19,27,34,37,40-heptaaxahexacyclo[15.15.9.1^{5,9}.1^{21,25}.0^{13,41}.0^{29,33}]tritetraconta-5(42),6,8,-13(41),14,16,21(43),22,24,29(33),30,32-dodecaene, C₄₂H₅₀O₉, adopts the 1,3-alternate conformation owing to the presence of a 1,3-polyether chain.

Comment

Homooxalixarenes are expanded calixarenes in which at least one methylene C atom is replaced by an ether –CH₂–O–CH₂– bridge (Masci, 2001, and references herein). In the course of our investigation of the crystal structures of homooxalix[*n*]arenes (*n* = 3–8) and of their uranyl ion complexes (Thuéry *et al.*, 1999; Thuéry, Nierlich, Vicens, Masci & Takemura, 2001; Thuéry *et al.*, 2001*a,b,c*) or *O*-substituted derivatives (Oueslati *et al.*, 2001), we have synthesized four methoxy-ether and one methoxy-ether/crown-ether derivatives, the structures of which are reported herein. Two different homooxalixarene skeletons have been used: tetrahomodioxacalix[4]arene and the larger octahomotetra-

oxacalix[4]arene, denoted [3.3.1.1]- and [3.3.3.3]-homooxalixarene, respectively, in the notation of Masci *et al.* (1998). The three first compounds bear four methoxy-ether groups, with different homooxalixarene cores: *p*-*tert*-butyl-tetrahomodioxacalix[4]arene, (I), *p*-methyloctahomotetraoxacalix[4]arene, (II), and octahomotetraoxacalix[4]arene with two diametrically located *p*-*tert*-butyl groups only, (III). The last compound, (IV), features two methoxy-ether groups and an –O–(CH₂)₂–O–(CH₂)₂–O– bridge linking two opposite phenolic units of *p*-methyloctahomotetraoxacalix[4]arene.



The asymmetric unit in (I) is composed of one calixarene molecule, which adopts a partial-cone conformation, the three phenolic rings bound by methylene bridges being in a cone conformation, and the last one, bound to the others by the ether bridges, being turned upside-down. The definition of a proper reference plane for homooxalixarene molecules is not as straightforward as in classical small calixarenes. In compound (I), the six C atoms of the bridges define a plane with a maximum deviation of 0.311 (3) Å, which can be used as a reference plane. The dihedral angles between this plane and those defined by the four aromatic rings are 80.85 (6), 53.52 (6), 84.87 (6) and 38.36 (6)°, which indicates that the reversed phenolic ring is closer to the mean plane than the three other rings. In the notation of Kanamathareddy &

Gutsche (1993), this conformation can be denoted as (*u, u, u, do*). As a result, the methoxy-ether substituent bound to this last ring is subject to self-inclusion, being directed towards the cavity centre. Such a self-inclusion phenomenon, which will be encountered also with compounds (II) and (III), has previously been observed with ester substituents in another compound of the same family, tetrahomodioxacalix[6]arene (Oueslati *et al.*, 2001). In calix[6]arene derivatives, the self-inclusion of three 1,3,5-methoxy groups was ascribed to weak $\text{CH}\cdots\pi$ interactions (van Duynhoven *et al.*, 1994). Such interactions have, however, been questioned in the case of a calix[4]arene derivative presenting a similar self-inclusion (Harrowfield *et al.*, 1994). In the present case, there is no H-atom \cdots ring centroid distance shorter than 3.15 Å, which precludes any $\text{CH}\cdots\pi$ interaction (Jeffrey & Saenger, 1994). As previously noted, two kinds of ether links can be distin-

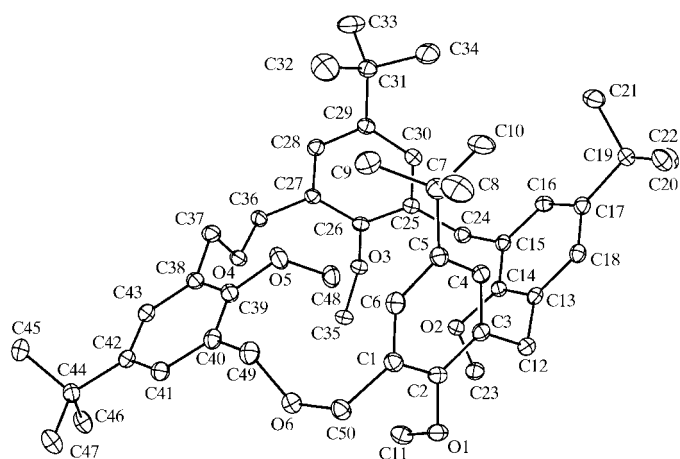


Figure 1
View of molecule (I) with the atomic numbering scheme. H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

guished in this family of compounds, corresponding to *anti/anti* or to *anti/gauche* C—O—C—C torsion angles (Thuéry *et al.*, 2001c). Both bridges in (I) are of the second type [80.4 (3) and -174.0 (2) $^\circ$ around O4, and 165.9 (2) and -81.2 (3) $^\circ$ around O6].

The centrosymmetric molecule (II), with four ether linkages, is in the 1,2-alternate conformation. The best reference plane in this compound, as well as in the two following ones, is given by the four ether O atoms. The dihedral angles between this plane and the two aromatic rings are 22.77 (7) and 81.97 (5) $^\circ$, indicating a (*u, uo, d, do*) conformation. The two methoxy-ether substituents of the rings closer to the mean plane are self-included, with a shorter C8 \cdots C13' distance of 3.727 (3) Å [symmetry code: (') $1 - x, -y, -z$]. There is no H-atom \cdots ring centroid distance shorter than 3.05 Å. C8 is not equally distant from the two nearest aromatic rings, the distortion of the calixarene being due to different ether bridge conformations. The bridge containing O2 is of the *anti/anti* type [torsion angles -176.1 (2) and 176.6 (2) $^\circ$], whereas that containing O4 is of the *anti/gauche* type [-172.3 (2) and 82.3 (2) $^\circ$]. The latter brings C8 in closer proximity to the aromatic ring than the former.

The same overall shape is encountered in compound (III), in which the molecule does not possess any crystallographic symmetry. The conformation is 1,2-alternate, but even more irregular than in compound (II). The four ether O atoms of the ring define a plane with a maximum deviation of 0.084 (2) Å, which cuts the four planes defined by the aromatic rings with dihedral angles of 81.06 (6), 32.00 (5), 85.45 (6) and 31.74 (5) $^\circ$. In this case also, the methoxy-ether groups of the two rings closer to the reference plane (which are those without a *p-tert-butyl* substituent) are self-included, with no H-atom \cdots ring centroid distance shorter than 3.13 Å. One of the ether bridges is different from the other three, which breaks the pseudo-symmetry centre of the molecule. The bridges associated with O2, O4 and O8 are of the *anti/gauche* type [torsion angles 72.6 (3) and -174.1 (2) $^\circ$ around O2, 173.0 (2) and -84.4 (3) $^\circ$ around O4, and 175.7 (2) and 81.9 (3) $^\circ$ around O8], whereas the bridge containing O6 is of the *anti/anti* type [-179.7 (2) and -177.4 (3) $^\circ$]. One of the H-atom \cdots ring centroid distances, involving the C36—C41 ring and a methoxy H atom of a neighbouring molecule, is 2.42 Å and can be considered, on a geometrical basis, to indicate a possible $\text{CH}\cdots\pi$ interaction.

The situation in compound (IV) is quite different. This molecule, related to the calixcrown family, for which a lot of structural information has been gathered (Thuéry *et al.*, 2000, and references therein), lacks any symmetry element and is in the 1,3-alternate conformation. The plane defined by the four ether O atoms has a maximum deviation of 0.580 (2) Å, but will be considered as the reference plane in spite of this large value in the absence of any better choice. The dihedral angles between this plane and those defined by the aromatic rings are 48.58 (7), 79.73 (7), 48.97 (6) and 80.56 (8) $^\circ$, the rings closer to the mean plane being those linked by the polyether bridge O1 \cdots O3. The two methoxy-ether groups are therefore directed away from the cavity. Two out of the four ether bridges, diametrically located, correspond to usual *anti/gauche* conformations [torsion angles -174.9 (2) and -79.9 (3) $^\circ$ around O4, and -177.3 (2) and -72.7 (3) $^\circ$ around O7], but the other two correspond to a third type not encountered up to now in this family of compounds, which is *gauche/gauche* [73.1 (3) and 72.9 (3) $^\circ$ around O6, and 78.8 (3) and 70.0 (3) $^\circ$

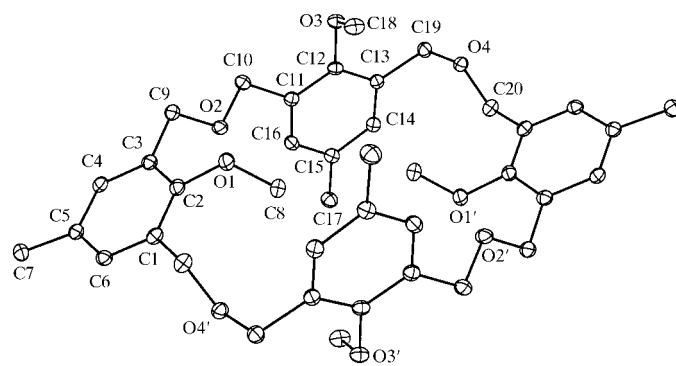


Figure 2
View of molecule (II) with the atomic numbering scheme. H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level [symmetry code: (') $1 - x, -y, -z$].

around O9]. This unusual conformation is likely due to the constraints arising from the O1...O3 polyether link bridging two aromatic rings. A self-inclusion phenomenon, different from the one observed in the previous compounds and involving two molecules related by the symmetry centre, appears in the packing. The *p*-methyl C30 atom of each molecule is included between the two polyether-linked aromatic rings of the neighbouring molecule, giving rise to dimers with shortest contacts between C30 and C7'' [3.480 (4) Å; symmetry code: (') 2 - x, -y, -z] and O1'' [3.419 (4) Å]. However, there is no H-atom...ring centroid distance shorter

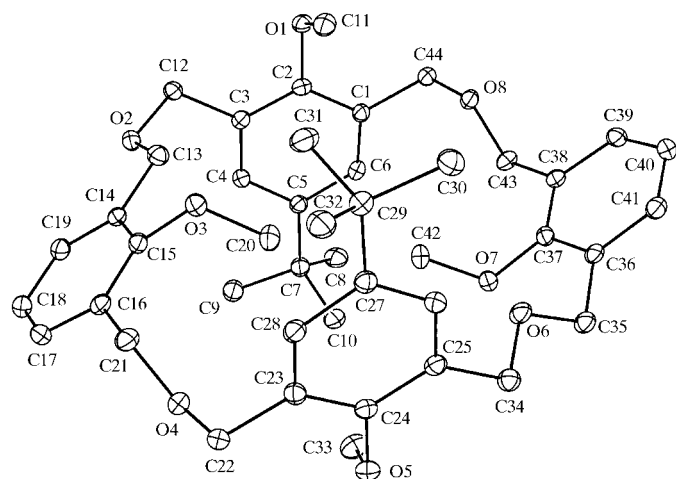


Figure 3
View of molecule (III) with the atomic numbering scheme. H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

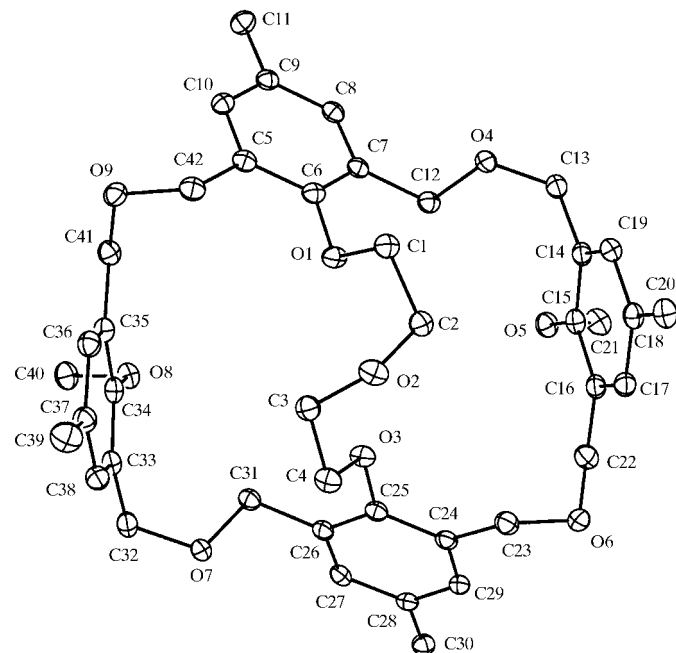


Figure 4
View of molecule (IV) with the atomic numbering scheme. H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

than 3.00 Å. It has been shown that calix[4]arene-mono- or bis(crown-6)s in the 1,3-alternate conformation were selective extractants for caesium ions (Ungaro *et al.*, 1994; Asfari *et al.*, 1995). However, it is doubtful that, even provided with an adequate polyether link containing six O atoms, compounds like (IV) could be better extractants than the latter compounds, owing to the increased cavity size and flexibility.

Experimental

Compound (I) was synthesized as reported elsewhere (Masci *et al.*, 1998). Compounds (II) and (IV) were also obtained as previously reported (Masci & Saccheo, 1993). Compound (III) was synthesized as reported for (II), from 2,6-bis(bromomethyl)anisole and 2,6-bis-(hydroxymethyl)-4-*tert*-butylanisole (yield 12%, m.p. 475–476 K).

Compound (I)

Crystal data

C₅₀H₆₈O₆
M_r = 765.04
Triclinic, P1̄
a = 11.3148 (8) Å
b = 14.2488 (5) Å
c = 15.3512 (11) Å
α = 84.280 (4)°
β = 69.132 (2)°
γ = 79.683 (4)°
V = 2273.5 (2) Å³

Z = 2
D_x = 1.118 Mg m⁻³
Mo Kα radiation
Cell parameters from 17232 reflections
θ = 2.7–25.7°
μ = 0.07 mm⁻¹
T = 100 (2) K
Parallelepiped, colourless
0.25 × 0.25 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
17 232 measured reflections
7972 independent reflections
5246 reflections with I > 2σ(I)

R_{int} = 0.072
θ_{max} = 25.7°
h = 0 → 13
k = -14 → 15
l = -17 → 18

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.061
wR(F²) = 0.158
S = 1.02
7972 reflections
521 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.0533P)² + 1.6661P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.39 e Å⁻³
Δρ_{min} = -0.21 e Å⁻³

Compound (II)

Crystal data

C₄₀H₄₈O₈
M_r = 656.78
Monoclinic, P2₁/n
a = 10.6466 (5) Å
b = 11.0343 (7) Å
c = 15.1801 (7) Å
β = 105.842 (3)°
V = 1715.59 (16) Å³
Z = 2

D_x = 1.271 Mg m⁻³
Mo Kα radiation
Cell parameters from 6275 reflections
θ = 2.7–25.7°
μ = 0.09 mm⁻¹
T = 100 (2) K
Platelet, colourless
0.25 × 0.25 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
6275 measured reflections
3245 independent reflections
2366 reflections with I > 2σ(I)

R_{int} = 0.041
θ_{max} = 25.7°
h = -12 → 12
k = -13 → 13
l = -18 → 18

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.112$
 $S = 1.02$
 3245 reflections
 221 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.4886P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

Compound (III)

Crystal data

$\text{C}_{44}\text{H}_{56}\text{O}_8$
 $M_r = 712.89$
 Monoclinic, $P2_1/c$
 $a = 23.2320 (15) \text{ \AA}$
 $b = 9.0186 (3) \text{ \AA}$
 $c = 19.6065 (12) \text{ \AA}$
 $\beta = 108.819 (2)^\circ$
 $V = 3888.4 (4) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.218 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 14012 reflections
 $\theta = 2.6\text{--}25.7^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 100 (2) \text{ K}$
 Platelet, colourless
 $0.20 \times 0.20 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ scans
 14012 measured reflections
 7332 independent reflections
 4351 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.078$
 $\theta_{\max} = 25.7^\circ$
 $h = -28 \rightarrow 28$
 $k = -10 \rightarrow 10$
 $l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.144$
 $S = 1.01$
 7332 reflections
 479 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.2708P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

Compound (IV)

Crystal data

$\text{C}_{42}\text{H}_{50}\text{O}_9$
 $M_r = 698.82$
 Triclinic, $P\bar{1}$
 $a = 8.6669 (6) \text{ \AA}$
 $b = 13.7665 (11) \text{ \AA}$
 $c = 16.8072 (9) \text{ \AA}$
 $\alpha = 113.671 (4)^\circ$
 $\beta = 94.723 (4)^\circ$
 $\gamma = 97.119 (3)^\circ$
 $V = 1803.1 (2) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.287 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 13815 reflections
 $\theta = 2.7\text{--}25.7^\circ$
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 100 (2) \text{ K}$
 Parallelepiped, colourless
 $0.30 \times 0.30 \times 0.20 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ scans
 13 815 measured reflections
 6346 independent reflections
 4286 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.063$
 $\theta_{\max} = 25.7^\circ$
 $h = 0 \rightarrow 10$
 $k = -16 \rightarrow 16$
 $l = -20 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.135$
 $S = 1.02$
 6346 reflections
 466 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 1.2698P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

All H atoms were introduced at calculated positions as riding atoms (C–H = 0.93–0.97 Å) with a displacement parameter equal to 1.2 (CH, CH₂) or 1.5 (CH₃) times that of the parent atom.

For all compounds, data collection: *KappaCCD Software* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL* and *PARST97* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1520). Services for accessing these data are described at the back of the journal.

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