Refinement

Refinement on F^2
$R(F) = 0.033$
$wR(F^2) = 0.063$
$S = 1.08$
757 reflections
54 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.0025F^2]$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

U_{iso} for H atoms, $U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j a_i.a_j$ for C and N atoms.

	x	y	z	U_{iso}/U_{eq}
Cl	0.67959 (15)	0.81283 (3)	0.06751 (10)	0.0378 (3)
N1	0.8140 (7)	0.89041 (14)	−0.3591 (4)	0.0475 (14)
N2	0.9522 (5)	0.97172 (11)	0.2038 (3)	0.0303 (10)
C1	0.8998 (6)	0.94546 (13)	−0.1801 (4)	0.0305 (12)
C2	0.8597 (6)	0.91998 (12)	0.0281 (4)	0.0286 (11)
H1	0.819 (6)	0.9172 (13)	−0.491 (4)	0.052 (8)
H2	0.658 (6)	0.8492 (13)	−0.354 (4)	0.057 (9)

Table 2. *Selected geometric parameters (Å, °)*

Cl—C2	1.7361 (19)	N2—Cl^i	1.347 (3)
N1—C1	1.362 (3)	N2—C2	1.321 (3)
N1—H1	0.91 (2)	C1^i—N2	1.347 (3)
N1—H2	0.84 (2)	C1—C2	1.388 (3)
C1—N1—H1	116.4 (13)	N1—C1—C2	124.07 (19)
C1—N1—H2	116.4 (16)	N2^i—C1—C2	117.63 (19)
H1—N1—H2	118 (2)	C1—C2—N2	116.18 (15)
C1^i—N2—C2	117.80 (17)	Cl—C2—C1	119.25 (16)
N1—Cl—N2^i	118.2 (2)	N2—C2—C1	124.57 (17)

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

The structure was solved using direct methods. The H atoms were found on a difference map and were refined isotropically.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1994). Cell refinement: *CAD-4-PC Software*. Data reduction: *DATRD2* in *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX*.

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1,5,7,11-Tetraoxaspiro[5.5]undecane, 3,9-Dimethylidene-1,5,7,11-tetraoxaspiro-[5.5]undecane and 1,5-Dioxa-7,11-dithia-spiro[5.5]undecane

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Abstract

In all three title compounds, $C_7H_{12}O_4$, (1), $C_9H_{12}O_4$, (2), and $C_7H_{12}O_2S_2$, (3), the spiro C—O distances are substantially shorter than the non-spiro C—O distances as a result of the anomeric effect. In contrast, the spiro C—S distances of compound (3) are similar to the non-spiro C—S distances. In all three compounds, steric repulsions between the lone pairs on the O or S atoms and the axial H atoms of the opposite ring result in a distorted geometry around the spiro-C atoms.

Comment

Bicyclic spiro-orthocarbonates (SOCs) and spiro-thio-orthocarbonates (STOCs) have been extensively studied, particularly in the area of polymer chemistry, the depth of work leading to the publication of a monograph (Sadhir & Luck, 1992). As O-heteroatom SOCs have demonstrated more potential for polymerization than their S- and N-heteroatom counterparts, these compounds have been studied in greater detail. Very little attention has been given to mixed-heteroatom systems, which appears to be due mainly to the lack of appropriate synthetic procedures. Our recent work (Bromley *et al.*, 1998) has developed a synthetic route to O/S-hybrid

SOCs, enabling a number of new hybrid SOCs to be prepared. In order to increase our knowledge of the factors involved in the polymerizations of these monomers, we have determined the structures of the title compounds (1), (2) and (3).
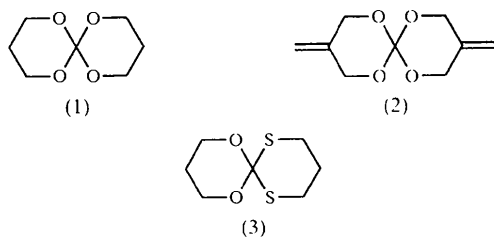
In all three compounds, the six-membered rings exist in chair conformations. The four spiro C—O distances of (1) (Fig. 1) are significantly shorter than the other C—O distances, consistent with the anomeric effect (Kirby, 1983). In addition, the bond between the spiro-C atom and the axial O atom is slightly longer than that to the equatorial O atom, again consistent with the anomeric effect. These results are in contrast to those obtained for the tetrathia analogue (Korp & Bernal, 1985), where there was no significant variation in the C—S distances. The bond angles around the spiro-C atom are, however, similar in both compounds. The endocyclic O—C—O angles in (1) are significantly larger than the standard sp^3 value of 109.5°, presumably due to the strain in accommodating the partial double-bond character of the O atoms. The largest exocyclic angle is that between the O atoms which are axial with respect to the opposite ring, while the smallest angle is that involving the equatorial O atoms. This is due to the unfavourable 1,3-diaxial interaction between the axial O atom and the axial H atoms on the C atoms in the opposite ring, the separations [O2$\cdots$H2A^i 2.48 (2) and O2$\cdots$H4A^i 2.56 (2) Å; symmetry code: (i) $-x$, y, $\frac{1}{2} - z$] being less than the sum of the van der Waals radii of 2.72 Å (Bondi, 1964). In the tetrathia analogue, the corresponding separations are S2$\cdots$H5A 2.94 (4),

S2$\cdots$H7A 3.19 (3), S4$\cdots$H2A 3.11 (3) and S4$\cdots$H4A 2.73 (3) Å, compared with the sum of the van der Waals radii of 3.00 Å. The sum of the endocyclic torsion-angle moduli for both rings is 345°, similar to the value of 353° found in 2-(p-chlorophenyl)-1,3-dioxane (De Kok & Romers, 1970), suggesting, as in the analogous tetrathia compound, that spiro attachment causes little change in the conformation of the rings and that any axial strain is transmitted around the ring and results in the equatorial O atoms being forced into closer proximity.

The only major difference between compound (1) and the 3,9-dimethylidene derivative, (2), lies in the conformation of the six-membered rings. The influence of the exocyclic double bond results in a noticeable flattening of the rings (Fig. 2), as evidenced by the reduction in the sum of the endocyclic torsion angles to 320°.

Fig. 2. The molecular structure of (2). Displacement ellipsoids are at the 50% probability level. H atoms are shown as spheres of radius 0.1 Å. [Symmetry code: (i) $1 - x$, y, $\frac{1}{2} - z$.]

As was found for (1) and (2), the spiro C—O distances for (3) (Fig. 3) are substantially shorter than the non-spiro C—O distances, while there is no significant variation in the spiro C—S and non-spiro C—S distances, similar to the situation in the tetra-thia analogue (Korp & Bernal, 1985). The two bond distances between the the spiro-C and the O atoms are similar, however, the distance between the spiro-
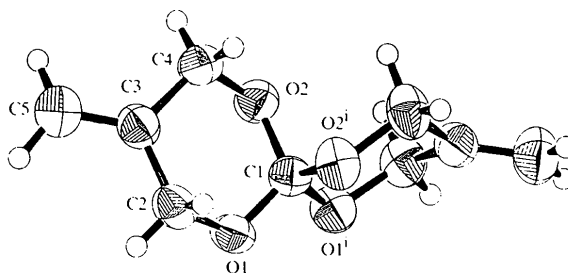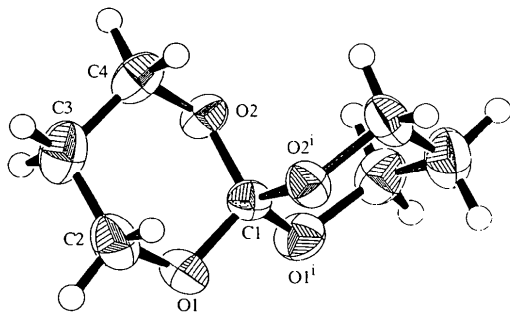

Fig. 1. The molecular structure of (1). Displacement ellipsoids are at the 50% probability level. H atoms are shown as spheres of radius 0.1 Å. [Symmetry code: (i) $-x$, y, $\frac{1}{2} - z$.]
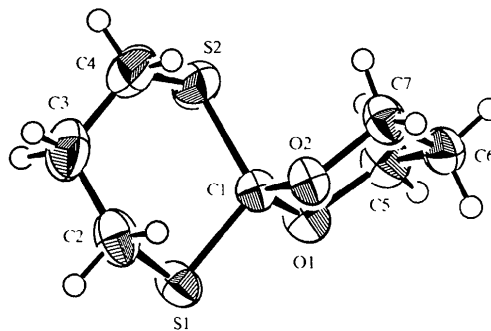
Fig. 3. The molecular structure of (3). Displacement ellipsoids are at the 50% probability level. H atoms are shown as spheres of radius 0.1 Å.

C and the axial S atoms is significantly longer than the distance involving the equatorial S atom, indicating that the anomeric effect is large for the O atoms, but not for the S atoms. Again, the geometry around the spiro-C atom is similar to that of the tetrathia and tetraoxa analogues, in particular, the S—C—O angle involving the axial S and O atoms is greater than the corresponding angle involving the equatorial S and O atoms, as a result of repulsions between the axial atoms and the axial H atoms on the opposite ring; the relevant separations are O2···H2A 2.69 (2), O2···H4A 2.78 (2), S2···H5A 2.80 (2) and S2···H7A 2.81 (2) Å, compared with the sum of the corresponding van der Waals radii of 2.72 and 3.00 Å, respectively.

Experimental

Crystals of all three compounds were obtained by sublimation of powder samples prepared as described previously (Mues & Buysch, 1990; Bromley *et al.*, 1998). All three crystals used for data collection were coated in epoxy resin to prevent decomposition due to contact with atmospheric moisture.

Compound (1)

Crystal data

$C_7H_{12}O_4$	Mo $K\alpha$ radiation
$M_r = 160.17$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 16
$Pbcn$	reflections
$a = 7.7068\,(11)$ Å	$\theta = 12.0–15.8°$
$b = 10.1645\,(12)$ Å	$\mu = 0.116$ mm^{-1}
$c = 9.691\,(2)$ Å	$T = 293\,(2)$ K
$V = 759.2\,(2)$ Å^3	Tabula.·
$Z = 4$	$0.40 \times 0.20 \times 0.10$ mm
$D_x = 1.437$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Rigaku AFC-5*R* diffractom-	533 reflections with
eter	$I > 2\sigma(I)$
ω–2θ scans	$\theta_{max} = 25.04°$
Absorption correction:	$h = 0 \rightarrow 9$
ψ scans (North *et al.*,	$k = 0 \rightarrow 12$
1968)	$l = -11 \rightarrow 0$
$T_{min} = 0.969$, $T_{max} = 0.988$	3 standard reflections
672 measured reflections	every 150 reflections
672 independent reflections	intensity decay: 0.71%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$\Delta\rho_{max} = 0.156$ e Å^{-3}
$wR(F^2) = 0.088$	$\Delta\rho_{min} = -0.131$ e Å^{-3}
$S = 1.147$	Extinction correction: none
671 reflections	Scattering factors from
75 parameters	*International Tables for*
All H atoms refined	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2$	
$+ 0.0735P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.06720 (14)	0.24644 (10)	0.15113 (11)	0.0478 (4)
O2	0.12579 (13)	0.40598 (9)	0.31408 (9)	0.0412 (3)
C1	0	0.3285 (2)	1/4	0.0362 (5)
C2	0.1639 (2)	0.3154 (2)	0.0461 (2)	0.0551 (5)
C3	0.3015 (2)	0.3983 (2)	0.1104 (2)	0.0613 (5)
C4	0.2230 (2)	0.4846 (2)	0.2183 (2)	0.0523 (5)

Table 2. *Selected geometric parameters (Å, °) for (1)*

O1—C1	1.3720 (15)	O2—C4	1.436 (2)
O1—C2	1.443 (2)	C2—C3	1.491 (3)
O2—C1	1.3948 (14)	C3—C4	1.493 (3)
C1—O1—C2	113.10 (11)	O2'—C1—O2	111.26 (15)
C1—O2—C4	112.91 (10)	O1—C2—C3	110.32 (14)
O1'—C1—O1	105.10 (15)	C2—C3—H3A	110.1 (11)
O1—C1—O2'	107.14 (6)	O2—C4—C3	109.68 (15)
O1—C1—O2	113.07 (6)		

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

Compound (2)

Crystal data

$C_9H_{12}O_4$	Mo $K\alpha$ radiation
$M_r = 184.19$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 16
$Pbcn$	reflections
$a = 10.175\,(2)$ Å	$\theta = 12.2–17.8°$
$b = 9.6082\,(14)$ Å	$\mu = 0.103$ mm^{-1}
$c = 9.577\,(2)$ Å	$T = 293\,(2)$ K
$V = 936.3\,(3)$ Å^3	Block
$Z = 4$	$0.30 \times 0.20 \times 0.20$ mm
$D_x = 1.307$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Rigaku AFC-5*R* diffractom-	537 reflections with
eter	$I > 2\sigma(I)$
ω–2θ scans	$\theta_{max} = 25.04°$
Absorption correction:	$h = 0 \rightarrow 12$
ψ scans (North *et al.*,	$k = 0 \rightarrow 11$
1968)	$l = -11 \rightarrow 0$
$T_{min} = 0.844$, $T_{max} = 0.980$	3 standard reflections
831 measured reflections	every 150 reflections
831 independent reflections	intensity decay: 2.38%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$\Delta\rho_{max} = 0.196$ e Å^{-3}
$wR(F^2) = 0.125$	$\Delta\rho_{min} = -0.139$ e Å^{-3}
$S = 1.042$	Extinction correction: none
830 reflections	Scattering factors from
84 parameters	*International Tables for*
All H atoms refined	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2$	
$+ 0.0125P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^ja_i.a_j.$$

	x	y	z	U_{eq}
O1	0.55915 (13)	0.26159 (14)	0.15585 (15)	0.0566 (5)
O2	0.58969 (14)	0.0928 (2)	0.32308 (15)	0.0592 (5)
C1	1/2	0.1745 (3)	1/4	0.0487 (7)
C2	0.6397 (2)	0.1910 (3)	0.0555 (2)	0.0599 (6)
C3	0.7351 (2)	0.0983 (2)	0.1259 (2)	0.0544 (6)
C4	0.6720 (3)	0.0100 (3)	0.2329 (3)	0.0648 (7)
C5	0.8605 (3)	0.0947 (3)	0.0946 (3)	0.0768 (8)

Table 4. *Selected geometric parameters ($\mathring{A}$, °) for (2)*

O1—C1	1.369 (2)	C2—C3	1.480 (3)
O1—C2	1.434 (2)	C3—C5	1.310 (3)
O2—C1	1.392 (2)	C3—C4	1.477 (3)
O2—C4	1.443 (3)		
C1—O1—C2	113.80 (15)	O1—C2—C3	110.7 (2)
C1—O2—C4	112.98 (15)	C5—C3—C4	124.5 (2)
O1—C1—O1^i	104.7 (2)	C5—C3—C2	123.3 (2)
O1—C1—O2	112.79 (8)	C4—C3—C2	112.1 (2)
O1^i—C1—O2	107.54 (8)	O2—C4—C3	110.5 (2)
O2—C1—O2^i	111.4 (2)		

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

Compound (3)

Crystal data

$C_7H_{12}O_2S_2$	Mo $K\alpha$ radiation
$M_r = 192.29$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 6.1062$ (12) Å	$\theta = 13.5–17.1°$
$b = 8.404$ (2) Å	$\mu = 0.536$ mm^{-1}
$c = 17.721$ (3) Å	$T = 293$ (1) K
$\beta = 93.478$ (15)°	Block
$V = 907.7$ (3) Å^3	0.60 × 0.44 × 0.44 mm
$Z = 4$	Colourless
$D_x = 1.407$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	1633 reflections with
MachS diffractometer	$I > 2\sigma(I)$
ω–2θ scans	$R_{int} = 0.014$
Absorption correction:	$\theta_{max} = 25.96°$
Gaussian, by integration	$h = -1 \rightarrow 7$
(Sheldrick, 1976)	$k = -1 \rightarrow 10$
$T_{min} = 0.784$, $T_{max} = 0.856$	$l = -21 \rightarrow 21$
2627 measured reflections	3 standard reflections
1783 independent reflections	frequency: 160 min
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$\Delta\rho_{max} = 0.288$ e Å^{-3}
$wR(F^2) = 0.074$	$\Delta\rho_{min} = -0.180$ e Å^{-3}
$S = 1.084$	Extinction correction:
1783 reflections	SHELXL96
149 parameters	Extinction coefficient:
All H atoms refined	0.048 (3)
$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2$	Scattering factors from
$+ 0.2508P]$	*International Tables for*
where $P = (F_o^2 + 2F_c^2)/3$	*Crystallography* (Vol. C)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (3)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^ja_i.a_j.$$

	x	y	z	U_{eq}
C1	0.5241 (2)	0.27431 (16)	0.33889 (7)	0.0351 (3)
S1	0.48210 (6)	0.43071 (5)	0.40666 (2)	0.04559 (15)
S2	0.52463 (8)	0.07699 (5)	0.38457 (3)	0.05698 (17)
C2	0.2119 (3)	0.3750 (2)	0.43389 (10)	0.0522 (4)
C3	0.1990 (3)	0.2123 (3)	0.46910 (11)	0.0655 (5)
C4	0.2467 (4)	0.0786 (3)	0.41561 (12)	0.0678 (5)
O1	0.73355 (15)	0.30389 (13)	0.31491 (6)	0.0455 (3)
O2	0.36066 (14)	0.28837 (12)	0.28118 (5)	0.0387 (2)
C5	0.7900 (2)	0.2100 (2)	0.25024 (10)	0.0509 (4)
C6	0.6164 (3)	0.2241 (2)	0.18707 (9)	0.0456 (4)
C7	0.3951 (3)	0.1890 (2)	0.21645 (9)	0.0459 (4)

Table 6. *Selected geometric parameters ($\mathring{A}$, °) for (3)*

C1—O2	1.3897 (16)	C2—C3	1.507 (3)
C1—O1	1.3944 (15)	C3—C4	1.510 (3)
C1—S1	1.8091 (14)	O1—C5	1.450 (2)
C1—S2	1.8452 (14)	O2—C7	1.4448 (18)
S1—C2	1.8086 (17)	C5—C6	1.499 (2)
S2—C4	1.816 (2)	C6—C7	1.506 (2)
O2—C1—O1	113.05 (11)	C3—C2—S1	114.64 (13)
O2—C1—S1	107.60 (9)	C2—C3—C4	113.47 (15)
O1—C1—S1	104.02 (9)	C3—C4—S2	114.52 (14)
O2—C1—S2	112.42 (9)	C1—O1—C5	114.22 (11)
O1—C1—S2	108.46 (9)	C1—O2—C7	113.72 (11)
S1—C1—S2	110.99 (7)	O1—C5—C6	110.85 (12)
C2—S1—C1	99.05 (7)	C5—C6—C7	109.56 (13)
C4—S2—C1	98.60 (8)	O2—C7—C6	109.75 (12)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994) for (1) and (2); *CAD-4 Software* (Enraf–Nonius, 1989) for (3). Cell refinement: *MSC/AFC Diffractometer Control Software* for (1) and (2); *CAD-4 Software* for (3). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995) for (1) and (2); *PROCESS_DATA* (Gable *et al.*, 1993) for (3). For all compounds, program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993) for (1) and (2); *SHELXL96* (Sheldrick, 1996) for (3). Molecular graphics: *TEXSAN* for (1) and (2); *ORTEPII* (Johnson, 1976) for (3). Software used to prepare material for publication: *TEXSAN* for (1) and (2); *SHELXL96* for (3).

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5,17-Dinitro-11,23-diphthalimido-25,26,27,28-tetrapropoxycalix[4]arene

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Abstract

The aromatic phthalimido moieties of the title compound, $C_{56}H_{52}N_4O_{12}$, do not (mutually) stack either intra- or intermolecularly, but rather intermolecularly with the nitrobenzyl moieties. The molecules show twist-distorted C_{2v} symmetry.

Comment

The calix[4]arene class of compounds is well known for the substantial number of functionalized derivatives having the ability to complex guest molecules (Böhmer, 1995). The title dinitrodiphthalimidocalix[4]arene, (I), has previously been used as an intermediate in the synthesis of a potential receptor molecule (Timmerman *et al.*, 1995). Interest in compound (I) was renewed by its possible application in large well organized molecular structures (Vreekamp *et al.*, 1996; Timmerman *et al.*, 1997). A crystal structure determination was carried out to elucidate whether the two large aromatic moieties (*i.e.* the phthalimido groups) prefer intermolecular stacking, giving equally directed molecules, or intramolecular stacking, resulting in a 'tweezer' conformation of the individual molecules.
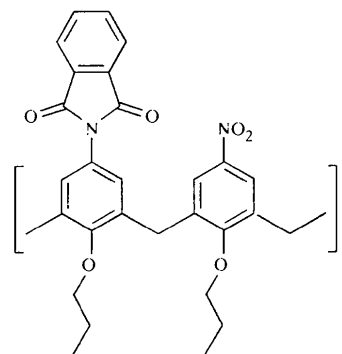
(I)

Although, in the solid-state structure, the phthalimido groups exhibit intermolecular stacking to some extent, the molecules are alternating and not equally directed, which might prove to be a disadvantage for applications in larger molecular structures. The closest intermolecular ring–ring interaction is found between N2,C21,C22,C27.C28 and C1–C6, with a center-of-gravity distance of 4.081 (2) Å and a dihedral angle of 21.2 (1)°.

The molecule is positioned on a crystallographic twofold axis. The molecular non-crystallographic symmetry of the central core may be described as twist distorted by 4.3 (1)° about this axis from exact C_{2v} symmetry (Fig. 1). One of the two crystallographically independent side chains is in the all-*trans* conformation, whereas the other one involves one *gauche* conformation in order to avoid the symmetry-related chain. The dihedral angle between the two rings connected through N2—C15 amounts to 63.9 (1)°.

The structure contains no guest molecules and no significant solvent-accessible voids (checked with *SOLV* in *PLATON*; Spek, 1994) larger than 11 Å³.