

Cis- and trans-bis(2-cyanoethylsulfanyl)(decane-1,10-diylthio)-tetrathiafulvaleneSune Nygaard,^a Amar H. Flood,^b Jan O. Jeppesen^a and Andrew D. Bond^{a*}^aUniversity of Southern Denmark, Department of Physics and Chemistry, Campusvej 55, 5230 Odense M, Denmark, and ^bIndiana University, Chemistry Department, 800 East Kirkwood Avenue, Bloomington, IN 47405, USA
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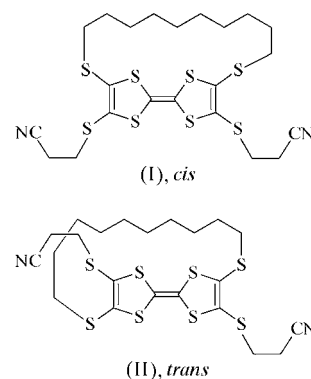
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The isomeric title compounds, 2,7-bis(2-cyanoethylsulfanyl)-3,6-(decane-1,10-diylthio)tetrathiafulvalene and 2,6-bis(2-cyanoethylsulfanyl)-3,7-(decane-1,10-diylthio)tetrathiafulvalene, both $C_{22}H_{28}N_2S_8$, comprise bis(2-cyanoethylsulfanyl)tetrathiafulvalene units tethered by a saturated decamethylenedithio linker attached in either a *cis* or a *trans* manner. The tetrathiafulvalene (TTF) group is planar in the *cis* isomer, but distorted significantly from planarity and twisted about its long axis in the *trans* isomer. In both structures, intermolecular interactions are segregated into regions in which TTF units are brought into close contact and regions where the polymethylene chains are brought into close contact. In the *cis* isomer, TTF units exhibit π - π stacking interactions, while in the *trans* isomer they do not.

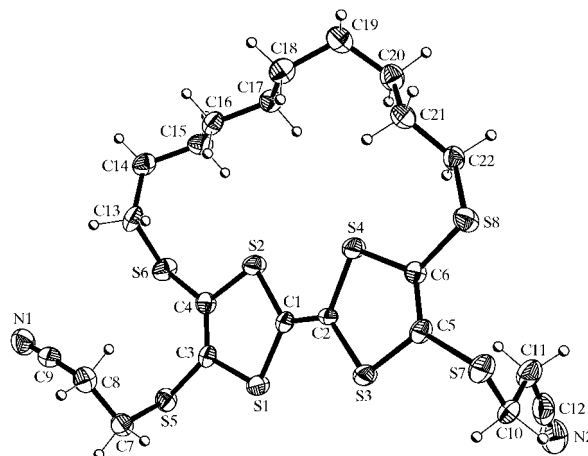
Comment

The chemistry of organothio derivatives of tetrathiafulvalene (TTF) has been studied extensively, and there are numerous crystal structures of such molecules in the literature [for example, the polymorphic parent compound, tetra(methylthio)tetrathiafulvalene; Cambridge Structural Database (CSD; Version 5.27 plus January, May and August 2006 updates; Allen, 2002) refcodes DIFVET (Katayama *et al.*, 1985) and DIFVET01 (Endres, 1986)]. One reason for this is that TTF derivatives find extensive use in the preparation of various interlocked compounds, including bistable [2]rotaxanes (Tseng *et al.*, 2004) and [2]catenanes (Asakawa *et al.*, 1998), which are prime candidates for future construction of molecular electronics (DeIonno *et al.*, 2006), artificial molecular muscles (Liu *et al.*, 2005) and molecular switches (Kang *et al.*, 2004). Amongst the derivatives that have been characterized crystallographically, there are several in which the two ends of the TTF molecule are tethered *via* a covalent linker. Various simple chain linkers have been employed for this purpose, including, for example, ether (GUJZAM and

GUJZEQ; Le Derf *et al.*, 2001), thioether (HOJNID; Le Derf *et al.*, 1999a) and 2,4-hexadiyne (PUGGAZ; Simonsen, Thorup & Becher, 1997) chains. More complex linkers have also been prepared, incorporating functional groups such as pyromellitic dianhydride (WISXOL, WISXUR and WISYAY; Hansen *et al.*, 2000), 4,4'-bipyridinium (RICWEF; Simonsen, Zong *et al.*, 1997), 2-thioxo-1,3-dithiole-4,5-dithiolate (LOMZOC; John *et al.*, 2000) and methylenediphenyl (NIHZEJ and NIHZIN; Lau *et al.*, 1997). One crystal structure has been reported in which a TTF molecule is tethered by saturated thioalkyl chains, namely *cis,cis*-bis(hexamethylenedithio)-TTF (JECXAQ; Suresh Kumar *et al.*, 1998), which includes two hexamethylenedithio chain linkers. We describe here the *cis* and *trans* isomers of bis(2-cyanoethylsulfanyl)tetrathiafulvalene tethered by a single decamethylenedithio chain.



The molecular structures of the *cis*, (I), and *trans*, (II), isomers are shown in Figs. 1 and 2, respectively. In (I), the TTF unit is approximately planar, with an r.m.s. deviation of 0.053 Å from the least-squares plane defined by atoms S1–S8 and C1–C6. The decamethylenedithio chain in (I) lies approximately in the plane of the TTF group, so that the molecule as a whole resembles a flat disc (Fig. 1), with the 2-cyanoethylsulfanyl groups pointing to either side. The decamethylenedithio chain is arranged so that its longest straight section (C14–C19) resembles *n*-hexane (Fig. 1). By contrast, the TTF unit in (II) deviates considerably from

**Figure 1**

The molecular structure of (I), showing displacement ellipsoids at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radius.

planarity: the least-squares plane through one outer ring of the TTF unit (S1/S2/C3/C4, referred to as plane 1) forms a dihedral angle of $21.7(1)^\circ$ with the least-squares plane through the inter-ring region (S1–S4/C1/C2; plane 2), which in turn forms a dihedral angle of $18.6(1)^\circ$ with the least-squares plane through the other outer ring (S3/S4/C5/C6; plane 3) (Fig. 2). The constraining influence of the decamethylenedithio linker is reflected further by the positions of atoms S5–S8; atoms S6 and S7, part of the decamethylenedithio linker, lie $0.087(3)$ and $0.126(3)$ Å from plane 1 and plane 3, respectively, while atoms S5 and S8, part of the two cyanoethylsulfanyl arms, lie $0.404(3)$ and $0.370(3)$ Å, respectively, from the same planes. Thus, as well as inducing non-planarity, the linker also twists the molecule about its long axis (*i.e.* the C1–C2 inter-ring vector of TTF). In the *trans* isomer, the longest straight section of the decamethylenedithio linker (C14–C21) resembles *n*-octane (Fig. 2).

In both (I) and (II), interactions between molecules are largely segregated so that TTF units are brought into close

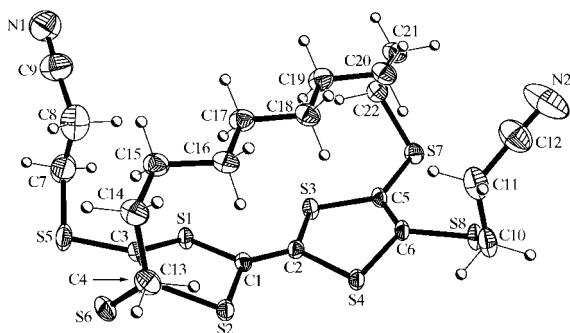


Figure 2
The molecular structure of (II), showing displacement ellipsoids at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radius.

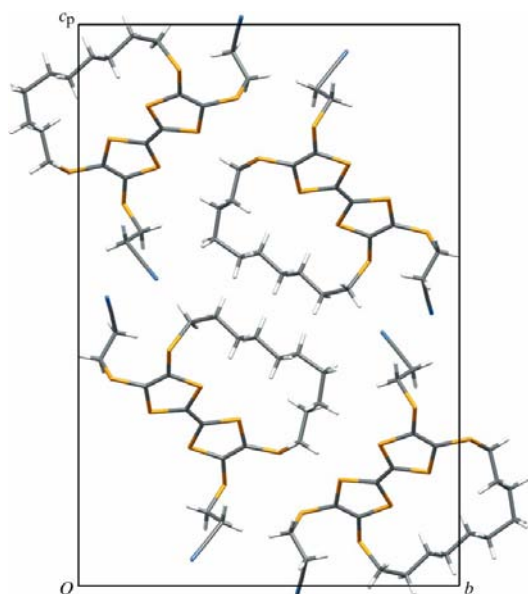


Figure 3
The unit-cell contents of (I), viewed in projection along *a*. Each molecule represents a stack in projection.

contact with each other, and the alkyl chains are brought into close contact with each other. In (I), molecules form stacks along *a* (Fig. 3), in which the TTF groups adopt an interplanar separation of $3.71(1)$ Å. For adjacent molecules within a stack [symmetry code: (i) $1 + x, y, z$], the straight *n*-hexyl sections (C14–C19) of the decamethylenedithio linker are arranged typically for *n*-alkyl chains, with a lateral offset of *ca* 2.5 Å (*i.e.* $2 \times \text{CH}_2$) that allows the CH_2 groups of one chain to project into the gaps between CH_2 groups in the neighbouring chain (Fig. 4). Between molecules in adjacent stacks [symmetry code: (ii) $1 - x, 1 - y, 1 - z$], the *n*-hexyl sections are arranged with no lateral offset, with a translation of *ca* 4.7 Å between chains. This arrangement is essentially identical to that in the crystal structure of *n*-hexane itself [HEXANE01; the corresponding lattice dimension is $4.696(1)$ Å; Boese *et al.*, 1999]. Pairs of stacks are aligned in a herring-bone manner (Fig. 3), with the $\text{C}\equiv\text{N}$ bonds adopting typical antiparallel and ‘crossed’ arrangements. The shortest $\text{S}\cdots\text{S}$ contacts in (I) [$3.4657(16)$ Å] occur between atoms S1 and S8ⁱⁱⁱ [symmetry code: (iii) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$]. The geometry is such that a lone pair of electrons on S1, lying in the plane of the TTF unit, can be envisaged to approach the $\sigma^*(\text{S8}-\text{C6})$ orbital in the neighbouring molecule (Rosenfield *et al.*, 1977).

In (II), the intermolecular interactions are segregated clearly into layered regions lying parallel to the *ac* planes (Fig. 5). In the plane at $y = \frac{1}{2}$, the straight *n*-octyl sections (C14–C21) of the decamethylenedithio chains are brought into close contact (Fig. 6). As for (I), pairs of molecules can be envisaged in this region [symmetry code: (iv) $1 - x, 1 - y, 1 - z$], with their *n*-octyl sections lying parallel with no lateral offset, and with an inter-chain translation of *ca* 4.7 Å. This arrangement again resembles closely that in *n*-octane itself [the corresponding lattice dimension is $4.752(1)$ Å; Boese *et al.*, 1999].

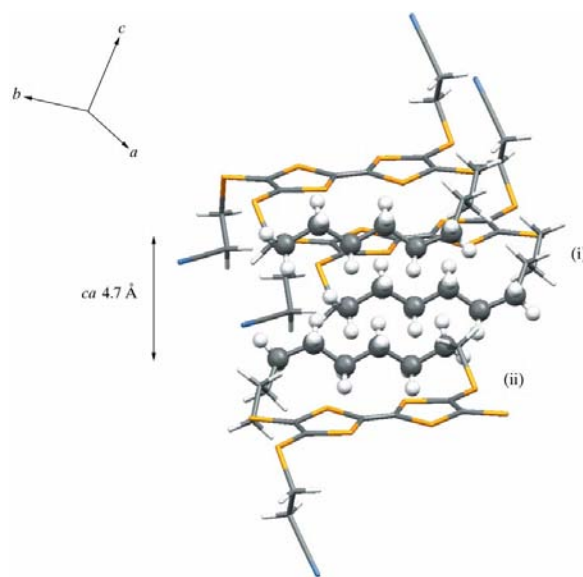


Figure 4
The arrangement of the straight *n*-hexyl sections of the decamethylenedithio chains in (I). Symmetry codes refer to those given in the *Comment*. For clarity, one cyanoethyl chain has been omitted from the molecule at (ii).

In the perpendicular direction, adjacent chains [symmetry code: (v) $2 - x, 1 - y, 1 - z$] are arranged with a much greater lateral offset, so that only approximately half of each *n*-octyl section is in contact with its neighbour (Fig. 6). In the *ac* planes at $y = \frac{1}{4}$ and $\frac{3}{4}$ (Fig. 5), the TTF units are brought into contact. Where the molecules meet in a face-to-face manner, one S atom of the decamethylenedithio chain lies over the centroid of a neighbouring five-membered ring [$S7 \cdots Cg(S1/S2/C1/C3/C4)^{vi} = 3.53 \text{ \AA}$; symmetry code: (vi) $-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$]. The shortest in-plane S \cdots S contact in (II) is 3.3399 (9) Å, between S5 and S8^{vii} [symmetry code: (vii) $x, y, -1 + z$], displaying no clear directional features. The 2-cyanoethylsulfanyl groups adopt antiparallel and crossed arrangements similar to those in (I).

From the CSD, 24 comparable non-tethered structures were identified, for which three-dimensional coordinates are available (Table 1). Of these, the TTF unit deviates significantly from planarity in only three, namely DIFVET (Katayama *et*

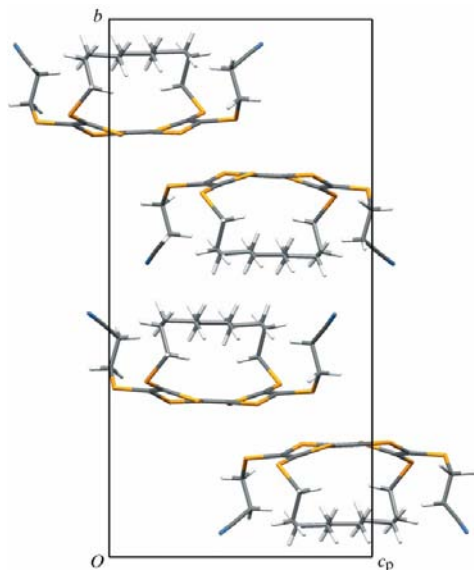


Figure 5
The unit-cell contents of (II), viewed in projection along *a*.

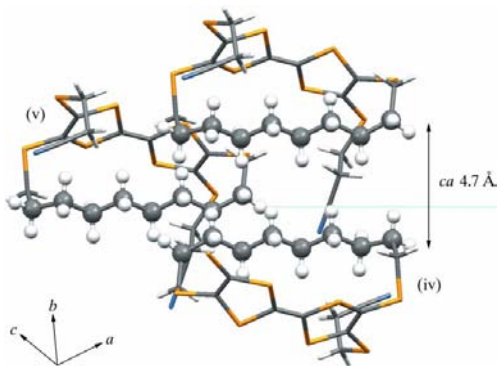


Figure 6
The arrangement of the straight *n*-octyl sections of the decamethylenedithio chains in (II). Symmetry codes refer to those given in the *Comment*. For clarity, one cyanoethyl chain has been omitted from the molecule at (iv).

al., 1985), FIQBUD (Bond & Jeppesen, 2005) and KUSLEP (Nakano *et al.*, 1992). By contrast, for 26 tethered examples identified (with three-dimensional coordinates available; Table 1), only three contain planar TTF units. Two of these, KAQXAB (Le Derf *et al.*, 1999b) and NIHZIN (Lau *et al.*, 1997), are *cis* isomers, while the third (WISXUR; Hansen *et al.*, 2000) is a *trans* isomer. For NIHZIN, the related *trans* isomer has also been characterized (NIHZEJ; Lau *et al.*, 1997) and it contains a planar TTF unit. For WISXUR, the linker incorporates a pyromellitic dianhydride group, and the planar TTF conformation appears to arise as a consequence of intra- and intermolecular π - π stacking interactions.

Experimental

2,3,6,7-Tetrakis(2-cyanoethylsulfanyl)tetrathiafulvalene (1.07 g, 2.0 mmol) was dissolved in anhydrous dimethylformamide (DMF; 20 ml) and degassed thoroughly (Ar, 15 min). CsOH·H₂O (0.69 g, 4.1 mmol) dissolved in anhydrous methanol (2 ml) was added dropwise over a period of 30 min and the solution was stirred for 1 h. The resulting solution and a solution of 1,10-dibromodecane (0.30 g, 1.0 mmol) in anhydrous DMF (22 ml) were added simultaneously over a period of 6 h to DMF (100 ml), under pseudo-high-dilution conditions using a perfusor pump. After the addition was completed, stirring was continued for a further 10 h. The reaction mixture was then concentrated *in vacuo*, redissolved in CH₂Cl₂ (100 ml), washed with water (150 ml) and dried over MgSO₄. Removal of the solvent gave a black oil, from which the title compound was isolated by column chromatography (SiO₂, CH₂Cl₂) as an analytically pure yellow solid (yield 0.84 g, 1.5 mmol, 75%) that comprised a mixture of the *cis* and *trans* isomers (m.p. 378–380 K). Elemental analysis found: C 45.85, H 4.94, N 4.87, S 44.68%; calculated C 45.79, H 4.89, N 4.86, S 44.46%. The isomers were separated in approximately 90% purity by preparative thin-layer chromatography using CH₂Cl₂ as eluant. Compound (I): ¹H NMR (CDCl₃, 300 MHz): δ 1.32–1.42 (*m*, 12H), 1.66–1.71 (*m*, 4H), 2.70 (*t*, $J = 7.2 \text{ Hz}$, 4H), 2.79–2.84 (*m*, 4H), 3.04 (*t*, $J = 7.2 \text{ Hz}$, 4H); ¹³C NMR (CDCl₃): δ 18.7, 27.5, 27.6, 28.2, 30.6, 31.3, 35.7, 112.5, 117.6, 120.9, 134.4. Compound (II): ¹H NMR (CDCl₃, 300 MHz): 0.89–1.17 (*m*, 4H), 1.26–1.41 (*m*, 8H), 1.67–1.70 (*m*, 4H), 2.68–2.79 (*m*, 6H), 2.98–3.23 (*m*, 6H); ¹³C NMR (CDCl₃): 18.8, 26.8, 28.8, 30.7, 31.2, 31.6, 35.7, 114.5, 117.3, 125.1, 132.4. Crystals used for X-ray analysis were grown from CH₂Cl₂/*n*-pentane (1:1) in both cases.

Compound (I)

Crystal data

C₂₂H₂₈N₂S₈
 $M_r = 576.94$
 Monoclinic, $P2_1/c$
 $a = 5.3573 (8) \text{ \AA}$
 $b = 18.296 (3) \text{ \AA}$
 $c = 27.041 (5) \text{ \AA}$
 $\beta = 90.753 (8)^\circ$
 $V = 2650.3 (8) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.446 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.69 \text{ mm}^{-1}$
 $T = 180 (2) \text{ K}$
 Lath, orange
 $0.30 \times 0.10 \times 0.05 \text{ mm}$

Data collection

Bruker–Nonius X8 APEX-II CCD diffractometer
 Thin-slice ω and φ scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.649$, $T_{\max} = 0.966$

28437 measured reflections
 4935 independent reflections
 2471 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.129$
 $\theta_{\text{max}} = 25.6^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{\max} = 0.001$
4935 reflections	$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
289 parameters	$\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$

Compound (II)

Crystal data

$C_{22}H_{28}N_2S_8$	$Z = 4$
$M_r = 576.94$	$D_x = 1.452 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.8916 (4) \text{ \AA}$	$\mu = 0.69 \text{ mm}^{-1}$
$b = 26.1798 (16) \text{ \AA}$	$T = 180 (2) \text{ K}$
$c = 12.9931 (8) \text{ \AA}$	Plate, yellow
$\beta = 100.576 (2)^\circ$	$0.35 \times 0.10 \times 0.05 \text{ mm}$
$V = 2638.8 (3) \text{ \AA}^3$	

Data collection

Bruker–Nonius X8 APEX-II CCD diffractometer	63502 measured reflections
Thin-slice ω and φ scans	5891 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	3807 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.817$, $T_{\max} = 0.966$	$R_{\text{int}} = 0.060$
	$\theta_{\max} = 27.9^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 1.4311P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.099$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.07$	$\Delta\rho_{\max} = 1.04 \text{ e } \text{\AA}^{-3}$
5891 reflections	$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$
289 parameters	
H-atom parameters constrained	

Table 1

CSD refcodes (Allen, 2002) for tethered and non-tethered TTF units.

Tethered	BIGBAU, EBAYOV, EBAYUB, GUJZAM, GUJZEO, HOJNID, HUHHEX, JAZFOF, JECXAO, KAQXAB, LOMZOC, NEJQIC, [†] NIHZEJ, NIHZIN, NOCHAO, OKINAX, PAMJAO, PEHMIY, PUGGAZ, RICWEF, RIYBOQ, RIYBUW, RIYCIL, WISXOL, WISXUR, WISYAY, ZECNAW
Non-tethered	COMQIE, DATNIV, [†] DIFVET, DOLMIA, DUXKOW, DUXKUC, EVAQAT, FIJYAY, [†] FIJYEC, [†] FIOBUD, FOJFUF, [†] FOJGAM, [†] FOJGEO, [†] FOMREF, GEDPUB, GIRGOD, [†] JOBSOI, JOBSUO, JOFSUS, KUSLEP, KUSLUF, KUSMUG, MAYMIJ, MAYMOP, MUFNUW, NAWSUA, NOGKUP, SAJFOY, [†] SAJGAL, [†] SOVWII, WUMPEZ, YUZLIO, YUZLOU

Note: (†) three-dimensional coordinates not available.

H atoms were positioned geometrically and allowed to ride during the subsequent refinement, with C—H distances of 0.99 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. For (II), the largest peak in the difference density map is located in the vicinity of one cyanoethylsulfanyl arm, viz. 1.24 Å from C7.

For both compounds, data collection: APEX2 (Bruker–Nonius, 2004); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3047). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Asakawa, M., Ashton, P. R., Balzani, V., Credi, A., Hamers, C., Mattersteig, G., Montalti, M., Shipway, A. N., Spencer, N., Stoddart, J. F., Tolley, M. S., Venturi, M., White, A. J. P. & Williams, D. J. (1998). *Angew. Chem. Int. Ed.* **37**, 333–337.
- Boese, R., Bläser, D. & Weiss, H.-C. (1999). *Angew. Chem. Int. Ed.* **38**, 988–992.
- Bond, A. D. & Jeppesen, J. O. (2005). *Acta Cryst.* **E61**, o765–o766.
- Bruker (2003). SAINT. Version 7.06a. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker–Nonius (2004). APEX2. Version 1.0-22. Bruker–Nonius BV, Delft, The Netherlands.
- DeIono, E., Tseng, H.-R., Harvey, D. D., Stoddart, J. F. & Heath, J. R. (2006). *J. Phys. Chem. B*, **110**, 7609–7612.
- Endres, H. (1986). *Z. Naturforsch. Teil B*, **41**, 1351–1356.
- Hansen, J. G., Bang, K. S., Thorup, N. & Becher, J. (2000). *Eur. J. Org. Chem.* pp. 2135–2144.
- John, D. E., Batsanov, A. S., Bryce, M. R. & Howard, J. A. K. (2000). *Synthesis*, pp. 824–830.
- Kang, S., Vignon, S. A., Tseng, H.-R. & Stoddart, J. F. (2004). *Chem. Eur. J.* **10**, 2555–2564.
- Katayama, C., Honda, M., Kumagai, H., Tanaka, J., Saito, G. & Inokuchi, H. (1985). *Bull. Chem. Soc. Jpn.*, **58**, 2272–2278.
- Lau, J., Blanchard, P., Riou, A., Jubault, M., Cava, M. P. & Becher, J. (1997). *J. Org. Chem.* **62**, 4936–4942.
- Le Derf, F., Mazari, M., Mercier, N., Levillain, E., Richomme, P., Becher, J., Garin, J., Orduna, J., Gorgues, A. & Salle, M. (1999a). *Chem. Commun.* pp. 1417–1418.
- Le Derf, F., Mazari, M., Mercier, N., Levillain, E., Richomme, P., Becher, J., Garin, J., Orduna, J., Gorgues, A. & Salle, M. (1999b). *Inorg. Chem.* **38**, 6096–6100.
- Le Derf, F., Mazari, M., Mercier, N., Levillain, E., Trippe, G., Riou, A., Richomme, P., Becher, J., Garin, J., Orduna, J., Gallego-Plana, N., Gorgues, A. & Salle, M. (2001). *Chem. Eur. J.* **7**, 447–455.
- Liu, Y., Flood, A. H., Bonvallet, P. A., Vignon, S. A., Northrop, B. H., Tseng, H.-R., Jeppesen, J. O., Huang, T. J., Brough, B., Baller, M., Magonov, S., Solares, S. D., Goddard, W. A., Ho, C.-M. & Stoddart, J. F. (2005). *J. Am. Chem. Soc.* **127**, 9745–9759.
- Nakano, C., Mori, T., Imaeda, K., Yasuoka, N., Maruyama, Y., Inokuchi, H., Iwasawa, N. & Saito, G. (1992). *Bull. Chem. Soc. Jpn.*, **65**, 1878–1883.
- Rosenfield, R. E. Jr, Parthasarathy, R. & Dunitz, J. D. (1977). *J. Am. Chem. Soc.* **99**, 4860–4862.
- Sheldrick, G. M. (2000). SHELXTL. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2003). SADABS. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Simonsen, K. B., Thorup, N. & Becher, J. (1997). *Synthesis*, pp. 1399–1404.
- Simonsen, K. B., Zong, K., Rogers, R. D., Cava, M. P. & Becher, J. (1997). *J. Org. Chem.* **62**, 679–686.
- Suresh Kumar, E. V. K., Singh, J. D., Singh, H. B., Das, K., Yakhmi, J. V. & Butcher, R. J. (1998). *J. Chem. Soc. Perkin Trans. 1*, pp. 1769–1778.
- Tseng, H.-R., Vignon, S. A., Celestre, P. C., Perkins, J., Jeppesen, J. O., Di Fabio, A., Ballardini, R., Gandolfi, M. T., Venturi, M., Balzani, V. & Stoddart, J. F. (2004). *Chem. Eur. J.* **10**, 155–172.