H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Cl1—C1	1.743 (3)	C7—O2	1.313 (4)
C1—C6	1.376 (4)	O3—N1	1.322 (3)
C1—C2	1.382 (5)	N1—C8	1.350 (4)
C2—C3	1.386 (6)	N1—C12	1.357 (3)
C3—C4	1.383 (5)	C8—C9	1.358 (5)
C4—C5	1.392 (4)	C9—C10	1.374 (6)
C5—C6	1.396 (4)	C10—C11	1.382 (6)
C5—C7	1.485 (4)	C11—C12	1.387 (5)
C7—O1	1.206 (4)	C12—C13	1.492 (5)
C6—C1—C2	121.9 (3)	O2—C7—C5	112.9 (2)
C6—C1—Cl1	118.0 (2)	O3—N1—C8	120.2 (3)
C2—C1—Cl1	120.1 (2)	O3—N1—C12	118.1 (2)
C1—C2—C3	118.5 (3)	C8—N1—C12	121.6 (3)
C4—C3—C2	120.8 (3)	N1—C8—C9	121.2 (3)
C3—C4—C5	120.0 (3)	C8—C9—C10	119.4 (3)
C6—C5—C4	119.5 (3)	C11—C10—C9	118.9 (3)
C6—C5—C7	121.0 (2)	C10—C11—C12	121.3 (3)
C4—C5—C7	119.5 (2)	N1—C12—C11	117.6 (3)
C1—C6—C5	119.3 (2)	N1—C12—C13	117.6 (3)
O1—C7—O2	123.9 (3)	C11—C12—C13	124.8 (3)
O1—C7—C5	123.1 (3)		

The ring and methyl H atoms were included at geometrically idealized positions. The HO2 atom was located from a difference map and its coordinates were refined. An isotropic displacement parameter of 6.0 Å^2 was assigned to all H atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *VAXSDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *VAXSDP*.

The authors want to thank FINEP, CNPq and FAPESP (Brazilian agencies), and Universidad del Valle (Colombia) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1020). Services for accessing these data are described at the back of the journal.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Frenz, B. A. (1978). *The Enraf–Nonius CAD*-4 *SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.

Gougoutas, Z. J. & Lessinger, L. (1975). *J. Solid State Chem.* **12**, 51–62.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Moreno-Fuquen, R., De Almeida Santos, R. H. & Lechat, J. R. (1996). *Acta Cryst.* C**52**, 220–222, and references therein.

Moreno-Fuquen, R., Gambardella, M. T. do P. & De Almeida Santos, R. H. (1996). *Acta Cryst.* C**52**, 1745–1747.

Prasad, P. N. & Williams, D. J. (1991). In *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, 1st ed. New York: John Wiley.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1997). C**53**, 1637–1640

Steric Inhibition of Molecular Weaving: Non-Woven Nets of $R^6_6(40)$ and $R^6_6(60)$ Rings in 1,1,3-Tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane–Hexamethylenetetramine (1/1)

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(*Received 8 May 1997; accepted 24 June 1997*)

Abstract

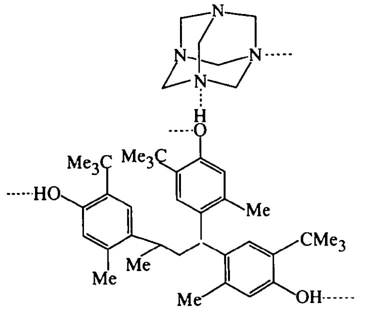
In the 1:1 adduct formed by 1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane and hexamethylenetetramine (HMTA; alternative name: 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane), $C_{37}H_{52}O_3.C_6H_{12}N_4$, the tris-phenol [alternative name: 4,4′,4″-(butane-1,1,3-triyl)-tris(2-*tert*-butyl-5-methylphenol)] acts as a triple donor and a single acceptor of hydrogen bonds, while the HMTA acts as a double acceptor. The tris-phenol and HMTA units are linked into $C^2_2(16)$ chains along [101] by means of O—H···N hydrogen bonds, with O···N distances of 2.759 (4) and 2.828 (4) Å; the tris-phenol units are themselves linked into $C(14)$ chains along [010] by O—H···O hydrogen bonds, each having an O···O distance of 2.828 (4) Å. These two types of chain intersect to generate two-dimensional nets built from alternating $R^6_6(40)$ and $R^6_6(60)$ rings; despite the size of these rings, interweaving of the nets is prevented by the presence of the *tert*-butyl groups in the tris-phenol.

Comment

The successful construction of microporous molecular solids requires the production of two- or three-dimensional supramolecular networks containing continuous voids with dimensions that exceed those of small molecules, but the interweaving of such networks is a common occurrence. For example, in 4,4′-sulfonyldiphenol, $O_2S(C_6H_4OH)_2$ (Glidewell & Ferguson, 1996), there is pairwise interweaving of square nets

Acta Crystallographica Section C
ISSN 0108-2701 © 1997

of $R^4_4(32)$ rings (Bernstein, Davis, Shimoni & Chang, 1995), and in the 1:1 adduct of 1,1,1-tris(4-hydroxyphenyl)ethane, $CH_3C(C_6H_4OH)_3$, and hexamethylenetetramine (HMTA), $C_6H_{12}N_4$, there is pairwise interweaving of hexagonal $R^6_6(48)$ nets (Coupar, Ferguson, Glidewell & Meehan, 1997). In 1,1′-bis(4-hydroxybenzoyl)ferrocene, $[Fe(C_5H_4COC_6H_4OH)_2]$, two independent stacks of $R^4_4(40)$ nets are continuously interwoven (Benyei, Glidewell, Lightfoot, Royles & Smith, 1997). One approach to the prevention of such weaving is to increase the dimensions of the strands of the net relative to the size of the reticulations; here we report the structure of 1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane–hexamethylenetetramine (1/1), $C_{37}H_{52}O_3.C_6H_{12}N_4$, (I), in which the interweaving of two-dimensional nets is prevented by the steric demands of the tris-phenol component.



(I)

In compound (I), the tris-phenol component acts as a triple donor of hydrogen bonds, as generally observed in such adducts (Coupar, Glidewell & Ferguson, 1997; Ferguson, Bell, Coupar & Glidewell, 1997; Coupar, Ferguson, Glidewell & Meehan, 1997), and the HMTA acts as a double acceptor of hydrogen bonds, so that the structure contains both O—H···N and O—H···O hydrogen bonds. In this respect, the structure of (I) differs from that of the related 1:1 adduct formed by 1,1,1-tris(4-hydroxyphenyl)ethane and HMTA, where the HMTA acts as a triple acceptor of hydrogen bonds and the structure is built from O—H···N hydrogen bonds only (Coupar, Ferguson, Glidewell & Meehan, 1997). Within the asymmetric unit of (I) (Fig. 1), atom O1 acts as a hydrogen-bond donor to N1. The network structure of (I) can be described in terms of two simple chain motifs, involving atoms O2 and O3, respectively, which intersect to generate the nets.

Atom O2 in the asymmetric unit at (x, y, z) acts as donor to N2 in the unit at ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$), while O2 in this second unit acts as donor to N2 at ($1+x$, y, $1+z$); hence the hydrogen bonds involving O1, O2 and the HMTA units give rise to a chain generated by the n glide plane and running parallel to the [101] direction. The unitary and binary level graph-set descriptors (Bernstein, Davis, Shimoni & Chang, 1995) are $N_1 = DD$, $N_2 = C^2_2(16)$. The remaining O atom, O3, in the tris-phenol at (x, y, z) acts as donor to O1 in the unit at ($-\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$), while O3 in this second unit acts as donor to O1 at (x, $-1+y$, z); the hydrogen bonds involving O3 thus form a $C(14)$ chain running parallel to the [010] direction and generated by a 2_1 screw axis. These two orthogonal sets of chains intersect (Fig. 2) to generate a continuous two-dimensional network, parallel to the $(10\bar{1})$ plane and characterized by two types of centrosymmetric reticulation: there are $R^6_6(40)$ rings centred, for example, at $(0,0,\frac{1}{2})$ and $R^6_6(60)$ rings centred, for example, at $(\frac{1}{2},0,1)$ and $(-\frac{1}{2},0,0)$ (Fig. 2). These two types of ring form a checkerboard pattern on the $(10\bar{1})$ plane. A single net involves each of the four molecular aggregates in the unit cell, and hence is sufficient to define the entire structure. There are no contacts between neighbouring nets which are less than the sum of the van der Waals radii and, in particular, there is no interweaving of the nets such as is observed in the analogous 1:1 adduct of 1,1,1-tris(4-hydroxyphenyl)ethane and HMTA.

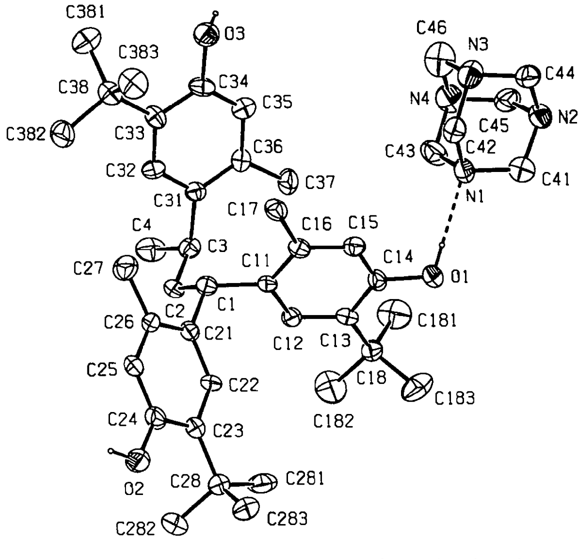


Fig. 1. A view of the asymmetric unit of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The structure of 1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane has not been reported previously. There is a stereogenic centre at C3, but the sample employed here was racemic, so that the observation of a centrosymmetric space group for (I) is as expected. The bond lengths in the tris-phenol are all typical of their types, but some of the bond angles within the planar aromatic rings show significant deviations from 120° (Table 1). The internal angles at Cn3 and Cn6 (n = 1–3), *ipso* to the *tert*-butyl and methyl substituents, are all significantly less than 120°, and those at Cn2 and Cn5, the unsubstituted C atoms, are very much larger than 120°. The conformations of the *tert*-butyl

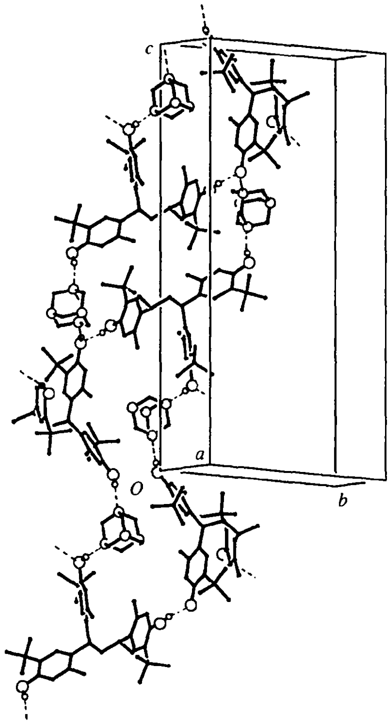


Fig. 2. A view of the crystal structure showing the formation of $R_6^6(40)$ and $R_6^6(60)$ rings. For clarity, only the hydroxy H atoms are shown.

groups are all such that two of the methyl C atoms in each CMe$_3$ fragment are essentially equidistant from the neighbouring O atom, with C···O distances in the range 2.984 (5)–3.072 (5) Å; it is possible that such short intramolecular C—H···O interactions are actually repulsive rather than attractive (Desiraju, 1996). A very similar conformation was observed in 2,5-di-*tert*-butylhydroquinone (Ermer & Röbke, 1994). Although there is no disorder of the methyl C atoms in the CMe$_3$ groups, there is evidence for considerable librational motion of each such group about the C*n*3—C*n*8 (*n* = 1–3) bonds. Similarly, there is evidence for librational motion of the HMTA cage about the N1···N2 vector. There are no significant differences between the C—N bond lengths involving the two different types of N atom, hydrogen-bond acceptors and non-acceptors; the acceptor N atoms are usually associated with longer C—N bonds (Coupar, Glidewell & Ferguson, 1997).

Examination of the structure with *PLATON* (Spek, 1996*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

Equimolar quantities of the tris-phenol and HMTA (5 mmol) were separately dissolved in methanol (50 ml). The solutions were mixed and the mixture was set aside to crystallize, yielding analytically pure (I). Analysis found: C 75.2, H 9.9, N 8.3%; $C_{43}H_{64}N_4O_3$ requires: C 75.4, H 9.4, N 8.2%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_6H_{12}N_4.C_{37}H_{52}O_3$
M_r = 684.98
Monoclinic
$P2_1/n$
a = 10.1144 (9) Å
b = 13.4212 (11) Å
c = 30.576 (3) Å
β = 98.919 (9)°
V = 4100.4 (6) Å^3
Z = 4
D_x = 1.110 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 8.64–12.93°
μ = 0.069 mm^{-1}
T = 294 (1) K
Block
0.42 × 0.26 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
7912 measured reflections
7150 independent reflections
2188 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.013

$\theta_{\rm max}$ = 25.0°
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 36$
3 standard reflections frequency: 120 min intensity decay: no decay, variation 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.137
S = 0.815
7150 reflections
457 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.172 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.201 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C41	1.464 (4)	N4—C46	1.465 (5)
N1—C42	1.473 (5)	C1—C2	1.544 (4)
N1—C43	1.463 (5)	C2—C3	1.539 (4)
N2—C41	1.468 (4)	C3—C4	1.536 (5)
N2—C44	1.455 (4)	C1—C11	1.526 (4)
N2—C45	1.474 (5)	C1—C21	1.536 (5)
N3—C42	1.462 (5)	C3—C31	1.516 (5)
N3—C44	1.464 (4)	C14—O1	1.380 (4)
N3—C46	1.463 (6)	C24—O2	1.373 (4)
N4—C43	1.462 (5)	C34—O3	1.373 (4)
N4—C45	1.453 (5)		
C1—C2—C3	114.7 (3)	C21—C22—C23	124.9 (4)
C2—C1—C11	113.2 (3)	C21—C26—C25	118.5 (4)
C2—C1—C21	109.7 (3)	C22—C21—C26	118.0 (4)
C11—C1—C21	113.5 (3)	C22—C23—C24	115.5 (4)
C2—C3—C4	110.3 (3)	C23—C24—C25	120.7 (4)
C2—C3—C31	113.9 (3)	C24—C25—C26	122.4 (4)
C4—C3—C31	111.2 (3)	C31—C32—C33	124.9 (3)
C11—C12—C13	125.3 (3)	C32—C31—C36	118.3 (3)
C11—C16—C15	117.3 (3)	C32—C33—C34	114.9 (3)
C12—C11—C16	118.5 (3)	C31—C36—C35	117.6 (3)
C12—C13—C14	114.5 (3)	C33—C34—C35	120.7 (3)
C13—C14—C15	120.8 (3)	C34—C35—C36	123.6 (3)
C14—C15—C16	123.5 (3)		

C11—C1—C2—C3	−48.9 (4)
C21—C1—C2—C3	−176.8 (3)
C1—C2—C3—C4	−172.9 (3)
C2—C1—C11—C12	−41.8 (5)
C2—C1—C21—C22	81.1 (4)
C2—C3—C31—C32	−49.7 (5)
C14—C13—C18—C181	−62.1 (5)
C14—C13—C18—C182	178.7 (4)
C14—C13—C18—C183	59.3 (5)
C24—C23—C28—C281	−178.9 (4)
C24—C23—C28—C282	61.7 (5)
C24—C23—C28—C283	−58.7 (5)
C34—C33—C38—C381	58.9 (5)
C34—C33—C38—C382	178.1 (4)
C34—C33—C38—C383	−62.8 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.82	1.95	2.759 (4)	170
O2—H2···N2^{i}	0.82	2.03	2.828 (4)	165
O3—H3···O1^{ii}	0.82	2.05	2.828 (4)	158

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

Compound (I) crystallized in the monoclinic system; space group $P2_1/n$ was indicated by the systematic absences. H atoms were treated as riding atoms (C—H 0.93–0.98 and O—H 0.82 Å), except for those treated as part of rigid methyl groups (allowed to rotate but not tip). Starting coordinates for methyl and OH groups were taken from difference syntheses.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*96. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1996*a*) and *PLUTON* (Spek 1996*b*). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*93 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997).

GF thanks NSERC (Canada) for Research Grants. RMG thanks EPSRC (UK) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1228). Services for accessing these data are described at the back of the journal.

References

Benyei, A. C., Glidewell, C., Lightfoot, P., Royles, B. J. L. & Smith, D. M. (1997). *J. Organomet. Chem.* **539**, 177–186.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Coupar, P. I., Ferguson, G., Glidewell, C. & Meehan, P. R. (1997). *Acta Cryst.* In the press.

Coupar, P. I., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* B**53**, 521–533.

Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.

Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ermer, O. & Röbke, C. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1755–1757.

Ferguson, G. (1997). *PRPCIF*97. A *WordPerfect*-5.1 *Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL93 Programs*. University of Guelph, Canada.

Ferguson, G., Bell, W., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 534–543.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Glidewell, C. & Ferguson, G. (1996). *Acta Cryst.* C**52**, 2528–2530.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1996*a*). *PLATON. Molecular Geometry Program*. Version of November 1996. University of Utrecht, The Netherlands.

Spek, A. L. (1996*b*). *PLUTON. Molecular Graphics Program*. Version of August 1996. University of Utrecht, The Netherlands.

Acta Cryst. (1997). C**53**, 1640–1642

Perylo[1,12-*b*,*c*,*d*]thiophene†

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(*Received 24 February 1997; accepted 27 May 1997*)

Abstract

The title compound, $C_{20}H_{10}S$, contains discrete molecules which are essentially planar and are regularly stacked along the *b* axis [interplanar separation 3.474 (4) Å]; columns are bridged by short S···S interstack contacts of 3.506 (2) Å about inversion centres.

Comment

Perylene ($C_{20}H_{12}$) is a well known donor molecule used in the preparation of conducting and semiconducting radical cation salts (Akamutu, Inokuchi & Matsunaga, 1954; Alcácer & Maki, 1974, 1976; Endres, Keller, Müller & Schweitzer, 1985; Almeida & Henriques, 1997). In our research group, special attention has been given to the (quasi) one-dimensional family of conductors (perylene)$_2M$(mnt)$_2$, where *M* is a transition metal and mnt is maleonitriledithiolate or *cis*-2,3-disulfanylbut-2-enedinitrile (Gama *et al.*, 1991, 1993). In the search for perylene derivatives, perylo[1,12-*b*,*c*,*d*]thiophene, hereafter designated by pet, was chosen, aiming at the introduction of both an increase of intermolecular interaction, due to the presence of the outer S atom, and possible effects on lowering molecular symmetry. So far, instead of the common 2:1 stoichiometry, only (pet)$_3$[Ni(mnt)$_2$]$_2$ compounds were obtained (Alcácer, Morgado, Henriques & Almeida, 1995). In order to gain

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† Alternative name: 1,12-epithioperylene.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997