structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *CRYSTAN* (Burzlaff & Rothammel, 1988). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1314). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Burzlaff, H. & Rothammel, W. (1988). *Proceedings of the CIC Meeting, Tübingen*, edited by G. Gauglitz, pp. 415–421. Berlin: Springer-Verlag.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Grisar, J. M., Claxton, G. P., Carr, A. A. & Wiech, N. L. (1973). *J. Med. Chem.* **16**, 679–683.
Hartmann, S., Brecht, V. & Frahm, A. W. (1999). *Magn. Reson. Chem.* **37**, 69–72.
Kabsch, W. (1993). *J. Appl. Cryst.* **26**, 795–800.
Knupp, G. & Frahm, A. W. (1983). *Chem. Ber.* **117**, 2076–2098.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Wiehl, W. & Frahm, A. W. (1986). *Chem. Ber.* **119**, 2668–2677.

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Imide and tribenzyl ester derivatives of Kemp's triacid

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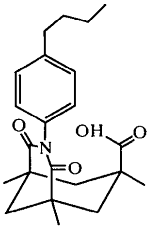
Abstract

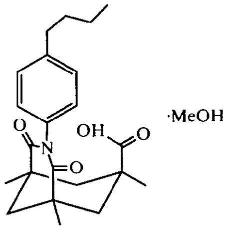
Two derivatives of Kemp's triacid (*cis,cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid) have been structurally characterized. The imide *cis,cis*-*N*-(4-*n*-butylphenyl)-5-carboxy-1,3,5-trimethylcyclohexane-1,3-dicarboximide crystallizes either pure ($C_{22}H_{29}NO_4$) or as a methanol solvate ($C_{22}H_{29}NO_4 \cdot CH_3OH$) in which the solvent molecule is hydrogen bonded to imide and carboxyl-O atoms. The triester derivative, tribenzyl *cis,cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylate ($C_{33}H_{36}O_6$), presents the concave shape characteristic of many such derivatives.

Comment

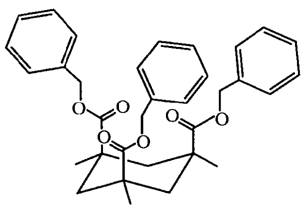
Kemp's triacid is well known as a useful and versatile building block in systems designed for molecular recognition (Rebek, 1990) or for ion transport. The crystal structures of its pure and acetonitrile-solvate forms have been determined (Rebek *et al.*, 1985; Chan *et al.*, 1991; Hirose *et al.*, 1998). The imide derivative, *N*-(4-*n*-butylphenyl)-5-carboxy-1,3,5-trimethylcyclohexane-1,3-dicarboximide, (1), has been shown to be both an efficient alkaline-earth metal-ion transport agent with a marked selectivity for calcium ions (Hirose *et al.*, 1995), and a transition-metal-ion complexant selective for divalent mercury ions (Hirose *et al.*, 1996). Chromogenic reagents for mercury ions have been synthesized using an azobenzene moiety in place of the *n*-butyl group in the *N*-substituent (Wang *et al.*, 1997). Bis(Kemp's acid imide) compounds, where the two moieties are bridged by the *N*-substituent, have also been synthesized and their complexing properties investigated (Tanase *et al.*, 1994; Herold *et al.*, 1995; Yun *et al.*, 1995). The complexing properties of the ester derivative tribenzyl *cis,cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylate, (3), have not yet been investigated.



(1)



(2)



(3)

The bond distances and angles are as expected for the three structures reported here, *i.e.* (1), its methanol solvate (2), and (3). The chair cyclohexane skeleton is rigid and prevented from epimerization and conformational change by the methyl groups which prefer the equatorial position. The bulky *N*-substituent assumes slightly different positions in (1) and (2), with dihedral angles between the benzene ring plane and the plane defined by the atoms of the imide bridge (C1, C12, O2, N1, O1, C11 and C3) of 69.44 (5) and 86.30 (6)° for (1) and (2), respectively. The plane defined by the carboxyl group (C5, C9, O3 and O4) makes a dihedral angle with the imide bridge of 27.38 (6) and 24.25 (8)° in (1) and (2), respectively, and is thus roughly parallel to it. Some O···O distances in both compounds are indicative of the formation of hydrogen bonds. In (1), those bonds involve the carboxyl groups [shortest intermolecular contact O3···O4($2-x$, $-y$, $-z$) of 2.642 (3) Å], whereas in (2), the methanol molecule possibly forms two hydrogen bonds with one of the carboxyl-O atoms [O5···O4 2.616 (3) Å] and one of the imide bridge O atoms from a neighboring molecule [O5···O2($-x$, $1-y$, $-z$) 2.740 (3) Å]. The location of the corresponding H atoms from the final Fourier map confirms the existence of such bonds.

In the tribenzyl ester derivative (3), the three benzyl groups are directed outside and the C=O bonds roughly parallel to the sides of the cyclohexane ring. The three aromatic rings are slightly inclined with respect to the plane defined by the three atoms C1, C3 and C5, with dihedral angles of 33.73 (8), 17.91 (10) and 26.85 (9)°, respectively. The triaxial geometry is analogous to that observed in the trimethyl ester derivative (Rebek *et al.*, 1985; Chan *et al.*, 1991). However, due to the benzyl substituents, the overall shape of the molecule is that of a bowl whose complexing abilities deserve further investigation.

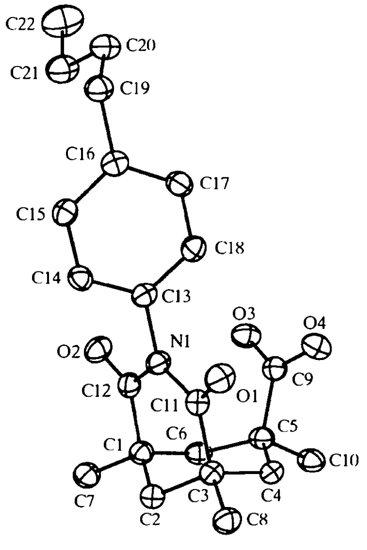


Fig. 1. The molecule of (1) with the atom-labelling scheme. H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 25% probability level.

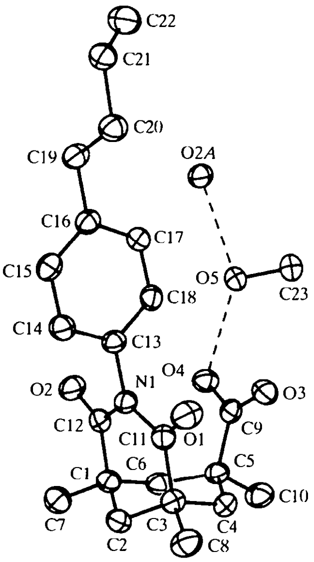


Fig. 2. The molecule of (2) with the atom-labelling scheme. H atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 25% probability level. [Symmetry code: (A) $-x$, $1-y$, $-z$.]

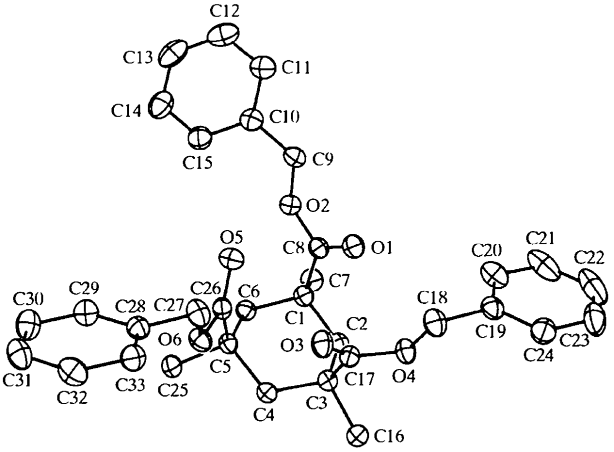


Fig. 3. The molecule of (3) with the atom-labelling scheme. H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 25% probability level.

Experimental

Compound (1) was synthesized as described previously (Rebek, 1985) and further recrystallized from benzene. Recrystallization from methanol gave compound (2). Kemp's anhydride acid chloride was prepared by reacting Kemp's triacid and $SOCl_2$ under reflux, then reacted with a small excess (2.5 equivalents) of benzyl alcohol in the presence of NEt_3 (3 equivalents) in dry tetrahydrofuran (THF) under reflux to give Kemp's triacid dibenzyl ester. The diester was then further reacted with $SOCl_2$ to give the acid chloride, which was reacted with benzyl alcohol again in the presence of NEt_3 and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) in dry THF under reflux to yield the Kemp's triester (3), which was recrystallized from toluene (70–80% yield).

Compound (1)

Crystal data

$C_{22}H_{29}NO_4$
$M_r = 371.46$
Monoclinic
$P2_1/n$
$a = 13.2852\,(4)$ Å
$b = 11.4419\,(3)$ Å
$c = 13.5434\,(4)$ Å
$\beta = 98.438\,(2)^\circ$
$V = 2036\,(2)$ Å^3
$Z = 4$
$D_x = 1.212$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14594 reflections
$\theta = 3\text{–}26^\circ$
$\mu = 0.083$ mm^{-1}
$T = 123\,(2)$ K
Platelet
$0.30 \times 0.30 \times 0.25$ mm
Colourless

Data collection

Nonius Kappa-CCD diffractometer
φ rotation scans with 2° steps
Absorption correction: none
14 594 measured reflections
4059 independent reflections

3191 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\rm max} = 26.36^\circ$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 14$
$l = -16 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.123$
$S = 1.066$
4033 reflections
248 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 1.0733P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.39$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (2)

Crystal data

$C_{22}H_{29}NO_4 \cdot CH_4O$
$M_r = 403.50$
Monoclinic
$P2_1/n$
$a = 9.1757\,(4)$ Å
$b = 13.1247\,(6)$ Å
$c = 18.6567\,(9)$ Å
$\beta = 97.412\,(3)^\circ$
$V = 2228\,(3)$ Å^3
$Z = 4$
$D_x = 1.203$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15184 reflections
$\theta = 3\text{–}26^\circ$
$\mu = 0.084$ mm^{-1}
$T = 123\,(2)$ K
Platelet
$0.40 \times 0.40 \times 0.20$ mm
Colourless

Data collection

Nonius Kappa-CCD diffractometer
φ rotation scans with 2° steps
Absorption correction: none
15 184 measured reflections
4441 independent reflections

3181 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\rm max} = 26.39^\circ$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = -23 \rightarrow 23$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.162$
$S = 1.083$
4388 reflections
267 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 1.9183P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.41$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (3)

Crystal data

$C_{33}H_{36}O_6$
$M_r = 528.62$
Monoclinic
$P2_1/c$
$a = 14.5445\,(5)$ Å
$b = 9.6680\,(2)$ Å
$c = 19.8101\,(7)$ Å
$\beta = 90.186\,(1)^\circ$
$V = 2785\,(2)$ Å^3
$Z = 4$
$D_x = 1.260$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 21241 reflections
$\theta = 3\text{–}26^\circ$
$\mu = 0.086$ mm^{-1}
$T = 123\,(2)$ K
Platelet
$0.60 \times 0.60 \times 0.30$ mm
Colourless

Data collection

Nonius Kappa-CCD diffractometer
φ rotation scans with 2° steps
Absorption correction: none
21 241 measured reflections
5104 independent reflections

4030 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\rm max} = 26.38^\circ$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 10$
$l = -23 \rightarrow 23$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.115$
$S = 1.032$
5082 reflections
353 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 1.2102P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0135 (17)
Scattering factors from *International Tables for Crystallography* (Vol. C)

For all compounds, data collection: *Kappa-CCD Software* (Nonius, 1997); cell refinement: *HKL* (Otwinowski & Minor, 1997); data reduction: *HKL*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1450). Services for accessing these data are described at the back of the journal.

References

Chan, T. L., Cui, Y. X., Mak, T. C. W., Wang, R. J. & Wong, H. N. C. (1991). *J. Crystallogr. Spectrosc. Res.* **21**, 297–308.
Herold, S., Pence, L. E. & Lippard, S. J. (1995). *J. Am. Chem. Soc.* **117**, 6134–6135.
Hirose, T., Baldwin, B. W., Uchimaru, T., Tsuzuki, S., Uebayashi, M. & Taira, K. (1995). *Chem. Lett.* pp. 231–232.
Hirose, T., Baldwin, B. W., Wang, Z. H., Kasuga, K., Uchimaru, T. & Yliniemelä, A. (1996). *Chem. Commun.* pp. 391–392.
Hirose, T., Baldwin, B. W., Wang, Z. H. & Kennard, C. H. L. (1998). *Acta Cryst.* **C54**, 1143–1144.
Nonius (1997). *Kappa-CCD Software.* Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. London and New York: Academic Press.
Rebek, J. Jr (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 245–255.
Rebek, J. Jr, Marshall, L., Wolak, R., Parris, K., Killoran, M., Askew, B., Nemeth, D. & Islam, N. (1985). *J. Am. Chem. Soc.* **107**, 7476–7481.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL.* Version 5.03. Distributed by Bruker-AXS, Madison, Wisconsin, USA.
Tanase, T., Watton, S. P. & Lippard, S. J. (1994). *J. Am. Chem. Soc.* **116**, 9401–9402.
Wang, Z. H., Hirose, T., Baldwin, B. W. & Yang, Y. (1997). *Chem. Commun.* pp. 297–298.
Yun, J. W., Tanase, T., Pence, L. E. & Lippard, S. J. (1995). *J. Am. Chem. Soc.* **117**, 4407–4408.

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3-Phenyl-1-(2-pyridyl)thiourea†

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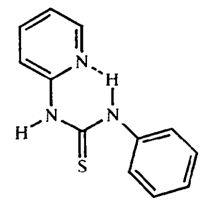
Abstract

The title compound, $C_{12}H_{11}N_3S$, contains an intramolecular N3—H···N_{py} hydrogen bond, which stabilizes the coplanarity of the thiourea moiety and the pyridine (py) ring. The molecules form centrosymmetric hydrogen-bonded dimers, with the S atom forming bifurcated intermolecular hydrogen bonds involving the N2—H group of the thiourea moiety and the C3—H group of the pyridyl ring.

Comment

Although ^{1}H NMR analysis has correctly predicted intramolecular hydrogen bonding involving the pyridyl N atom (N_{py}) and the N3—H group (Kascheres & Ueno, 1991), no structures have been reported for 1-(2-pyridyl)-3-arylthioureas, which are biologically significant molecules (Hall *et al.*, 1996). We report here the crystal structure and lattice arrangement of 3-phenyl-1-(2-pyridyl)thiourea, (I), in order to compare its intramolecular hydrogen bonding with that of benzoylthioureas (Dago *et al.*, 1987, 1988; Zhang *et al.*, 1996; Cao *et al.*, 1996) and its intermolecular hydrogen bonding with that of 1,3-substituted thioureas (Ramnathan *et al.*, 1995*a*; Ramnathan, Sivakumar, Subramanian, Meerarani *et al.*, 1996; Ramnathan, Sivakumar, Janarthanan *et al.*, 1996; Ramnathan, Sivakumar, Subramanian, Srinivasan *et al.*, 1996).



(I)

The unit cell of (I) with the atomic numbering scheme and the intra- and intermolecular hydrogen bonding is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The S1—C7 bond distance [1.682 (3) Å] is essentially identical to that of 1,3-diphenylthiourea [1.681 (5) Å; Ramnathan *et al.*, 1995*b*], but longer than that of 1-benzoyl-3-*p*-nitrophenylthiourea [1.658 (2) Å; Zhang *et al.*, 1996] and 1-benzoyl-3-*p*-methoxyphenylthiourea [1.659 (3) Å; Cao *et al.*, 1996]. In contrast, the N2—C7 bond distance [1.371 (4) Å] is considerably longer than found for 1,3-diphenylthiourea [1.349 (4) Å; Ramnathan *et al.*, 1995*b*], but shorter than that of both 1-benzoyl-3-*p*-nitrophenylthiourea [1.393 (3) Å; Zhang *et al.*, 1996] and 1-benzoyl-3-*p*-methoxyphenylthiourea [1.392 (4) Å; Cao *et al.*, 1996]. The N3—C7 bonds in (I), in the three thioureas mentioned above and in nine other substituted thioureas whose structures have been solved (Dago *et al.* 1987, 1988, 1989; Koch *et al.*, 1995; Ramnathan *et al.*, 1995*a*; Ramnathan, Sivakumar, Subramanian, Meerarani *et al.*, 1996; Ramnathan, Sivakumar, Janarthanan *et al.*, 1996; Ramnathan, Sivakumar, Subramanian, Srinivasan *et al.*, 1996), all have bond distances of about 1.335 (7) Å.

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