Table 5. *Selected geometric parameters (Å, °) of the peracid groups in compounds (I)–(IV)*

	(I) (n = 11)	(II) (n = 12)	(III) (n = 13)	(IV) (n = 14)
O*n*0—C*n*	1.228 (7)	1.190 (2)	1.167 (7)	1.202 (5)
O*n*1—C*n*	1.252 (8)	1.340 (2)	1.348 (7)	1.345 (5)
O*n*1—O*n*2	1.357 (7)	1.461 (2)	1.446 (6)	1.462 (4)
C*n*—O*n*1—O*n*2	109.7 (5)	110.73 (13)	110.4 (4)	110.9 (3)
O*n*0—C*n*—O*n*1	122.7 (7)	124.9 (2)	124.5 (6)	124.3 (4)
O*n*0—C*n*—C($n-1$)	123.6 (7)	126.6 (2)	126.9 (5)	126.4 (4)
O*n*1—C*n*—C($n-1$)	113.6 (6)	108.47 (14)	108.5 (5)	109.3 (4)
O*n*2—O*n*1—C*n*—O*n*0	−0.2 (9)	−0.3 (2)	−0.8 (9)	−0.8 (5)
O*n*2—O*n*1—C*n*—C($n-1$)	178.1 (5)	178.24 (13)	−178.7 (4)	177.9 (3)
C($n-2$)—C($n-1$)—C*n*—O*n*0	−73.2 (8)	55.1 (2)	25.0 (9)	−44.4 (6)
C($n-2$)—C($n-1$)—C*n*—O*n*1	108.6 (7)	−123.4 (2)	−157.2 (5)	136.9 (4)

The peroxy H atom was not located in any of the four title compounds. All other H atoms were placed at the expected positions, riding with $U_{\rm iso}$ refined for each. The terminal peroxy O atom (O112) of compound (I) was found to be disordered over two sites. Refinement of the atom at these sites with a range of occupancies significantly lowered the R value for the structure. The displacement parameters of the atoms at these sites, however, were found to be unacceptably high and hence it was concluded that the data were not of sufficient quality to model the disorder in this way. Finally, the atom position was refined starting at some mean of the two sites with full occupancy. This accounts for the high $U_{\rm eq}$ value for this atom and also for the slightly high R value reported.

For all compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software* (*SETANG*); data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *TEXSAN*; software used to prepare material for publication: *SHELXL*93.

The authors acknowledge support from the SERC (studentship for NF) and are grateful to Solvay Interox (and in particular Dr A. James) for the provision of samples and numerous discussions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1155). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Belitskus, D. & Jeffrey, G. A. (1965). *Acta Cryst.* **18**, 458–463.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
Feeder, N. (1992). PhD thesis, University of Cambridge, England.
Feeder, N. & Jones, W. (1994*a*). *Acta Cryst.* **C50**, 820–823.
Feeder, N. & Jones, W. (1994*b*). *Acta Cryst.* **C50**, 1347–1349.
Feeder, N. & Jones, W. (1996*a*). *Acta Cryst.* **C52**, 913–919.
Feeder, N. & Jones, W. (1996*b*). *Acta Cryst.* **C52**, 919–923.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kim, H. S., Chu, S.-C. & Jeffrey, G. A. (1970). *Acta Cryst.* **B26**, 896–900.
Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sax, M., Beurskens, P. & Chu, S. (1965). *Acta Cryst.* **18**, 252–258.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). **C52**, 1520-1523

(±)-2-Oxocyclododecaneacetic Acid: Structure and Hydrogen-Bonding Pattern of a Large-Ring γ-Keto Acid

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(*Received 3 January 1995; accepted 24 July 1995*)

Abstract

In the title compound, $C_{14}H_{24}O_3$, the ring adopts a typical 'square' [3333] cyclododecane conformation and enantiomeric pairs of molecules form centrosymmetric dimers across the cell corners by mutual hydrogen bonding of carboxy groups, O(2)···O(3)($-x$, $2-y$, $-z$) [2.662 (4) Å]. The ketonic O(1) atom does not participate in the hydrogen bonding but has a close contact [2.487 (3) Å] with the ring H(12*B*)($x-1$, y, z) atom of an adjacent molecule. The observed carboxy C—O and C═O bond lengths and angles correspond to accepted values for a well ordered dimer.

Comment

The crystalline states of acetic and formic acids involve chains (catemers) created by repeating intermolecular O—H···O═C hydrogen bonds (Jones & Templeton, 1958; Nahringbauer, 1978). This pattern is otherwise unusual among carboxylic acids, which typically form hydrogen-bonded dimers (Leiserowitz, 1976). Our interest in the X-ray structures of simple keto-carboxylic acids concerns such hydrogen-bonding motifs, of which four are known. The commonest forms acid dimers without the involvement of the ketone. Less frequently, intermolecular carboxy-to-ketone hydrogen bonds repeat infinitely along one cell axis to yield a catemer. A third, rare arrangement is an internal hydrogen bond, and one instance is known of acid-to-ketone dimerization. We have previously referenced and discussed numerous examples (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1996).

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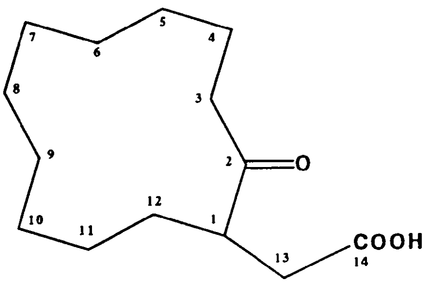
The category of γ-keto acids is especially rich in hydrogen-bonding types, embracing dimers, internal hydrogen bonds and catemers of both the helical and translational type. The title γ-keto acid, (I), m.p. 392 K, was prepared by enamine alkylation of cyclododecanone with ethyl chloroacetate (Stork, Brizzolara, Landesman, Szmuszkovicz & Terrell, 1963; Brannock, Burpitt, Goodlett & Thweatt, 1963). The compound's crystal density ($1.147\,\text{Mg}\,\text{m}^{-3}$) is significantly lower than is typical for small-ring aliphatic keto acids (*ca* $1.25\,\text{Mg}\,\text{m}^{-3}$). This is common in simple macrocycles and reflects empty volume presumably associated, at least in part, with the central hole (Dunitz & Shearer, 1960; Groth, 1974, 1976; Lewis, Rettig, Scheffer, Trotter & Wireko, 1990).



(I)

Fig. 1 presents a view of the molecule with its numbering scheme. The 12-membered ring adopts a sawtoothed 'square' [3333] conformation like that of cyclododecane itself and many cyclododecane and cyclododecanone derivatives (Dunitz & Shearer, 1960; Groth, 1980; Lei, Doubleday & Turro, 1986). This arrangement staggers the methylene units so that they dovetail across adjacent and opposite edges of the ring with minimum interference and it has inherent chirality apart from the substituents present. The ketone C=O is oriented nearly 'axial', *i.e.* nearly orthogonal [82.7 (1)°] to the least-squares ring plane.

The carboxymethyl group projects outward from a corner of the square on the ketone face of the ring, with the substituent methylene adopting a staggered conformation relative to its ring C atom [H—C—C—H torsion angles −62.2 (1) and 179.8 (2)°] and with the carboxy directed toward the ketone. The carbonyl group of the carboxy is turned toward the ketone and the dihedral angle between the carboxy and ketone planes is 70.3 (2)°.

Disordering of the carboxy group, as evidenced by the C—O bond lengths and C—C—O angles, is common in dimeric acids (Dieterich, Paul & Curtin, 1974), but is not significant here. The lengths here are 1.227 (7) and 1.301 (6) Å, with angles 113.6 (5) and 123.3 (4)°, respectively. Typical values for highly ordered carboxy dimers are 1.21 and 1.31 Å, with angles 112 and 123° (Borthwick, 1980). The carboxy H was not found but was added riding on its O atom and its position was refined to optimize the bond angle. The dimer hydrogen bond between O(2) and O(3^{i}) is 2.662 (4) Å [symmetry code: (i) $-x, 2-y, -z$].

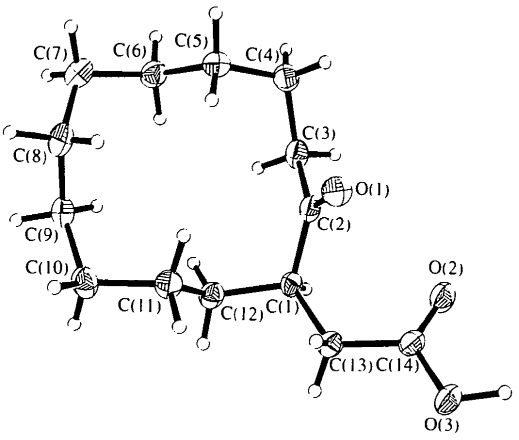


Fig. 1. A view of the title compound with its numbering scheme. Ellipsoids are at the 40% probability level. The crown-like square [3333] conformation is typical of saturated cyclododecane rings, including ketones.

Fig. 2 illustrates the packing ($Z = 2$) and includes extracellular molecules to show the centrosymmetric dimers formed through carboxy pairing of enantiomers across the cell corners. Chirality is differentiated by patterning of the skeletal bonds and atoms. Also shown is a 2.487 (3) Å close contact from the ketone O(1) to H($12B^{\text{ii}}$) of an adjacent, translationally equivalent molecule [symmetry code: (ii) $x-1, y, z$]. This probably represents a significant polar attraction contributing to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

The solid-state IR (KBr) spectrum of the compound has a single, relatively sharp C=O stretching absorption centered at $1709\,\text{cm}^{-1}$ for both ketone and carboxy,

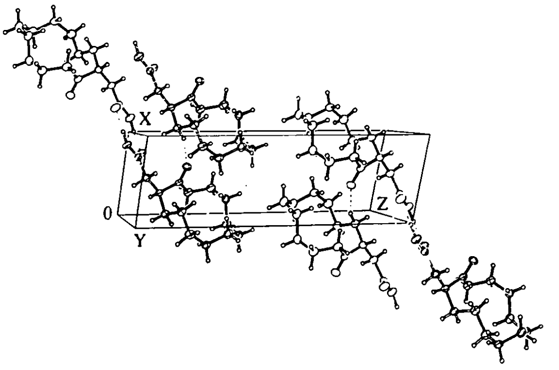


Fig. 2. A partial packing diagram for the title compound. Extracellular molecules show the centrosymmetric carboxy dimerization across the corners of the cell and a 2.487 (3) Å intermolecular close contact. The chirality of enantiomers is differentiated by patterning of the skeletal bonds and atoms.

normal for a compound with dimeric acid hydrogen bonding and a free ketone (Vanderhoff, Lalancette & Thompson, 1990).

Experimental

The title compound was crystallized from 60:40 ethanol/ethyl butyl ketone at room temperature.

Crystal data

$C_{14}H_{24}O_3$
$M_r = 240.3$
Triclinic
$P\bar{1}$
$a = 5.536\,(2)$ Å
$b = 7.901\,(2)$ Å
$c = 16.540\,(3)$ Å
$\alpha = 83.98\,(1)°$
$\beta = 82.55\,(2)°$
$\gamma = 76.76\,(2)°$
$V = 696.1\,(3)$ Å^3
$Z = 2$
$D_x = 1.147$ Mg m^{-3}
$D_m = 1.14\,(1)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 16 reflections
$\theta = 5.25–9.36°$
$\mu = 0.079$ mm^{-1}
$T = 297$ K
Parallelepiped
0.48 × 0.16 × 0.12 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical
$T_{\min} = 0.984$, $T_{\max} = 0.992$
2044 measured reflections
1815 independent reflections
932 observed reflections $[F > 4\sigma(F)]$

$R_{\rm int} = 0.0334$
$\theta_{\max} = 22.5°$
$h = 0 \rightarrow 5$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 47 reflections
intensity decay: 6.51%

Refinement

Refinement on F
$R = 0.0504$
$wR = 0.0582$
$S = 1.19$
932 reflections
157 parameters
H atoms: see below
$w = 1/[\sigma^2(F) + 0.0006F^2]$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

Extinction correction: $F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$
Extinction coefficient: $\chi = 0.012\,(2)$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(1)	0.4161 (6)	0.8385 (4)	−0.2266 (2)	0.068 (2)
O(2)	0.2719 (6)	0.9988 (5)	−0.0589 (2)	0.073 (2)
O(3)	0.1490 (6)	0.7753 (4)	0.0144 (2)	0.072 (2)
C(1)	0.7170 (8)	0.7798 (6)	−0.1306 (3)	0.050 (2)
C(2)	0.6065 (9)	0.8661 (6)	−0.2070 (3)	0.050 (2)
C(3)	0.7431 (9)	0.9921 (6)	−0.2591 (3)	0.059 (2)
C(4)	0.6982 (9)	1.0148 (7)	−0.3489 (3)	0.069 (2)
C(5)	0.8106 (9)	0.8538 (6)	−0.3942 (3)	0.065 (2)
C(6)	1.0964 (9)	0.8091 (6)	−0.4068 (3)	0.066 (2)
C(7)	1.2136 (10)	0.6326 (7)	−0.4401 (3)	0.076 (3)
C(8)	1.1657 (10)	0.4769 (7)	−0.3833 (3)	0.074 (2)
C(9)	1.2872 (8)	0.4535 (6)	−0.3038 (3)	0.062 (2)
C(10)	1.1454 (9)	0.3688 (6)	−0.2304 (3)	0.069 (2)
C(11)	0.9013 (9)	0.4876 (6)	−0.1981 (3)	0.059 (2)
C(12)	0.9451 (8)	0.6330 (6)	−0.1521 (3)	0.056 (2)
C(13)	0.5286 (8)	0.7113 (6)	−0.0687 (3)	0.059 (2)
C(14)	0.3047 (9)	0.8423 (8)	−0.0380 (3)	0.055 (2)

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

O(1)—C(2)	1.213 (7)	O(2)—C(14)	1.227 (7)
O(3)—C(14)	1.301 (6)	C(1)—C(2)	1.505 (7)
C(1)—C(12)	1.538 (6)	C(1)—C(13)	1.514 (6)
C(2)—C(3)	1.517 (7)	C(3)—C(4)	1.522 (7)
C(4)—C(5)	1.511 (7)	C(5)—C(6)	1.532 (7)
C(6)—C(7)	1.524 (7)	C(7)—C(8)	1.520 (7)
C(8)—C(9)	1.529 (8)	C(9)—C(10)	1.537 (7)
C(10)—C(11)	1.526 (6)	C(11)—C(12)	1.522 (7)
C(13)—C(14)	1.492 (6)	O(2)···O(3$^{\rm i}$)	2.662 (4)
C(2)—C(1)—C(12)	110.3 (4)	C(2)—C(1)—C(13)	112.6 (4)
C(12)—C(1)—C(13)	110.7 (4)	O(1)—C(2)—C(1)	122.3 (4)
O(1)—C(2)—C(3)	120.7 (4)	C(1)—C(2)—C(3)	117.0 (5)
C(2)—C(3)—C(4)	114.5 (5)	C(3)—C(4)—C(5)	113.5 (4)
C(4)—C(5)—C(6)	114.6 (5)	C(5)—C(6)—C(7)	115.3 (5)
C(6)—C(7)—C(8)	114.5 (4)	C(7)—C(8)—C(9)	114.3 (5)
C(8)—C(9)—C(10)	114.6 (4)	C(9)—C(10)—C(11)	113.5 (4)
C(10)—C(11)—C(12)	112.2 (4)	C(1)—C(2)—C(11)	116.7 (4)
C(1)—C(13)—C(14)	116.5 (4)	O(2)—C(14)—O(3)	123.1 (4)
O(2)—C(14)—C(13)	123.3 (4)	O(3)—C(14)—C(13)	113.6 (5)
C(14)—O(3)—H(3*C*)	109.5 (3)	C(14)—O(2)···H(3*C*$^{\rm i}$)	119.9 (3)
O(3)—H(3*C*)···O(2$^{\rm i}$)	172.8 (2)		

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

All diffractometer software was provided by Siemens Analytical X-ray Instruments Inc., including *SHELXTL/PC* (Sheldrick, 1990). The structure was solved by direct methods. Integrated intensities were corrected for Lorentz and polarization effects. Full-matrix least-squares refinement was performed. All non-H atoms were refined anisotropically. The carboxy H atom was placed in a calculated position and allowed to refine on its associated O atom using a riding model. The second carboxy is symmetry-related and was not involved in the refinement. All other H atoms were placed in calculated positions and allowed to refine as riding on their associated C atoms for optimum R factor and goodness-of-fit.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Berkovitch-Yellin, Z. & Leiserowitz, L. (1982). *J. Am. Chem. Soc.* **104**, 4052–4064.

Borthwick, P. W. (1980). *Acta Cryst.* B**36**, 628–632.

Brannock, K. C., Burpitt, R. D., Goodlett, V. W. & Thweatt, J. G. (1963). *J. Org. Chem.* **28**, 1464–1468.

Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1996). *Acta Cryst.* C**52**, 684–687.

Dieterich, D. A., Paul, I. C. & Curtin, D. Y. (1974). *J. Am. Chem. Soc.* **96**, 6372–6380.

Dunitz, J. D. & Shearer, H. M. M. (1960). *Helv. Chim. Acta*, **43**, 18–35.

Groth, P. (1974). *Acta Chem. Scand. Ser. A*, **28**, 294–298, 808–810.

Groth, P. (1976). *Acta Chem. Scand. Ser. A*, **30**, 294–296.

Groth, P. (1980). *Acta Chem. Scand. Ser. A*, **34**, 609–620.

Jones, R. E. & Templeton, D. H. (1958). *Acta Cryst.* **11**, 484–487.
Jönsson, P. -G. (1972). *Acta Chem. Scand.* **26**, 1599–1619.
Lei, X., Doubleday, C. Jr & Turro, N. J. (1986). *Tetrahedron Lett.* **27**, 4671–4674.
Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.
Lewis, T. J., Rettig, S. J., Scheffer, J. R., Trotter, J. & Wireko, F. (1990). *J. Am. Chem. Soc.* **112**, 3679–3680.
Nahringbauer, I. (1978). *Acta Cryst.* **B34**, 315–318.
Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Release 4.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stork, G., Brizzolara, A., Landesman, H., Szmuszkovicz, J. & Terrell, R. (1963). *J. Am. Chem. Soc.* **85**, 207–222.
Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). *Acta Cryst.* **C48**, 66–70.
Vanderhoff, P. A., Lalancette, R. A. & Thompson, H. W. (1990). *J. Org. Chem.* **55**, 1696–1698.

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Cyclohexane-Linked Indenyl Rings in 5,8-Bis(trimethylsilyl)-6,7,12b,12c-tetrahydroindeno[2,1-*c*]fluorene

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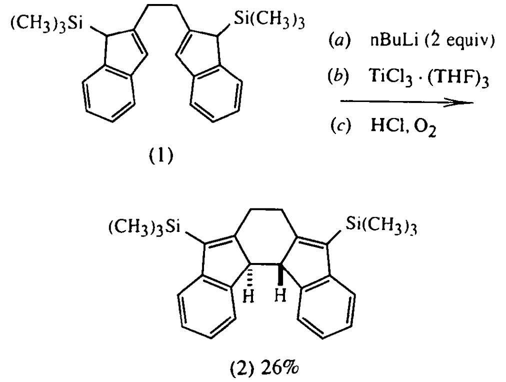
Abstract

A novel ring structure of formula $C_{26}H_{32}Si_2$ has been formed by oxidation of 1,2-bis(1-trimethylsilyl-2-indenyl)ethane during attempted $TiCl_3(thf)_3$ complexation. Two indenyl groups are linked by a cyclohexane ring having a chair conformation and the resulting dihedral angle between the planes of the indenyl groups is 10.6 (1)°.

Comment

ansa-Metallocenes based on Group 4 transition metals have drawn attention because of their role in reactions such as asymmetric hydrogenation (Willoughby & Buchwald, 1994) and asymmetric carbomagnesation (Hoveyda & Morken, 1993). Recently, we reported the synthesis of novel *ansa*-titanocenes based on 1,2-bis(2-indenyl)ethane (Hitchcock, Situ, Covel, Olmstead & Nantz, 1995). In the course of our studies, we encountered an *ansa* ligand, (1), that did not undergo facile $TiCl_3$ complexation. Rather, an unforeseen oxidative coupling process took place resulting in compound (2). This oxidative process was believed to occur as a result of the steric demands of the resident trimethylsilyl groups.



In the title compound, (2), short C1—C20 and C16—C17 bond distances of 1.356 (4) and 1.354 (3) Å, respectively, confirm the presence of indenyl double

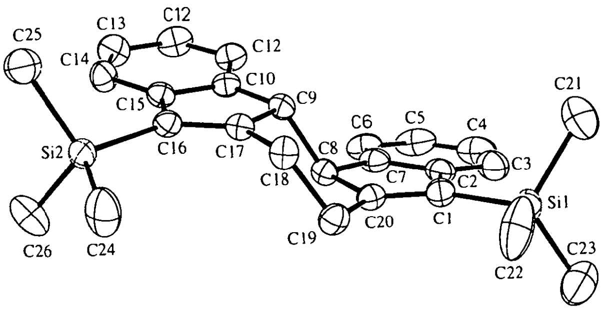


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

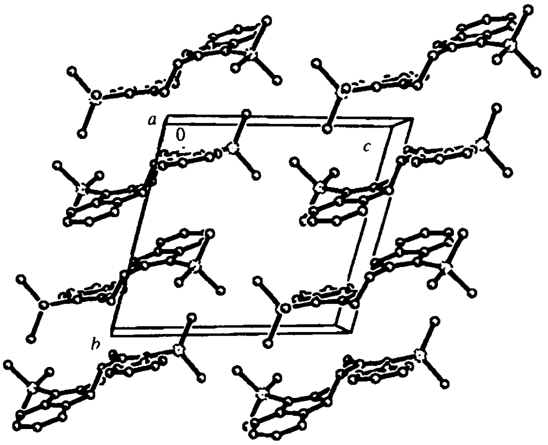


Fig. 2. A packing diagram of (2) showing the alignment of the indenyl rings. Si atoms are displayed as dotted spheres.

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