Prince, P., Evans, K. L., Boss, K. R., Fronczek, F. R. & Gandour, R. D. (1990). *Acta Cryst.* C**46**, 1150–1152.
Prince, P., Evans, K. L., Rosas-García, V. M., Gandour, R. D. & Fronczek, F. R. (1992). *Tetrahedron Lett.* **33**, 6431–6434.
Prince, P., Fronczek, F. R. & Gandour, R. D. (1989). *Acta Cryst.* C**45**, 1256–1258.
Prince, P., Fronczek, F. R. & Gandour, R. D. (1990). *Acta Cryst.* C**46**, 1720–1723.
Sy, W.-W., Lodge, B. A. & By, A. W. (1990). *Synth. Commun.* **20**, 877–880.

Acta Cryst. (1996). C**52**, 947–949

trans-1,1′-Bis(indenylidene)

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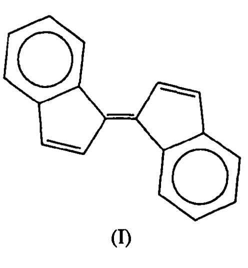
Abstract

The title compound, $(C_9H_6)_2$, was obtained by the coupling of the carbene C_9H_6: derived from 1-diazoindene, $C_9H_6N_2$, in the presence of $[Ru_3(CO)_{12}]$. The molecule is centrosymmetric and completely planar. The six-membered rings have aromatic character and are connected by an extended π-electron system.

Comment

In spite of being a relatively simple hydrocarbon, 1,1′-bis(indenylidene), (I), has not been described in the literature. It was obtained during our synthetic and structural studies on the reaction between metal carbonyl clusters and diazo compounds (Arce, De Sanctis, Manzur & Capparelli, 1994; Arce, De Sanctis, Machado, Manzur & Capparelli, 1995). The title compound was formed by the coupling of the carbene C_9H_6: derived from 1-diazoindene, $C_9H_6N_2$, in the presence of $[Ru_3(CO)_{12}]$.



(I)

The crystal structure analysis showed that the molecule of (I) (Fig. 1) is centrosymmetric and that the asymmetric unit consists of only one half of a molecule. The two halves are linked by a double bond, C1=C1$^{\rm i}$, in a *trans* configuration imposed by the inversion centre. This bond and the double bond in the five-membered ring, C2=C3, form an hexatriene system (C3=C2—C1=C1$^{\rm i}$—C2$^{\rm i}$=C3$^{\rm i}$). Within experimental error, both double bonds have equal lengths which are similar to the 1.345 (12) Å reported for hexatrienes (Allen *et al.*, 1987). The lengths of the single bonds (C1—C2, C1—C5 and C3—C4) indicate that they have partial double-bond character. The C1—C5 distance is comparable to 1.489 (5) Å, in agreement with equivalent bonds in five-membered rings (carbocyclic and heterocyclic) fused to benzene rings (Allen, 1981), but the C3—C4 bond length is significantly shorter. The C1—C2 distance is long when compared with 1.443 (13) Å for known hexatrienes (Allen *et al.*, 1987), or *ca* 1.44–1.47 Å observed in butadienes (Capparelli & Codding, 1993, and references therein). In general, the lengths of these $C_{sp^2}{=}C_{sp^2}$ double and $C_{sp^2}{-}C_{sp^2}$ single bonds reveal the existence of an extended π-electron system connecting both phenyl rings.

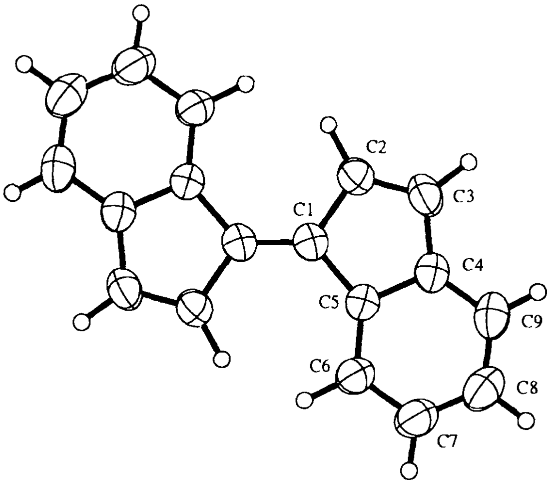


Fig. 1. Molecular structure of the title compound showing the displacement ellipsoids drawn at 40% probability.

The six-membered ring is aromatic and there is no indication that the ring fusion produces any double-bond fixation, in agreement with the findings of Allen (1981). In contrast, η^5 bonding of the five-membered rings to transition metals results in an aromatic character of these rings and a clear loss of aromaticity of the six-membered rings. This is indicated by the significant shortening of the C6—C7 and C8—C9 distances observed in $[Ru_3(C_{18}H_{12})(CO)_8]$, (II) (Arce, De Sanctis, Machado, Manzur & Capparelli, 1995). The average C—C bond length in the six-membered ring of (I), 1.386 (1) Å, coincides with the value given by Allen (1981) for benzene rings fused to five-membered rings. However, the expected lengthening of the C4—C5 bond is several times larger than the tabulated value. In general, the ring does not display the average *mm* symmetry found by Allen (1981). The endocyclic C—C—C angles do not quite follow the expected pattern: the angles at C4, C7 and C8 show the predicted opening, but the angle at C5 is smaller than 120°, and the average narrowing of the angles at C6 and C9 [1.1 (2)°] is half the reported value.

The molecule is quite planar (mean deviation from the least-squares plane 0.003 Å). The exact coplanarity of both halves, imposed by the inversion centre, maximizes the π overlap across the $C1{=}C1^i$ bridge and, therefore, the delocalization of the π system. In comparison, in (II) the two halves of the organic ligand are twisted by 43.2° about the bridging bond, due to strain caused by the η^5 bonding to the metal cluster. As expected, the bridging bond in (II) [1.48 (1) Å] is significantly longer than in (I).

In the crystal structure the molecular inversion centres lie on Wyckoff sites *a*. The crystal packing is entirely the result of van der Waals interactions.

Experimental

Freshly distilled 1-diazoindene, $C_9H_6N_2$ (1 ml, 0.9 mmol), prepared as described by Rewicki & Tuchscherer (1972), was added to a solution of $[Ru_3(CO)_{12}]$ (200 mg, 0.32 mmol) in dried tetrahydrofuran (50 ml). The mixture was refluxed under N_2 for 60 min and then the solvent was removed. TLC separation [SiO_2, *n*-hexane/dichloromethane (8:1 *v*/*v*)] of the dark red residue produced several yellow–orange–red Ru complexes (Arce, De Sanctis, Machado, Manzur & Capparelli, 1995) and the orange title compound, (I) (40 mg, 0.17 mmol, 38% yield based on diazoindene). Crystals suitable for X-ray analysis were obtained by slow evaporation of a *n*-hexane/dichloromethane solution with volume ratio 1:1. ^1H NMR ($CDCl_3$, δ, p.p.m.): 7.0 (2H, *d*, J = 5.7 Hz), 7.3 (6H, *m*), 7.4 (2H, *d*, J = 5.7 Hz), 7.9 (2H, *m*).

Crystal data

$C_{18}H_{12}$
$M_r = 228.29$
Monoclinic
$P2_1/a$
$a = 8.289\ (5)$ Å
$b = 6.312\ (4)$ Å
$c = 11.786\ (4)$ Å
$\beta = 93.19\ (3)°$
$V = 615.7\ (6)$ Å^3
$Z = 2$
$D_x = 1.231$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7.0–19.2°$
$\mu = 0.070$ mm^{-1}
$T = 295\ (1)$ K
Prism
0.48 × 0.28 × 0.18 mm
Orange

Data collection

AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none

$\theta_{max} = 25.0°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 7$
$l = -13 \rightarrow 13$

1281 measured reflections
1236 independent reflections
771 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0372$

3 standard reflections monitored every 150 reflections
intensity decay: 1.67%

Refinement

Refinement on F
$R = 0.0421$
$wR = 0.0428$
$S = 2.908$
771 reflections
107 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.0002$

$\Delta\rho_{max} = 0.12$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ e Å^{-3}
Extinction correction: Zachariasen (1968) type II Gaussian isotropic
Extinction coefficient: 0.35 (6) × 10^{-5}
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)*

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

	x	y	z	U_{eq}
C1	0.0007 (2)	0.0429 (3)	0.9479 (2)	0.0559 (6)
C2	0.0762 (3)	0.2480 (4)	0.9208 (2)	0.0686 (8)
C3	0.0525 (3)	0.2878 (4)	0.8087 (2)	0.0735 (8)
C4	−0.0365 (2)	0.1167 (4)	0.7540 (2)	0.0609 (7)
C5	−0.0692 (2)	−0.0360 (3)	0.8368 (2)	0.0535 (6)
C6	−0.1538 (3)	−0.2163 (4)	0.8040 (2)	0.0677 (8)
C7	−0.2044 (3)	−0.2415 (5)	0.6900 (2)	0.0839 (9)
C8	−0.1714 (3)	−0.0926 (5)	0.6103 (2)	0.088 (1)
C9	−0.0873 (3)	0.0889 (5)	0.6412 (2)	0.0784 (9)

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

C1—C1^i	1.342 (4)	C4—C9	1.383 (3)
C1—C2	1.481 (3)	C5—C6	1.382 (3)
C1—C5	1.488 (3)	C6—C7	1.394 (3)
C2—C3	1.347 (3)	C7—C8	1.367 (4)
C3—C4	1.441 (3)	C8—C9	1.379 (4)
C4—C5	1.409 (3)		
C1^i—C1—C2	125.2 (2)	C1—C5—C4	107.5 (2)
C1^i—C1—C5	130.3 (3)	C1—C5—C6	133.6 (2)
C2—C1—C5	104.5 (2)	C4—C5—C6	118.9 (2)
C1—C2—C3	109.6 (2)	C5—C6—C7	119.0 (2)
C2—C3—C4	110.0 (2)	C6—C7—C8	121.5 (3)
C3—C4—C5	108.4 (2)	C7—C8—C9	120.5 (3)
C3—C4—C9	130.3 (2)	C4—C9—C8	118.8 (3)
C5—C4—C9	121.3 (2)		

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

The structure was solved by direct methods. All H atoms were located in a $\Delta\rho$ map and were refined isotropically. Reflections were not corrected for absorption effects, but an extinction correction was applied such that $|F_c^*| = k|F_c|[gI_c + (1 + g^2I_c^2)^{1/2}]^{-1/2}$ (k = scale factor), with g refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1295). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H. (1981). *Acta Cryst.* B**37**, 900–906.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Arce, A. J., De Sanctis, Y., Machado, R., Manzur, J. & Capparelli, M. V. (1995). *J. Am. Chem. Soc.* Submitted.
Arce, A. J., De Sanctis, Y., Manzur, J. & Capparelli, M. V. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 2193–2195.
Capparelli, M. V. & Codding, P. W. (1993). *Can. J. Chem.* **71**, 942–950.
Molecular Structure Corporation (1993*a*). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1993*b*). *TEXSAN. Single Crystal Structure Analysis Software.* Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Rewicki, D. & Tuchscherer, C. (1972). *Angew. Chem. Int. Ed. Engl.* **11**, 44–45.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

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N,*N*-Bis(2-hydroxybenzyl)-*N*-(2-pyridylmethyl)amine, H_2BBPA

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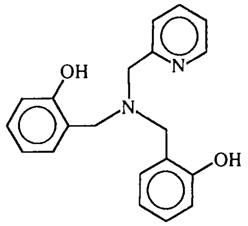
Abstract

In connection with our interest in the use of multidentate ligands for the preparation of iron complexes as models for the active site of the metalloenzyme transferrin, we have prepared the title compound [*N*-(2-pyridylmethyl)-2,2′-(iminodimethyl)diphenol, $C_{20}H_{20}N_2O_2$], which contains one amine and one pyridine N atom and two phenolate O atoms capable of forming a N_2O_2 donor set.

Comment

Multidentate ligands derived from amines containing phenolate-type and α-pyridyl groups as pendant arms are recognized as an important class of ligands, since they are able to mimic the amino acid residues tyrosine and histidine, respectively, in the active site of certain metalloenzymes such as transferrins (Pyrz, Roe, Stern & Que, 1985) and purple acid phosphatases (Que, 1990). In this work, we report the synthesis and crystal structure of a new tetradentate ligand, H_2BBPA, which may act as a potent chelator for M^{3+} transition metals. This is part of our programme of preparation and characterization of iron and vanadium complexes with bioinorganic relevance (Neves, Brito *et al.*, 1993; Neves, Vencato & Mascarenhas, 1994; Neves, Ceccato *et al.*, 1993).



H_2BBPA

The crystal structure reveals that H_2BBPA exhibits adequate geometry of the N1, N2 and O2 donor atoms for facial coordination in octahedral complexes. The bond angles around the amine N atom range from 108.5 (7) to 110.6 (6)° and show that the N2 atom lies in a slightly distorted tetrahedral environment. The C—O(phenol) distances are very similar [C13—O1 = 1.411 (9) and C20—O2 = 1.39 (1) Å] and agree very well with the corresponding distances detected in related ligands (Campbell, Parsons & Pennington, 1993; Neves *et al.*, 1995). The pyridine ring in the title compound is planar and forms dihedral angles of 81.2 (2) and 14.6 (9)° with the C8–C13 and C15–C20 phenol rings, respectively.

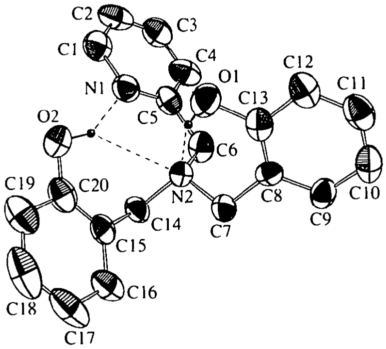


Fig. 1. The atomic numbering scheme and hydrogen bonds. Displacement ellipsoids are plotted at the 50% probability level. H atoms of the phenol O atoms have arbitrary size and other H atoms are omitted.