Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: LI1058). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 313–315

2,4,7,9-Tetra-*tert*-butyl-1,3,7,9-decatetraene

Jason S. Overby and Timothy P. Hanusa*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, USA

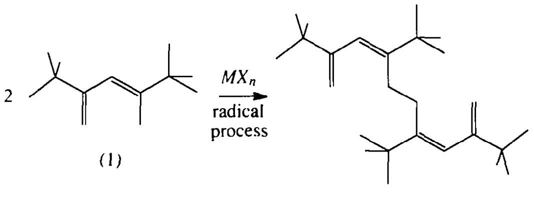
(*Received* 15 *February* 1994; *accepted* 7 *June* 1994)

Abstract

The structure of 2,4,7,9-tetra-*tert*-butyl-1,3,7,9-decatetraene, $C_{26}H_{46}$, is reported. The compound is isolated as a Wurtz coupling product of 2,4-di-*tert*-butyl-1,3-pentadiene from the reaction of the potassium salt of the pentadiene with various metal halides. The molecule lies on an inversion center and the conjugated portions of the molecule adopt 'U'-shaped geometries that are distorted from planarity.

Comment

Metal–pentadienyl complexes display a variety of metal–ligand bonding modes (η^1,η^3,η^5) that have been associated with reactivity patterns distinctively different from their cyclopentadienyl counterparts (Ernst, 1988). In the absence of structural information for the parent pentadienes, the energetic significance of particular conformations of the metal-coordinated ligands can be difficult to evaluate. We have been investigating the synthesis of pentadienyl complexes of the heavy alkaline earth metals (Ca–Ba), whose absence of valence electrons simplifies comparisons with transition metal analogs (Overby & Hanusa, 1994). As a by-product of the reaction of the potassium salt of 2,4-di-*tert*-butyl-1,3-pentadiene (1) with alkaline earth diiodides, we isolated a substantial amount of the Wurtz-coupled product 2,4,7,9-tetra-*tert*-butyl-1,3,7,9-decatetraene (2). This compound was identified previously from the reaction of the anion of (1) and various other metal halides, including ZnI_2 and the transition metal chlorides $TiCl_2(THF)_x$, $MoCl_4$, $NiCl_2$ and $ZrCl_4$; it has been characterized spectroscopically (Ernst, Freeman, Swepston & Wilson, 1991). Crystals of the tetraene were grown from hexane; their structure is reported here.



(2)

The molecule lies on an inversion center, with each half in a 'U'-shaped configuration (Fig. 1). The bond lengths are as expected, including the shortened distance [1.479 (5) Å] between the two vinylic C atoms C(2) and C(3). Unexpectedly, however, the 'U' portion is twisted substantially from planarity; although the four atoms C(2)–C(5) define a nearly perfect plane (maximum deviation 0.002 Å), C(1) lies 0.98 Å out of this plane, away from the inversion center. This distortion is also reflected in the C(1)—C(2)—C(3)—C(4) torsion angle of −59.0 (6)°. The bending may be driven by the need to avoid a close C(1)···C(5) contact; if the atoms C(1)–C(5) were all coplanar, the C(1)···C(5) separation would be only 2.89 Å, well within the sum of the van der Waals radii for two methylene units (*ca* 4.0 Å; Pauling, 1960). With the twist, they achieve a separation of 3.332 (6) Å.

The 2,4-di-*tert*-butyl-1,3-pentadiene ligand is found in the zinc complex $(\eta^1\text{-}2,4\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_5)_2\text{Zn}$ (Ernst, Freeman, Swepston & Wilson, 1991). Interestingly, the conjugated portions of the ligands adopt a 'U' configuration resembling that in the tetraene and there is a similar twist from planarity, although by a smaller amount (torsion angle of 34.9°). The twisting in the metal complex was ascribed to an interaction of the outer double bonds of the ligands with the zinc center. A comparison with the tetraene demonstrates that some distortion is inherent to the diene portions of the molecule and thus in the zinc complex need not arise from metal–ligand interactions alone.

Acta Crystallographica Section C
ISSN 0108-2701 © 1995

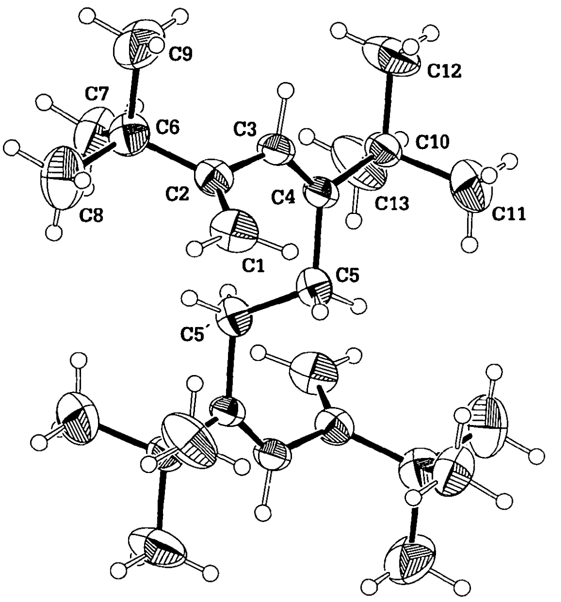


Fig. 1. *ORTEP* (Johnson, 1976) view of the title compound with displacement ellipsoids drawn at the 40% level.

Experimental

Crystal data

$C_{26}H_{46}$
$M_r = 358.65$
Monoclinic
$P2_1/n$
$a = 9.559$ (2) Å
$b = 12.464$ (2) Å
$c = 10.478$ (2) Å
$\beta = 94.37$ (1)°
$V = 1244.7$ (3) Å^3
$Z = 2$
$D_x = 0.957$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–16.7°
$\mu = 0.049$ mm^{-1}
$T = 293$ (1) K
Prism
0.85 × 0.40 × 0.31 mm
Colorless

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: none
2462 measured reflections
2320 independent reflections
789 observed reflections [$F > 3.00\sigma(F)$]

$R_{\rm int} = 0.039$
$\theta_{\rm max} = 25.05°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 14$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 150 reflections
intensity decay: <2%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.050$
$S = 1.54$
789 reflections
119 parameters
H-atom parameters not refined

$\Delta\rho_{\rm max} = 0.13$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}
Extinction correction: estimated from low-angle data
Extinction coefficient: refined second parameter, 1.3756×10^{-6}

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.002$

Atomic scattering factors from Cromer & Waber (1974)

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
C(1)	0.0688 (4)	0.2622 (3)	0.9057 (4)	5.2 (2)
C(2)	0.0727 (4)	0.1914 (3)	0.8127 (4)	3.7 (2)
C(3)	−0.0500 (4)	0.1218 (3)	0.7789 (3)	3.5 (2)
C(4)	−0.1148 (3)	0.0522 (3)	0.8493 (3)	3.2 (2)
C(5)	−0.0685 (3)	0.0294 (3)	0.9904 (3)	3.9 (2)
C(6)	0.1934 (4)	0.1840 (3)	0.7264 (4)	4.5 (2)
C(7)	0.1471 (5)	0.2352 (4)	0.5972 (4)	7.8 (3)
C(8)	0.3250 (5)	0.2413 (4)	0.7812 (5)	7.7 (3)
C(9)	0.2331 (4)	0.0679 (4)	0.7049 (4)	5.9 (2)
C(10)	−0.2425 (4)	−0.0106 (3)	0.7938 (3)	3.7 (2)
C(11)	−0.3678 (5)	0.0111 (4)	0.8723 (5)	7.6 (3)
C(12)	−0.2889 (4)	0.0195 (4)	0.6572 (4)	7.1 (3)
C(13)	−0.2112 (5)	−0.1298 (4)	0.7972 (5)	7.2 (3)

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

The torsion angles carry a poitive sign if when looking from atom (2) to atom (3), a clockwise motion of atom (1) would superimpose it on atom (4).

C(1)—C(2)	1.318 (5)	C(6)—C(7)	1.531 (5)
C(2)—C(3)	1.479 (5)	C(6)—C(8)	1.520 (5)
C(2)—C(6)	1.523 (5)	C(6)—C(9)	1.516 (5)
C(3)—C(4)	1.323 (4)	C(10)—C(11)	1.528 (5)
C(4)—C(5)	1.537 (5)	C(10)—C(12)	1.512 (5)
C(4)—C(10)	1.528 (5)	C(10)—C(13)	1.515 (5)
C(5)—C(5^{i})	1.500 (6)		
C(1)—C(2)—C(3)	120.2 (4)	C(2)—C(6)—C(9)	110.8 (3)
C(1)—C(2)—C(6)	123.1 (4)	C(7)—C(6)—C(8)	108.2 (4)
C(3)—C(2)—C(6)	116.4 (3)	C(7)—C(6)—C(9)	109.0 (4)
C(2)—C(3)—C(4)	130.3 (3)	C(8)—C(6)—C(9)	107.2 (4)
C(3)—C(4)—C(5)	123.0 (3)	C(4)—C(10)—C(11)	109.9 (3)
C(3)—C(4)—C(10)	121.2 (3)	C(4)—C(10)—C(12)	113.6 (3)
C(5)—C(4)—C(10)	115.7 (3)	C(4)—C(10)—C(13)	110.0 (3)
C(4)—C(5)—C(5^{i})	113.8 (4)	C(11)—C(10)—C(12)	106.3 (3)
C(2)—C(6)—C(7)	108.6 (3)	C(11)—C(10)—C(13)	108.8 (4)
C(2)—C(6)—C(8)	113.0 (4)	C(12)—C(10)—C(13)	108.0 (4)

C(1)—C(2)—C(3)—C(4)	−59.0 (6)
C(1)—C(2)—C(6)—C(7)	−103.0 (5)
C(1)—C(2)—C(6)—C(8)	17.1 (6)
C(1)—C(2)—C(6)—C(9)	137.3 (4)
C(2)—C(3)—C(4)—C(5)	−0.5 (6)
C(2)—C(3)—C(4)—C(10)	179.2 (4)
C(3)—C(2)—C(6)—C(7)	70.8 (5)
C(3)—C(2)—C(6)—C(8)	−169.2 (3)
C(3)—C(2)—C(6)—C(9)	−48.9 (4)
C(3)—C(4)—C(5)—C(5^{i})	−69.7 (6)
C(3)—C(4)—C(10)—C(11)	−122.0 (4)
C(3)—C(4)—C(10)—C(12)	−3.1 (5)
C(3)—C(4)—C(10)—C(13)	118.1 (4)
C(4)—C(3)—C(2)—C(6)	127.1 (4)
C(4)—C(5)—C(5^{i})—C(4)	180
C(5)—C(4)—C(10)—C(11)	57.7 (4)
C(5)—C(4)—C(10)—C(12)	176.6 (3)
C(5)—C(4)—C(10)—C(13)	−62.2 (4)
C(5^{i})—C(5)—C(4)—C(10)	−110.6 (4)

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

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1985) using the *TEXSAN* set of programs (Molecular Structure Corporation, 1990). H atoms were inserted in calculated positions based on packing considerations (C—H 0.95 Å). The positions were fixed for the final cycles of refinement.

This work was supported by the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the University Research Council of Vanderbilt University. Funds for the X-ray diffraction facility were provided through NSF Grant CHE-8908065.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AS1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 315–318

Thiamin Thiothiazolone Acetone Solvate, $C_{12}H_{16}N_4OS_2.0.5C_3H_6O$

Whanchul Shin* and Byung Chul Lim†

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-742, Korea

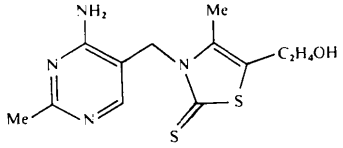
(*Received* 29 *September* 1993; *accepted* 7 *April* 1994)

Abstract

The structure of thiamin thiothiazolone {TTT; 3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methyl-2(3*H*)-thiazolethione}, originally known as a transition-state analogue of thiamin, is quite different from that of its congener thiamin thiazolone (TT). TTT assumes the *S* conformation [$\varphi_T = \pm 83\,(1)°$; $\varphi_P = \mp 176\,(1)°$], while TT assumes the *V* conformation [$\varphi_T = \pm 104\,(1)°$; $\varphi_P = \mp 74\,(1)°$] with an intramolecular N—H···O hydrogen bond. The conformations of the hydroxyethyl side chains are also different, so that TTT has a close $^{\delta+}S\cdots O^{\delta-}$ electrostatic interaction while TT does not. Crystal packing consists of a three-dimensional hydrogen-bonding network formed by three unique hydrogen bonds. There are two kinds of hydrogen-bonded molecular dimer. The acetone molecule is statistically disordered in the cavity formed by the two centrosymmetrically related pyrimidine base pairs.

Comment

The diphosphate esters of thiamin thiothiazolone (TTT) and thiamin thiazolone (TT) were originally proposed to be transition-state analogues for thiamin diphosphate-dependent enzymic reactions owing to their structural resemblance to the enamine, a reactive intermediate in thiamin catalysis, together with a very high binding affinity (Gutowski & Lienhard, 1976). However, it was suggested later that they are intermediate analogues rather than transition-state analogues and that the lower polarity of these compounds may be the major factor governing their high affinity for the hydrophobic binding site of the apoenzyme (Kluger, Gish & Kauffman, 1984; Kuo & Jordan, 1983). Whether TT and TTT are the transition-state or intermediate analogues or not, these compounds are interesting from a structural viewpoint. In the crystalline state, TT assumes a *V* conformation with an intramolecular N—H···O hydrogen bond (Shin & Kim, 1986). This remains the only crystal structure that remotely resembles Schellenberger's *active V* model of thiamin (Schellenberger, 1967), which has been confirmed from the recently determined crystal structures of transketolase (Lindqvist, Schneider, Ermler & Sundström, 1992), pyruvate oxidase (Muller & Schulz, 1993) and pyruvate decarboxylase (Dyda *et al.*, 1993). Although it is tempting to predict that TTT assumes the same *V* conformation as congeneric TT since the N—H···S hydrogen bond can easily be formed, the X-ray structure of TTT reveals a quite different conformation.



TTT

An *ORTEP*II (Johnson, 1976) drawing of the TTT molecule with the atomic numbering scheme is presented in Fig. 1. The bond distances of the Δ^4-thiazoline-2-thione ring moiety are in excellent agreement (within 1σ) with those of compounds containing the same ring system (Rochester, Berg, Pierrot & Sandström, 1987). The thioketo bond distance of 1.656 (4) Å is also in agreement with those found in thio derivatives of nucleic acid components (Saenger & Suck, 1971). The

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† Present address: Samsung Corning Co., Suwon, Korea.