C1—N1—C13	110.3 (6)	N3—C17—O2	110.4 (5)
C4—N2—C15	111.8 (5)	N3—C17—C18	112.5 (5)
C16—N3—C17	123.3 (5)	N3—C17—C26	107.3 (5)
C18—N4—C25	111.7 (5)	C18—C17—C26	112.3 (6)
C20—N5—C21	121.8 (5)	N4—C18—C17	108.1 (5)
C21—N5—C24	111.2 (6)	N4—C19—C20	111.7 (6)
N1—C1—C2	110.3 (6)	C20—C19—C27	107.9 (5)
C1—C2—C14	104.7 (6)	N5—C20—C19	119.3 (6)
C2—C3—C4	107.5 (6)	N5—C21—C22	104.9 (5)
N2—C4—C8	111.1 (5)	C22—C23—C24	101.6 (6)
N2—C5—C6	106.8 (5)	N5—C24—C25	110.3 (6)
C5—C6—C16	109.2 (6)	N4—C25—O2	104.9 (5)
C6—C7—C8	121.1 (7)	O2—C25—O5	109.6 (5)
C4—C8—C9	113.1 (5)	O2—C25—C24	109.9 (6)
C8—C9—C10	128.2 (5)	C19—C27—C28	115.9 (6)
C10—C9—C14	116.5 (7)	C29—C30—C31	120.1 (6)
C10—C11—C12	119.3 (9)	C31—C32—C33	120.0 (6)
N1—C13—C12	134.6 (7)	C27—C28—C29	119.9 (6)
C12—C13—C14	121.9 (7)	C29—C28—C33	120.0 (6)
C2—C14—C13	111.3 (6)	C35—C34—O7	117.9 (7)
N3—C16—O1	125.5 (5)	C34—C35—O8	106.7 (6)
O1—C16—C6	122.5 (6)	O8—C35—C35^{i}	111.7 (5)
C4—N2—C5	112.5 (5)	O40—C39—C41	109.1 (17)
C5—N2—C15	108.2 (5)	O2—C17—C18	104.3 (5)
C18—N4—C19	127.6 (5)	O2—C17—C26	110.1 (5)
C19—N4—C25	120.5 (4)	N4—C18—O3	126.4 (6)
C20—N5—C24	126.7 (5)	O3—C18—C17	125.4 (5)
C17—O2—C25	110.9 (5)	N4—C19—C27	114.8 (5)
C1—C2—C3	135.2 (6)	N5—C20—O4	122.2 (5)
C3—C2—C14	120.1 (5)	O4—C20—C19	118.6 (6)
N2—C4—C3	109.3 (6)	C21—C22—C23	103.2 (7)
C3—C4—C8	113.4 (5)	N5—C24—C23	102.9 (5)
C5—C6—C7	110.7 (6)	C23—C24—C25	117.1 (6)
C7—C6—C16	109.7 (6)	N4—C25—O5	113.3 (6)
C4—C8—C7	123.8 (6)	N4—C25—C24	107.1 (5)
C7—C8—C9	123.0 (6)	O5—C25—C24	111.8 (5)
C8—C9—C14	115.3 (6)	C30—C29—C28	120.0 (6)
C9—C10—C11	122.2 (6)	C32—C33—C28	120.0 (6)
C11—C12—C13	118.4 (8)	C27—C28—C33	120.0 (6)
N1—C13—C14	103.5 (7)	C35—C34—O6	116.1 (7)
C2—C14—C9	127.0 (7)	O6—C34—O7	125.7 (8)
C9—C14—C13	121.6 (7)	C34—C35—C35^{i}	113.8 (9)
N3—C16—C6	111.9 (5)	O37—C36—C38	109.1 (15)

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

Table 3. *Conformations of the various rings*

The atoms comprising the rings are as follows: ring *C* = C8, C9, C14, C2, C3, C4; ring *D* = N2, C5, C6, C7, C8, C4; ring *F* = C24, N5, C20, C19, N4, C25; ring *G* = C23, C22, C21, N5, C24.

Ring	Conformation	Puckering Coordinates		
		Q (Å)	φ (°)	θ (°)
C	E_6	0.468 (7)	−63.8 (10)	56.7 (9)
D	$^{1}H_2$	0.530 (7)	48.8 (9)	50.7 (7)
F	E_6	0.454 (7)	−61.8 (9)	55.4 (8)
G	E_1	0.397 (8)	−177.6 (10)	

SDP software (B. A. Frenz & Associates, Inc., 1985) was used for measurement, data reduction and cell refinement. *SHELXS*86 (Sheldrick, 1985) was used to solve the structure. The structure was refined by block-diagonal least squares in six blocks using *SHELX*76 (Sheldrick, 1976). Since a difference map revealed only a few H atoms, their positions were calculated from ideal geometry and held constant during refinement, with displacement factors taken from their bond partners. The H atom of the hydroxy group of the tartrate molecule was not found. The C28–C33 phenyl ring (Fig. 1) was refined by assumption of its ideal geometry. The final difference electron density synthesis revealed the presence of two ethanol molecules. The bond distances and angles involving atoms of the two independent molecules of ethanol were chemically unreasonable, they were fixed at ideal geometry and anisotropically refined with constraints and unit occupancy factors. The molecular geometry was calculated using *PARST* (Nardelli, 1991).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Methoxy-5-(4-nitrostyryl)phenol

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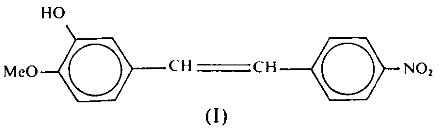
Abstract

The title compound, $C_{15}H_{13}NO_4$, has a *trans* conformation at the central C=C double bond; the dihedral angle between the phenyl rings is 6.1 (1)°.

Comment

The molecular configuration and the packing of molecules in the unit cell of the title compound, (I), are shown in Fig. 1 and Fig. 2, respectively. The H atoms are *trans* in the —C=C— group and the dihedral angle between the phenyl rings is 6.1 (1)°.



(I)

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3-Methyl-4-methoxy-4′-nitrostilbene is representative of newly developed organic crystals with high nonlinear optical coefficients (Bierlein, Cheng, Wang & Tam, 1990). It has a very large second-harmonic generation (SHG) efficiency (1250 × urea) in the powder form. In order to explore the relationship between their structure and nonlinear optical properties, we synthesized a series of substituted stilbenes. The title compound, however, crystallizes in a centrosymmetric space group and therefore has no nonlinear optical properties. This has been confirmed by SHG efficiency measurements on a powder sample using the method of Kurtz & Perry (1968).

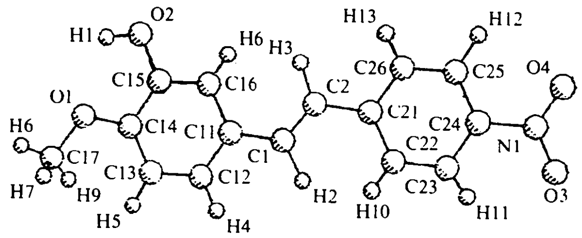

Fig. 1. The molecular structure of the title compound with atom labelling.

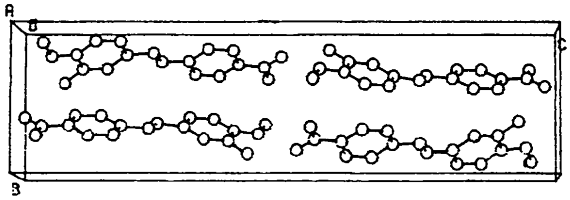

Fig. 2. The packing of the title compound in the unit cell.

Experimental

Crystal data

$C_{15}H_{13}NO_4$
$M_r = 271.27$
Monoclinic
$P2_1/n$
$a = 6.281\ (4)$ Å
$b = 7.613\ (5)$ Å
$c = 27.78\ (2)$ Å
$\beta = 92.45\ (6)°$
$V = 1327\ (2)$ Å^3
$Z = 4$
$D_x = 1.36$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 5–9°$
$\mu = 0.093$ mm^{-1}
$T = 296$ K
Plate
1.5 × 1.2 × 0.1 mm
Transparent yellow

Data collection

AFC-5 diffractometer
ω–2θ scans
Absorption correction: refined from ΔF (Walker & Stuart, 1983)
2777 measured reflections
2535 independent reflections
1263 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.0239$
$\theta_{\rm max} = 25.0°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 9$
$l = -33 \rightarrow 33$
3 standard reflections
frequency: 250 min
intensity decay: 1.6%

Refinement

Refinement on F
$R = 0.066$
$wR = 0.077$
$S = 1.91$
1263 reflections
181 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

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

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
O(1)	0.4339 (4)	0.1888 (4)	0.06046 (7)	4.1 (1)
O(2)	0.0689 (4)	0.3427 (4)	0.07641 (8)	5.1 (2)
O(3)	−0.3019 (5)	0.1297 (6)	0.4784 (1)	7.0 (2)
O(4)	−0.5811 (7)	0.2623 (6)	0.4510 (1)	9.4 (3)
N(1)	−0.4108 (7)	0.1924 (6)	0.4453 (1)	5.4 (2)
C(1)	0.0941 (6)	0.1383 (6)	0.2435 (1)	3.5 (2)
C(2)	−0.0959 (6)	0.1828 (6)	0.2562 (1)	3.6 (2)
C(11)	0.1823 (5)	0.1573 (3)	0.1956 (1)	2.9 (2)
C(12)	0.3784 (6)	0.0801 (6)	0.1878 (1)	3.7 (2)
C(13)	0.4682 (5)	0.0856 (6)	0.1435 (1)	3.5 (2)
C(14)	0.3670 (5)	0.1707 (5)	0.1059 (1)	2.9 (2)
C(15)	0.1705 (5)	0.2537 (5)	0.1131 (1)	3.0 (2)
C(16)	0.0796 (5)	0.2460 (5)	0.1572 (1)	3.2 (2)
C(17)	0.6302 (7)	0.1104 (8)	0.0493 (1)	6.4 (3)
C(21)	−0.1773 (5)	0.1726 (5)	0.3054 (1)	3.1 (2)
C(22)	−0.0643 (6)	0.0984 (6)	0.3440 (1)	3.9 (2)
C(23)	−0.1378 (6)	0.1002 (6)	0.3899 (1)	4.2 (2)
C(24)	−0.3329 (6)	0.1804 (5)	0.3970 (1)	3.7 (2)
C(25)	−0.4523 (5)	0.2518 (6)	0.3592 (1)	3.8 (2)
C(26)	−0.3729 (6)	0.2462 (6)	0.3141 (1)	3.7 (2)

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

O(1)—C(14)	1.354 (4)	C(12)—C(13)	1.375 (5)
O(1)—C(17)	1.416 (5)	C(13)—C(14)	1.365 (5)
O(2)—C(15)	1.360 (4)	C(14)—C(15)	1.409 (5)
O(3)—N(1)	1.221 (5)	C(15)—C(16)	1.376 (4)
O(4)—N(1)	1.212 (5)	C(21)—C(26)	1.381 (5)
N(1)—C(24)	1.449 (4)	C(21)—C(22)	1.388 (5)
C(1)—C(2)	1.304 (5)	C(22)—C(23)	1.375 (5)
C(1)—C(11)	1.470 (4)	C(23)—C(24)	1.391 (5)
C(2)—C(21)	1.481 (5)	C(24)—C(25)	1.376 (5)
C(11)—C(12)	1.390 (5)	C(25)—C(26)	1.370 (5)
C(11)—C(16)	1.396 (5)		
C(14)—O(1)—C(17)	118.0 (3)	O(2)—C(15)—C(16)	119.3 (3)
O(4)—N(1)—O(3)	122.8 (4)	O(2)—C(15)—C(14)	120.2 (3)
O(4)—N(1)—C(24)	119.0 (4)	C(16)—C(15)—C(14)	120.5 (3)
O(3)—N(1)—C(24)	118.2 (4)	C(15)—C(16)—C(11)	120.4 (3)
C(2)—C(1)—C(11)	127.1 (4)	C(26)—C(21)—C(22)	117.6 (3)
C(1)—C(2)—C(21)	126.3 (3)	C(26)—C(21)—C(2)	119.1 (3)
C(12)—C(11)—C(16)	117.9 (3)	C(22)—C(21)—C(2)	123.3 (3)
C(12)—C(11)—C(1)	118.1 (3)	C(23)—C(22)—C(21)	122.3 (3)
C(16)—C(11)—C(1)	124.0 (3)	C(22)—C(23)—C(24)	118.4 (3)
C(13)—C(12)—C(11)	121.8 (3)	C(25)—C(24)—C(23)	121.3 (3)
C(14)—C(13)—C(12)	120.3 (3)	C(25)—C(24)—N(1)	119.1 (4)
O(1)—C(14)—C(13)	127.6 (3)	C(23)—C(24)—N(1)	119.6 (4)
O(1)—C(14)—C(15)	113.3 (3)	C(26)—C(25)—C(24)	118.6 (3)
C(13)—C(14)—C(15)	119.1 (3)	C(25)—C(26)—C(21)	122.4 (4)

All calculations were performed on a VAX computer using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985).

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

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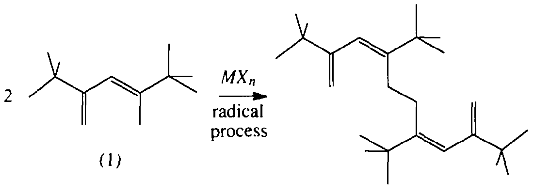
Abstract

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.



(1)

(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.

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