

Table 2. Selected bond lengths (Å) and angles (°)

P(1)—N(1)	1.701 (6)	P(1)—N(2)	1.741 (5)
P(1)—N(3)	1.715 (5)	N(1)—C(1)	1.432 (9)
N(2)—C(19)	1.281 (8)	C(19)—C(20)	1.502 (9)
C(19)—C(31)	1.521 (9)	N(3)—C(32)	1.278 (9)
C(32)—C(38)	1.516 (10)	C(32)—C(44)	1.486 (9)
N(1)—P(1)—N(2)	101.0 (2)	N(1)—P(1)—N(3)	97.4 (3)
N(2)—P(1)—N(3)	98.2 (2)	P(1)—N(1)—C(1)	119.2 (4)
N(1)—C(1)—C(2)	121.3 (5)	N(1)—C(1)—C(6)	118.9 (5)
C(2)—C(1)—C(6)	119.6 (6)	P(1)—N(2)—C(19)	120.5 (4)
N(2)—C(19)—C(20)	125.7 (5)	N(2)—C(19)—C(31)	117.8 (6)
C(20)—C(19)—C(31)	116.5 (6)	P(1)—N(3)—C(32)	126.5 (4)
N(3)—C(32)—C(38)	124.0 (6)	N(3)—C(32)—C(44)	117.8 (6)
C(38)—C(32)—C(44)	118.1 (6)		

angles in Table 2. Fig. 1 shows a plot with the atom numbering.

**Related literature.** Recently we showed (Niecke, Nieger, Gärtner-Winkhaus & Kramer, 1990) that reaction of lithiated ketimines LiN=C(R)<sub>2</sub> (R<sub>2</sub> = 'Bu<sub>2</sub>, fluorenyl) with the chloro(arylimino)phosphane Cl—P=N—Ar (Ar = 2,4,6-'Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) gives the heterobutadienes R<sub>2</sub> = N—P=N—Ar with unusual short P—N single bonds in both *cis* and *trans* arrangements of the NPN skeleton. The reaction with the lithiated ketimine LiN=CPh<sub>2</sub> resulted in the structure described above.

*Acta Cryst.* (1990). C46, 2472–2474

## The Structure of (4*R*\*,7*R*\*)-4,10,11,11-Tetramethyl-5-oxobicyclo[5.3.1]undec-1(10)-en-4-carbaldehyde

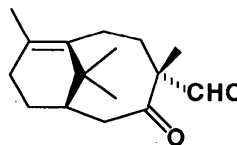
BY V. M. LYNCH, J.-M. ASSERCQ, S. F. MARTIN AND B. E. DAVIS

*Department of Chemistry, University of Texas at Austin, Austin, TX78712, USA*

(Received 9 February 1990; accepted 25 April 1990)

**Abstract.** C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>, *M<sub>r</sub>* = 248.36, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>, *a* = 9.0745 (9), *b* = 12.1499 (15), *c* = 12.8820 (10) Å, *V* = 1420.3 (3) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.16 g cm<sup>-3</sup>, *μ* = 0.6946 cm<sup>-1</sup>, Mo *Kα*, *λ* = 0.7107 Å, *F*(000) = 544, *T* = 298 K, *R* = 0.0624 for 1238 reflections where *F<sub>o</sub>* ≥ 4[σ(*F<sub>o</sub>*)]. The cyclooctane ring is in the usual boat-chair conformation. The bridgehead atom of the alkene group, C7, has one short [C7—C6 1.485 (6) Å] and one long [C7—C11, 1.541 (6) Å] C<sub>sp<sup>2</sup></sub>—C<sub>sp<sup>3</sup></sub> bond. The alkene group is presumably distorted due to ring strain. The six C atoms comprising the group are non-planar [max. dev. 0.114 (7) Å for C9]. The two nearly planar fragments (C6, C7, C8, C11 and C7, C8, C9, C18) are twisted by 8.9 (3)°.

**Experimental.** (1) was synthesized by sequential formylation and methylation of the corresponding [5.3.1]bicyclic ketone which was prepared by an anionic oxy-Cope rearrangement of the appropriate dienol precursor (Martin, White & Wagner, 1982).



(1)

The full details of the synthesis of (1) are presented elsewhere (Martin, White, Wagner, Guinn, Tanaka,

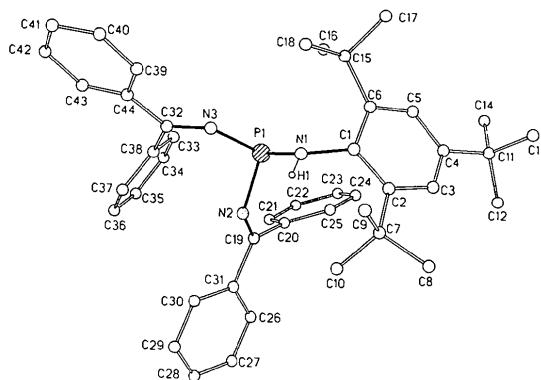


Fig. 1. A perspective view of the bis(ketimino)(amino)phosphine molecule with the atom numbering.

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Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{eq} (\text{\AA}^2)$
C1	0.6877 (5)	0.4572 (5)	0.2808 (3)	0.063 (2)
C2	0.8344 (6)	0.4592 (5)	0.2209 (3)	0.066 (2)
C3	0.9521 (5)	0.5379 (4)	0.2611 (3)	0.0536 (15)
C4	1.0900 (4)	0.4910 (3)	0.3129 (3)	0.0502 (14)
C5	1.0654 (6)	0.3968 (4)	0.3891 (4)	0.057 (2)
C6	0.9596 (6)	0.4193 (4)	0.4792 (3)	0.055 (2)
C7	0.8208 (5)	0.4716 (3)	0.4433 (3)	0.0406 (12)
C8	0.7988 (5)	0.5806 (3)	0.4465 (3)	0.0502 (14)
C9	0.6730 (7)	0.6333 (5)	0.3880 (6)	0.081 (2)
C10	0.6211 (7)	0.5702 (6)	0.2914 (5)	0.087 (2)
C11	0.7037 (5)	0.4016 (3)	0.3873 (3)	0.0489 (14)
C12	0.5574 (6)	0.4041 (5)	0.4478 (5)	0.066 (2)
C13	0.7430 (8)	0.2794 (4)	0.3756 (5)	0.073 (2)
C14	1.1891 (8)	0.4510 (6)	0.2227 (6)	0.085 (3)
C15	1.1774 (6)	0.5818 (4)	0.3625 (4)	0.065 (2)
O16	1.2487 (4)	0.5723 (3)	0.4401 (3)	0.093 (2)
O17	0.9457 (4)	0.6348 (3)	0.2392 (3)	0.0768 (13)
C18	0.8971 (9)	0.6619 (5)	0.5016 (6)	0.081 (2)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the non-H atoms of (1)

C2—C1	1.539 (7)	C7—C6	1.485 (6)
C10—C1	1.506 (9)	C8—C7	1.339 (5)
C11—C1	1.536 (6)	C11—C7	1.541 (6)
C3—C2	1.524 (7)	C9—C8	1.510 (8)
C4—C3	1.529 (6)	C18—C8	1.509 (8)
O17—C3	1.213 (6)	C10—C9	1.535 (10)
C5—C4	1.524 (6)	C12—C11	1.540 (7)
C14—C4	1.548 (8)	C13—C11	1.534 (6)
C15—C4	1.502 (6)	O16—C15	1.196 (6)
C6—C5	1.532 (7)		
C2—C1—C10	112.3 (5)	C8—C7—C11	117.3 (4)
C10—C1—C11	111.0 (4)	C8—C7—C6	122.7 (4)
C11—C1—C2	111.9 (4)	C11—C7—C6	119.6 (3)
C3—C2—C1	116.4 (4)	C9—C8—C18	113.8 (4)
C4—C3—O17	120.2 (4)	C9—C8—C7	121.1 (4)
C4—C3—C2	119.2 (4)	C18—C8—C7	125.0 (4)
O17—C3—C2	119.8 (4)	C10—C9—C8	115.1 (5)
C5—C4—C14	109.4 (4)	C1—C10—C9	113.9 (5)
C5—C4—C15	110.8 (4)	C12—C11—C13	105.6 (4)
C5—C4—C3	116.2 (4)	C12—C11—C1	111.2 (4)
C14—C4—C15	104.1 (4)	C12—C11—C7	110.3 (4)
C14—C4—C3	105.3 (4)	C13—C11—C1	111.2 (4)
C15—C4—C3	110.2 (4)	C13—C11—C7	114.8 (4)
C6—C5—C4	116.4 (4)	C1—C11—C7	103.9 (3)
C7—C6—C5	111.9 (4)	O16—C15—C4	124.8 (5)

Assercq, Gluchowski, Austin & Dantanarayana, 1990). The crystal was a colorless plate cut from a larger crystal and had approximate dimensions  $0.24 \times 0.29 \times 0.58$  mm. Crystals were obtained by slow evaporation from ether. Data were collected at room temperature on a Nicolet P3 diffractometer with a graphite monochromator. The lattice parameters were obtained from the least-squares refinement of 40 reflections with  $22.3 < 2\theta < 29.0^\circ$ . Data were collected using the  $\omega$ -scan technique (3790 reflections, 1875 unique,  $R_{int} = 0.0324$  from averaging  $hkl$  and  $h, -k, -l$  reflections), with a  $2\theta$  range  $4\text{--}50^\circ$ , and a  $1^\circ$   $\omega$  scan at  $4\text{--}8^\circ \text{min}^{-1}$  ( $h = 0 \rightarrow 11$ ,  $k = -15 \rightarrow 15$ ,

$l = -16 \rightarrow 16$ ). Four check reflections ( $211, 006, 130, 040$ ) were remeasured every 146 reflections to monitor instrument and crystal stability. The check reflections showed a steady decline in intensity throughout the course of the data collection. The maximum decay correction was 36%. Data were also corrected for Lp effects but not for absorption. Data reduction and decay correction were applied using the Nicolet XRD *SHELXTL-Plus* software package (Sheldrick, 1988). Reflections having  $F_o < 4[\sigma(F_o)]$  were considered unobserved (637 reflections). The structure was solved by direct methods (Sheldrick, 1988) and refined by full-matrix least-squares procedures (Sheldrick, 1976). The non-H atoms were refined with anisotropic thermal parameters. H atoms were obtained from an  $F$  map and refined with isotropic thermal parameters. A total of 259 parameters was refined. The function  $\sum w(|F_o| - |F_c|)^2$  was minimized, where  $w = 1/[\sigma(F_o)]^2$  and  $\sigma(F_o) = (0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2})$ . Intensity,  $I$ , given by  $(I_{peak} - I_{background}) \times (\text{scan rate})$ ; 0.02 is a factor to downweight intense reflections and to account for instrument instability and  $k$  is the correction due to Lp effects and decay.  $\sigma(I)$  was estimated from counting statistics;  $\sigma(I) = [(I_{peak} + I_{background})^{1/2} \times (\text{scan rate})]$ . The final  $R = 0.0624$  for 1238 reflections with  $wR = 0.0556$  ( $R = 0.0975$ ,  $wR = 0.0622$ ) and goodness of fit = 1.661. The max.  $|\Delta/\sigma| < 0.1$  in the final refinement cycle and the min. and max. peaks in the final  $F$  map were  $-0.27$  and  $0.19 \text{ e \AA}^{-3}$ , respectively. Differentiation between enantiomorphs could not be made on the basis of the X-ray results ( $wR = 0.0556$  for the enantiomorph). The scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with anomalous-dispersion corrections from Cromer & Liberman (1970). The scattering factors

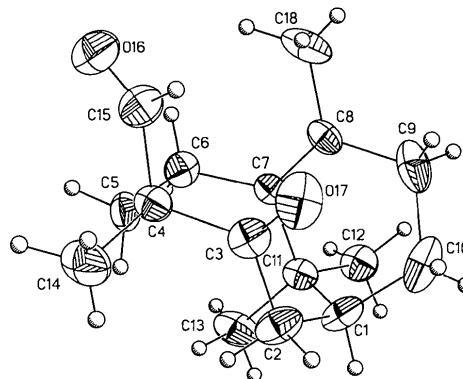


Fig. 1. View of (1) with the atom-labeling scheme showing the boat-chair conformation of the cyclooctane portion of the [5.3.1] ring system. The nearly parallel orientation of the endocyclic carbonyl group and the alkene moiety can also be seen. Ellipsoids are scaled to the 30% probability level. H atoms are of arbitrary size.

for the H atoms are from Stewart, Davidson & Simpson (1965). The values used to calculate the linear absorption coefficient are from *International Tables for X-ray Crystallography* (1974). Positional and thermal parameters for non-H atoms are listed in Table 1,\* while the bond lengths and angles for the non-H atoms are listed in Table 2. The atom-labelling scheme is shown in Fig. 1. The least-squares-planes program was supplied by Cordes (1983); other computer programs are listed in Gadol & Davis (1982).

**Related literature.** (1) is a bicyclic intermediate in a synthetic route aimed at preparing the tricyclic carbon framework of the taxane diterpenes (Martin, White & Wagner, 1982). The structures of related [5.3.1]undecenes have been reported (Lynch, Fishpaugh, Martin & Davis, 1990; Lynch, Tanaka, Fishpaugh, Martin & Davis, 1990). The alkene moiety in these structures is also highly distorted.

\* Lists of structure factors, anisotropic thermal parameters, torsion angles, least-squares planes, unit-cell packing diagram and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53032 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Funding for this project was supplied by the Robert A. Welch Foundation (F-652) and the National Institutes of Health (CA 37929).

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*Acta Cryst.* (1990). **C46**, 2474–2476

## Structure of the Eudesmanolide Gazaniolide\*

BY MICHAEL A. JANUSA, MARK S. JEANSONNE, FRANK R. FRONCZEK AND STEVEN F. WATKINS†

*Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, USA*

(Received 9 March 1990; accepted 21 May 1990)

**Abstract.** C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>,  $M_r = 230.31$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.129$  (1),  $b = 11.126$  (2),  $c = 16.112$  (2) Å,  $V = 1278.0$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.197$  g cm<sup>-3</sup>, at 293 (1) K,  $\lambda(\text{Cu } K\alpha) = 1.54184$  Å,  $\mu = 5.8$  cm<sup>-1</sup>,  $F(000) = 496$ , 1535 unique reflections measured, final  $R = 0.038$  over 1217 reflections having  $I > 1.0\sigma(I)$ . This sesquiterpene lactone of the eudesmanolide class, extracted from the roots of the plant *Rudbeckia subtomentosa*, has an unusual 1,3-cyclohexadiene ring which is highly susceptible to air

oxidation. The two six-membered rings are *trans*-fused, with the saturated ring in the chair conformation and the ring containing the diene in the half-chair conformation. The pseudo twofold axis of the half chair bisects the diene, and the torsion angle about the central bond of the diene is  $-16.1$  (4)°.

**Experimental.** A colorless, nearly isometric crystal of gazaniolide, (1),  $0.35 \times 0.38 \times 0.40$  mm, was mounted in a glass capillary in random orientation on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite crystal incident beam monochromator. Cell constants were obtained from least-squares refinement of the setting angles of 25 reflections in the range  $21 < \theta < 27^\circ$ . From systematic absences

\* *Chemical Abstracts* name: [3aS-(3a $\alpha$ ,5a $\beta$ ,9a $\alpha$ ,9b $\beta$ )]-3a-,4,5a,9a,9b-hexahydro-5a,9-dimethyl-3-methylenenaphtho[1,2-*b*]furan-2(3H)-one.

† Author to whom correspondence should be addressed.