

**Discussion.** The structure solution confirmed the chemical analysis. The title compound is similar to lemnacarnol (Karlsson & Losman, 1976), but the exchange of the C(12) methylene group for a carbonyl group gives the molecules different conformations.

In lemnacarnol, the cyclohexane ring has the boat-twisted-boat conformation, and the five-membered ring has the envelope conformation with the smallest twist about C(6)–C(7); in 2-deoxy-12-oxolemnacarnol, the lactone ring has the smallest twist about C(12)–O(2), giving a planar ester group and making the less energetic chair conformation possible for the cyclohexane ring. Table 2 shows the torsion angles of the three rings for the two independent molecules.

The two independent molecules are related by a non-crystallographic  $2_1$  axis inclined approximately  $1^\circ$  to  $y$  (Fig. 3). The twinning can now be explained struc-

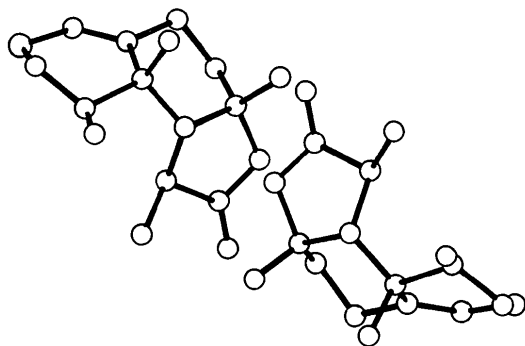


Fig. 3. The two independent molecules of 2-deoxy-12-oxolemnacarnol. A view down  $y$ .

turally as the sharing by the two members of the twin of the (160) crystal face to which  $y$  is nearly perpendicular. In the crystal face, the molecules have positions such that they can belong simultaneously to both twin members. The molecules are catenated by the hydrogen bonds O(3) $A$ –O(1) $B$  and O(3) $B$ –O(1) $A$ , both with an O–O distance of 2.75 Å.

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Calculations were performed with programs written by GMS.

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## 2-Nitro-3,5,5-trimethylcyclopentanone\*†

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**Abstract.**  $C_8H_{13}O_3N$ , orthorhombic,  $P2_12_12_1$ ,  $a = 8.164$  (1),  $b = 17.119$  (3),  $c = 6.825$  (1) Å,  $V = 953.9$

\* Cyclic 2-Nitroketones. I.

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Å<sup>3</sup>;  $D_m = 1.19$ ,  $D_c = 1.19$  g cm<sup>-3</sup> ( $Z = 4$ ); 1021 data (769 observed); Mo  $K\alpha$  ( $\lambda = 0.7107$  Å) on a  $\kappa$ -geometry diffractometer. Structure determination employed *MULTAN/NQUEST*, and final residuals are:  $R_{obs} = 0.049$ ,  $R_w = 0.078$ . The ring is a highly twisted  $C_1$  half-chair; the nitro group is approximately perpen-

dicular to the cyclopentane ring; the 2-nitro and 3-methyl substituents are *trans* with respect to one another.

**Introduction.** Crystals of the title compound were grown by slow cooling of a saturated cyclohexane solution. A brick-shaped crystal was covered with grease and mounted in a capillary. Cell constants were obtained by a least-squares fit of the  $2\theta$  values of 55 high-angle reflections to preliminary values calculated from equi-inclination Weissenberg photographs, which were taken to check the crystal quality and space group. Intensity data were measured in the  $\theta-2\theta$  scan mode on a  $\kappa$ -geometry diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) and a dispersion-corrected scan width of  $(0.8 + 0.2 \tan \theta)^\circ$ . The data were corrected for Lorentz and polarization effects. Of the 1021 data measured to a  $\sin \theta/\lambda$  limit of  $0.70 \text{ \AA}^{-1}$ , 769 were considered observed and were employed in the refinement of the structure.

The structure was determined by application of multi-solution tangent-refinement techniques (Germain, Main & Woolfson, 1971); the most promising phase set was identified with a negative-quartet figure of merit (NQEST; De Titta, Edmonds, Langs & Hauptman,

1975). The 12 nonhydrogen atomic positions were identified in the first  $E$  map. H atomic positions were identified in subsequent difference Fourier maps, but for the purpose of refinement the positions were fixed at the theoretical values and the H isotropic thermal parameters were held fixed at  $4.0 \text{ \AA}^2$ .

The positional and anisotropic thermal parameters of the nonhydrogen atoms were refined by full-matrix least-squares techniques. 109 parameters were varied and 769 data were included (7.06 observations per parameter). The function minimized was  $\sum w(F_o^2 - F_c^2)$ , where  $w = 4F_o^2/\sigma_i^2$  and  $\sigma_i^2 = [\sigma_{i,raw}^2 + (0.06I)^2]^{1/2}/Lp$ . The final conventional residual is 0.049 for the observed data, and the weighted residual is 0.078.\* The estimated standard deviation of an observation of unit weight is 1.70. The refinement was considered complete when all shift/error ratios were less than 0.01. A final difference map was featureless.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32472 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional parameters* ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
C(1)	6980 (4)	4419 (2)	3936 (4)	H(2)	8296	3950	1451
C(2)	7869 (4)	3752 (2)	2891 (4)	H(3)	6502	2759	3892
C(3)	6567 (4)	3111 (2)	2583 (5)	H(3A1)	8124	2306	1029
C(3A)	6922 (5)	2582 (2)	849 (6)	H(3A2)	6002	2148	694
C(4)	5005 (4)	3608 (2)	2362 (6)	H(3A3)	6979	2939	-495
C(5)	5136 (4)	4262 (2)	3900 (5)	H(4A)	4935	3838	897
C(5A)	4159 (5)	5002 (2)	3376 (7)	H(4B)	3949	3251	2651
C(5B)	4667 (5)	3980 (2)	5963 (5)	H(5A1)	2896	4857	3268
N(1)	9294 (4)	3498 (2)	4088 (5)	H(5A2)	4351	5434	4528
O(1)	7678 (4)	4966 (2)	4656 (4)	H(5A3)	4611	5237	2003
O(1N)	10635 (4)	3563 (3)	3396 (8)	H(5B1)	5520	3518	6349
O(2N)	9032 (5)	3232 (2)	5719 (5)	H(5B2)	4790	4459	6967
				H(5B3)	3448	3765	5913

Table 2. *The torsion angles* ( $^\circ$ )

A torsion angle  $\alpha-\beta-\gamma-\delta$  is positive, if, when viewed down the  $\beta-\gamma$  bond, the  $\alpha-\beta$  bond will eclipse the  $\gamma-\delta$  bond when rotated less than  $180^\circ$  in a clockwise direction.

C(5)-C(1)-C(2)-C(3)	-10.9 (3)	C(5)-C(1)-C(2)-N(1)	-134.0 (3)
O(1)-C(1)-C(2)-C(3)	168.7 (3)	O(1)-C(1)-C(2)-N(1)	45.6 (4)
C(2)-C(1)-C(5)-C(4)	-14.0 (3)	C(2)-C(1)-C(5)-C(5A)	-136.0 (3)
C(2)-C(1)-C(5)-C(5B)	103.9 (3)	O(1)-C(1)-C(5)-C(4)	166.4 (3)
O(1)-C(1)-C(5)-C(5A)	44.4 (5)	O(1)-C(1)-C(5)-C(5B)	-75.7 (4)
C(1)-C(2)-C(3)-C(3A)	153.8 (3)	C(1)-C(2)-C(3)-C(4)	31.0 (3)
N(1)-C(2)-C(3)-C(3A)	-86.0 (4)	N(1)-C(2)-C(3)-C(4)	151.2 (3)
C(1)-C(2)-N(1)-O(1N)	-118.0 (4)	C(1)-C(2)-N(1)-O(2N)	62.2 (4)
C(3)-C(2)-N(1)-O(1N)	124.0 (4)	C(3)-C(2)-N(1)-O(2N)	-55.7 (4)
C(2)-C(3)-C(4)-C(5)	-41.0 (3)	C(3A)-C(3)-C(4)-C(5)	-163.3 (3)
C(3)-C(4)-C(5)-C(1)	34.2 (3)	C(3)-C(4)-C(5)-C(5A)	154.6 (3)
C(3)-C(4)-C(5)-C(5B)	-79.5 (3)		

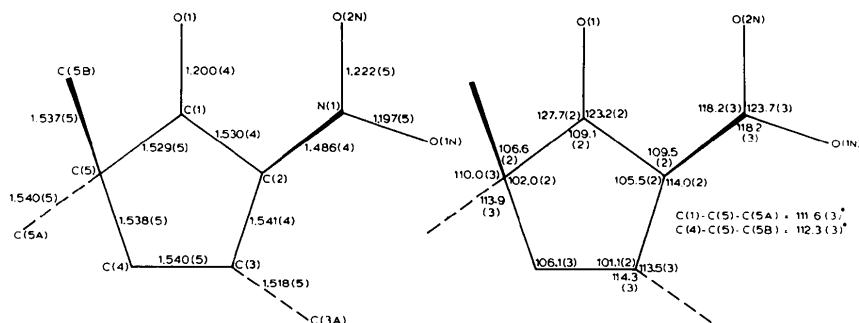


Fig. 1. Atomic nomenclature, bond distances (Å) and bond angles ( $^{\circ}$ ) for 2-nitro-3,5,5-trimethylcyclopentanone.

Positional parameters are collected in Table 1. Bond distances and angles are shown in Fig. 1 and torsion angles are collected in Table 2.

**Discussion.** During the course of studies on the synthesis of  $\alpha$ -nitroketones under both acidic and basic conditions we had synthesized a series of 2-nitrocyclopentanones (Elfehail, 1975) and 2-nitrocyclohexanones (Ozbal, 1975). Many of the 2-nitroketones synthesized had a substituent at position 3 and were therefore capable of *cis-trans* isomerism. In the cyclohexanone series the configuration of the ketones was readily determined by proton NMR studies with the Karplus relationship (Jackman & Sternhell, 1969) of coupling constant to dihedral angle. In the 3-substituted 2-nitrocyclopentanone series, however, the assignment of configuration by NMR was ambiguous. Since *cis* coupling constants can be larger than *trans* coupling constants in these systems (Jackman & Sternhell, 1969) it is not immediately clear how to relate the vicinal coupling constant to the dihedral angle. In this latter series of compounds the NMR has a low-field proton ( $CHNO_2$ ) at  $\delta$  4.85 which appears as a doublet with an 11 Hz coupling constant in each case. So although it was tempting to assign the *trans* configuration on this basis, in this system of compounds a vicinal torsion angle of close to  $0^{\circ}$  would also lead to a large coupling constant and would suggest the *cis* configuration.

Before speculation as to the mechanism of nitration of the cyclopentanones was attempted, we chose to determine unambiguously the configuration of 2-nitro-3,5,5-trimethylcyclopentanone by X-ray crystallographic techniques. This compound is representative of the series of 2-nitro 3-substituted cyclopentanones synthesized. The compound had also been synthesized by Feuer & Pivawer (1966), but no stereochemistry was suggested at that time.

The molecular conformation, as observed in the crystal-structure determination, is shown in Fig. 2. As can be seen, the 2-nitro and 3-methyl substituents are

on opposite faces of the cyclopentanone ring, *i.e.* the *trans* assignment from the NMR results is correct. The torsion angles  $H(2)-C(2)-C(3)-H(3)$  and  $N(1)-C(2)-C(3)-C(3A)$  are  $157.3$  and  $-86.0^{\circ}$  respectively. The cyclopentanone ring is severely puckered; it can best be described as a  $C_1$  half-chair with an asymmetry parameter (Duax, Weeks & Rohrer, 1976)  $\Delta C_2$

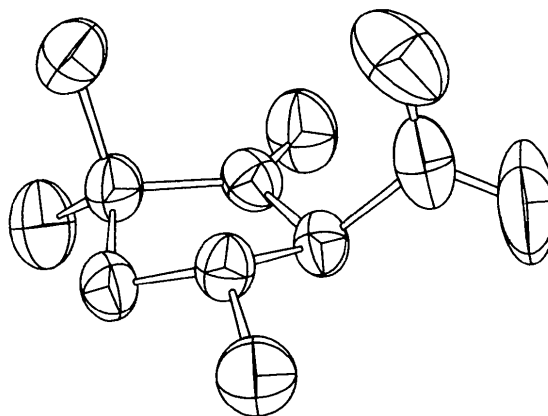


Fig. 2. The molecular conformation of 2-nitro-3,5,5-trimethylcyclopentanone. The 3-methyl group is at the lower edge of the picture.

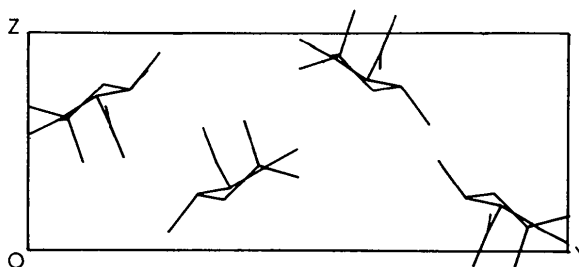


Fig. 3. Crystal packing of 2-nitro-3,5,5-trimethylcyclopentanone, as viewed down *a*, showing the herringbone packing of the molecules.

= 3.2°. The nitro group is roughly perpendicular to the five-membered ring, with the dihedral angle between the least-squares planes\* equal to 95°. Bond distances and angles appear to be within the normal range for similar compounds.

The crystal packing (Fig. 3) is of the familiar herringbone design. There are a number of short intermolecular contacts which may possibly be described as CH...O bonding interactions. In particular the contact C(2)H...O(1) with C...O 3.15 Å and H...O 2.36 Å is a reasonable candidate for this description. In this case the tertiary H is expected to be quite acidic in view of the electron-withdrawing effects of the nitro group.

In a future communication we will describe the molecular conformation of a 2-nitrocyclohexanone and at that time discuss more fully the relationship of the observed conformations of cyclic nitroketones and the observed NMR spectra of these compounds.

\* Atoms defining the planes are C(1) through C(5), and C(2), N(1), O(1N) and O(2N).

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### Acetylacetonato(1,*cis*-3,*trans*-tetraphenyl-4-ethoxybutadien-1-yl)- (dimethylphenylphosphine)palladium(II)

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**Abstract.** C<sub>43</sub>H<sub>43</sub>O<sub>3</sub>PPd, *M<sub>r</sub>* = 745.07, triclinic, *P*1 or *P*1̄ (latter confirmed); *a* = 11.54 (2), *b* = 15.68 (2), *c* = 23.29 (3) Å, α = 96.27 (1), β = 117.07 (1), γ = 91.47 (1)°; *V* = 3717 Å<sup>3</sup>; *D<sub>c</sub>* (for *Z* = 4) = 1.33, *D<sub>m</sub>* = 1.31 g cm<sup>-3</sup>; μ(Mo *K*α) = 5.3 cm<sup>-1</sup>. The structure, refined to a final residual of 0.059 from 9538 diffractometric intensity data, consists of two independent molecules of opposite chirality in each asymmetric unit. The tetraphenylbutadienyl moiety is one of four square-planar ligands about Pd (using a terminal *sp*<sup>2</sup> C atom), the other three ligands being P and the planar bidentate acetylacetonate group (itself coplanar with the Pd coordination plane).

**Introduction.** Diphenylacetylene is dimerized by PdCl<sub>2</sub> in ethanol and forms an equilibrium mixture of tetraphenylbutadienyl and tetraphenylcyclobutadienyl complexes (I) with Pd. To understand the reaction mecha-

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nism it is of importance to know whether the ethoxy group is *cis* or *trans* to the central single bond. To this end, and to ensure that the cyclobutadiene ring was opened, (I) has been treated with thallium acetylacetonate (acac) and then with dimethylphenylphosphine to form the complex (II) (Cheng, Jack, May, Nyburg & Powell, 1975), whose crystal and molecular structure analysis is reported here.

