

C(6)—C(7)—C(8)	173.8 (11)	O(12)—C(8)—C(7)	109.3 (9)
O(12)—C(8)—C(9)	103.3 (8)	C(7)—C(8)—C(9)	108.8 (8)
O(12)—C(8)—C(10)	111.6 (8)	C(7)—C(8)—C(10)	110.5 (9)
C(9)—C(8)—C(10)	113.0 (9)	C(8)—C(10)—C(11)	118.1 (11)
C(8)—C(10)—C(15)	126.4 (10)	C(11)—C(10)—C(15)	115.6 (12)
C(10)—C(11)—C(12)	120.6 (13)	C(11)—C(12)—C(13)	121.9 (13)
C(12)—C(13)—C(14)	116.6 (14)	C(13)—C(14)—C(15)	123.2 (12)
C(10)—C(15)—C(14)	122.1 (10)	C(3)—C(16)—C(17)	121.2 (11)
C(16)—C(17)—C(18)	119.9 (12)	C(17)—C(18)—C(19)	120.5 (13)
C(18)—C(19)—C(20)	121.1 (11)	C(3)—C(20)—C(19)	120.1 (10)

2,7-Diphenyl-3,5-octadiyne-2,7-diol (I) was prepared by treatment of (±)-2-phenyl-3-butyn-2-ol dissolved in methanol containing pyridine with cuprous chloride in an oxygen-containing atmosphere. Diastereomeric (I) was isolated in near quantitative yield as an off-white solid melting over a wide range (313–473 K). Recrystallization from benzene gave the less-soluble diastereomer as colorless needles; m.p. 472–473 K (literature value 465 K; Strauss, Kollek & Hauptmann, 1930). Suitable crystals for X-ray analysis were obtained from the same solvent by slow evaporation.

The mother liquors from *meso*-(I) were systematically pooled and, following several recrystallizations from benzene, produced the more-soluble diastereomer; m.p. 420–421 K (literature value 415–416 K; Popova, 1959). Suitable crystals for X-ray analysis were slowly grown from benzene.

In both cases, a crystal was mounted on a glass fiber in a random orientation and a preliminary examination was carried out. Final cell parameters and an orientation matrix were obtained by least-squares refinement. Axial photographs confirmed the cell dimensions and lattice symmetry; ω scans of representative reflections indicated acceptable crystal quality. No absorption correction was applied. Data reduction, structure solution and refinement were performed using *SHELXTL-Plus* (Sheldrick, 1991). Both structures were solved by direct methods and the remaining non-H atoms were located from subsequent difference Fourier maps. Full-matrix least-squares refinement was carried out by minimizing the function $\sum w(F_o - F_c)^2$. H atoms were included in their idealized positions. O atoms were refined to convergence anisotropically and C atoms isotropically.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71404 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1054]

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Di-*tert*-butyl 4-[2-(*tert*-Butoxycarbonyl)-ethyl]-4-nitroheptanedioate, C₂₂H₃₉NO₈

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Abstract

The molecule has an extended conformation with approximate mirror symmetry. 15 of the 16 *anti* torsion angles are in the range 171.7 (3)–179.1 (4)° in magnitude, with a mean value of 176.6°. The major deviation from mirror symmetry is the C—C—C—C torsion angle in the *tert*-butoxycarbonylethyl group, which is nearly coplanar with the nitro group, having a magnitude of 163.0 (2)°. The C—N bond has a length of 1.555 (3) Å.

Comment

During the synthesis of cascade polymers (Newkome, Nayak, Behera, Moorefield & Baker,

1992; Newkome, Moorefield & Baker, 1992; Newkome, Behera, Moorefield & Baker, 1991), it was necessary to shorten the overall iterative procedure for cascade construction. A new building block, di-*tert*-butyl 4-[2-(*tert*-butoxycarbonyl)ethyl]-4-nitroheptanedioate was synthesized by a modification of a literature procedure (Bruson & Riener, 1943). Uniquely, this *tert*-butyl ester does not undergo facile intramolecular lactam formation (Allen & Napler, 1950; Butler, 1984) during hydrogenation of the nitro moiety, so its structure determination was undertaken to ascertain the rationale for this timely observation.

The conformation of the molecule has the three *tert*-butoxycarbonyl ethyl groups fully extended, and approximate mirror symmetry with a nitro N—O bond *anti* to one of the chains; the O1—N1—C1—C2 torsion angle is 179.0 (2)°. The largest deviation from mirror symmetry is in this same chain with torsion angle C1—C2—C3—C4 deviating 17.0 (2)° from the *anti* position. Thermal parameters are generally high for the carbonyl O atoms, the *tert*-butyl methyl groups and particularly for atom O2 of the nitro group. The unequal N—O distances [1.213 (3) and 1.165 (3) Å] of the nitro group are a result of the large thermal parameters, with the shorter distance to the atom with the larger thermal parameters, O2. Thus, the true internuclear distances may not be significantly different. The C—C distances of the *tert*-butyl groups average 1.500 Å, while the average C—C distances along the chains from the central C atom are 1.524, 1.520 and 1.494 Å.

Molecules stack along the *a* direction, with the shorter dimension of the molecule aligned approximately along *a*. The central atoms C1 are spaced at 5.791 (4) Å, approximately *a*/2. No intermolecular distances between heavy atoms are shorter than 3.3 Å.

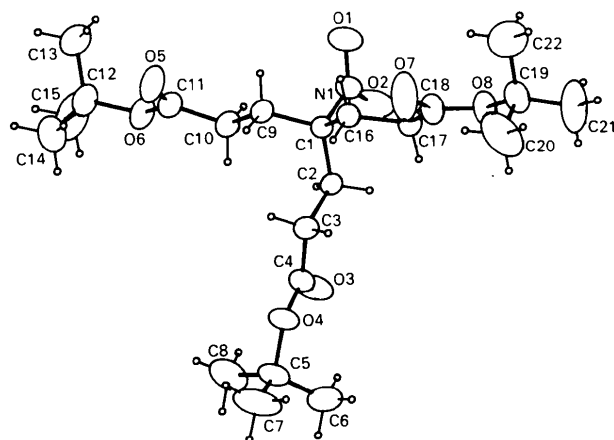


Fig. 1. The title compound with ellipsoids drawn at the 30% probability level.

Experimental

Crystal data

$C_{22}H_{39}NO_8$
 $M_r = 445.6$
 Orthorhombic
Pbca
 $a = 11.552$ (2) Å
 $b = 22.165$ (1) Å
 $c = 20.890$ (2) Å
 $V = 5349$ (2) Å³
 $Z = 8$
 $D_x = 1.107$ Mg m⁻³

Cu $K\alpha$ radiation
 $\lambda = 1.54184$ Å
 Cell parameters from 25 reflections
 $\theta = 25$ –30°
 $\mu = 0.66$ mm⁻¹
 $T = 298$ K
 Rectangular prism
 0.38 × 0.35 × 0.23 mm
 Colorless
 Crystal source: EtOH (95%)

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: empirical
 $T_{\min} = 0.961$, $T_{\max} = 0.999$
 5204 measured reflections
 5204 independent reflections

3456 observed reflections
 $[I > 3\sigma(I)]$
 $\theta_{\max} = 75^\circ$
 $h = 0 \rightarrow 14$
 $k = 0 \rightarrow 24$
 $l = 0 \rightarrow 26$
 3 standard reflections
 frequency: 167 min
 intensity variation: -6.4%

Refinement

Refinement on F
 $R = 0.069$
 $wR = 0.090$
 $S = 4.092$
 3456 reflections
 281 parameters
 H-atom parameters not refined
 $w = 4F_o^2 / [\sigma^2(I) + (0.02F_o^2)^2]$
 $(\Delta/\sigma)_{\max} = 0.02$

$\Delta\rho_{\max} = 0.54$ e Å⁻³
 $\Delta\rho_{\min} = -0.38$ e Å⁻³
 Extinction correction: $(1 + gI_c)^{-1}$ applied to F_c
 Extinction coefficient: $g = 9.9$ (3) × 10⁻⁷
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B, 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

	$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
O1	0.7520 (2)	0.47184 (9)	0.7990 (1)	7.55 (6)
O2	0.5860 (2)	0.4360 (1)	0.8025 (2)	10.88 (9)
O3	0.4869 (2)	0.2293 (1)	0.7729 (1)	7.71 (6)
O4	0.5992 (2)	0.16943 (9)	0.7128 (1)	5.86 (5)
O5	0.9892 (2)	0.3088 (1)	0.8938 (1)	7.55 (6)
O6	0.8554 (2)	0.2892 (1)	0.9677 (1)	6.48 (5)
O7	0.8654 (2)	0.4263 (1)	0.5769 (1)	10.38 (8)
O8	0.6994 (2)	0.4706 (1)	0.5505 (1)	6.30 (5)
N1	0.6837 (2)	0.4312 (1)	0.7898 (1)	4.70 (5)
C1	0.7321 (2)	0.3720 (1)	0.7601 (1)	3.58 (5)
C2	0.6307 (2)	0.3287 (1)	0.7549 (1)	3.80 (5)
C3	0.6627 (2)	0.2674 (1)	0.7282 (1)	4.48 (6)
C4	0.5733 (3)	0.2209 (1)	0.7411 (1)	4.76 (7)
C5	0.5267 (3)	0.1149 (1)	0.7191 (2)	6.62 (9)
C6	0.4065 (4)	0.1272 (2)	0.6954 (3)	10.1 (1)
C7	0.5900 (4)	0.0714 (2)	0.6757 (3)	11.7 (1)
C8	0.5283 (5)	0.0937 (2)	0.7873 (2)	11.0 (1)
C9	0.8277 (2)	0.3496 (1)	0.8048 (1)	4.01 (6)
C10	0.7896 (2)	0.3249 (1)	0.8694 (1)	4.76 (7)
C11	0.8902 (3)	0.3069 (1)	0.9107 (1)	4.96 (7)
C12	0.9336 (3)	0.2673 (2)	1.0175 (2)	7.34 (9)
C13	1.0213 (4)	0.3151 (2)	1.0343 (2)	9.7 (1)

C14	0.9952 (5)	0.2099 (2)	0.9935 (3)	11.2 (1)
C15	0.8545 (4)	0.2541 (3)	1.0724 (2)	13.2 (2)
C16	0.7847 (2)	0.3901 (1)	0.6960 (1)	4.16 (6)
C17	0.7030 (3)	0.4204 (1)	0.6487 (1)	5.04 (7)
C18	0.7638 (3)	0.4378 (1)	0.5882 (1)	5.70 (7)
C19	0.7386 (3)	0.4924 (2)	0.4869 (1)	6.05 (8)
C20	0.7779 (6)	0.4416 (2)	0.4464 (2)	13.9 (2)
C21	0.6347 (4)	0.5208 (3)	0.4588 (2)	12.5 (1)
C22	0.8336 (5)	0.5372 (3)	0.4962 (2)	12.9 (2)

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2,4-Dinitrophenylhydrazone Derivative of Acetone

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Table 2. Geometric parameters (Å, °)

O1—N1	1.213 (3)	C1—C9	1.528 (4)
O2—N1	1.165 (3)	C1—C16	1.525 (3)
O3—C4	1.214 (4)	C2—C3	1.516 (4)
O4—C4	1.318 (3)	C3—C4	1.484 (4)
O4—C5	1.477 (4)	C5—C6	1.499 (6)
N1—C1	1.555 (3)	C5—C7	1.511 (6)
C1—C2	1.518 (4)	C5—C8	1.500 (6)
C4—O4—C5	122.7 (2)	C2—C3—C4	112.7 (2)
O1—N1—O2	121.8 (3)	O3—C4—O4	124.4 (3)
O1—N1—C1	117.2 (2)	O3—C4—C3	124.4 (3)
O2—N1—C1	121.0 (2)	O4—C4—C3	111.2 (2)
N1—C1—C2	106.6 (2)	O4—C5—C6	110.2 (3)
N1—C1—C9	106.9 (2)	O4—C5—C7	101.2 (3)
N1—C1—C16	105.8 (2)	O4—C5—C8	109.5 (3)
C2—C1—C9	113.4 (2)	C6—C5—C7	111.5 (4)
C2—C1—C16	114.2 (2)	C6—C5—C8	112.5 (4)
C9—C1—C16	109.5 (2)	C7—C5—C8	111.3 (3)
C1—C2—C3	113.9 (2)		
C5—O4—C4—C3	178.2 (3)	C9—C1—C16—C17	−173.1 (2)
C4—O4—C5—C7	177.1 (3)	C1—C2—C3—C4	163.0 (2)
C12—O6—C11—C10	178.1 (3)	C2—C3—C4—O4	174.8 (2)
C11—O6—C12—C15	179.1 (4)	C1—C9—C10—C11	−177.3 (2)
C19—O8—C18—C17	−178.4 (3)	C9—C10—C11—O6	176.2 (3)
C18—O8—C19—C21	173.5 (3)	C1—C16—C17—C18	178.5 (2)
O1—N1—C1—C2	179.0 (2)	C16—C17—C18—O8	−171.7 (3)
C16—C1—C9—C10	−175.4 (2)	N1—C1—C2—C3	−178.5 (2)

The structure was solved using *RANTAN* (Yao, 1981) and refined using the Enraf–Nonius *SDP* programs (Frenz & Okaya, 1980). All the H atoms but a few in the methyl groups were clearly evident in difference maps. However, H atoms were placed in calculated positions with C—H distance 0.95 Å and $B_{\text{iso}} = 1.3B_{\text{eq}}$ for the bonded C atom.

This work was supported, in part, by the National Science Foundation.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71399 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1056]

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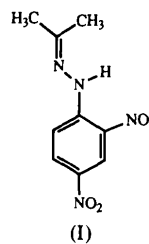
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Abstract

The molecule propanone 2,4-dinitrophenylhydrazone, C₉H₁₀N₄O₄, is nearly planar, with the non-H atoms exhibiting a mean deviation of 0.052 Å from their best plane. The largest deviation from coplanarity is 0.194 (3) Å, for one of the methyl groups. The N—N bond has length 1.380 (2) Å and the N=C bond length is 1.289 (4) Å. The nitro groups are essentially coplanar with the phenyl group, forming C—C—N—O torsion angles with magnitudes 1.8 (4) and 3.8 (4)°. The N—H group forms an intramolecular hydrogen bond with an O atom of the *ortho* nitro group, having an N...O distance of 2.601 (3) Å and an angle at H of 132 (2)°.

Comment

The title compound, (I), was isolated as an impurity in the 2,4-dinitrophenylhydrazone derivation of a ketone of unknown structure, presumably as a result of the presence of acetone from previous recrystallizations. The structure of (I) was determined to ascertain its identity.



A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for 2,4-dinitrophenylhydrazones yielded 51 compounds for which crystal-structure determinations have been carried out. Those most closely related to the title compound are propanal 2,4-dinitrophenylhydrazone and dimethyl 2-oxopropanedioate 2,4-dinitrophenylhydrazone (Vickery, Willey & Drew, 1981). Both these compounds exhibit intramolecular N—H...O hydrogen bonds; however, in the former the hydrogen bond is bifurcated, involving an intermolecular