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)

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 $B_{iso} = 1.3B_{eq}$ 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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2,4-Dinitrophenylhydrazone Derivative of Acetone

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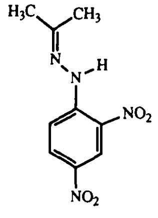
Abstract

The molecule propanone 2,4-dinitrophenylhydrazone, $C_9H_{10}N_4O_4$, 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.



(I)

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 contact about a center of symmetry, and in the latter, a bifurcated intramolecular hydrogen bond exists. The N—N and N=C bonds of (I) agree well with these observations.

Structure determinations of both the *para* (Menczel, Samay & Simon, 1972) and *meta* (Menczel, 1969) isomers of propanone nitrophenylhydrazone have been reported. Lacking the *ortho* NO_2 substituent, both these molecules form intermolecular N—H···O hydrogen bonds.

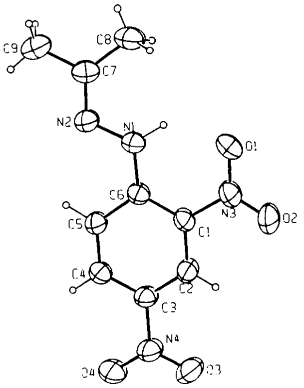


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound with thermal ellipsoids drawn at the 40% probability level.

Experimental

Crystal data

$C_9H_{10}N_4O_4$
$M_r = 238.2$
Triclinic
$P\bar{1}$
$a = 7.2032\ (10)$ Å
$b = 8.2781\ (13)$ Å
$c = 10.121\ (2)$ Å
$\alpha = 66.709\ (13)^\circ$
$\beta = 89.607\ (12)^\circ$
$\gamma = 79.451\ (12)^\circ$
$V = 543.5\ (2)$ Å^3
$Z = 2$
$D_x = 1.455$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 25\text{-}30^\circ$
$\mu = 0.96$ mm^{-1}
$T = 296$ K
Plate
0.40 × 0.35 × 0.10 mm
Yellow
Crystal source: recrystallization from ethanol

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.873$, $T_{\max} = 0.989$
2229 measured reflections
2229 independent reflections

1629 observed reflections $[I > \sigma(I)]$
$\theta_{\max} = 75^\circ$
$h = 0 \rightarrow 9$
$k = -9 \rightarrow 10$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 166.67 min
intensity variation: <2%

Refinement

Refinement on F
$R = 0.058$

$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

$wR = 0.062$
$S = 2.643$
1629 reflections
195 parameters
All H-atom parameters refined
$w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$
$(\Delta/\sigma)_{\max} = 0.01$

Extinction correction: $(1 + gI_c)^{-1}$ applied to F_c
Extinction coefficient: $g = 7.7\ (5) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B, 2.3.1)

Programs used include *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *DIRDIF* (Beurskens, 1984), *MolEN* (Fair, 1990) and *ORTEP* (Johnson, 1965).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal 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	$B_{\rm eq}$
O1	0.1997 (2)	0.0729 (3)	0.1390 (2)	6.52 (5)
O2	0.3159 (3)	0.0326 (3)	0.3468 (2)	6.62 (5)
O3	0.8488 (3)	0.2634 (3)	0.4043 (2)	7.76 (6)
O4	0.9969 (2)	0.4015 (2)	0.2214 (2)	5.92 (4)
N1	0.3682 (3)	0.2235 (2)	−0.0937 (2)	4.28 (4)
N2	0.4006 (3)	0.2831 (3)	−0.2382 (2)	4.62 (5)
N3	0.3205 (3)	0.0883 (3)	0.2171 (2)	4.80 (5)
N4	0.8719 (3)	0.3191 (3)	0.2765 (2)	4.96 (5)
C1	0.4721 (3)	0.1795 (5)	0.1491 (2)	3.75 (5)
C2	0.5959 (3)	0.2058 (3)	0.2390 (2)	4.01 (5)
C3	0.7421 (3)	0.2902 (3)	0.1818 (2)	3.93 (5)
C4	0.7684 (3)	0.3481 (3)	0.0358 (2)	4.05 (5)
C5	0.6474 (3)	0.3231 (3)	−0.0539 (2)	4.14 (5)
C6	0.4902 (3)	0.2405 (3)	−0.0009 (2)	3.65 (5)
C7	0.2715 (4)	0.2721 (3)	−0.3201 (2)	4.76 (6)
C8	0.0955 (4)	0.2022 (4)	−0.2708 (3)	5.78 (7)
C9	0.3013 (5)	0.3364 (4)	−0.4755 (3)	6.98 (8)

Table 2. *Geometric parameters* (Å, °)

N1—N2	1.380 (2)	N3—O2	1.210 (3)
N1—C6	1.355 (3)	N3—C1	1.455 (3)
N2—C7	1.289 (4)	N4—O3	1.211 (2)
C7—C8	1.490 (4)	N4—O4	1.227 (3)
C7—C9	1.477 (3)	N4—C3	1.458 (3)
N3—O1	1.236 (3)		
N2—N1—C6	119.5 (2)	O1—N3—C1	118.3 (2)
N1—N2—C7	115.4 (2)	O2—N3—C1	119.1 (2)
N2—C7—C8	125.4 (2)	O3—N4—O4	123.6 (2)
N2—C7—C9	116.6 (2)	O3—N4—C3	118.5 (2)
C8—C7—C9	118.0 (3)	O4—N4—C3	117.8 (2)
O1—N3—O2	122.6 (2)		
C6—N1—N2—C7	−175.8 (2)	O1—N3—C1—C6	−3.8 (4)
N2—N1—C6—C5	1.5 (3)	O3—N4—C3—C2	1.8 (4)
N1—N2—C7—C9	179.4 (2)	C4—C5—C6—C1	−2.7 (4)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes data, torsion angles and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71433 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1066]

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Structure of a Tetracyclic Intermediate in the Synthesis of *Daphniphyllum* Alkaloids

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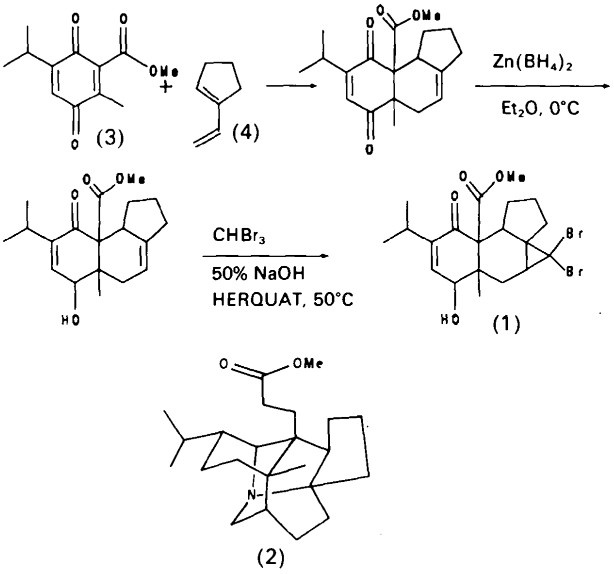
Abstract

Methyl 14,14-dibromo-4-hydroxy-6-isopropyl-3-methyl-7-oxotetracyclo$[11.1.0.0^{3,8}.0^{9,13}]$tetradec-5-ene-8-carboxylate, $C_{20}H_{26}Br_2O_4$, adopts an overall hemispherical conformation with the three major rings all having *cis* ring fusion and the cyclopropane ring pointing outward from the hemisphere.

Comment

Compound (1) forms part of a many-step sequence of reactions in the projected synthesis of methyl homodaphniphylate (2), a *Daphniphyllum* alkaloid of considerable structural, biological and synthetic interest (Yamamura, 1986). Compound (1) was prepared from thymoquinone-2-carboxylate methyl ester (3) and 1-vinylcyclopentene (4), as shown below. The synthetic complexity involved translates into a compound containing six contiguous asymmetric centres, whose complete structure elucidation can only be obtained by single-crystal X-ray diffraction. Furthermore, this structure determination is also necessary for planning the most appropriate sequence of reactions that will lead to the desired final product (2).



The hydroxycyclohexenone ring is in a sofa conformation with the methylated ring-junction C atom out of the plane. The fused cyclopropane ring forces the central cyclohexane ring into a half-chair conformation. The cyclopentane ring is in an envelope conformation with C(12) 0.521 (5) Å out of the plane through the other four atoms.

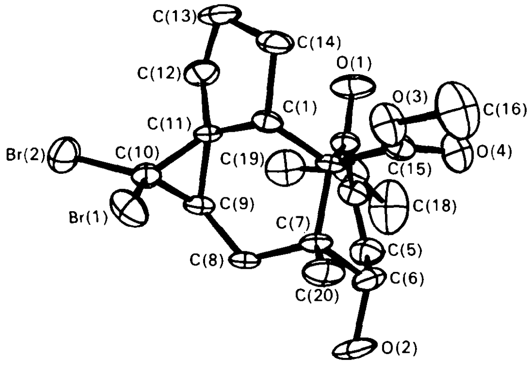


Fig. 1. Projection of $C_{20}H_{26}Br_2O_4$; atoms C(2), C(3) and C(4), which are not labeled, make a six-membered ring with C(5), C(6) and C(7); C(17), also unlabeled and behind this ring, is a substituent at C(4). 50% probability thermal ellipsoids are shown.

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