

N(1a)—C(1a)	1.468 (8)	C(6a)—C(6)	1.512 (9)
N(1a)—C(1)	1.477 (8)	C(6)—C(7)	1.377 (9)
N(1a)—C(2)	1.491 (8)	C(7)—C(8)	1.539 (8)
N(4)—C(3)	1.481 (8)	C(8a)—C(8)	1.400 (8)
N(4)—C(4a)	1.338 (7)	C(8a)—C(9)	1.520 (8)
N(4)—C(9a)	1.478 (7)	C(9a)—C(9)	1.563 (9)
N(7)—C(7)	1.332 (7)	C(9)—C(10)	1.508 (9)
N(11)—C(11)	1.335 (9)		
C(10)—O(10)—C(11)	117.4 (6)	N(7)—C(7)—C(6)	124.7 (6)
C(1a)—N(1a)—C(1)	112.8 (5)	N(7)—C(7)—C(8)	113.0 (6)
C(1a)—N(1a)—C(2)	114.8 (5)	C(6)—C(7)—C(8)	122.3 (6)
C(1)—N(1a)—C(2)	61.3 (4)	C(4a)—C(8a)—C(8)	120.3 (6)
C(3)—N(4)—C(4a)	130.8 (6)	C(4a)—C(8a)—C(9)	108.6 (6)
C(3)—N(4)—C(9a)	113.0 (5)	C(8)—C(8a)—C(9)	128.9 (6)
C(4a)—N(4)—C(9a)	110.3 (5)	O(8)—C(8)—C(7)	117.3 (6)
N(1a)—C(1)—C(2)	59.8 (4)	O(8)—C(8)—C(8a)	126.0 (6)
N(1a)—C(1)—C(9a)	114.2 (5)	C(7)—C(8)—C(8a)	116.5 (6)
C(2)—C(1)—C(9a)	107.2 (6)	O(9a)—C(9a)—N(4)	110.5 (5)
N(1a)—C(2)—C(1)	58.9 (4)	O(9a)—C(9a)—C(1)	104.8 (5)
N(1a)—C(2)—C(3)	113.2 (5)	O(9a)—C(9a)—C(9)	116.1 (6)
C(1)—C(2)—C(3)	109.7 (6)	N(4)—C(9a)—C(1)	103.3 (5)
N(4)—C(3)—C(2)	102.5 (6)	N(4)—C(9a)—C(9)	104.0 (5)
N(4)—C(4a)—C(5)	122.9 (6)	C(1)—C(9a)—C(9)	117.5 (6)
N(4)—C(4a)—C(8a)	113.0 (6)	C(8a)—C(9)—C(9a)	101.7 (5)
C(5)—C(4a)—C(8a)	124.2 (6)	C(8a)—C(9)—C(10)	116.4 (5)
O(5)—C(5)—C(4a)	119.3 (6)	C(9a)—C(9)—C(10)	112.0 (5)
O(5)—C(5)—C(6)	124.7 (7)	O(10)—C(10)—C(9)	103.6 (5)
C(4a)—C(5)—C(6)	115.9 (6)	O(10)—C(11)—O(11)	123.9 (7)
C(5)—C(6)—C(6a)	119.0 (6)	O(10)—C(11)—N(11)	109.1 (7)
C(5)—C(6)—C(7)	120.6 (6)	O(11)—C(11)—N(11)	127.1 (7)
C(6a)—C(6)—C(7)	120.4 (6)		
O(10)—C(10)—C(9)—C(8a)	178.1 (5)		
C(9)—C(10)—O(10)—C(11)	156.4 (6)		
O(11)—C(11)—O(10)—C(10)	1 (1)		

All non-H atoms were located by the direct methods using the programs *SAPI90* (Fan, 1990) and *DIRDIF* (Beurskens *et al.*, 1992). All H atoms except those of water molecules (which were not located) were found from difference Fourier maps. All non-H atoms were refined anisotropically and all H atoms were fixed. One water molecule is located on the twofold axis.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SAPI90* (Fan, 1990), *DIRDIF* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992). Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acetone 4,4-Dimethyl-5-oxo-2-pyrazolin-3-ylhydrazone

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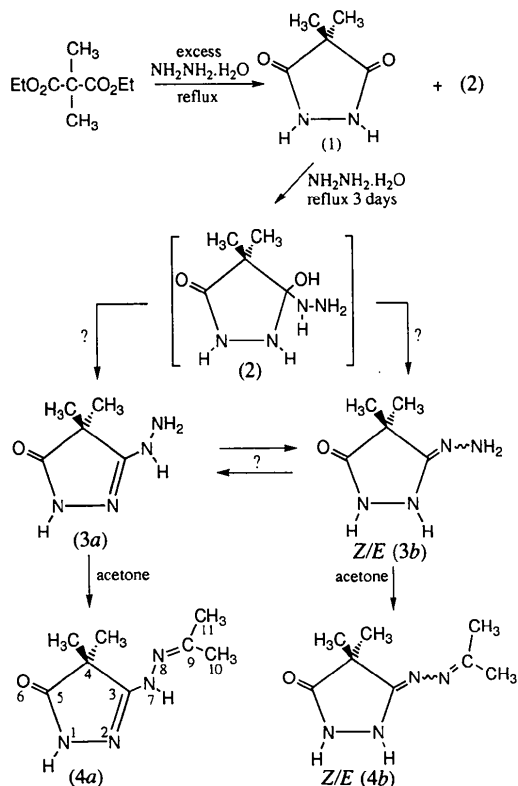
Abstract

The title compound, C₈H₁₄N₄O, exhibits an overall molecular coplanarity and trigonal planar geometry of all four N atoms, suggesting resonance interaction extending over eight contiguous atoms. Strong hydrogen bonding between hydrazidic-N donor and carbonyl-O acceptor atoms results in an almost-planar octagonal bridge between two molecules. These dimers are interconnected through a second octagonal bridge of weaker hydrogen bonds between side-chain hydrazine-N donor and ring-N acceptor atoms, leading to an almost-flat linear polymeric structure. The acetone–hydrazone N atom does not participate in hydrogen bonding. From the structure of the title compound, the unequivocal identification of 4,4-dimethyl-5-oxo-2-pyrazolin-3-ylhydrazine, an unexpected byproduct of the reaction of 4,4-dimethylpyrazolidine-3,5-dione with hydrazine, was made.

Comment

We recently prepared 4,4-dimethylpyrazolidine-3,5-dione (1) by refluxing diethyl dimethylmalonate with hydrazine hydrate for 5–8 days (Kolb, Colloton, Robinson, Lutfi & Meyers, 1996) following the methodology reported by Gillis & Izydore (1969) for the preparation of the 4,4-diethyl analog of (1). While Gillis & Izydore did not report the formation of byproducts, our analogous reaction carried out under varying temperatures, produced a mixture of products. Under moderate reaction temperatures, the desired compound (1) was isolated by selective solubility or chromatography. Higher temperatures led to an additional product which could be identified by ¹H and ¹³C NMR only as (3a), or Z or E (3b) and which, on recrystallization from acetone, afforded yet another compound identifiable by ¹H and ¹³C only as (4a), or Z or E (4b). Further study revealed that (3) was produced when (1) reacted with hydrazine hydrate and that (4) was formed from (3) reacting with acetone. These reactions are summarized in the scheme

below. Unequivocal identification of the structure of (4) would also define the structure of its precursor, (3), and thereby assist in understanding the reaction mechanisms leading to these unanticipated products.



The X-ray structure of (4) with its atom numbering, shown in Fig. 1, identifies it as (4a). The ring is essentially planar, with an average deviation from planarity of the ring atoms of 0.008 Å. The torsion angles given in Table 2 illustrate the overall molecular coplanarity of (4a), including H1, H7, O6 and the side-chain atoms. The molecular coplanarity and trigonal planar geometry of the hydrazidic N1 and, less expected, the hydrazino N7, strongly suggest a resonance interaction extending over O6, C5, N1, N2, C3, N7, N8 and C9.

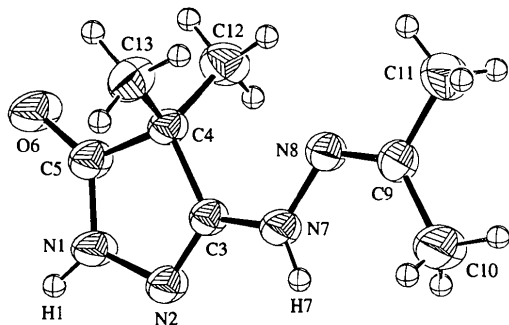


Fig. 1. Molecular structure and atom-numbering scheme for (4a) with displacement ellipsoids at the 50% probability level. H atoms are shown as isotropic spheres of arbitrary radius.

The intermolecular hydrogen-bonding data in Table 3 show that N1 is a strong donor and O6 is a strong acceptor, leading to a dimeric structure in which two molecules are linked *via* an almost-planar octagon composed of two crystallographically equivalent hydrogen bonds, N1—H1ⁱ...O6ⁱ and N1ⁱ—H1ⁱ...O6. The data in Table 3 also suggest a weaker interaction linking dimer to dimer through a second octagonal bridge also composed of two crystallographically equivalent hydrogen bonds, N7—H7ⁱⁱ...N2ⁱⁱ and N7ⁱⁱ—H7ⁱⁱ...N2. If both types of hydrogen bonds play a role, crystalline (4a) is an almost-flat linear polymeric structure, as shown in Fig. 2, which would account for its high melting point (*cf.* Meyers, Lutfi, Kolb & Robinson, 1994; Meyers, Lutfi, Hou & Robinson, 1995). N8 does not participate in hydrogen bonding. The poor acceptor character of the four N atoms is undoubtedly associated with their *sp*² hybridization.

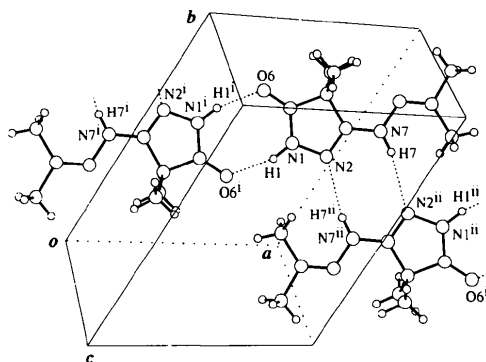


Fig. 2. Hydrogen-bonding scheme for (4a) showing infinite one-dimensional molecular chains propagating in the [101] direction. Symmetry codes: (i) 1 - x, 1 - y, -z; (ii) 2 - x, 1 - y, 1 - z.

The definitive characterization of (4) as (4a) through its crystal structure positively identifies its precursor (3) as isomer (3a) which is, therefore, formed from intermediate (2). In reactions of ketones and aldehydes with hydrazines, elimination of H₂O from the initially formed intermediate affords the hydrazone product. While reactions of hydrazides like (1) with hydrazines are rare and have received little if any attention, the direction of elimination from intermediate (2) would be difficult to predict in any case, since elimination from either direction would lead to a 'hydrazone'. The observed formation only of (3a) suggests two possibilities: it is the kinetically preferred isomer and does not isomerize to (3b) or both are formed but, under the reaction conditions, equilibration leads exclusively to thermodynamically preferred (3a).

Experimental

A mixture of diethyl dimethylmalonate (Aldrich), hydrazine hydrate (Sigma) and a small amount of water was gently refluxed for several days, then concentrated and dried *in vacuo* leaving a hard resinous residue; trituration with cold acetone

afforded crystals identified as (1) (Kolb, Colloton, Robinson, Lutfi & Meyers, 1996). Carried out under more vigorous conditions (oil bath temperature 423 K; reflux temperature 377 K; 8 days) the reaction also yielded a solid residue upon concentrating the mixture to dryness. A portion of this residue, recrystallized from ethanol, provided crystals (3) identified later as (3a): m.p. 513–515 K (corr., dec.); ^1H NMR (300 MHz, DMSO- d_6) δ : 1.11 (s, 6 H, CH $_3$), 3.87 (s, 2 H, NH $_2$), 7.59 (s, 1 H, NH) and 10.11 (s, 1 H, NH); ^{13}C NMR (75 MHz, DMSO- d_6) δ : 21.18 (CH $_3$), 43.25 [C(CH $_3$) $_2$], 165.56 (C=N) and 177.32 (C=O). A second portion of the residue, recrystallized from acetone, yielded a different product, a colorless crystalline compound, subsequently identified by X-ray diffraction as (4a): m.p. 483–485 K (corr.), ^1H NMR (CDCl $_3$) δ : 1.48 [s, 6 H, C $_4$ (H $_3$) $_2$], 1.87 (s, 3 H, C $_{10}$ H $_3$), 1.99 (s, 3 H, C $_{11}$ H $_3$), 8.55 (s, 1 H, N7H), 9.53 (s, 1 H, N1H); ^{13}C NMR (CDCl $_3$) δ : 15.78 (C $_{11}$ H $_3$), 21.11 C $_4$ (CH $_3$) $_2$, 25.13 (C $_{10}$ H $_3$), 46.06 (C $_4$), 147.69 (C $_9$ =N), 163.68 (C $_3$ =N) and 178.67 (C=O). Refluxing crystalline (1) with hydrazine hydrate for 3 days produced (3) which, when treated with acetone, was converted into (4a), thereby identifying (3) as (3a).

Crystal data

C $_8$ H $_{14}$ N $_4$ O

$M_r = 182.22$

Triclinic

$P\bar{1}$

$a = 8.956(2) \text{ \AA}$

$b = 10.322(2) \text{ \AA}$

$c = 5.905(2) \text{ \AA}$

$\alpha = 101.04(2)^\circ$

$\beta = 95.46(2)^\circ$

$\gamma = 68.42(2)^\circ$

$V = 498.0(5) \text{ \AA}^3$

$Z = 2$

$D_x = 1.215 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Rigaku AFC-5S diffractometer

$\omega/2\theta$ scans (rate 6° min^{-1} in ω , 3 repeats maximum)

Absorption correction: none

3480 measured reflections

1740 independent reflections

1419 observed reflections

$[I > \sigma(I)]$

Refinement

Refinement on F

$R = 0.045$

$wR = 0.052$

$S = 1.93$

1419 reflections

124 parameters

H atoms riding, except

H1 & H7 for which coordinates refined

$w = 4F_o^2/\sigma^2(F_o^2)$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 14.4\text{--}15.0^\circ$

$\mu = 0.08 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Irregular fragment

$0.49 \times 0.46 \times 0.21 \text{ mm}$

Colorless

$R_{\text{int}} = 0.023$

$\theta_{\text{max}} = 25^\circ$

$h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -7 \rightarrow 7$

3 standard reflections

monitored every 150 reflections

intensity decay: 1.2%

$(\Delta/\sigma)_{\text{max}} = 0.0002$

$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

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

	x	y	z	U_{eq}
N1	0.68047 (19)	0.52967 (17)	0.1611 (3)	0.0496 (6)
N2	0.82682 (17)	0.52626 (16)	0.2794 (3)	0.0433 (5)
C3	0.8517 (2)	0.63520 (18)	0.2396 (3)	0.0348 (5)
C4	0.7218 (2)	0.72550 (18)	0.0931 (3)	0.0355 (6)
C5	0.6143 (2)	0.6384 (2)	0.0479 (3)	0.0440 (6)
O6	0.48904 (17)	0.66394 (15)	-0.0706 (3)	0.0639 (6)
N7	0.98120 (18)	0.66627 (18)	0.3315 (3)	0.0454 (6)
N8	1.00774 (17)	0.77664 (16)	0.2634 (3)	0.0430 (5)
C9	1.1363 (2)	0.7989 (2)	0.3308 (3)	0.0442 (7)
C10	1.2660 (3)	0.7137 (3)	0.4756 (5)	0.0877 (11)
C11	1.1590 (3)	0.9203 (3)	0.2558 (4)	0.0636 (9)
C12	0.7757 (3)	0.7372 (2)	-0.1373 (3)	0.0529 (7)
C13	0.6289 (2)	0.8710 (2)	0.2298 (3)	0.0509 (7)
H1	0.638 (2)	0.458 (2)	0.161 (3)	0.0571†
H7	1.049 (2)	0.617 (2)	0.426 (3)	0.0528†

† U_{iso} (calculated).

Table 2. Selected geometric parameters (\AA , $^\circ$)

N1—N2	1.417 (2)	C4—C13	1.531 (3)
N1—C5	1.334 (2)	C5—O6	1.233 (2)
N2—C3	1.290 (2)	N7—N8	1.382 (2)
C3—C4	1.513 (2)	N8—C9	1.268 (2)
C3—N7	1.353 (2)	C9—C10	1.484 (3)
C4—C5	1.518 (2)	C9—C11	1.492 (3)
C4—C12	1.526 (3)		
N2—N1—C5	113.91 (16)	C12—C4—C13	111.63 (15)
N1—N2—C3	105.53 (16)	N1—C5—C4	107.10 (16)
N2—C3—C4	114.48 (16)	N1—C5—O6	126.60 (19)
N2—C3—N7	121.39 (17)	C4—C5—O6	126.30 (18)
C4—C3—N7	124.08 (16)	C3—N7—N8	117.93 (16)
C3—C4—C5	98.94 (14)	N7—N8—C9	118.78 (17)
C3—C4—C12	115.52 (17)	N8—C9—C10	125.5 (2)
C3—C4—C13	111.99 (15)	N8—C9—C11	116.98 (19)
C5—C4—C12	108.97 (16)	C10—C9—C11	117.5 (2)
C5—C4—C13	108.88 (15)		
H1—N1—N2—C3	178.2 (13)	N7—N8—C9—C10	1.4 (3)
H1—N1—C5—O6	0.9 (13)	N7—N8—C9—C11	179.21 (18)
N2—C3—N7—H7	-3.4 (15)	H7—N7—N8—C9	3.9 (14)
N2—C3—N7—N8	173.93 (17)		

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N1—H1 \cdots O6 i	0.95 (2)	1.961 (19)	2.873 (3)	160.7 (16)
N7—H7 \cdots N2 ii	0.869 (19)	2.420 (19)	3.266 (3)	164.5 (17)

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $2 - x, 1 - y, 1 - z$.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*; *PLATON* (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1180). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Racemic 3,6-Dimethyl-3,6-bis(*tert*-butyldimethylsilyloxy)-1,7-cyclododecadiyne

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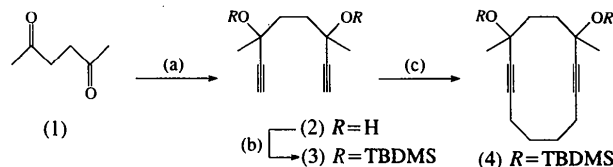
Abstract

The title compound, C₂₆H₄₈O₂Si₂, has been prepared and its structure determined. The bond angles at the triple bond are close to 174.5° (average) and the length of the triple bond is 1.179 (3) Å. The alkylene chains maintain a screw-type arrangement similar to that found in unsubstituted cyclododecane.

Comment

Medium-sized ring compounds are of considerable interest because of their unique structure and transannular reactivity (Dunitz & Meyer, 1965; Johnson, 1986;

Gleiter, Merger, Irgartinger & Nuber, 1993). The title cyclododecadiyne, (4), has been prepared in order to investigate the reactions of juxtaposed triple bonds with doubly functionalized reagents.



- (a) THF, 273K, 2 eq. ClMgC≡CH
 (b) THF, NEt₃, 2 eq. TBDMS-triflate
 (c) (i) THF, 253K, 2 eq. *n*-BuLi;
 (ii) 298K, DMPU, 1 eq. 1,4-dibromobutane

TBDMS: *tert*-butyldimethylsilyl
 DMPU: 1,3-dimethyl-3,4,5,6-tetrahydro-2 (1*H*)-pyrimidinone

The expected C₂ symmetry of racemic compound (4) is apparent from the structural analysis (Fig. 1). The orientation of the two alkylene chains relative to each other corresponds to the screw-type arrangement found in unsubstituted cyclododecane (Dale, 1978). The length of the triple bond is 1.179 (3) Å.

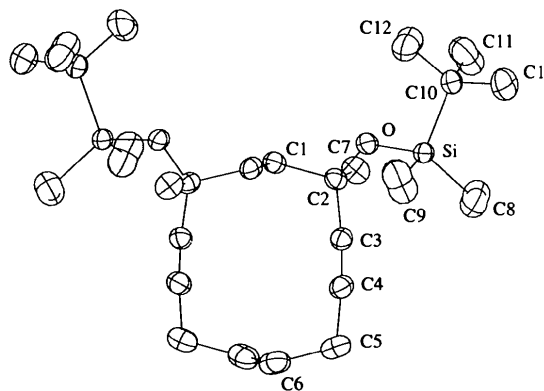


Fig. 1. The molecular structure of title compound (site occupancy 0.799) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 20% probability level.

The bond angles at the triple bond are 174.2 (3) (C2—C3—C4) and 174.7 (3)° (C3—C4—C5), which deviate only slightly from 180°. The transannular distance of the two alkyne units is 3.871 (4) Å [C3···C3A 3.891 (4) and C4···C4A 3.886 (4) Å]. These structural features are well within the range found in cyclododecadiynes and cyclododecadiynes, extracted from the Cambridge Structural Database (Allen *et al.*, 1979). The silyloxy groups are highly disordered. For every Si, C8, C9, C10, C11, C12 and C13 atom, two different positions with acceptable geometric and displacement parameters have been found. The unit cell contains two pairs of enantiomeric molecules of (4). The value of the density of (4) is rather low. It is apparent from the crystal