| | | | | |
|---|---|---|---|---|
| C(2) | 1.6264 (3) | 0.4175 (3) | −0.1684 (4) | 3.14 (9) |
| C(3) | 1.4778 (3) | 0.3147 (3) | −0.1301 (3) | 2.80 (8) |
| C(4) | 1.3317 (3) | 0.3277 (3) | −0.1816 (3) | 2.03 (7) |
| C(5) | 1.3420 (3) | 0.4429 (3) | −0.2724 (3) | 2.54 (8) |
| C(6) | 1.4966 (3) | 0.5413 (3) | −0.3035 (3) | 2.62 (8) |
| C(7) | 1.1718 (3) | 0.2158 (2) | −0.1361 (3) | 2.18 (7) |
| C(11) | 0.7470 (3) | 0.0672 (3) | −0.2840 (3) | 2.40 (7) |
| C(12) | 0.7931 (5) | −0.0167 (4) | −0.4154 (5) | 4.5 (1) |
| C(13) | 0.5861 (4) | −0.0298 (4) | −0.2263 (4) | 3.7 (1) |
| H(2) | 1.731 (4) | 0.4111 (3) | −0.133 (3) | 3.9 (6) |
| H(3) | 1.480 (4) | 0.232 (3) | −0.066 (4) | 4.3 (7) |
| H(5) | 1.246 (3) | 0.456 (3) | −0.314 (3) | 2.9 (5) |
| H(6) | 1.507 (3) | 0.622 (3) | −0.364 (4) | 3.7 (6) |
| H(9) | 1.038 (3) | 0.321 (3) | −0.192 (3) | 3.5 (6) |
| H(10*A*) | 0.907 (3) | 0.073 (3) | −0.073 (3) | 2.7 (5) |
| H(10*B*) | 0.850 (4) | 0.204 (4) | −0.008 (4) | 6.5 (9) |
| H(11) | 0.738 (3) | 0.151 (3) | −0.330 (3) | 3.1 (6) |
| H(12*A*) | 0.706 (4) | −0.063 (4) | −0.519 (5) | 5.8 (8) |
| H(12*B*) | 0.813 (4) | −0.083 (4) | −0.358 (4) | 4.3 (8) |
| H(12C) | 0.898 (4) | 0.046 (4) | −0.445 (4) | 5.3 (8) |
| H(13*A*) | 0.556 (4) | 0.023 (4) | −0.136 (5) | 5.6 (8) |
| H(13*B*) | 0.491 (4) | −0.064 (4) | −0.323 (5) | 6.0 (8) |
| H(13C) | 0.592 (5) | −0.106 (4) | −0.184 (5) | 7.0 (1) |
| H(14) | 0.870 (4) | 0.370 (4) | 0.501 (4) | 5.6 (9) |
| H(15) | 1.151 (5) | 0.354 (4) | 0.281 (5) | 7.0 (1) |

Table 2. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bond lengths* (Å)

| | | | |
|---|---|---|---|
| P(1)—O(1) | 1.565 (2) | O(1)—H(14) | 0.82 (3) |
| P(1)—O(2) | 1.557 (2) | O(2)—H(15) | 0.89 (4) |
| P(1)—O(3) | 1.502 (2) | N(9)—H(9) | 0.83 (3) |
| P(1)—O(4) | 1.508 (2) | N(10)—H(10*A*) | 0.89 (3) |
| O(8)—C(7) | 1.226 (3) | N(10)—H(10*B*) | 1.24 (4) |
| N(1)—C(2) | 1.333 (3) | C(2)—H(2) | 0.98 (3) |
| N(1)—C(6) | 1.337 (3) | C(3)—H(3) | 1.01 (3) |
| N(9)—N(10) | 1.418 (2) | C(5)—H(5) | 0.95 (3) |
| N(9)—C(7) | 1.341 (3) | C(6)—H(6) | 0.95 (3) |
| N(10)—C(11) | 1.504 (3) | C(11)—H(11) | 0.98 (3) |
| C(2)—C(3) | 1.377 (3) | C(12)—H(12*A*) | 0.96 (3) |
| C(3)—C(4) | 1.386 (3) | C(12)—H(12*B*) | 0.90 (3) |
| C(4)—C(5) | 1.385 (3) | C(12)—H(12*C*) | 0.95 (3) |
| C(4)—C(7) | 1.500 (3) | C(13)—H(13*A*) | 1.00 (4) |
| C(5)—C(6) | 1.378 (3) | C(13)—H(13*B*) | 0.97 (4) |
| C(11)—C(12) | 1.512 (4) | C(13)—H(13*C*) | 0.88 (4) |
| C(11)—C(13) | 1.508 (4) | | |
| O(1)—P(1)—O(2) | 105.3 (1) | C(3)—C(4)—C(5) | 118.0 (2) |
| O(1)—P(1)—O(3) | 106.3 (1) | C(3)—C(4)—C(7) | 118.1 (2) |
| O(1)—P(1)—O(4) | 110.1 (1) | C(5)—C(4)—C(7) | 123.9 (2) |
| O(2)—P(1)—O(3) | 110.4 (1) | C(4)—C(5)—C(6) | 118.9 (2) |
| O(2)—P(1)—O(4) | 109.74 (9) | N(1)—C(6)—C(5) | 123.4 (2) |
| O(3)—P(1)—O(4) | 114.6 (1) | O(8)—C(7)—N(9) | 121.9 (2) |
| C(2)—N(1)—C(6) | 117.4 (2) | O(8)—C(7)—C(4) | 121.5 (2) |
| N(10)—N(9)—C(7) | 118.6 (2) | N(9)—C(7)—C(4) | 116.7 (2) |
| N(9)—N(10)—C(11) | 112.5 (2) | N(10)—C(11)—C(12) | 111.6 (2) |
| N(1)—C(2)—C(3) | 123.5 (2) | N(10)—C(11)—C(13) | 107.4 (2) |
| C(2)—C(3)—C(4) | 119.0 (2) | C(12)—C(11)—C(13) | 113.8 (3) |

| *D* (at *x*, *y*, *z*) | *A* | *D*· · ·*A* | Symmetry code |
|---|---|---|---|
| O(2) | N(1) | 2.670 (3) | i |
| N(10) | O(3) | 2.553 (3) | ii |
| N(9) | O(4) | 2.761 (3) | iii |
| O(1) | O(4) | 2.615 (3) | iv |
| N(10) | O(8) | 2.939 (3) | v |

Symmetry code: (i) $3 - x, 1 - y, -z$; (ii) $x, y, z$; (iii) $2 - x, 1 - y, -z$; (iv) $2 - x, 1 - y, 1 - z$; (v) $-2 - x, -y, -z$.

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Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71205 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1009]

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*Acta Cryst.* (1993). C**49**, 1678–1680

# Structure of 2,4-Dinitrophenylhydrazine

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(*Received* 11 *November* 1992; *accepted* 10 *March* 1993)

## Abstract

The crystal structure of a potential DNA damaging and mutagenic agent, 2,4-dinitrophenylhydrazine, has been determined. The four nitro O atoms and the amino N atom of the hydrazine side chain are almost in the same plane as the phenyl ring. The three-dimensional arrangement of the molecules is held together by hydrogen bonds between nitro O atoms and the imino and amino groups of the hydrazine side chain.

## Comment

A number of hydrazine derivatives have been widely used in the medical and industrial fields. They have been shown to be potentially carcinogenic in animals having DNA damaging activity or mutagenicity (Toth, 1975; Parodi *et al.*, 1981; Mori *et al.*, 1988; Morpurgo *et al.*, 1988). However, the modes of action of hydrazine derivatives have not yet been clarified. In order to investigate their biological activity, it is important to determine their precise structures. In this study, as one of structural determinations of hydrazine derivatives, the structure of 2,4-dinitrophenylhydrazine has been determined.

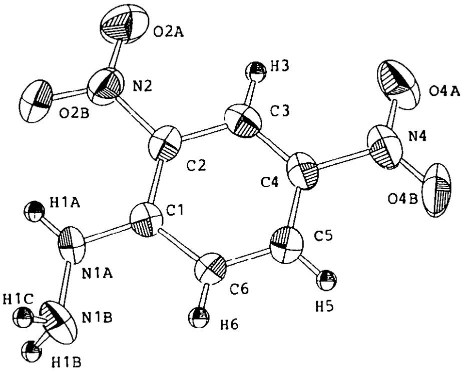

Fig. 1. Perspective view of the molecule with the atomic numbering scheme.

## Experimental

### *Crystal data*

$C_6H_6N_4O_4$
$M_r$ = 198.14
Monoclinic
$P2_1/c$
$a$ = 4.819 (3) Å
$b$ = 11.625 (4) Å
$c$ = 14.268 (4) Å
$\beta$ = 97.04 (4)°
$V$ = 793.3 (5) Å$^3$
$Z$ = 4
$D_x$ = 1.659 Mg m$^{-3}$
$D_m$ = 1.659 (1) Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda$ = 0.71069 Å
Cell parameters from 25 reflections
$\theta$ = 4.25-9.8°
$\mu$ = 0.133 mm$^{-1}$
$T$ = 296 K
Plate
0.30 × 0.20 × 0.10 mm
Orange
Crystal source: crystallized from ethanol

### *Data collection*

Rigaku AFC-5$R$ diffractometer
$\omega$-$2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min}$ = 0.87, $T_{\max}$ = 1.05
2138 measured reflections
1920 independent reflections
581 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int}$ = 0.081
$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 13$
$l = -16 \rightarrow 17$
3 standard reflections monitored every 150 reflections
intensity variation: 2.37%

### *Refinement*

Refinement on $F$
Final $R$ = 0.040
$wR$ = 0.043
$S$ = 1.16
581 reflections
151 parameters
All H-atom parameters refined

$w = 4F_o^2/[\sigma^2(F_o)^2]$
$(\Delta/\sigma)_{\max}$ = 0.01
$\Delta\rho_{\max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.18 e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $B_{\rm eq}$ |
|---|---|---|---|---|
| O(2*A*) | 0.5646 (9) | 0.0172 (4) | 0.6910 (3) | 5.2 (2) |
| O(2*B*) | 0.2348 (8) | 0.1200 (3) | 0.7365 (3) | 4.8 (2) |
| O(4*A*) | 0.9543 (8) | 0.1006 (4) | 0.4081 (3) | 5.3 (2) |
| O(4*B*) | 0.7937 (9) | 0.2435 (4) | 0.3210 (3) | 5.9 (2) |
| N(1*A*) | 0.115 (1) | 0.3226 (4) | 0.6617 (3) | 3.3 (2) |
| N(1*B*) | −0.014 (1) | 0.4309 (5) | 0.6513 (4) | 4.2 (3) |
| N(2) | 0.411 (1) | 0.1011 (4) | 0.6822 (3) | 3.6 (2) |
| N(4) | 0.804 (1) | 0.1853 (5) | 0.3928 (3) | 3.9 (3) |
| C(1) | 0.281 (1) | 0.2869 (4) | 0.5981 (3) | 2.5 (2) |
| C(2) | 0.431 (1) | 0.1812 (5) | 0.6061 (3) | 2.8 (2) |
| C(3) | 0.604 (1) | 0.1493 (5) | 0.5395 (4) | 3.0 (3) |
| C(4) | 0.628 (1) | 0.2195 (5) | 0.4642 (4) | 3.0 (3) |
| C(5) | 0.480 (1) | 0.3217 (5) | 0.4529 (4) | 3.5 (3) |
| C(6) | 0.314 (1) | 0.3553 (5) | 0.5182 (4) | 3.1 (3) |

Table 2. *Bond lengths* (Å), *hydrogen-bond distances* (Å) *and bond angles* (°)

| | | | |
|---|---|---|---|
| O(2*A*)—N(2) | 1.222 (5) | N(4)—C(4) | 1.460 (6) |
| O(2*B*)—N(2) | 1.237 (5) | C(1)—C(2) | 1.423 (6) |
| O(4*A*)—N(4) | 1.226 (6) | C(1)—C(6) | 1.415 (7) |
| O(4*B*)—N(4) | 1.223 (6) | C(2)—C(3) | 1.391 (6) |
| N(1*A*)—N(1*B*) | 1.405 (6) | C(3)—C(4) | 1.364 (7) |
| N(1*A*)—C(1) | 1.347 (6) | C(4)—C(5) | 1.383 (7) |
| N(2)—C(2) | 1.442 (6) | C(5)—C(6) | 1.359 (7) |
| N(1*B*)···O(2*A*$^{\rm i}$) | 3.092 (8) | N(1*A*)···O(4*B*$^{\rm iii}$) | 3.004 (5) |
| N(1*B*)···O(2*B*$^{\rm ii}$) | 2.990 (6) | | |
| N(1*B*)—N(1*A*)—C(1) | 119.8 (5) | N(2)—C(2)—C(1) | 122.5 (4) |
| O(2*A*)—N(2)—O(2*B*) | 122.1 (5) | N(2)—C(2)—C(3) | 116.4 (5) |
| O(2*A*)—N(2)—C(2) | 119.7 (4) | C(1)—C(2)—C(3) | 121.1 (5) |
| O(2*B*)—N(2)—C(2) | 118.2 (5) | C(2)—C(3)—C(4) | 119.6 (5) |
| O(4*A*)—N(4)—O(4*B*) | 123.7 (5) | N(4)—C(4)—C(3) | 119.8 (5) |
| O(4*A*)—N(4)—C(4) | 118.5 (5) | N(4)—C(4)—C(5) | 119.1 (5) |
| O(4*B*)—N(4)—C(4) | 117.8 (5) | C(3)—C(4)—C(5) | 121.0 (5) |
| N(1*A*)—C(1)—C(2) | 123.3 (5) | C(4)—C(5)—C(6) | 120.3 (6) |
| N(1*A*)—C(1)—C(6) | 120.3 (5) | C(1)—C(6)—C(5) | 121.6 (6) |
| C(2)—C(1)—C(6) | 116.4 (5) | | |

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$.

The scan rate was 32° min $^{-1}$ (in $\omega$) and the scan width was $(1.05 + 0.30 \tan\theta)$°. The ratio of peak counting time to background counting time was 2:1. Data collection and cell refinement: *Rigaku MSC/AFC Data Collection and Refinement Software* (Rigaku Corporation, 1988). Programs used to solve structure: *MITHRIL* (Gilmore, 1984); *DIRDIF* (Beurskens, 1984). All calculations, including data reduction: *TEXSAN* (Molecular Structure Corporation, 1985).

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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 71158 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1037]

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*Acta Cryst.* (1993). C**49**, 1680–1683

# Cyclobutane Structures Fused to a 13-Membered Ring

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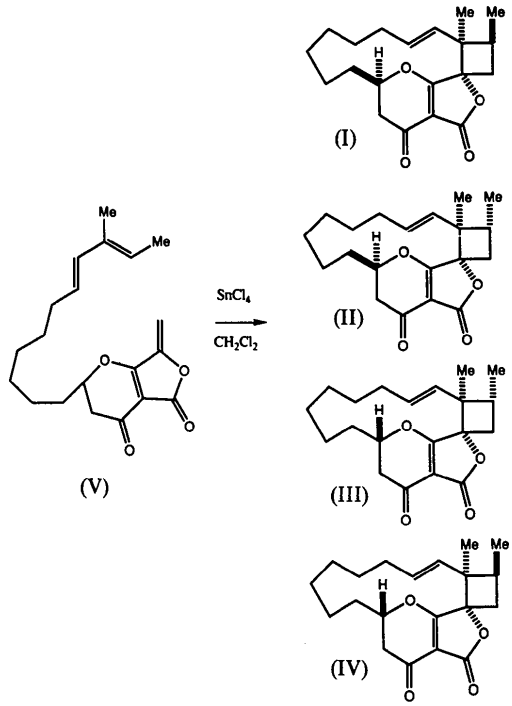
(*Received* 25 *January* 1993; *accepted* 15 *March* 1993)

## Abstract

The structures of two diastereomers, (1$R^*$,6a$S^*$,14a$S^*$,14b$R^*$,13$E$)- and (1$R^*$,6a$R^*$,14a$R^*$,14b$S^*$,13$E$)-1,14a-dimethyl-1,2,6,6a,7,8,9,10,11,12-decahydro-4$H$,5$H$,14a$H$-6a,14c-epoxy-3-cyclobuta[1′,2′:1,2]cyclopentadeca[2,3,4-$b$,$c$]furan-4,5-dione, in which a cyclobutane moiety is fused to a 13-membered ring are reported for the first time. The two diastereomers exhibit similar conformations except for the configuration about the methyl carbon (C15).

## Comment

In the course of our synthetic studies on the antibiotic okilactomycin, we have found the unexpected formation of intramolecular [2 + 2] cycloadducts (Takeda, Shimotani, Yoshii & Yamaguchi, 1992). This cycloaddition was performed from compound (V), a precursor of okilactomycin. The cycloaddition of (V), carried out at low temperature in $CH_2Cl_2$ in the presence of $SnCl_4$, afforded four diastereomeric [2 + 2] cycloadducts [(I)-(IV)]. Cyclobutane structures fused to a 13-membered ring, previously unreported, were confirmed by X-ray crystallographic analysis on (I) and (II).



Figs. 1 and 2 show *ORTEP* (Johnson, 1976) drawings of molecules (I) and (II), with the respective crystallographic numbering systems. The two diastereomers exhibit similar conformations except for the configuration at C15 [*trans* in (I) and *cis* in (II) relative to C16]. In the 13-membered ring, the most significant difference found between these two molecules was in the torsion angles C21—C22—C23—C24 and C23—C24—C6—O1 [−165.3 (3) in (I), 59 (1)° in (II) and 49.2 (3) in

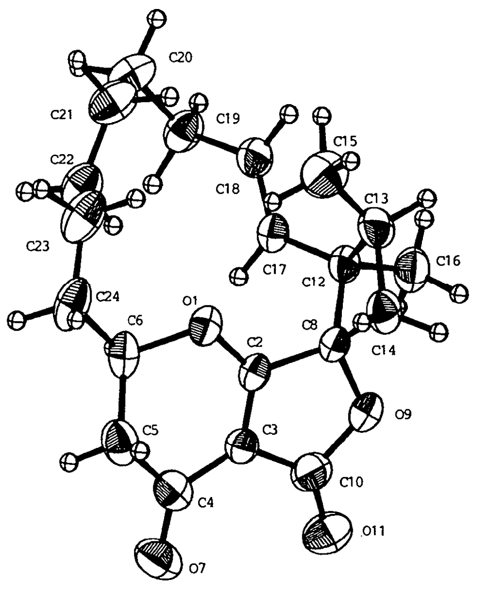


Fig. 1. *ORTEP* (Johnson, 1976) drawing of (I). Ellipsoids are drawn at the 50% probability level while isotropic H-atom thermal parameters are represented by spheres of arbitrary size.

*Acta Crystallographica* Section C
ISSN 0108-2701 ©1993