

5',6',7',8'-Tetrahydro-4a'-hydroperoxyspiro[cyclohexane-1,2'(2'H)-quinazoline]-4'(3'H)-one

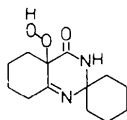
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Abstract. $C_{13}H_{20}N_2O_3$, $M_r = 252.30$, monoclinic, $P2_1/c$, $a = 10.390$ (3), $b = 11.923$ (3), $c = 10.989$ (6) Å, $\beta = 108.01$ (4)°, $V = 1294.6$ Å³, $Z = 4$, $D_m = 1.294$ (5), $D_x = 1.294$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.710693$ Å, $\mu = 0.86$ cm⁻¹, $F(000) = 544$, $T = 293$ K, final $R = 0.044$ for 1514 observed reflections. The crystal structure consists of a central ten-membered quinazoline bicyclic system with spiro-cyclohexane and hydroperoxyl groups. The hydroperoxyl group is involved in inter- rather than intramolecular hydrogen bonding. The crystal packing is dominated by intermolecular interactions of both a localized and an extended nature.

Introduction. Cyclohexanone reacts with urea affording a 2:1 adduct (McKay, Podesva, Tarlton & Billy, 1963) which, in solution, readily absorbs molecular oxygen with concomitant formation of a peroxide (McKay, Billy & Tarlton, 1963) later identified as the hydroperoxide (I) (Zigeuner & Gübitz, 1970). Although (I) and its derivatives possess some structural characteristics of the biologically important hydroperoxy flavins, they are reported to have similar reactivity to α -hydroperoxy esters and ketones, including the epoxidation of olefins without the requirement for metal-ion catalysis (Bruce, Noar, Ball & Venkataram, 1983). This enhanced reactivity of the α -hydroperoxy carbonyl compounds has been rationalized in terms of intramolecular hydrogen bonding which weakens the O—O bond (Rebek & McCready, 1980). Consequently, this X-ray study was undertaken to assess the extent of intramolecular hydrogen bonding in the title compound (I).



(I)

Experimental. The hydroperoxide prepared by literature procedure (McKay, Billy & Tarlton, 1963); colourless needles (from hot absolute ethanol), $0.4 \times 0.3 \times 0.6$ mm; D_m by flotation in chloroform/hexane mixture.

Data collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation and ω - 2θ scanning; cell parameters derived from 20 reflections ($11 < \theta < 12^\circ$); over quadrant ($2 < \theta < 23^\circ$; $h -11 \rightarrow 11$, $k 0 \rightarrow 13$, $l 0 \rightarrow 12$) 1796 intensities measured of which 1514 considered observed [$I > 2\sigma(I)$], $R_{int} = 0.010$; two standard reflections monitored every 7200 s showed no significant decay in intensity; data not corrected for absorption. Structure solved by direct methods (SHELX84, Sheldrick, 1984) and refined on F using full-matrix least-squares analysis (SHELX76, Sheldrick, 1976); all H atoms located on difference Fourier maps but fixed at calculated positions, apart from H atoms directly bonded to O(2) and N(2), with fixed isotropic thermal parameter ($U_{iso} = 0.10$ Å²). Final $R = 0.044$ for 1514 reflections, $wR = 0.059$ where $w = 1/[\sigma^2(F) + 0.000149(F^2)]$; $S = 1.56$; $|\Delta/\sigma|_{max} = 0.09$; $\Delta\rho_{max} = 0.27$, $\Delta\rho_{min} = -0.17$ e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculation of geometrical parameters performed using CALC (Gould & Taylor, 1983). Figs. 1 and 2 plotted using ORTEP (Johnson, 1965) and PLUTO (Motherwell, 1976) respectively.

Discussion. Final atomic coordinates and isotropic thermal parameters are listed in Table 1;* derived bond lengths and angles in Table 2. Fig. 1 depicts the crystal structure of (I) together with the numbering scheme utilized in this study and confirms the general structural features of this molecule.

In the central quinazoline moiety, the heterocyclic ring is essentially planar (mean deviation from l.s. plane ± 0.04 Å) whereas the adjoining carbocyclic ring adopts a conventional chair conformation, as does the pendant spiro-cyclohexane group. The geometrical parameters around the three rings are generally well within the expected ranges (Dunitz, 1979) though the

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42731 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(3)—N(1) distance of 1.272 (3) Å lies at the lower limit of 1.28 Å observed for localized >C=N— bonds. For the hydroperoxyl group, the C—O and O—O bond lengths found in (I) are in good agreement with the generally accepted values for alkylhydroperoxides (Gougoutas, 1983): C(2)—O(1) 1.430 (3) and O(1)—O(2) 1.4631 (24) Å. Although the hydroperoxyl group H atom was readily located on difference Fourier maps, refinement of positional and thermal parameters together was unsatisfactory. When the latter was fixed ($U_{\text{iso}} = 0.12 \text{ \AA}^2$), the O(2)—H(10) distance refined to a

value of 0.99 (4) Å; no residual peaks of any significance were located close to the terminal peroxy oxygen O(2).

With organic hydroperoxides containing additional heteroatoms there is usually the possibility of *inter-* or *intramolecular* hydrogen bonding. Inspection of molecular models of (I) shows that an intramolecular interaction between the hydroperoxyl H atom and the adjacent carbonyl group O is possible [*cf.* the hydroperoxide derived from autoxidation of a cyclohexanone hydrazone (Bozzini, Gratton, Risaliti, Stener, Calligans & Nardin, 1977)]. In the crystal structure of (I), however, the torsion angle C(2)—O(1)—O(2)—H(10) of $-136 (2)^\circ$ and the large H(10)···O(3) separation of 3.64 (4) Å indicate that there is no significant intramolecular contact. In the solution phase, there is some evidence for an extended conformation of the hydroperoxyl group since the HOO— signal in the ^1H NMR spectrum is found downfield at $\delta 11.8$, indicative of a strong interaction with the solvent (Me₂SO).

The crystal packing is illustrated in Fig. 2. Localized intermolecular hydrogen bonding between the amido group hydrogen H(1N) and the carbonyl group oxygen O(3) of two adjacent molecules of (I) results in the formation of dimeric units clustered around the crystallographic inversion centres at the midpoints of the *b* and *c* axes [H(10)···O(3) 2.03 (3) Å, N(2)—H(10)···O(3) 170 (2)°]. The dimers are in turn stacked alternately in a head-to-tail fashion along the *c* axis linked by an extended network of hydrogen bonds between the hydroperoxyl group hydrogen H(1O) and the ring nitrogen N(1) [H(10)···N(1) 1.75 (4) Å, O(2)—H(10)···N(1) 166 (2)°].

In conclusion, extensive intramolecular hydrogen bonding with concomitant weakening of the O—O bond is not evident from this study of the crystal structure of hydroperoxide (I). Consequently it is unlikely that structural factors can solely account for the enhanced reactivity of peroxides related to (I).

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Table 1. Final fractional atomic coordinates and isotropic thermal parameters (Å²) with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i, a_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}$
O(1)	0.40427 (15)	0.62987 (13)	0.06345 (14)	0.0458 (10)
O(2)	0.35091 (20)	0.74375 (14)	0.06044 (17)	0.0647 (13)
O(3)	0.16043 (16)	0.49723 (17)	-0.01846 (18)	0.0711 (13)
C(1)	0.20006 (22)	0.54813 (19)	0.08478 (22)	0.0430 (14)
C(2)	0.34874 (20)	0.56819 (17)	0.14701 (20)	0.0363 (13)
C(3)	0.38044 (20)	0.62961 (18)	0.27321 (20)	0.0349 (13)
N(1)	0.29219 (17)	0.66741 (14)	0.32098 (17)	0.0367 (11)
C(4)	0.14827 (20)	0.65540 (17)	0.25876 (20)	0.0364 (13)
N(2)	0.11590 (19)	0.58057 (17)	0.14764 (18)	0.0448 (12)
C(5)	0.42499 (23)	0.45567 (19)	0.16523 (25)	0.0493 (16)
C(6)	0.57492 (25)	0.46931 (22)	0.2350 (3)	0.0563 (17)
C(7)	0.59715 (25)	0.52830 (24)	0.36186 (25)	0.0567 (17)
C(8)	0.52756 (21)	0.64244 (21)	0.34415 (22)	0.0466 (15)
C(9)	0.08915 (25)	0.77137 (20)	0.2187 (3)	0.0533 (17)
C(10)	-0.0660 (3)	0.76891 (25)	0.1737 (3)	0.0732 (21)
C(11)	-0.1204 (3)	0.7218 (3)	0.2759 (4)	0.0883 (26)
C(12)	-0.0645 (3)	0.6066 (3)	0.3167 (3)	0.0697 (20)
C(13)	0.08853 (24)	0.60694 (22)	0.35923 (23)	0.0508 (16)
H(1N)	0.027 (3)	0.5641 (20)	0.110 (3)	0.0641
H(1O)	0.323 (3)	0.765 (3)	-0.031 (4)	0.1200

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

O(1)—O(2)	1.4631 (24)	C(4)—N(2)	1.465 (3)
O(1)—C(2)	1.430 (3)	C(4)—C(9)	1.522 (3)
O(2)—H(1O)	0.99 (4)	C(4)—C(13)	1.537 (3)
O(3)—C(1)	1.240 (3)	N(2)—H(1N)	0.91 (3)
C(1)—C(2)	1.503 (3)	C(5)—C(6)	1.517 (4)
C(1)—N(2)	1.328 (3)	C(6)—C(7)	1.514 (4)
C(2)—C(3)	1.512 (3)	C(7)—C(8)	1.525 (4)
C(2)—C(5)	1.539 (3)	C(9)—C(10)	1.533 (4)
C(3)—N(1)	1.272 (3)	C(10)—C(11)	1.513 (5)
C(3)—C(8)	1.494 (3)	C(11)—C(12)	1.505 (5)
N(1)—C(4)	1.446 (3)	C(12)—C(13)	1.512 (4)
O(2)—O(1)—C(2)	105.46 (15)	N(1)—C(4)—C(13)	106.60 (18)
O(1)—O(2)—H(1O)	104.7 (22)	N(2)—C(4)—C(9)	110.12 (18)
O(3)—C(1)—C(2)	119.89 (21)	N(2)—C(4)—C(13)	109.29 (18)
O(3)—C(1)—N(2)	122.19 (22)	C(9)—C(4)—C(13)	109.44 (19)
C(2)—C(1)—N(2)	117.79 (20)	C(1)—N(2)—C(4)	126.32 (19)
O(1)—C(2)—C(1)	110.59 (17)	C(1)—N(2)—H(1N)	116.2 (18)
O(1)—C(2)—C(3)	108.86 (17)	C(4)—N(2)—H(1N)	116.6 (18)
O(1)—C(2)—C(5)	103.78 (17)	C(2)—C(5)—C(6)	112.27 (20)
C(1)—C(2)—C(3)	113.35 (18)	C(5)—C(6)—C(7)	110.82 (22)
C(1)—C(2)—C(5)	109.62 (18)	C(6)—C(7)—C(8)	111.45 (22)
C(3)—C(2)—C(5)	110.21 (18)	C(3)—C(8)—C(7)	110.09 (20)
C(2)—C(3)—N(1)	124.75 (19)	C(4)—C(9)—C(10)	111.47 (22)
C(2)—C(3)—C(8)	115.21 (18)	C(9)—C(10)—C(11)	111.4 (3)
N(1)—C(3)—C(8)	120.03 (20)	C(10)—C(11)—C(12)	111.2 (3)
C(3)—N(1)—C(4)	122.80 (18)	C(11)—C(12)—C(13)	111.2 (3)
N(1)—C(4)—N(2)	113.06 (17)	C(4)—C(13)—C(12)	113.51 (21)
N(1)—C(4)—C(9)	108.22 (18)		

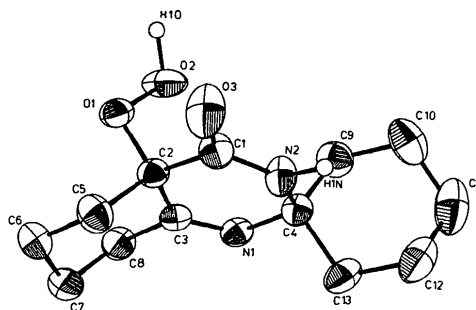


Fig. 1. Crystal structure of hydroperoxide (I) with numbering scheme. H atoms [except H(1O) and H(1N)] have been omitted for clarity.

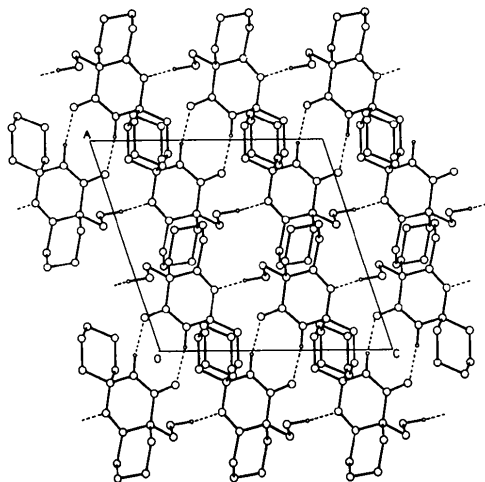


Fig. 2. Packing diagram for (I) viewed down the *b* axis.

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A Neutron Diffraction Study of the Crystal and Molecular Structure of Acenaphthene

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Abstract. $C_{12}H_{10}$, $M_r = 154.2$, orthorhombic, $Pcm2_1$, $a = 8.290$ (4), $b = 14.000$ (7), $c = 7.225$ (4) Å, $V = 838.5$ (7) Å³, $Z = 4$, $D_m = 1.19$, $D_x = 1.221$ (1) Mg m⁻³, 288 K [Ehrlich (1957). *Acta Cryst.* **10**, 699–705]. Neutron diffraction, $\lambda = 1.006$ Å, $\mu = 19.4$ mm⁻¹, $F(000) = 16.96$, room temperature. Final $R(F) = 0.038$ for 668 reflexions [$I > 3\sigma_c(I)$]. The two independent half-molecules are very closely planar with the dimensions of the naphthalene moiety close to those in naphthalene. The corrected length of the aliphatic bond C(7)–C(7') is 1.573 (6) Å. The mean C–H bond lengths are 1.091 (5) Å (aromatic) and 1.133 (7) Å (aliphatic). The results are compared with those of molecular-mechanics calculations.

Introduction. Acenaphthene, or 1,2-dihydroacenaphthylene, is not known to be carcinogenic but the moiety forms a component of several active non-alternant ring systems such as the benzfluoranthenes and the potent carcinogen 3-methylcholanthrene. That the five-membered ring induces some strain was apparent from an early crystal structure analysis (Ehrlich, 1957); twisting of the ethylene bridge occurs in two charge-transfer complexes of acenaphthene (Tickle & Prout, 1973*a,b*) and in *peri*-substituted acenaphthenes (Clough, Kung, Marsh & Roberts, 1976; Tanaka, Kasai, Takenaka & Sasada, 1981). The presence of two crystallographically independent half-molecules in the asymmetric unit makes this noncentrosymmetric