the dioxane ring in *trans*-2-isopropyl-*N*,*N*-dimethyl-1,3-dioxane-5-carbothioamide (Shoja & Kaloustian, 1983). The C(4)—C(12) bond length [1·554 (4) Å] is longer than C(2)—C(11) [1·533 (3) Å], the latter being close to the corresponding mean value of 1·526 (16) Å for α- and β-parachloral. The dioxin ring has a distorted half-boat conformation with its 'flap' at C(2). C(2) and O(3) are displaced by 0·846 (4) and 0·331 (5) Å respectively from the best plane through O(1), C(4), C(9) and C(10). The torsion angles are −64·0 (3)° for C(9)—O(1)—C(2)—O(3), 51·8 (3)° for O(1)—C(2)—O(3)—C(4) and −8·6 (3)° for C(2)—O(3)—C(4)—C(10). It is noticable that the C(11)Cl₃ group takes the equatorial position and C(12)Cl₃ the axial one. In each group, the Cl atoms are in staggered form with respect to the dioxin ring. The benzene ring is planar, the largest deviations from the best plane being −0·028 (3) Å for C(10) and 0·015 (4) Å for C(6). The N, O(1) and C(4) atoms deviate by 0·066 (5), 0·140 (4) and −0·172 (4) Å respectively from this plane. The plane of the nitro group makes an angle of 4·9 (2)° with the benzene ring. The crystal is composed of molecules held together by van der Waals interactions. The shortest intermolecular distance between Cl atoms is 3·597 (2) Å for Cl(2)···Cl(4); Cl(3)···H(1) [2·72 (4) Å] is slightly less than the van der Waals contact, 3·0 Å.

The ³⁵Cl NQR studies showed that the numbers of crystallographically independent chlorine atoms in (I) and (II) are nine and six, respectively, in accord with the present X-ray results. In (II) the thermal parameters of the Cl atoms of the C(11)Cl₃ group are somewhat larger than those of C(12)Cl₃. This observation may be

associated with the difference in V_0 which is proposed from the ³⁵Cl NQR results. However, no similar correlation was found for (I), possibly owing to its smaller V_0 magnitude suggested by the lower T_f's as compared with those of (II). The expected correlation would be observed if the X-ray work were done at lower temperatures, for instance at 150 K.

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2,3-Epoxy-2,3-dihydro-1,4-naphthoquinone

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Abstract. $C_{10}H_6O_3$, $M_r = 174·16$, monoclinic, $P2_1$, $a = 12·9845$ (19), $b = 4·2866$ (3), $c = 7·0192$ (9) Å, $\beta = 97·182$ (6)°, $V = 387·62$ (8) Å³, $Z = 2$, $D_x = 1·492$ Mg m⁻³, $\lambda(Mo\,K\alpha) = 0·7093$ Å, $\mu = 0·1207$ mm⁻¹, $F(000) = 180$, $T = 294$ K, $R = 0·033$ for 757 contributing reflections. The molecule adopts a shallow boat conformation with carbonyl groups bowed away from the oxirane ring. This conformation maximizes the conjugation between the carbonyl group and the oxirane ring with consequent shortening of the
oxirane C—O bond distance. Packing forces cause significant distortion as shown by the torsional angles about bonds C(4)—C(10) and C(9)—C(1).

Introduction. Epoxy compounds are powerful alkylating agents, thought to exert their biological activity by forming covalent bonds with information-carrying molecules like DNA and proteins. Chemicals of this class are antibiotics, mutagens, phytotoxins and carcinogens.

In our studies of the metabolites from the patulin pathway, we had determined the crystal structure of phyllostine (Kerr, 1986a) and wished to use molecular mechanics to explore the possibility of an alternative conformation with an intramolecular hydrogen bond. Determination of this structure was prompted by our need for precise dimensions for oxirane rings with carbonyl substituents in order to develop parameters for the molecular-mechanics calculation. It was an added bonus to discover that the conformation of the quinoid ring in the title compound is very close to that observed in phyllostine. Since the epoxynaphthoquinone is commercially available, it is much cheaper than phyllostine for studying the alkylation reactions of epoxides with protein and nucleic-acid fragments. These addition compounds are currently under study in this laboratory. Aldrich Chemical Co. of Milwaukee, Wisconsin, is our source of 2,3-epoxy-2,3-dihydro-1,4-naphthoquinone.

Experimental. Colourless needles (cut), $0 \cdot 11 \times 0 \cdot 16 \times 0 \cdot 32$ mm, Enraf–Nonius CAD-4F diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from least-squares refinement of 25 reflections with $11 \cdot 5 < \theta < 21 \cdot 1°$. Scan range, $\Delta\omega = 1 \cdot 5$-$(0 \cdot 74 + 0 \cdot 35 \tan\omega)°$ in $\omega/2\theta$ mode; hkl range, 0–15, 0–5, −8–8; three standard reflections monitored every 1200 s, decay of $4 \cdot 2\%$ over 20 measurements; after scaling 646 of 789 unique reflections observed with $I > 2 \cdot 0\sigma(I)$ to a max. $(\sin\theta)/\lambda$ value of $0 \cdot 5947$ Å⁻¹. No absorption correction. Structure solved using MULTAN (Germain, Main & Woolfson, 1971); refined by full-matrix least squares minimizing $\sum w |F_o - F_c|^2$ with $w = [\sigma^2(F) + 0 \cdot 0005 F^2]^{-1}$ to an R value of $0 \cdot 033$ and wR of $0 \cdot 034$ for 757 contributing reflections |reflections with $I < 2 \cdot 0\sigma(I)$ included if $F_o < F_c$]; $S = 1 \cdot 78$; scattering factors and anomalous-dispersion terms (real part only) from International Tables for X-ray Crystallography (1974). H atoms refined isotropically; max. $\Delta/\sigma = 0 \cdot 78 \times 10^{-3}$, average $\Delta/\sigma = 0 \cdot 19 \times 10^{-3}$; max. residual electron density $0 \cdot 104$ e Å⁻³. XRAY76 programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Final atomic coordinates are given in Table 1,* bond lengths, bond angles and torsional angles in Table 2.

Discussion. The molecular structure of 2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (EPQUIN) is displayed in Fig. 1. A striking feature is the shallow boat conformation of the quinoid ring, with the carbonyls

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* Lists of structure factors, anisotropic thermal parameters and bond angles and torsional angles involving H have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43562 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and isotropic thermal parameters* ($\times 10^4$ *for heavy atoms,* $\times 10^3$ *for* H)

	x	y	z	$U_{eq}*/U_{iso}(\text{Å}^2)$
C(1)	7615 (2)	6502 (11)	4654 (4)	491 (16)
C(2)	6482 (2)	5991 (11)	4632 (4)	494 (16)
C(3)	5804 (2)	6167 (11)	2792 (4)	500 (16)
C(4)	6293 (2)	6852 (11)	1015 (4)	462 (16)
C(5)	7652 (2)	10052 (11)	−246 (4)	509 (19)
C(6)	8614 (2)	11426 (20)	−32 (4)	587 (20)
C(7)	9257 (2)	11228 (12)	1686 (4)	578 (19)
C(8)	8934 (2)	9625 (11)	3204 (4)	514 (18)
C(9)	7955 (2)	8262 (11)	3028 (3)	412 (15)
C(10)	7304 (2)	8454 (11)	1272 (3)	404 (15)
O(1)	8227 (2)	5477	5954 (3)	758 (16)
O(4)	5872 (1)	6031 (10)	−550 (3)	647 (13)
O(3)	5867 (1)	8728 (10)	4122 (3)	534 (13)
H(2)	624 (2)	491 (9)	570 (4)	62 (9)
H(3)	513 (2)	521 (8)	256 (3)	50 (8)
H(5)	717 (2)	1013 (8)	−145 (4)	60 (9)
H(6)	886 (2)	1248 (8)	−108 (4)	66 (10)
H(7)	998 (2)	1211 (9)	175 (4)	72 (10)
H(8)	940 (2)	949 (9)	440 (4)	55 (8)

* The equivalent isotropic temperature factor U_{eq} for an anisotropic atom is one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsional angles* (°)

C(1)–C(2)	1·486 (4)	C(5)–H(5)	0·99 (3)
C(1)–C(9)	1·480 (5)	C(5)–C(6)	1·373 (5)
C(1)–O(1)	1·215 (3)	C(5)–C(10)	1·389 (5)
C(2)–C(3)	1·471 (4)	C(6)–C(7)	1·381 (4)
C(2)–O(3)	1·439 (5)	C(6)–H(6)	0·95 (3)
C(2)–H(2)	0·96 (3)	C(7)–C(8)	1·376 (5)
C(3)–C(4)	1·497 (4)	C(7)–H(7)	1·01 (3)
C(3)–O(3)	1·437 (5)	C(8)–C(9)	1·391 (4)
C(3)–H(3)	0·96 (3)	C(8)–H(8)	0·98 (3)
C(4)–C(10)	1·473 (4)	C(9)–C(10)	1·407 (3)
C(4)–O(4)	1·216 (3)		

C(2)–C(1)–C(9)	117·2 (2)	C(6)–C(5)–C(10)	120·4 (3)
C(2)–C(1)–O(1)	120·6 (3)	C(5)–C(6)–C(7)	120·8 (4)
C(9)–C(1)–O(1)	122·2 (3)	C(6)–C(7)–C(8)	119·8 (3)
C(1)–C(2)–C(3)	119·0 (3)	C(7)–C(8)–C(9)	120·3 (3)
C(1)–C(2)–O(3)	113·6 (3)	C(1)–C(9)–C(8)	120·2 (2)
C(3)–C(2)–O(3)	59·2 (2)	C(1)–C(9)–C(10)	120·0 (3)
C(2)–C(3)–C(4)	118·2 (3)	C(8)–C(9)–C(10)	119·7 (3)
C(2)–C(3)–O(3)	59·3 (2)	C(4)–C(10)–C(5)	120·4 (2)
C(4)–C(3)–O(3)	113·3 (3)	C(4)–C(10)–C(9)	120·6 (3)
C(3)–C(4)–C(10)	117·0 (2)	C(5)–C(10)–C(9)	118·9 (3)
C(3)–C(4)–O(4)	120·4 (3)	C(2)–O(3)–C(3)	61·5 (2)
C(10)–C(4)–O(4)	122·6 (3)		

C(9)	C(1)	C(2)	O(3)	−44·5 (3)	C(10) C(4) C(3) O(3)	43·6 (3)
C(9)	C(1)	C(2)	C(3)	22·0 (3)	C(10) C(4) C(3) C(2)	−22·9 (3)
O(1)	C(1)	C(2)	O(3)	136·1 (4)	O(4) C(4) C(3) O(3)	−138·1 (4)
O(1)	C(1)	C(2)	C(3)	−157·3 (4)	O(4) C(4) C(3) C(2)	155·4 (4)
C(1)	C(2)	O(3)	C(3)	110·8 (3)	C(2) O(3) C(3) C(4)	−110·0 (3)
C(1)	C(2)	C(3)	C(4)	0·1 (3)	C(1) C(9) C(10) C(4)	−1·5 (3)
C(1)	C(2)	C(3)	O(3)	−101·7 (4)	C(1) C(9) C(10) C(5)	−178·4 (4)
O(3)	C(2)	C(3)	C(4)	101·8 (4)	C(8) C(9) C(10) C(5)	−1·0 (3)
C(1)	C(9)	C(8)	C(7)	179·1 (4)	C(8) C(9) C(10) C(4)	175·9 (4)
C(9)	C(10)	C(5)	C(6)	0·0 (3)	C(4) C(10) C(5) C(6)	−177·0 (4)
C(10)	C(5)	C(6)	C(7)	0·5 (4)	C(10) C(9) C(8) C(7)	1·7 (3)
C(5)	C(6)	C(7)	C(8)	0·3 (4)	C(9) C(8) C(7) C(6)	−1·4 (4)
C(5)	C(10)	C(4)	O(4)	22·6 (3)	C(8) C(9) C(1) O(1)	−19·8 (3)
C(9)	C(10)	C(4)	O(4)	−154·2 (4)	C(10) C(9) C(1) O(1)	157·6 (4)
C(9)	C(10)	C(4)	C(3)	24·0 (3)	C(10) C(9) C(1) C(2)	−21·8 (3)
C(5)	C(10)	C(4)	C(3)	−159·2 (4)	C(8) C(9) C(1) C(2)	160·9 (4)

$$\chi_{C(10)} = \omega_1 - \omega_3 + \pi = -\omega_2 + \omega_4 + \pi$$
$$\chi_{C(4)} = \omega_2 - \omega_3 + \pi = -\omega_1 + \omega_4 + \pi \left.\right\} \text{ modulo } 2\pi.$$
$$\tau = (\omega_1 + \omega_2)/2.$$

that form the bow and stern of the boat pointing away from the oxirane ring.

Like cyclopropane, oxirane is capable of π-type conjugation with neighbouring π-acceptor substituents such as the carbonyl groups seen here. The important interaction stabilizing the observed conformation is the overlap of the Walsh orbital which is the HOMO of the oxirane system with the LUMO of the π-accepting group. This interaction is optimal when the orbitals are parallel. In cyclopropane derivatives, this occurs when the torsional angle about the bond linking the cyclopropane group to the carbonyl is about 30°. Hoffman (1970) invoked this concept to explain both the existence of 2,5-dimethyl-2,4-norcaradiene-7,7-dicarbonitrile and the highly asymmetric bond lengths in the cyclopropane ring observed in the X-ray structure of that compound (Fritchie, 1966). The delocalization weakens the antibonding component in the distal bond, thus shortening that bond while lengthening the adjacent bonds in the cyclopropane ring. The asymmetry so induced is well documented in the case of cyclopropyl groups (Allen, 1980) but not in oxirane systems (Allen, 1982). For an unperturbed oxirane ring, 'average' dimensions are $C-C = 1\cdot467$ (2), $C-O$ $1\cdot447$ (2) Å, $\angle COC = 60\cdot9$ (2), $\angle CCO = 59\cdot5$ (2)°. For EPQUIN, the corresponding dimensions are: $C-C = 1\cdot471$ (4), $\langle C-O \rangle = 1\cdot438$ (5) Å, $\angle COC = 61\cdot5$ (2), $\angle CCO = 59\cdot2$ (2)°. The shortening of the

$C-O$ bond by $0\cdot009$ Å would not be significant if this were an isolated observation. However, similar values have been observed for phyllostine (Kerr, 1986a) and in the immediate synthetic precursor of phyllostine (Kerr, 1986b). The corresponding values are $\langle C-O \rangle = 1\cdot434$ (4), $\Delta = 0\cdot013$ Å and $\langle C-O \rangle = 1\cdot432$ (2), $\Delta = 0\cdot015$ Å, respectively.

The methylene analogue of EPQUIN is 2,3-dihydro-2,3-methylene-1,4-naphthoquinone (HYMNAP, Grant & Speakman, 1962). HYMNAP crystallizes in space group $P2_1/m$ with two molecules in the unit cell. Thus the molecule is constrained to be symmetrical with the O(1)–O(4) vector parallel with the b axis. In contrast, the molecules of EPQUIN pack with the O(1)–O(4) vector roughly perpendicular to the b axis so that the epoxy O atoms point along the b axis (Fig. 2). The environments of O(1)–O(4) are dissimilar, resulting in significant distortion from mirror symmetry. The most significant non-bonded contacts involve the molecule at $-x+1$, $\frac{1}{2}+y$, $-z$: O(4)$\cdots$C(3) $3\cdot347$ (5), C(3)$\cdots$O(4) $3\cdot271$ (5), C(4)$\cdots$O(4) $3\cdot314$ (4), O(4)$\cdots$H(3) $2\cdot54$ (3) Å.

Analysis of the torsional angles about the C(4)–C(10) and C(9)–C(1) bonds using the formalism of Winkler & Dunitz (1971) allows description of the molecular distortion in terms of three parameters for each bond: two out-of-plane bends, χ, and a twist, τ: $\tau_{C(4)-C(10)} = 23\cdot3°$, $\chi_{C(10)} = -3\cdot2$, $\chi_{C(4)} = -1\cdot8°$; $\tau_{C(1)-C(9)} = 20\cdot8°$, $\chi_{C(9)} = 2\cdot6$, $\chi_{C(1)} = 0\cdot6°$. Since C(4), C(9) and C(10) show significantly pyramidal distortion the lengthening of the bonds C(3)–C(4) and C(9)–C(10) is not unexpected.
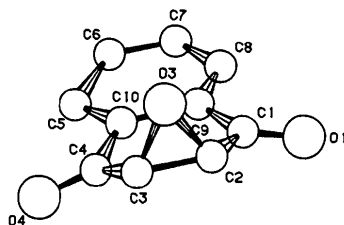
Fig. 1. Molecular structure and numbering scheme for EPQUIN as drawn by *PLUTO*78 (Motherwell & Clegg, 1978).
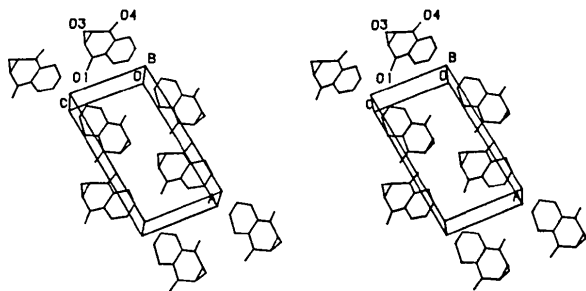

Fig. 2. Stereoscopic illustration of molecular packing. Note the orientation of the epoxy groups relative to the b axis.

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