The conformation is E with respect to the C(2)=N(3) bond; the methylthio methyl group is *cis* to N(3) in both molecules, torsion angles C(10)—S(1)—C(2)—N(3) 9·4 (4) and 3·7 (4)° in molecules A and B.

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Structure of 2,3-Dichloronaphthazarin

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Abstract. 2,3-Dichloro-5,8-dihydroxy-1,4-naphthoquinone, $C_{10}H_4Cl_2O_4$, $M_r = 259·0$, monoclinic, space group $P2_1/n$, $a = 14·110$ (1), $b = 7·070$ (1), $c = 9·810$ (1) Å, $\beta = 102·09$ (1)°, $V = 956·9$ (4) Å^3, $Z = 4$, $D_x = 1·798$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 62·174$ cm^{-1}, $F(000) = 520$, $T = 294$ K, $R = 0·058$ for 1531 observed reflections. The crystal is built up of molecules, possessing $2m$ symmetry, stacked along a diagonal axis; the molecules overlap to form a charge-transfer complex. The distance between the overlapping planes of neighbouring molecules is 3·40 (3) Å. There are intramolecular H bonds between the carbonyl and hydroxyl O atoms.

Introduction. According to the procedure previously described (Rodriguez, Vilches, Smith-Verdier & García-Blanco, 1983), the title compound was obtained by cycloaddition of 1,3-butadiene to 2,3-dichloro-*p*-benzoquinone and successive acetylation and oxidation of the adduct. Good crystals were obtained from an ethyl acetate solution by slow evaporation.

In chloroform solution, 2,3-dichloronaphthazarin shows absorption bands in the visible spectrum at 570 ($\varepsilon = 226$), 528 ($\varepsilon = 340$) and 496 nm ($\varepsilon = 284$ m^2 mol^{-1}) due to the annular chromophoric absorption of the carbonyl delocalization with the conjugated system and 468 nm ($\varepsilon = 178$ m^2 mol^{-1}) as a shoulder due to the charge-transfer complexation of the naphthazarin nucleus.

Analysis by ^{1}H NMR (200 MHz) in chloroform solution shows singlet signals at 12·34 (OH groups) and 7·33 (2 H aromatic or quinonoid protons). Chemical equivalence of the OH protons and also of the aromatic or quinonoid protons indicates that in solution the molecule has mirror symmetry.

The naphthazarin nucleus forms a charge-transfer self-complex (Rodriguez, Smith-Verdier, Florencio & García-Blanco, 1984). Verification of this fact and elucidation of the molecular stereochemistry requires determination of the structure.

Experimental. Crystal 0·02 × 0·15 × 0·30 mm, Philips 1100 automatic four-circle diffractometer, graphite monochromator, Cu $K\alpha$ radiation. Lattice parameters determined by least-squares refinement of θ values for 25 reflections; ω–2θ scan, $2 \leq \theta \leq 67$°; two reflections used as standard and remeasured after every 90 min, no decomposition observed. 1704 independent reflections ($-16 \leq h \leq 16$, $0 \leq k \leq 8$, $0 \leq l \leq 11$), 1531 observed with $I \geq 2\sigma(I)$, $\sigma(I)$ is the standard deviation based on

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counting statistics. No correction for absorption due to small size of crystal and since ψ-scan data showed effect to be quite small. $R_{\text{int}} = 0{\cdot}015$. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), subsequent refinement by least squares, function minimized $\sum w(|F_o| - |F_c|)^2$; difference electron density map revealed positions of all H atoms and further refinement of non-hydrogen atoms anisotropically and H atoms isotropically reduced R to 0·058 and wR to 0·059. Attempts to improve the refinement of the structure by applying an absorption correction by the technique of Walker & Stuart (1983) led to $R = 0{\cdot}044$ and $wR = 0{\cdot}059$ and slight but *significant* change in the overall geometry. Final difference map contains no peaks $>0{\cdot}14$ e Å^{-3}; max. $\Delta/\sigma = 0{\cdot}02$ for heavy atoms. Empirical weighting scheme (Martinez-Ripoll & Cano, 1975). $w = 1$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computations done on a Univac 1108 computer with programs of the *XRAY*70 system (Stewart, Kundell & Baldwin, 1970), *PESOS* (Martinez-Ripoll & Cano, 1975) and *PARST* (Nardelli, 1980).

Discussion. The final parameters are in Table 1.* Fig. 1 indicates the atomic numbering and the overlap of the molecules. Bond distances and angles are listed in Table 2.

The annular system consists of two rings, one benzenoid and one quinonoid. Although there are no crystallographically imposed symmetry elements, the molecular geometry deviates only trivially from $2m$. This is in good agreement with the work of Feutrill, Raston & White (1978) on a different crystal modification of the same compound and with ^{1}H NMR analysis of the title compound in chloroform solution.

The molecule is very near to planarity with an average torsion angle of 2·35 (3)° for all non-H-atom bonds. Best planarity is shown by the benzenoid ring [average torsion angle = 0·99 (2)°].

Bond lengths and angles are in the range found in other naphtharine compounds (Rodriguez *et al.*, 1984).

The crystal is built up from molecules stacked along a tilt axis, forming angles of 14·29 and 49·80° with the unit cell a and b axes respectively. Each stack contains symmetry centres that act in such a way that the quinonoid part of one molecule partially overlaps the benzenoid part of a symmetry-related neighbouring molecule (Fig. 1). The distance between the overlapping planes of neighbouring molecules is 3·40 (3) Å. Consequently, this crystal modification of 2,3-dichloronaphthazarin forms in the solid state a charge-transfer complex with itself, as expected from spectroscopic study.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^4)

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j \cos(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}
C(1)	0·03676 (18)	0·18940 (35)	0·22894 (28)	447 (9)
C(2)	0·00051 (19)	0·24246 (35)	0·07946 (29)	462 (9)
C(3)	0·06651 (18)	0·21516 (32)	−0·01403 (26)	419 (8)
C(4)	0·03933 (20)	0·27262 (36)	−0·15303 (29)	492 (9)
C(5)	0·10450 (25)	0·25485 (43)	−0·24251 (31)	597 (11)
C(6)	0·19376 (23)	0·17760 (47)	−0·19559 (31)	589 (11)
C(7)	0·22248 (19)	0·11438 (37)	−0·05708 (28)	477 (9)
C(8)	0·15942 (17)	0·13294 (33)	0·03409 (25)	408 (8)
C(9)	0·18896 (18)	0·06980 (34)	0·17685 (27)	431 (8)
C(10)	0·12233 (19)	0·10519 (35)	0·27237 (27)	450 (8)
O(1)	−0·08142 (13)	0·30772 (30)	0·04130 (23)	599 (8)
C(2)	−0·04809 (16)	0·34800 (32)	−0·20709 (24)	641 (8)
O(3)	0·31170 (15)	0·03866 (32)	−0·01886 (24)	623 (8)
O(4)	0·26721 (14)	−0·01107 (31)	0·22140 (21)	583 (8)
Cl(1)	−0·03878 (6)	0·24224 (12)	0·33896 (9)	640 (5)
Cl(2)	0·16368 (6)	0·03843 (12)	0·44090 (7)	646 (4)

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)–C(2)	1·496 (4)	C(9)–C(10)	1·481 (4)
C(1)–Cl(1)	1·710 (3)	C(10)–Cl(2)	1·701 (3)
C(2)–C(3)	1·450 (4)	C(8)–C(9)	1·446 (4)
C(2)–O(1)	1·228 (3)	C(9)–O(4)	1·239 (3)
C(3)–C(4)	1·397 (4)	C(7)–C(8)	1·393 (4)
C(4)–C(5)	1·404 (5)	C(6)–C(7)	1·407 (4)
C(4)–O(2)	1·346 (3)	C(7)–O(3)	1·347 (3)
C(1)–C(10)	1·334 (4)	O(3)–C(8)	1·421 (3)
C(5)–C(6)	1·362 (5)		
C(2)–C(1)–C(10)	121·7 (3)	C(1)–C(10)–C(9)	121·7 (2)
C(2)–C(1)–Cl(1)	115·7 (2)	C(9)–C(10)–Cl(2)	115·7 (2)
C(10)–C(1)–Cl(1)	122·6 (2)	C(1)–C(10)–Cl(2)	122·5 (2)
C(1)–C(2)–C(3)	117·0 (2)	C(8)–C(9)–C(10)	117·9 (2)
C(1)–C(2)–O(1)	120·0 (3)	C(10)–C(9)–O(4)	119·5 (2)
C(3)–C(2)–O(1)	123·1 (3)	C(8)–C(9)–O(4)	122·6 (2)
C(2)–C(3)–C(4)	119·8 (2)	C(7)–C(8)–C(9)	120·0 (2)
C(2)–C(3)–C(8)	121·0 (2)	C(3)–C(8)–C(9)	120·4 (2)
C(4)–C(3)–C(8)	119·2 (2)	C(3)–C(8)–C(7)	119·6 (2)
C(3)–C(4)–C(5)	120·2 (3)	C(6)–C(7)–C(8)	119·8 (3)
C(3)–C(4)–O(2)	122·8 (3)	C(8)–C(7)–O(3)	123·0 (2)
C(5)–C(4)–O(2)	117·1 (3)	C(6)–C(7)–O(3)	117·3 (3)
C(4)–C(5)–C(6)	120·4 (3)	C(5)–O(6)–C(7)	120·9 (3)

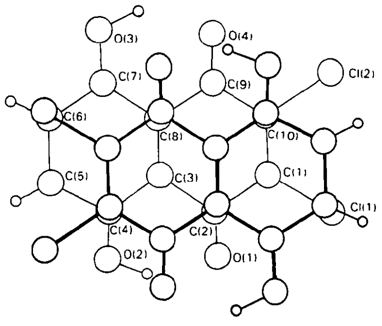

Fig. 1. A view of the overlap of two molecules related by an inversion centre.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42373 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The $O(1)\cdots O(2)$ [2·592 (3) Å] and $O(3)\cdots O(4)$ [2·587 (3) Å] distances seem to indicate the presence of intramolecular H bonds with $O{-}H\cdots O$ angles of 141 (4) and 143 (5)°, respectively. There is also a weak interaction $O(3)\cdots O(2)(\frac{1}{2}+x,\ \frac{1}{2}+y,\ \frac{1}{2}+z)$, 3·373 (3) Å, with an $O{-}H\cdots O$ angle of 130 (4)°.

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Nitro-2 Tétrahydro-6,7,8,9 Naphto[2,1-*b*]furanne

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Abstract. $C_{12}H_{11}NO_3$, mutagenic agent, $M_r = 217{\cdot}2$, triclinic, $P\bar{1}$, $a = 10{\cdot}968\ (2)$, $b = 7{\cdot}291\ (1)$, $c = 7{\cdot}395\ (3)$ Å, $\alpha = 92{\cdot}57\ (3)$, $\beta = 94{\cdot}89\ (3)$, $\gamma = 119{\cdot}56\ (2)°$, $V = 509{\cdot}9$ Å^3, $Z = 2$, $D_m = 1{\cdot}42$, $D_x = 1{\cdot}4152\ \mathrm{g\ cm^{-3}}$, $\bar{\lambda}(\mathrm{Cu}\ K\bar{\alpha}) = 1{\cdot}5418$ Å, $\bar{\mu} = 9{\cdot}7\ \mathrm{cm^{-1}}$, $F(000) = 228$, $T = 298$ K, final $R = 0{\cdot}043$ for 1513 independent observed reflections. The nitro group is practically coplanar with the benzofuran system. Stacking forces resulting from π–π interactions between parallel molecules play an important role in crystal cohesion.

Introduction. Dans la série des naphtofurannes de synthèse (Royer & Buisson, 1980; Cavier, Buisson, Lemoine & Royer, 1981) le méthoxy-7 nitro-2 naphto-[2,1-*b*]furanne (R7000), dont la structure cristalline a été déterminée récemment (Bravic, Bideau & Courseille, 1982), est le plus puissant des agents mutagènes connus (Weill-Thévenet, Buisson, Royer & Hofnung, 1981). Dans le but d'établir des relations structure–activité, nous avons entrepris l'étude structurale d'une série de molécules analogues du R7000, dont certaines présentent des propriétés bactéricides et protozoocides remarquables (Cavier, Buisson, Lemoine & Royer, 1981). Nous avons récemment présenté les structures cristallines des méthoxy-8 nitro-2 naphto[2,1-*b*]- et [2,3-*b*]furannes respectivement dénommés R6998 et R7105 (Bideau, Bravic, Cotrait & Courseille, 1983*a*,*b*) du méthyl-1 nitro-2 naphto[2,1-*b*]furanne ou R7371 (Bideau, Bravic & Cotrait, 1984) et du nitro-2 naphto[1,2-*b*]furanne ou R6614 (Bideau, Bravic & Cotrait, 1985). Le composé présentement étudié est le R7325, composé moyennement actif, qui est un analogue hydrogéné de l'homocycle extérieur des naphtofurannes précédents.

Partie expérimentale. Synthèse par l'équipe du Pr Royer (Institut Curie, Paris); D_m par flottation; prismes de couleur jaune orangée (benzène + méthanol) 0,2 × 0,2 × 0,3 mm; diffractomètre Enraf–Nonius CAD-4, monochromateur en graphite; 17 réflexions avec $\theta > 30°$ pour détermination des paramètres; $h_{\max} = 12$, $k_{\max} = 7$, $l_{\max} = 8$; balayage ω–2θ, $\Delta\theta = (0{,}8 + 0{,}15\ \mathrm{tg}\theta)°$, ouverture détecteur $(1{,}3 + 0{,}5\ \mathrm{tg}\theta)$ mm; $2\theta < 120°$; $\frac{1}{2}$ Ewald sphère; correction Lp; absorption négligée; pas de décroissance des intensités de référence (201 et $\bar{1}12$) avec le temps; 1513 réflexions indépendantes dont 1023 avec $I > 3\sigma(I)$; méthodes directes, programme *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); affinement B_i puis β_{ij} des atomes C, N, O par moindres carrés (blocs diagonaux); CII Mini-6/92; minimisation de

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