

Generally, the pyrene portion of the molecule shows no large deviations in bond lengths or bond angles compared to previous determinations of the structure of pyrene itself (Camerman & Trotter, 1965; Allmann, 1970; Hazell, Larsen & Lehmann, 1972; Kai, Hama, Yasuoka & Kasai, 1978). The C(1)–C(2) bond length [1.400 (4) Å], however, is slightly greater than in any of the pyrene structures [1.376 (12), 1.373 (2), 1.383 (3), 1.383 (2) Å, respectively].

The rings of the pyrene portion of the molecule are relatively planar with the exception of ring *D* (Fig. 1) which has a χ^2 value of 23, compared with a value of 15 expected on the basis of random errors. This ring is somewhat twisted to accommodate the planarity of the other three rings. The effect of this twisting is to give the entire molecule a slight fold along the line of atoms C(5) to C(10). The χ^2 value of the least-squares plane of the entire pyrene portion is 127, compared to a value of 28 expected on the basis of random errors. The torsion angle between the bromoethenyl group and the least-squares plane of the pyrene is 24.9 (4)°.

Layers of 1-(*trans*-2-bromoethenyl)pyrene are stacked herringbone fashion with 3.487 (4) Å between the layers. A stereoview of the contents of the unit cell is shown in Fig. 2 (Johnson, 1976).

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Structure of the Acetonitrile Solvate of the Antitumor Agent 4-Amino-*N*-(5-chloro-2-quinoxaliny)benzenesulfonamide, C₁₄H₁₁ClN₄O₂S·CH₃CN

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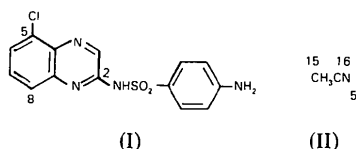
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Abstract. $M_r = 375.83$, monoclinic, $P2_1/c$, $a = 7.888$ (3), $b = 20.527$ (8), $c = 11.068$ (4) Å, $\beta = 98.64$ (3)°, $U = 1771$ (1) Å³, $Z = 4$, $D_m = 1.41$, $D_x = 1.41$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.45$ cm⁻¹, $T = 298$ K, $F(000) = 776$, final $R = 0.076$ ($S = 2.32$) for 2107 observed reflections measured on a diffractometer. The structure of the title compound was determined to be the 5-chloro isomer, and thus the condensation reaction between 1,2-diamino-3-chlorobenzene and butyl glyoxalate gives 5-chloro-2-quinoxalinol. Bond distances and angles are normal. There is probably a hydrogen bond between the molecule and the solvate (NH...N 1.98 Å).

Introduction. The 2-hydroxyquinoxaline ring system is conveniently made by the reaction of 1,2-diamino-

benzenes and butyl glyoxalate (Gowenlock, Newbold & Spring, 1945). When applied to substituted 1,2-diaminobenzenes, mixtures of isomers are often obtained. However, in the case of 1,2-diamino-3-chlorobenzene only one compound was produced (Wolf, Phister, Beutel, Wilson, Robinson & Stevens, 1949). In an investigation of compounds with serotonin-like activity (Lumma, Hartman, Saari & Engelhardt, 1981) the condensation product between 1,2-diamino-3-chlorobenzene and glyoxylic acid was presumed to be 5-chloro-2-quinoxalinol, but no reason for this conclusion was given. This material was converted to the title compound (I) for antimalarial testing (Wolf *et al.*, 1949) but whether it was the 5- or 8-chloro isomer was not known. Little further interest in compound (I) had been shown until recently, when it was discovered to

have strong and reproducible antitumor activity. Since (I) has been selected as a potential clinical candidate, it was important to determine its exact structure.



Experimental. Compound (I) was supplied to us by the Developmental Therapeutics Program, Division of Cancer Treatment, National Cancer Institute. Slow recrystallization from acetonitrile-ethanol (2:1) gave suitable crystals. ^1H NMR analysis showed that the crystals contained one mole of acetonitrile (II) per mole of (I).

Density measured by flotation in hexane-carbon tetrachloride; crystal ca $0.2 \times 0.3 \times 0.4$ mm; Syntex $P2_1$ diffractometer, take-off angle 6.74° , Mo $K\alpha$ radiation, graphite monochromator; unit-cell parameters by least-squares refinement of 15 machine-centered reflections (2θ from 10.9 to 19.3°); 3137 independent reflections out to $2\theta = 50^\circ$ (maximum $\sin\theta/\lambda = 0.5947 \text{ \AA}^{-1}$) using θ - 2θ scans; background counts at beginning and end of each scan; quadrant $\pm h$, k and $l \geq 0$; intensities of three standard reflections measured every 97 scans varied by an average of 2.5%; 2107 observed reflections [$F > 3\sigma(F)$]; L_p correction but none for absorption or extinction; structure solved by direct method using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) which generated a series of E maps, one of which correctly located most non-H atoms; a difference synthesis located the other non-H atoms; full-matrix least-squares refinement on F with isotropic temperature factors gave $R = 0.193$; function minimized $\sum(|F_o| - |F_c|)^2$; all non-methyl H atoms located from difference synthesis, methyl H atoms added as group parameter; further refinement with all non-H atoms anisotropic (non-methyl H-atom coordinates not refined) reduced R to 0.076 ($wR = 0.064$ and $S = 2.32$); max. least-squares $\Delta/\sigma = 0.021$; final difference Fourier synthesis maximum 0.73, minimum

$-0.69 e \text{ \AA}^{-3}$; neutral atomic scattering factors as in *SHELX76* (Sheldrick, 1976); weighting scheme $w = 2.63/[\sigma^2(F) + 0.0001F^2]$ was used. The space group $P2_1/c$ was uniquely determined by the observed systematic absences, $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$).

Table 1. Fractional coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	$U_{eq} = \frac{1}{3} \sum U_{ii}$			
	x	y	z	U_{eq}
C(1)	0.1574 (8)	0.3647 (3)	0.2977 (5)	69
C(2)	0.1586 (8)	0.3872 (3)	0.4148 (5)	75
C(3)	0.1797 (8)	0.4535 (3)	0.4432 (5)	81
C(4)	0.1959 (8)	0.4959 (3)	0.3511 (5)	75
C(5)	0.1978 (6)	0.4754 (2)	0.2312 (4)	50
C(6)	0.1781 (6)	0.4086 (2)	0.2045 (4)	48
C(7)	0.1981 (6)	0.4284 (2)	0.0055 (4)	44
C(8)	0.2163 (7)	0.4961 (2)	0.0311 (5)	58
C(9)	0.4255 (6)	0.3103 (2)	-0.0794 (4)	41
C(10)	0.4372 (6)	0.2633 (2)	0.0117 (4)	48
C(11)	0.5960 (7)	0.2448 (2)	0.0712 (4)	54
C(12)	0.7443 (7)	0.2728 (2)	0.0413 (4)	53
C(13)	0.7316 (6)	0.3215 (2)	-0.0475 (5)	55
C(14)	0.5747 (7)	0.3397 (2)	-0.1086 (4)	50
N(1)	0.1793 (5)	0.3854 (2)	0.0886 (3)	48
N(2)	0.2159 (6)	0.5196 (2)	0.1410 (4)	63
N(3)	0.1983 (5)	0.4096 (2)	-0.1155 (3)	51
N(4)	0.9045 (6)	0.2530 (3)	0.0968 (5)	83
O(1)	0.2454 (4)	0.3426 (2)	-0.2865 (3)	71
O(2)	0.0989 (4)	0.2931 (2)	-0.1279 (3)	65
S	0.2302 (2)	0.33454 (7)	-0.1600 (1)	51
Cl	0.2178 (3)	0.57814 (8)	0.3834 (2)	143
C(15)	0.646 (1)	0.3575 (3)	0.3186 (7)	117
C(16)	0.6768 (9)	0.4233 (4)	0.2800 (5)	89
N(5)	0.7032 (9)	0.4747 (3)	0.2519 (5)	122

Table 2. Bond lengths (\AA) and angles ($^\circ$)

C(1)-C(2)	1.375 (7)	C(1)-C(6)	1.399 (6)
C(2)-C(3)	1.401 (8)	C(3)-C(4)	1.362(7)
C(4)-C(5)	1.395 (7)	C(4)-Cl	1.728 (5)
C(5)-C(6)	1.405 (6)	C(5)-N(2)	1.374 (5)
C(6)-N(1)	1.371 (5)	C(7)-C(8)	1.422 (6)
C(7)-N(1)	1.299 (5)	C(7)-N(3)	1.394 (5)
C(8)-N(2)	1.309 (6)	C(9)-C(10)	1.390 (6)
C(9)-C(14)	1.402 (6)	C(9)-S	1.733 (5)
C(10)-C(11)	1.378 (6)	C(11)-C(12)	1.388 (7)
C(12)-C(13)	1.395 (6)	C(12)-N(4)	1.381 (6)
C(13)-C(14)	1.370 (6)	N(3)-S	1.649 (4)
O(1)-S	1.433 (3)	O(2)-S	1.425 (3)
C(15)-C(16)	1.448 (8)	C(16)-N(5)	1.128 (7)
C(6)-C(1)-C(2)	119.6 (5)	C(3)-C(2)-C(1)	121.4 (5)
C(4)-C(3)-C(2)	118.4 (5)	C(5)-C(4)-C(3)	122.2 (5)
Cl-C(4)-C(3)	119.2 (4)	Cl-C(4)-C(5)	118.6 (4)
C(6)-C(5)-C(4)	118.6 (4)	N(2)-C(5)-C(4)	120.6 (4)
N(2)-C(5)-C(6)	120.8 (4)	C(5)-C(6)-C(1)	119.7 (4)
N(1)-C(6)-C(1)	118.9 (4)	N(1)-C(6)-C(5)	121.4 (4)
N(1)-C(7)-C(8)	122.8 (4)	N(3)-C(7)-C(8)	116.5 (4)
N(3)-C(7)-N(1)	120.6 (4)	N(2)-C(8)-C(7)	122.2 (4)
C(14)-C(9)-C(10)	119.9 (4)	S-C(9)-C(10)	122.0 (4)
S-C(9)-C(14)	118.1 (4)	C(11)-C(10)-C(9)	119.7 (4)
C(12)-C(11)-C(10)	120.7 (5)	C(13)-C(12)-C(11)	119.4 (5)
N(4)-C(12)-C(11)	121.4 (5)	N(4)-C(12)-C(13)	119.2 (5)
C(14)-C(13)-C(12)	120.5 (5)	C(13)-C(14)-C(9)	119.8 (4)
C(7)-N(1)-C(6)	116.3 (4)	C(8)-N(2)-C(5)	116.5 (4)
S-N(3)-C(7)	124.5 (3)	N(3)-S-C(9)	106.1 (2)
O(1)-S-C(9)	109.7 (2)	O(1)-S-N(3)	102.9 (2)
O(2)-S-C(9)	108.9 (2)	O(2)-S-N(3)	109.5 (2)
O(2)-S-O(1)	118.9 (2)	N(5)-C(16)-C(15)	178.6 (8)

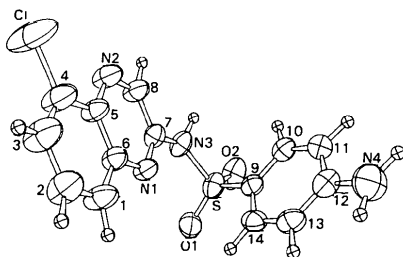


Fig. 1. An ORTEP diagram (Johnson, 1976) of compound (I).

Discussion. Fig. 1 is an *ORTEPII* diagram (Johnson, 1976) of the molecule (deleting the acetonitrile of crystallization) illustrating 50% probability ellipsoids for all non-H atoms and with an arbitrary sphere of radius about 0.4 Å for H atoms. Atomic positions are listed in Table 1 and distances and angles between all non-H atoms are shown in Table 2.* The structure determined for compound (I) shows that it is the 5-chloro (not 8-chloro) isomer. Thus the condensation reaction between 1,2-diamino-3-chlorobenzene and butyl glyoxalate produces 5-chloro-2-quinoxalinol. The distance between the proton on N(3) and N(5) is 1.98 Å which is shorter than the combined van der Waals radii of 2.7 Å suggesting a hydrogen bond between the molecule and solvate (Hamilton & Ibers, 1968).

* 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 42149 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Laserolide [*trans,trans*-Germacra-1(10),4-dien-*cis*-6,12-olide], C₂₂H₃₀O₆, from the Family Umbelliferae

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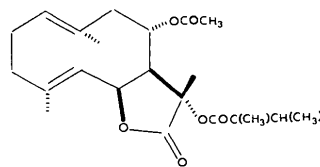
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Abstract. *M_r* = 390.48, monoclinic, *P*2₁, *a* = 6.566 (1), *b* = 12.551 (1), *c* = 12.836 (2) Å, β = 94.83 (1)°, *U* = 1054.1 (2) Å³, *Z* = 2, *D_m* = 1.25, *D_x* = 1.23 Mg m⁻³, Cu *K*α, λ = 1.54184 Å, μ = 0.73 mm⁻¹, *F*(000) = 420, *T* = 293 K, *R* = 0.044 for 1432 observed reflections. Laserolide (I) belongs to a relatively recently discovered stereochemical group of germacranolides which are derived from the (*E,E*)-6αH,7αH-germacra-1(10),4-dien-6,12-olide skeleton. It possesses stereochemical features characteristic for that group [chair-boat conformation of the 10-membered ring and *syn* α orientation of the methyl groups at C(4) and C(10)]. It differs from previously investigated compounds in the degree of saturation as well as in the conformational type of the γ-lactone.

Introduction. The sesquiterpene lactone laserolide (I) was isolated from the root of the species *Laser trilobium* (L.) Borkh. (family Umbelliferae, tribe Laserpitieae) (Holub, de Groote, Herout & Šorm, 1968), and its basic structure was deduced by means of chemical

and spectroscopic methods (Holub, Samek, Popa, Herout & Šorm, 1970). The present X-ray study verifies the stereochemistry of (I) and firmly establishes that laserolide belongs to the group of ursiniolides, relatively recently described *trans,trans*-germacranolides with the lactone ring closed at C(6) and *cis*-annulated to a ten-membered homocycle (Samek, Holub, Rychlewska, Grabarczyk & Drożdż, 1979; Herz, Govindan & Blount, 1980). Moreover, laserolide is the first native substance from the Umbelliferae family which has been demonstrated to belong to this stereochemical group.



(I)