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Structure of 1,4-Diazathianthrene at 163 K

By S. B. Larson and S. H. Simonsen

Department of Chemistry, University of Texas at Austin, Austin, TX 78712, *USA*

W. W. Lam and G. E. Martin

Department of Medicinal Chemistry and Pharmacognosy, College of Pharmacy, The University of Houston, Houston, Texas 77004, *USA*

and C. M. Lindsay and K. Smith

*Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA*2 8*PP, Wales*

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Abstract. $C_{10}H_6N_2S_2$, $M_r = 218\cdot29$, triclinic, $P\bar{1}$, $a = 8\cdot3751\ (11)$, $b = 10\cdot7988\ (12)$, $c = 11\cdot1715\ (13)$ Å, $\alpha = 83\cdot947\ (9)$, $\beta = 74\cdot611\ (12)$, $\gamma = 75\cdot073\ (10)°$, $V = 940\cdot5\ (2)$ Å^3, $Z = 4$, $D_x(163\ \text{K}) = 1\cdot541$, $D_m(295\ \text{K}) = 1\cdot519\ (1)$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0\cdot71069$ Å, $\mu = 5\cdot05$ cm^{-1}, $F(000) = 448$, $R = 0\cdot0387$ for 4176 observed reflections. There are two independent molecules per asymmetric unit. The benzene and pyrazine rings are planar with dihedral angles of 138·93 (7) and 137·00 (7)°; with S atoms included in these planes, the dihedral angles are 136·66 (3) and 134·74 (3)° respectively. A trend of increasing CSC and CCS angles through the series of thianthrene, 1-azathianthrene and 1,4-diazathianthrene is observed.

Introduction. As part of our ongoing studies of the effects of annular substitutions on the dihedral angles of thianthrenes (Larson, Simonsen, Martin, Smith & Puig-Torres, 1984) we present this report on the structure of 1,4-diazathianthrene.

Experimental. The title compound was prepared by condensation of the dianion of 1,2-benzenedithiol with 2,3-dichloropyrazine in dry, distilled *N,N*-dimethylformamide under an inert argon atmosphere (Lam, 1984). Crystals, grown by sublimation, were large colorless, transparent prisms. Density measured by flotation in aqueous $ZnCl_2$. A summary of data collection and structural refinement is given in Table 1.

Structure solved by a combination of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and Fourier techniques and refined by full-matrix least-squares method [$\sum w(F_o - F_c)^2$ minimized, $w = \sigma_F^{-2}$]. Scattering factors and anomalous-dispersion corrections for S, N and C from *International Tables for X-ray Crystallography* (1974); H scattering factors from Stewart, Davidson & Simpson (1965). All atomic positional parameters refined as well as anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. H atoms located in an electron density difference map as peaks of 0·61–0·74 e Å^{-3}. Atomic

Table 1. *Summary of data collection and structure refinement for* 1,4-*diazathianthrene*

(*A*) Data collection (163 K)[i,ii]	
Radiation	Mo $K\alpha$
Mode	ω scan
Scan range	Symmetrically over 1·0° about $K\alpha_{1,2}$ maximum
Background	Offset 1·0 and −1·0° in ω from $K\alpha_{1,2}$ maximum
Scan rate (° min^{-1})	3·0–6·0
Exposure time (h)	74·1
Stability analysis[ii]	
Computed s	−0·00011 (10)
t	0·000000 (1)
Max. correction (on I)	1·000–1·008
2θ range (°)	4·0–60·0
Range in *hkl*, min.	0,−14,−15
max.	11, 15, 15
Total reflections measured	5834
Crystal dimensions (mm)	0·45 × 0·40 × 0·19
Crystal volume (mm^3)	0·0311
Crystal faces	$00\bar{1}$;$0\bar{1}0$;$0\bar{2}1$;$\{01\bar{1}\}$ $\{1\bar{1}1\}$;$\{100\}$;$\{101\}$;$\{110\}$; cut face
Absorption correction transmission-factor range	0·821–0·914
(*B*) Structure refinement	
Instability factor p[ii]	0·04
Reflections used ($F \geq 4\sigma_F$)	4176
No. of variables	301
Goodness of fit, S	1·529
R, wR	0·0387, 0·0478
R for all data	0·0573
Max. shift/e.s.d.	0·0004
Max. density in difference map (e Å^{-3})	0·44
Min. density in difference map (e Å^{-3})	−0·24

Notes: (i) Unit-cell parameters were obtained by least-squares refinement of the setting angles of 60 reflections with $25\cdot07 < 2\theta < 29\cdot97°$. (ii) Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described by Riley & Davis (1976). Crystal and instrument stability were monitored by re-measurement of four check reflections after every 96 reflections. These data were analyzed as detailed by Henslee & Davis (1975).

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parameters are found in Table 2.* Least-squares planes calculated with a program provided by Cordes (1983). Principal computer programs given by Gadol & Davis (1982).

Discussion. Atom labeling, bond lengths and bond angles are shown in Figs. 1 and 2. The compound crystallizes with two molecules per asymmetric unit. Bond lengths and angles of the two independent molecules are in excellent agreement. The distances in the pyrazine rings are very similar to those found in the corresponding ring in 1,4,9-triazaphenoxathiin (Larson, Simonsen, Martin & Smith, 1985) in which the C(2)—C(3) distance is short and the inside C—N distances are shorter than the outside C—N distances. There is little effect on the bond lengths in the central heterocyclic ring when N replaces C in the aromatic rings. This is shown by the averages of the C—S and C—C bond lengths in the series consisting of thianthrene [1·771 (3), 1·396 (1) Å], 1-azathianthrene [1·770 (2), 1·398 (2) Å] (Larson *et al.*, 1984) and the title compound [1·768 (3), 1·399 (3) Å]. However, the interior angles of this central ring change considerably. Both CSC and CCS angles increase through the series thianthrene, 1-azathianthrene and 1,4-diazathianthrene [averages, 100·1 (4), 100·5 (4), 101·4 (4)°, respectively, for CSC angles and averages, 120·5 (1), 121·1 (1), 122·2 (2)°, respectively, for CCS angles]. These effects are accompanied by the increase in the dihedral angle through this series: 127·14 (3)° for thianthrene, 130·37 (3)° for 1-azathianthrene and 135·7 (14)° averaged over the two independent molecules of 1,4-diazathianthrene. The dihedral angles between the planes consisting of only the non-H atoms of the aromatic rings in the two independent molecules of 1,4-diazathianthrene are 138·93 (7) and 137·00 (7)°.

Table 2. *Positions in fractional coordinates and* U_{iso} (H *atoms) or* U_{eq} *for atoms in two independent molecules of* 1,4-*diazathianthrene*

	x	y	z	U_{eq}*/U_{iso}(Å^2)
S(10)	1·00452 (6)	0·58443 (5)	0·21380 (5)	0·0350 (2)
C(10A)	0·9678 (2)	0·6343 (2)	0·3664 (2)	0·0282 (6)
N(1)	1·1065 (2)	0·63167 (15)	0·4046 (2)	0·0343 (6)
C(2)	1·0794 (3)	0·6788 (2)	0·5163 (2)	0·0376 (8)
C(3)	0·9179 (3)	0·7238 (2)	0·5896 (2)	0·0384 (8)
N(4)	0·7776 (2)	0·72435 (15)	0·5530 (2)	0·0322 (6)
C(4A)	0·8036 (2)	0·6805 (2)	0·4408 (2)	0·0268 (6)
S(5)	0·61864 (6)	0·69342 (4)	0·38818 (4)	0·0294 (2)
C(5A)	0·6747 (2)	0·5518 (2)	0·3048 (2)	0·0255 (5)
C(6)	0·5491 (2)	0·4859 (2)	0·3137 (2)	0·0315 (6)
C(7)	0·5846 (3)	0·3769 (2)	0·2460 (2)	0·0371 (7)
C(8)	0·7465 (3)	0·3324 (2)	0·1705 (2)	0·0375 (7)
C(9)	0·8739 (3)	0·3962 (2)	0·1622 (2)	0·0331 (7)
C(9A)	0·8380 (2)	0·5065 (2)	0·2292 (2)	0·0269 (6)
S(10)*B*	0·53814 (6)	−0·02530 (5)	0·79394 (5)	0·0340 (2)
C(10A)*B*	0·4869 (2)	0·1223 (2)	0·8669 (2)	0·0283 (6)
N(1)*B*	0·6146 (2)	0·1787 (2)	0·8538 (2)	0·0370 (6)
C(2)*B*	0·5783 (3)	0·2863 (2)	0·9162 (2)	0·0430 (8)
C(3)*B*	0·4181 (3)	0·3367 (2)	0·9883 (2)	0·0402 (8)
N(4)*B*	0·2876 (2)	0·2822 (2)	0·99929 (15)	0·0329 (6)
C(4A)*B*	0·3226 (2)	0·1745 (2)	0·9389 (2)	0·0264 (6)
S(5)*B*	0·15377 (6)	0·09847 (5)	0·96031 (4)	0·0313 (2)
C(5A)*B*	0·1898 (2)	0·0431 (2)	0·8095 (2)	0·0253 (5)
C(6)*B*	0·0492 (2)	0·0524 (2)	0·7618 (2)	0·0310 (6)
C(7)*B*	0·0712 (3)	0·0013 (2)	0·6480 (2)	0·0358 (7)
C(8)*B*	0·2337 (3)	−0·0554 (2)	0·5795 (2)	0·0356 (7)
C(9)*B*	0·3746 (3)	−0·0604 (2)	0·6244 (2)	0·0317 (6)
C(9A)*B*	0·3535 (2)	−0·0120 (2)	0·7399 (2)	0·0259 (6)
H(2)	1·171 (3)	0·683 (2)	0·540 (2)	0·042 (6)
H(3)	0·900 (3)	0·761 (2)	0·665 (2)	0·049 (7)
H(6)	0·435 (3)	0·519 (2)	0·364 (2)	0·043 (6)
H(7)	0·499 (3)	0·334 (2)	0·254 (2)	0·039 (6)
H(8)	0·770 (3)	0·252 (2)	0·123 (2)	0·048 (7)
H(9)	0·990 (3)	0·370 (2)	0·108 (2)	0·050 (7)
H(2)*B*	0·671 (3)	0·331 (2)	0·905 (2)	0·063 (8)
H(3)*B*	0·391 (3)	0·424 (2)	1·031 (2)	0·042 (6)
H(6)*B*	−0·057 (3)	0·093 (2)	0·804 (2)	0·042 (6)
H(7)*B*	−0·027 (3)	0·013 (2)	0·614 (2)	0·043 (6)
H(8)*B*	0·248 (3)	−0·088 (2)	0·497 (2)	0·045 (6)
H(9)*B*	0·490 (3)	−0·093 (2)	0·572 (2)	0·038 (6)

* For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{A}_{ij}$ where $\mathbf{A}_{ij}$ is the dot product of the ith and jth direct-space unit-cell vectors.

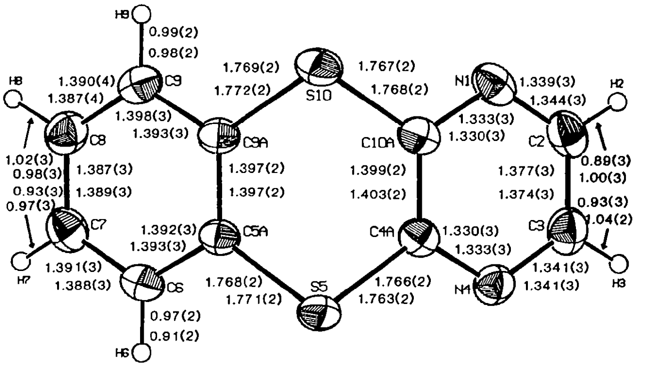

Fig. 1. View of molecule *A* illustrating atom labeling. Bond lengths (Å) with e.s.d.'s are indicated for both molecule *A* (upper numbers) and molecule *B*. Thermal ellipsoids scaled to 50% probability.

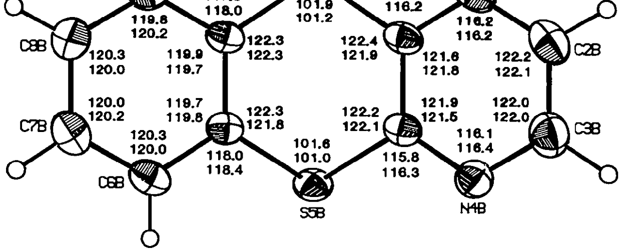

Fig. 2. View of molecule *B* giving bond angles (°). Upper values are for molecule *A*. E.s.d.'s are in the range 0·1 to 0·2°.

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* Tables of anisotropic thermal parameters, bond lengths and angles involving H, torsion angles, least-squares planes and structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42432 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

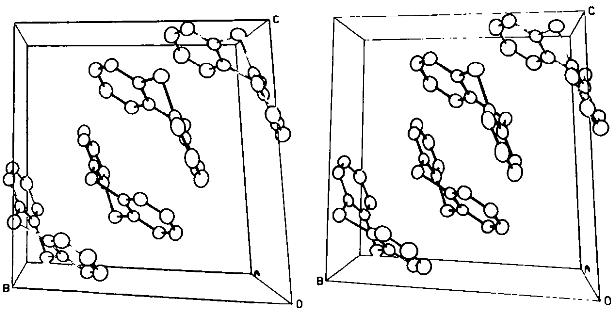

Fig. 3. Stereoview of molecular packing as viewed down the *a* axis.

The packing diagram is found in Fig. 3. One molecule appears to snuggle into the fold of the other independent molecule. The closest non-bonding contacts less than the sum of the van der Waals radii are: $S(10)\cdots H(2)B(2-x,1-y,1-z)$, 3·01 (3); $N(1)\cdots H(6)(1+x,y,z)$, 2·64 (2); $N(4)\cdots H(9)B(x,1+y,z)$, 2·67 (2); $N(1)B\cdots H(6)B(1+x,y,z)$, 2·60 (2); $N(4)B\cdots H(9)(x-1,y,1+z)$, 2·45 (3); $H(7)B\cdots H(7)B(\bar{x},\bar{y},1-z)$, 2·50 (3); $H(7)B\cdots H(8)B$, 2·43 (3); and $H(9)B\cdots H(9)B(1-x,\bar{y},1-z)$, 2·45 (3) Å.

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Structures of Umbelliferone and 7-Ethoxycoumarin

BY KATSUHIKO UENO

Research Institute for Polymers and Textiles, Yatabe-Higashi 1-1-4, *Tsukuba, Ibaraki* 305, *Japan*

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Abstract. Umbelliferone (U), $C_9H_6O_3$, $M_r = 162{\cdot}1$, monoclinic, $P2_1/c$, $a = 3{\cdot}892$ (1), $b = 11{\cdot}022$ (2), $c = 16{\cdot}722$ (3) Å, $\beta = 90{\cdot}58$ (2)°, $V = 717{\cdot}3$ (3) Å^3, $Z = 4$, $D_m = 1{\cdot}50$, $D_x = 1{\cdot}50$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}114$ mm^{-1}, $F(000) = 336$, $T = 298$ K, $R = 0{\cdot}042$ for 1255 observed reflexions. 7-Ethoxycoumarin (7-*O*-ethylumbelliferone; U7E), $C_{11}H_{10}O_3$, $M_r = 190{\cdot}2$, monoclinic, $P2_1/n$, $a = 4{\cdot}001$ (1), $b = 9{\cdot}770$ (2), $c = 24{\cdot}213$ (3) Å, $\beta = 93{\cdot}12$ (2)°, $V = 945{\cdot}1$ (3) Å^3, $Z = 4$, $D_m = 1{\cdot}33$, $D_x = 1{\cdot}33$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}934$ mm^{-1}, $F(000) = 400$, $T = 298$ K, $R = 0{\cdot}041$ for 1691 observed reflexions. The coumarin moiety of U has a different resonance structure from coumarin itself, because the hydroxylation at the 7-position appears to change the resonance system of the coumarin moiety. The plane composed of the O—C—C atoms of the ethoxy group in U7E is approximately coplanar with the mean plane of the coumarin moiety. The torsion angle around the C_{ring}—O_{ethoxy} bond is 2·6 (3)°, and such an 'in-plane' conformation causes the C—O—C angle of the ethoxy group to expand up to 117·7 (1)°.

Introduction. It has been revealed that the structures of 6,7-dihydroxycoumarin (esculetin: E; Ueno & Saito, 1977) and 7,8-dihydroxycoumarin (daphnetin: D; Ueno & Saito, 1976) are well explained in terms of the resonance system as shown in Fig. 1. The glucosidation at the 7-hydroxy group in esculetin (E7G; Ueno, Shiraki, Sato & Saito, 1985) or daphnetin (D7G; Ueno, Sato & Saito, 1983), significantly decreases the contribution of the limiting structure (II), while the glucosidation at the 6-hydroxy group (E6G; Ueno *et al.*, 1985) or 8-hydroxy group (D8G; Ueno, Saito &

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