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Structure of Ethyl 3-Methylene-2a-phenyl-2a,3-dihydro[1,2]diazeto[3,2-*c*]-[1,4]benzothiazine-2-carboxylate, $C_{19}H_{16}N_2O_2S$

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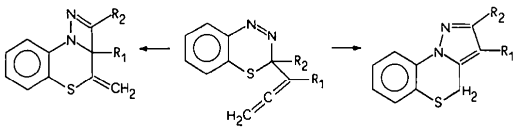
Abstract. $M_r = 336{\cdot}4$, monoclinic, $P2_1/c$, $a = 14{\cdot}677\,(3)$, $b = 8{\cdot}308\,(1)$, $c = 16{\cdot}008\,(3)$ Å, $\beta = 116{\cdot}79\,(2)°$, $V = 1742{\cdot}4\,(6)$ Å^3, $Z = 4$, $D_m = 1{\cdot}275$, $D_x = 1{\cdot}282$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}19$ mm^{-1}, $F(000) = 704$, $R = 0{\cdot}045$ for 2532 ($I > \sigma$) reflections, room temperature. The heterocyclic six-membered ring has an unusual conformation, midway between E and S. The four-membered ring is not planar and is very distorted, the two diagonals being 2·091 (3) and 1·963 (2) Å. The packing of the molecules does not involve any short contacts.

Introduction. Garanti & Zecchi (1984) studied the thermal isomerization of some substituted 3*H*-4,1,2-benzothiadiazines (I). All derivatives give the tricyclic compound (III), whose structure was determined by NMR studies. Only in the case $R_1 = C_6H_5$ and $R_2 = CO_2C_2H_5$ is the title isomer (II) obtained, together with (III). The X-ray study of (II) was undertaken because it was impossible to determine its structure on the basis of spectroscopic techniques.



(II) (I) (III)

$R_1 = H_2C_6H_5$. $R_2 = CO_2C_2H_5$. *p*-$NO_2C_6H_4$

Experimental. D_m by flotation in dilute K_2HgI_4 solution. Yellow prism 0·28 × 0·24 × 0·20 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω-scan technique. Cell constants from setting angles of 25 reflections with $10 < \theta < 14°$. Lorentz and polarization correction, but no absorption correction. No significant variation of intensity in three standard reflections. 3066 independent reflections measured with $\theta < 25°$; range of *hkl*: 0 to 16, 0 to 9, −18 to 18; 2532 with $I > \sigma(I)$ used in calculations. Heavy atoms from *MULTAN* (Germain, Main & Woolfson, 1971), with the exception of C(6), C(10) and C(19) which where obtained from Fourier synthesis as H atoms. Anisotropic heavy atoms, isotropic H atoms, final secondary-extinction parameter $g = 21\,(2) \times 10^{-6}$ (Larson, 1967, equation 3). Full-matrix least-squares refinement on F. $w = 4F_o^2/|\sigma^2(F_o^2) + 0{\cdot}0009F_o^4|$. Final $R = 0{\cdot}045$, $wR = 0{\cdot}043$, $S = 1{\cdot}53$, $\Delta_{\max}/\sigma = 0{\cdot}1$, $\Delta\rho = \pm 0{\cdot}15$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Programs used included the Enraf–Nonius (1979) *Structure Determination Package, ORTEP* (Johnson, 1965), and various in-house programs running on a Gould SEL 32/7780 computer.

Discussion. The final positional parameters and their e.s.d.'s are given in Table 1.* A view of the molecule with the numbering scheme is given in Fig. 1. Table 2 reports bond lengths, bond angles and selected torsion angles involving the heterocycles. Geometrical parameters concerning H atoms are in the expected range. The most interesting feature of the molecule is the conformation of the heterocycles. The ring S,C(1),C(2),N(2),C(4),C(9) has an unusual conformation, midway between E_2 and $^1S_2$, with spherical puckering coordinates (Cremer & Pople, 1975) $Q_t = 0{\cdot}559\,(2)$ Å, $\varphi = 47{\cdot}8\,(2)°$ and $\theta = 61{\cdot}8\,(2)°$. This is in contrast with that found in all phenothiazine derivatives (McDowell, 1976, and references therein), which have a $B_{1,4}$ conformation. The 'excited' situation found in our compound is probably due to the strain-energy minimization of the substituents at C(1), C(2) and C(3). Nevertheless, the bond distances and angles involving the S atom agree well with those found in phenothiazine derivatives. As a consequence of the deformation of this ring, the C(4),C(5),C(6),C(7),C(8),C(9) benzene group deviates significantly from planarity $[Q_t = 0{\cdot}027\,(2)$ Å], assuming a $^1T_3$ conformation. In contrast, the phenyl group bonded at C(2) is planar within experimental error. The four-membered ring, in spite of the N(1)–C(3) double bond, is not planar, with $Q_t = 0{\cdot}0128\,(5)$ Å. The asymmetric force field due to the presence of the phenyl and ethoxycarbonyl groups deforms the internal angles of

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39457 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final coordinates and isotropic thermal parameters*

For non-H atoms $U_{eq} = (\sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j)/6\pi^2$.

	x	y	z	U_{eq} or U_{iso}(Å^2)
S	0·34888 (4)	−0·14834 (7)	−0·03414 (5)	0·0596 (3)
O(1)	0·22023 (12)	0·45556 (18)	0·12926 (10)	0·0575 (7)
O(2)	0·37847 (13)	0·42893 (24)	0·14141 (13)	0·0812 (9)
N(1)	0·16238 (12)	0·17560 (20)	0·02006 (11)	0·0466 (8)
N(2)	0·17907 (11)	0·08188 (19)	−0·04612 (11)	0·0406 (7)
C(1)	0·36533 (15)	0·02443 (27)	0·03587 (15)	0·0497 (10)
C(2)	0·28510 (13)	0·15067 (24)	−0·01177 (13)	0·0409 (8)
C(3)	0·25019 (15)	0·24776 (25)	0·04840 (13)	0·0453 (9)
C(4)	0·15350 (14)	−0·08268 (24)	−0·05752 (13)	0·0396 (8)
C(5)	0·05661 (16)	−0·13146 (28)	−0·07289 (15)	0·0497 (10)
C(6)	0·02756 (18)	−0·28942 (28)	−0·09152 (17)	0·0596 (11)
C(7)	0·09430 (19)	−0·40156 (31)	−0·09676 (19)	0·0640 (12)
C(8)	0·19068 (18)	−0·35613 (28)	−0·08013 (17)	0·0557 (11)
C(9)	0·22218 (15)	−0·19723 (25)	−0·05920 (14)	0·0454 (9)
C(10)	0·44470 (19)	0·04066 (43)	0·11898 (20)	0·0704 (13)
C(11)	0·30005 (14)	0·24454 (23)	−0·08599 (13)	0·0403 (8)
C(12)	0·22083 (18)	0·27091 (27)	−0·17442 (15)	0·0501 (10)
C(13)	0·23584 (22)	0·36413 (30)	−0·23812 (18)	0·0622 (12)
C(14)	0·32935 (23)	0·43189 (32)	−0·21495 (20)	0·0663 (14)
C(15)	0·40872 (21)	0·40621 (32)	−0·12829 (20)	0·0662 (13)
C(16)	0·39447 (17)	0·31304 (29)	−0·06320 (18)	0·0561 (11)
C(17)	0·29096 (17)	0·38638 (28)	0·11110 (15)	0·0535 (10)
C(18)	0·25129 (28)	0·59829 (44)	0·18839 (28)	0·0840 (18)
C(19)	0·15815 (34)	0·66856 (47)	0·18725 (31)	0·0938 (20)
H(5)	0·013 (2)	−0·057 (3)	−0·072 (1)	0·050 (6)
H(6)	−0·038 (2)	−0·322 (3)	−0·098 (1)	0·068 (7)
H(7)	0·074 (2)	−0·513 (3)	−0·107 (2)	0·071 (7)
H(8)	0·239 (2)	−0·433 (3)	−0·079 (1)	0·054 (6)
H(101)	0·495 (2)	−0·048 (3)	0·144 (2)	0·092 (9)
H(102)	0·454 (2)	0·145 (3)	0·153 (1)	0·059 (7)
H(12)	0·156 (2)	0·225 (3)	−0·190 (2)	0·065 (7)
H(13)	0·182 (2)	0·384 (3)	−0·299 (2)	0·073 (8)
H(14)	0·337 (2)	0·495 (3)	−0·257 (2)	0·079 (8)
H(15)	0·473 (2)	0·452 (3)	−0·110 (2)	0·083 (8)
H(16)	0·450 (2)	0·297 (3)	−0·001 (2)	0·068 (7)
H(181)	0·294 (3)	0·566 (5)	0·249 (3)	0·140 (16)
H(182)	0·283 (2)	0·672 (4)	0·166 (2)	0·106 (11)
H(191)	0·170 (2)	0·758 (4)	0·221 (2)	0·097 (10)
H(192)	0·105 (3)	0·693 (4)	0·127 (3)	0·126 (14)
H(193)	0·126 (3)	0·582 (5)	0·214 (2)	0·137 (14)

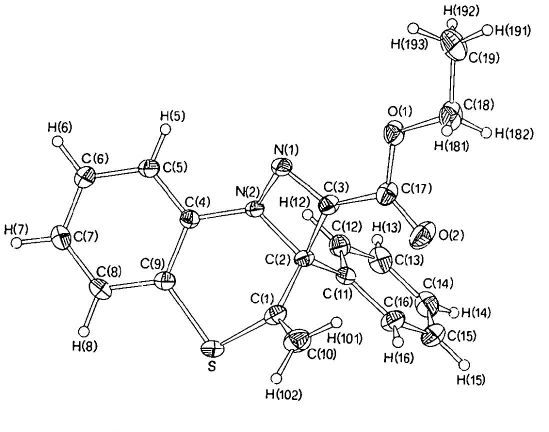

Fig. 1. A drawing of the molecule with the numbering scheme. Thermal ellipsoids for heavy atoms are at the 20% probability level; those of H atoms are not to scale.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

S–C(1)	1·769 (2)	S–C(9)	1·764 (2)
N(1)–N(2)	1·422 (3)	N(1)–C(3)	1·304 (3)
N(2)–C(2)	1·510 (2)	N(2)–C(4)	1·408 (3)
C(1)–C(2)	1·503 (3)	C(1)–C(10)	1·322 (3)
C(2)–C(3)	1·512 (3)	C(2)–C(11)	1·518 (3)
C(3)–C(17)	1·466 (3)	C(4)–C(5)	1·390 (3)
C(4)–C(9)	1·395 (3)	C(5)–C(6)	1·371 (3)
C(6)–C(7)	1·382 (4)	C(7)–C(8)	1·369 (4)
C(8)–C(9)	1·389 (3)	C(11)–C(12)	1·386 (3)
C(11)–C(16)	1·386 (3)	C(12)–C(13)	1·375 (4)
C(13)–C(14)	1·371 (4)	C(14)–C(15)	1·368 (4)
C(15)–C(16)	1·388 (5)	C(17)–O(1)	1·328 (3)
C(17)–O(2)	1·203 (3)	C(18)–O(1)	1·456 (4)
C(18)–C(19)	1·479 (7)		

C(1)–S–C(9)	99·2 (1)	C(17)–O(1)–C(18)	116·6 (2)
N(2)–N(1)–C(3)	92·1 (2)	N(1)–N(2)–C(2)	91·0 (1)
N(1)–N(2)–C(4)	120·2 (2)	C(2)–N(2)–C(4)	125·9 (2)
S–C(1)–C(2)	113·1 (2)	S–C(1)–C(10)	121·8 (2)
C(2)–C(1)–C(10)	125·0 (2)	N(2)–C(2)–C(1)	111·3 (2)
N(2)–C(2)–C(3)	81·0 (2)	N(2)–C(2)–C(11)	113·5 (2)
C(1)–C(2)–C(3)	117·5 (2)	C(1)–C(2)–C(11)	113·5 (2)
C(3)–C(2)–C(11)	115·8 (2)	N(1)–C(3)–C(2)	95·7 (2)
N(1)–C(3)–C(17)	129·3 (2)	C(2)–C(3)–C(17)	134·8 (2)
N(2)–C(4)–C(5)	119·9 (2)	N(2)–C(4)–C(9)	120·8 (2)
C(5)–C(4)–C(9)	119·2 (2)	C(4)–C(5)–C(6)	120·7 (2)
C(5)–C(6)–C(7)	120·0 (3)	C(6)–C(7)–C(8)	120·1 (2)
C(7)–C(8)–C(9)	120·8 (3)	S–C(9)–C(4)	122·4 (2)
S–C(9)–C(8)	118·4 (2)	C(4)–C(9)–C(8)	119·2 (2)
C(2)–C(11)–C(12)	122·0 (2)	C(2)–C(11)–C(16)	119·0 (2)
C(12)–C(11)–C(16)	118·9 (2)	C(11)–C(12)–C(13)	120·4 (2)
C(12)–C(13)–C(14)	120·4 (3)	C(13)–C(14)–C(15)	120·1 (3)
C(14)–C(15)–C(16)	120·1 (3)	C(11)–C(16)–C(15)	120·2 (2)
O(1)–C(17)–C(3)	111·8 (2)	O(1)–C(17)–O(2)	125·6 (2)

C(1)–C(2)–N(2)–C(4)	−16·7 (3)	C(2)–N(2)–C(4)–C(9)	−15·8 (3)
N(2)–C(4)–C(9)–S	7·4 (3)	C(4)–C(9)–S–C(1)	24·7 (2)
C(9)–S–C(1)–C(2)	−54·9 (2)	S–C(1)–C(2)–N(2)	53·9 (2)
S–C(1)–C(2)–C(3)	144·8 (2)	S–C(1)–C(2)–C(11)	−75·6 (2)
C(10)–C(1)–C(2)–C(3)	−39·3 (4)	C(10)–C(1)–C(2)–C(11)	100·3 (3)
N(2)–N(1)–C(3)–C(2)	−4·2 (2)	N(1)–C(3)–C(17)–O(2)	170·2 (3)
C(1)–C(2)–C(3)–C(17)	80·0 (3)	C(11)–C(2)–C(3)–C(17)	−58·7 (3)

the four-membered ring in such a way that the two diagonals became extremely different: 1·963 (2) and 2·091 (3) Å respectively for N(2)···C(3) and N(1)···C(2).

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