Acta Cryst. (1983). C**39**, 1693–1695

Ethyl 3-[4,5-Dimethoxy-2-(3-methyl-2-pyridylsulphamoyl)phenyl]propionate, $C_{19}H_{24}N_2O_6S$

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(*Received* 26 *April* 1983; *accepted* 5 *August* 1983)

Abstract. $M_r = 408{\cdot}47$, triclinic, $P\bar{1}$, $a = 8{\cdot}630\,(5)$, $b = 10{\cdot}490\,(9)$, $c = 11{\cdot}952\,(14)$ Å, $\alpha = 94{\cdot}52\,(5)$, $\beta = 94{\cdot}28\,(4)$, $\gamma = 108{\cdot}44\,(5)^\circ$, $V = 1017{\cdot}47$ Å^3, $Z = 2$, $D_m = 1{\cdot}34$, $D_x = 1{\cdot}33$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}63$ mm^{-1}, $F(000) = 432$, $T = 293$ K. Final $R = 0{\cdot}070$ for 2439 observed reflections. The methoxy groups are nearly coplanar with the phenyl ring [max. deviation from plane 0·34 (1) Å]. There is a possible intramolecular N—H···O hydrogen bond.

Introduction. Derivatives of benzothiazinone have anti-inflammatory activity (Lombardino & Wiseman, 1971) and are known to affect the central nervous system (Sianesi, Redaelli, Magistretti & Massarani, 1973).

Sulphonamides, similar in structure to benzothiazinone, have been synthesized (Camoutsis & Catsoulakos, 1976, 1980; Catsoulakos & Camoutsis, 1980) and are being tested for pharmacological properties.

Crystallographic studies of a series of these compounds are being carried out (Hamodrakas & Filippakis, 1977; Hamodrakas, Filippakis & Sheldrick, 1977; Hamodrakas, Akrigg, Sheldrick & Camoutsis, 1978; Perdikatsis, Catsoulakos & Filippakis, 1979; Panagiotopoulos & Filippakis, 1980; Panagiotopoulos, Filippakis & Catsoulakos, 1980) in attempts to relate structure and activity. The title compound is a member of this series.

Experimental. Crystal 0·07 × 0·08 × 0·60 mm. Enraf–Nonius CAD-4 diffractometer, Ni-filtered Cu $K\alpha$, moving-crystal/moving-counter technique, $2 < 2\theta \leq 140^\circ$. 25 reflections used to measure lattice parameters. Index range −10 to 10(h), −12 to 12(k), −14 to 14(l), 203 used as intensity standard, average count 10167 with $\sigma = 474$. 7737 reflections measured (two hemispheres), of which, after merging ($R_{\mathrm{int}} = 0{\cdot}06$), 2439 had $I > 3{\cdot}0\sigma(I)$. No absorption corrections applied. Structure solved in $P1$ by direct methods using *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). Phase set with lowest value of ψ_o (2·298) gave coordinates for all but four non-H atoms, revealed by subsequent difference Fourier map. 15 H atoms located from difference Fourier maps, remaining nine positions calculated. Refinement by least squares on F; in final cycles space group $P\bar{1}$ adopted, anisotropic temperature factors for non-H atoms, overall scale factor refined anisotropically (Shakked & Rabinovich, 1977); unit weights. Final $R = 0{\cdot}070$. $(\Delta/\sigma)_{\max} = 0{\cdot}04$. $\Delta\rho = -0{\cdot}16$–$0{\cdot}11$ e Å^{-3}. Refinement calculations with *SHELX*76 (Sheldrick, 1976); atomic scattering factors as supplied by the program.

Discussion. Atomic parameters are given in Table 1,* bond distances and angles in Table 2. Fig. 1 is a view of the molecule showing the atom numbering and Fig. 2 shows the molecular packing.

The results of this study are in close agreement with those of related compounds (Hamodrakas *et al.*, 1978; Hamodrakas, Filippakis & Sheldrick, 1977; Hamodrakas & Filippakis, 1977). The ester group, C(13), C(14), O(3), O(4), C(15), is almost planar [max. deviation from the plane 0·032 (5) Å] with dimensions similar to other observations (Hamodrakas *et al.*, 1978; Eliopoulos, Sheldrick & Hamodrakas, 1983). A major difference is in the value of the torsion angle C(14)—O(4)—C(15)—C(16) at 93·6 (9)° (previously observed at 155·9 and 165·8°) which places C(16) 1·293 (11) Å above the ester-group plane.

The propionate side chain, C(12), C(13), C(14), O(4), O(3) [max. deviation from least-squares plane 0·017 (3) Å], is arranged at an angle of 79·1 (3)° to the phenyl ring [torsion angle C(2)—C(12)—C(13)—C(14)

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38796 (19 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. *Fractional atom coordinates* (× 10^4) *for non*-H *atoms with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å^2 × 10^4)

	x	y	z	U_{eq}*
S(1)	−505 (2)	−312 (1)	2163 (1)	440
N(1)	−2383 (5)	−1221 (4)	2044 (3)	474
N(2)	−2969 (5)	−888 (4)	130 (3)	471
O(1)	272 (5)	−602 (4)	3166 (3)	555
O(2)	244 (4)	−444 (4)	1126 (3)	497
O(3)	−4941 (6)	974 (5)	3472 (4)	774
O(4)	−4945 (6)	2465 (6)	4889 (4)	953
O(5)	−228 (5)	5408 (4)	2563 (3)	678
O(6)	962 (5)	4460 (4)	883 (3)	661
C(1)	−467 (6)	1394 (5)	2364 (4)	417
C(2)	−1043 (6)	1899 (5)	3292 (4)	453
C(3)	−997 (7)	3252 (5)	3356 (4)	474
C(4)	−330 (7)	4077 (5)	2542 (4)	480
C(5)	289 (6)	3569 (5)	1636 (4)	478
C(6)	204 (6)	2230 (5)	1534 (4)	438
C(7)	−3422 (7)	−1382 (5)	1119 (4)	481
C(8)	−5138 (7)	−2123 (6)	1147 (5)	531
C(9)	−6158 (7)	−2290 (6)	193 (6)	635
C(10)	−5648 (7)	−1767 (7)	−807 (5)	609
C(11)	−4046 (8)	−1085 (6)	−817 (5)	600
C(12)	−1702 (7)	1057 (6)	4240 (4)	545
C(13)	−2754 (7)	1593 (6)	4980 (4)	566
C(14)	−4311 (8)	1622 (7)	4348 (5)	611
C(15)	−6513 (11)	2532 (11)	4411 (8)	1124
C(16)	−6263 (12)	3593 (11)	3696 (10)	1347
C(17)	−1172 (9)	5896 (6)	3304 (6)	762
C(18)	1667 (9)	3968 (6)	−23 (6)	790
C(19)	−5685 (8)	−2655 (8)	2218 (6)	820

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$(Hamilton, 1959).

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S(1)—N(1)	1·589 (4)	C(1)—C(2)	1·383 (7)
S(1)—O(1)	1·430 (3)	C(1)—C(6)	1·411 (6)
S(1)—O(2)	1·456 (4)	C(2)—C(3)	1·403 (7)
S(1)—C(1)	1·777 (5)	C(2)—C(12)	1·524 (6)
N(1)—C(7)	1·334 (6)	C(3)—C(4)	1·388 (7)
N(2)—C(7)	1·363 (6)	C(4)—C(5)	1·385 (7)
N(2)—C(11)	1·369 (7)	C(5)—C(6)	1·378 (7)
O(3)—C(14)	1·193 (7)	C(7)—C(8)	1·442 (7)
O(4)—C(14)	1·330 (7)	C(8)—C(9)	1·351 (8)
O(4)—C(15)	1·454 (9)	C(8)—C(19)	1·486 (8)
O(5)—C(4)	1·369 (6)	C(9)—C(10)	1·397 (8)
O(5)—C(17)	1·418 (7)	C(10)—C(11)	1·342 (8)
O(6)—C(5)	1·374 (5)	C(12)—C(13)	1·512 (7)
O(6)—C(18)	1·421 (7)	C(13)—C(14)	1·501 (8)
		C(15)—C(16)	1·429 (13)

O(1)—S(1)—C(1)	108·1 (2)	O(5)—C(4)—C(3)	124·2 (5)
O(1)—S(1)—N(1)	107·4 (2)	C(4)—C(5)—C(6)	119·5 (5)
O(2)—S(1)—O(1)	116·6 (2)	O(6)—C(5)—C(4)	116·6 (5)
O(2)—S(1)—C(1)	106·2 (2)	O(6)—C(5)—C(6)	123·8 (5)
O(2)—S(1)—N(1)	111·6 (2)	C(5)—C(6)—C(1)	120·1 (5)
C(1)—S(1)—N(1)	106·4 (2)	N(1)—C(7)—C(8)	119·1 (5)
S(1)—N(1)—C(7)	124·0 (4)	N(1)—C(7)—N(2)	124·1 (5)
C(7)—N(2)—C(11)	123·3 (5)	C(8)—C(7)—N(2)	116·8 (5)
C(14)—O(4)—C(15)	117·8 (6)	C(7)—C(8)—C(9)	117·8 (5)
C(4)—O(5)—C(17)	117·9 (4)	C(7)—C(8)—C(19)	118·4 (5)
C(5)—O(6)—C(18)	117·2 (4)	C(9)—C(8)—C(19)	123·8 (6)
S(1)—C(1)—C(2)	122·3 (4)	C(8)—C(9)—C(10)	123·7 (6)
S(1)—C(1)—C(6)	116·7 (4)	C(9)—C(10)—C(11)	117·6 (5)
C(2)—C(1)—C(6)	120·9 (5)	N(2)—C(11)—C(10)	120·7 (5)
C(1)—C(2)—C(3)	117·8 (4)	C(2)—C(12)—C(13)	115·6 (4)
C(1)—C(2)—C(12)	123·0 (5)	C(12)—C(13)—C(14)	112·9 (5)
C(3)—C(2)—C(12)	119·2 (5)	O(4)—C(14)—C(13)	111·7 (6)
C(2)—C(3)—C(4)	121·3 (5)	O(3)—C(14)—C(13)	125·7 (6)
C(5)—C(4)—O(5)	115·6 (4)	O(3)—O(14)—O(4)	122·6 (6)
C(5)—C(4)—C(3)	120·3 (5)	O(4)—C(15)—C(16)	110·4 (8)

63·5 (6)°], although the value of the torsion angle C(1)—C(2)—C(12)—C(13) is 161·4 (5)°, in disagreement with the other two similar structures (Hamodrakas *et al.*, 1978; Eliopoulos *et al.*, 1983). The high temperature factor of C(16) indicates that this side chain is probably involved in some disorder. The methoxy groups O(5)—C(17) and O(6)—C(18) are almost coplanar with the phenyl ring [torsion angles −14·6 (8) and 2·7 (8)° respectively] with C(17) and C(18) being 0·34 (1) and 0·13 (1) Å from the plane of the ring. This planar arrangement has been observed in more than 60 structures while the O(5)—C(4) and O(6)—C(5) bond lengths of 1·369 (6) and 1·374 (5) Å indicate partial double-bond character and compare well with the average calculated value of 1·36 Å for similar bonds (Hamodrakas, 1974). The tendency of

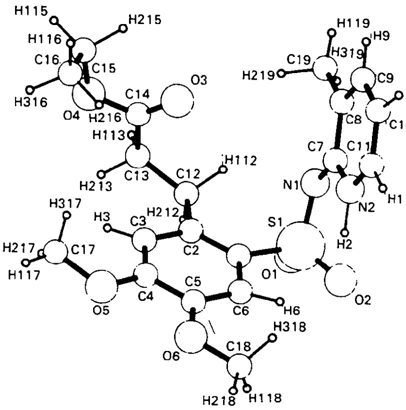


Fig. 1. *PLUTO*78 (Motherwell, 1978) drawing of the molecule showing numbering of the atoms.

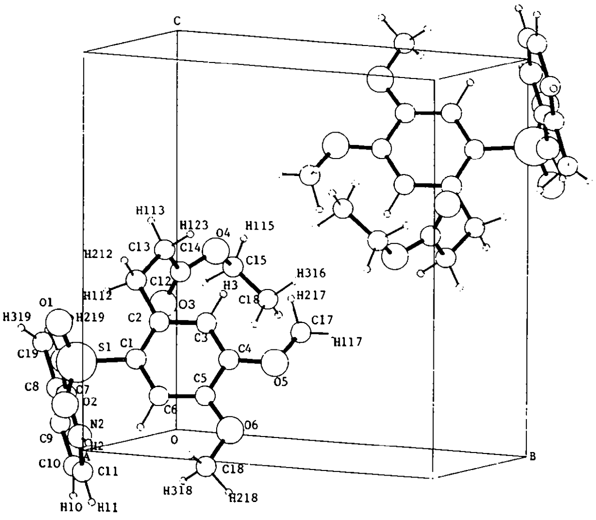
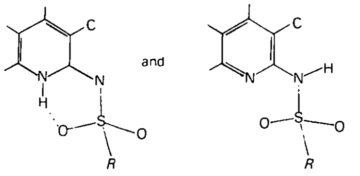


Fig. 2. x-axis projection packing diagram drawn by the program *PLUTO*78.

the methoxy groups to be coplanar with the phenyl ring has resulted in some close contacts between C(17) and C(3), and C(18) and C(6) and the H atoms attached to them, which have been relieved by increase of the angles C(3)—C(4)—O(5) and C(6)—C(5)—O(6) from 120 to 124·2 (5) and 123·8 (5)° respectively.

The tetrahedral coordination around the S atom is distorted, with the O(1)—S(1)—O(2) angle being 116·6 (2)°, larger than the normal tetrahedral value, possibly due to repulsions between the sulphonamide O atoms (Kálmán, Duffin & Kucsman, 1971). The S(1)—O(1) and S(1)—O(2) bond lengths of 1·430 (3) and 1·456 (4) Å indicate π-bond character of over 60% (Cruickshank, 1961), while the S(1)—C(1) and S(1)—N(1) bond lengths of 1·777 (5) and 1·589 (4) Å are very close to values obtained for similar structures (Hamodrakas *et al.*, 1978).

Some structural differences between this structure and others of the same family (Hamodrakas *et al.*, 1978; Eliopoulos *et al.*, 1983) occur, in addition to the position of the methyl group attached to the phenyl ring. The length of the bond N(1)—C(7) [1·334 (6) Å] suggests a possible partial double bond. The final electron density map shows no peaks close to N(1) while a peak with height one third of an electron appears 1·07 (3) Å from the pyridine N(2). This peak, 2·06 (3) Å from O(2), suggests a hydrogen bond [N(2)—H···O(2)]. This unusual situation could be explained by tautomerism of the two forms with the balance shifted in favour of the first form.



In the 4-methyl member of this series of compounds (Eliopoulos *et al.*, 1983), where an intermolecular hydrogen-bond scheme N(1)···H—N(2) was proposed, the hydrogen peak was observed 1·08 Å from N(2).

We wish to thank Dr Ch. Camoutsis for providing the material, Mr D. Akrigg for assisting us with the calculations and diagrams and the Leeds University Computing Service for the provision of computing facilities.

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Acta Cryst. (1983). C**39**, 1695–1697

Structure of 11,12-Dichloro-3,8-bis(2,4,6-trimethylphenyl)-1,4,7,10-tetraoxa-2,9-diazadispiro[4.0.4.2]dodeca-2,8,11-triene (DTDD), $C_{24}H_{22}Cl_2N_2O_4$

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(*Received* 14 *March* 1983; *accepted* 3 *August* 1983)

Abstract. $M_r = 473{\cdot}36$, monoclinic $P2_1/c$, $a = 16{\cdot}661\ (3)$, $b = 9{\cdot}011\ (1)$, $c = 24{\cdot}231\ (7)$ Å, $\beta = 139{\cdot}01\ (1)°$, $Z = 4$, $V = 2386{\cdot}2$ Å^3, $D_x = 1{\cdot}318$, $D_m = 1{\cdot}307$ Mg m^{-3}, m.p. = 448–449 K, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}305$ mm^{-1}, $F(000) = 984$, $T = 293$ K. Final $R = 0{\cdot}056$ for 815 independent non-zero

0108-2701/83/121695-03$01.50