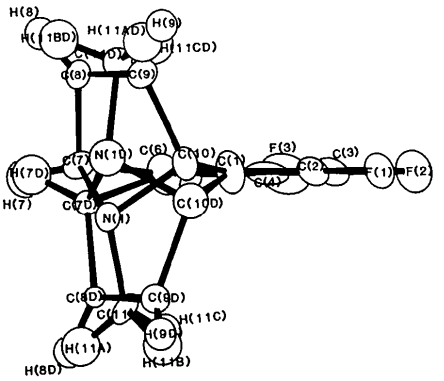

Fig. 2. *ORTEP* drawing of the disordered N(1) molecule. Atoms F(4), H(10) and H(10*D*) are omitted for clarity.

The structure analysis confirms the position of the *N*-methyl group over the benzene ring with a distance from the center of the benzene ring to the methyl carbon atom of 3·608 (8) for C(30) and 3·616 (11) Å for C(11).

As expected, the N(1) and N(2) imine bridge bond angles of 95·0 (7) and 96·0 (4)° are very small for an sp^3-hybridized nitrogen, accounting for the relatively high barrier to nitrogen inversion observed for this compound (Gribble, Easton & Eaton, 1970). Similarly small bond angles of 92·3 (7) and 96° are found for the methano bridge of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropyl-1,4-methanonaphthalene and the epoxy bridge of the photodimer of 1,4-epoxy-1,4-dihydronaphthalene, respectively (Brown & Mason, 1978; Bordner, Stanford & Dickerson, 1970).

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Structures of 2-(5-Amino-1,3,4-thiadiazol-2-yl)benzenesulphonamide (I), $C_8H_8N_4O_2S_2$, and 2-(5-Amino-1,3,4-thiadiazol-2-yl)-*N*-methylbenzenesulphonamide (II), $C_9H_{10}N_4O_2S_2$

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Abstract. (I): $M_r = 256·3$, monoclinic, $P2_1/n$, $a = 14·604$ (5), $b = 14·605$ (6), $c = 5·206$ (3) Å, $\beta = 94·78$ (1)°, $V = 1106·5$ (9) Å^3, $Z = 4$, $D_x = 1·539$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 0·413$ mm^{-1}, $F(000) = 528$, $R = 0·038$ for 1781 observed reflections, $T = 295$ K. (II): $M_r = 270·3$, monoclinic, $P2_1/a$, $a = 21·308$ (8), $b = 13·420$ (6), $c = 8·155$ (2) Å, $\beta = 94·49$ (1)°, $V = 2325$ (1) Å^3, $Z = 8$,

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$D_x = 1{\cdot}545$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}395$ mm^{-1}, $F(000) = 1120$, $R = 0{\cdot}053$ for 3900 observed reflections, $T = 295$ K. The two independent molecules (A and B) in compound (II) have different conformations, the first being an approximate mirror image of the second. Compound (I), the demethylated derivative of (II), exhibits only one of the two conformers. The two samples, chosen among a series of synthetic products believed to possess antiviral activity, are shown to have a different hydrogen-bonding pattern: this feature is correlated to the difference in lipophilic character.

Introduction. In the search for new synthetic molecules with antiviral activity, we have concentrated on a series of 2-(5-amino-1,3,4-thiadiazol-2-yl)benzenesulphonamides (Saramet, 1975; Tonew & Limki, 1974) obtained by reaction between *o*-sulphobenzoic acid imide, P_2S_5 and thiosemicarbazide (De Regis, Orzalesi, Volpato, Cecchetti, Fravolini & Schiaffella, 1980). Both IR and NMR spectra gave signals compatible either with a thiadiazole-type rearrangement of the thiosemicarbazide chain or with an open-chain structure of the thiosemicarbazone type. To resolve this ambiguity, a crystal structure analysis of the two compounds of major pharmacological interest was undertaken.

Experimental. Colourless crystals of both compounds were grown from ethanol at room temperature, dimensions $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}4$ mm (I) and $0{\cdot}15 \times 0{\cdot}25 \times 0{\cdot}50$ mm (II). Philips PW 1100 diffractometer, graphite monochromator, ω–2θ scan, $2° \le \theta \le 26°$, scan width $1{\cdot}20°$ (θ), scan speed $0{\cdot}03$ ° s^{-1}, background measuring time 20 s. Cell parameters from 25 independent reflections ($3 \le \sigma \le 12°$ for both compounds). hkl values respectively -17 to 17, 0 to 18 and 0 to 6 (I), and -28 to 27, 0 to 17 and 0 to 10 (II). Two standard reflections [251 and 362 for (I) and 261 and $\bar{2}52$ for (II)], measured every 124 reflections, no significant change in intensity. Systematic absences $h0l$ for $h+l$ odd and $0k0$ for k odd (I), $h0l$ for h odd and $0k0$ for k odd (II). No absorption correction. (I): 2506 reflections collected, 2174 unique ($R_{int} = 0{\cdot}023$), 1781 with $I > 2{\cdot}5\sigma(I)$ considered observed; (II): 5999 reflections collected, 5399 unique ($R_{int} = 0{\cdot}018$), 3900 with $I > 2{\cdot}5\sigma(I)$ considered observed. 170 parameters refined for (I), 228 for (II). Both structures solved by direct methods using the *SHELX*76 system of programs (Sheldrick, 1976). H atoms located mainly from ΔF maps, the rest placed in calculated positions. Full-matrix least-squares refinement with anisotropic thermal parameters for all heavy atoms (I) and for all heavy atoms of the aminothiadiazole moiety (II). $\sum w(|F_o - F_c|)^2$ minimized with $w = 3{\cdot}266/[\sigma^2(F_o) + 0{\cdot}000229(F_o)^2]$, final $R = 0{\cdot}038$ and $R_w = 0{\cdot}040$ for (I), and $w = 3{\cdot}756/[\sigma^2(F_o) + 0{\cdot}000449(F_o)^2]$, final $R = 0{\cdot}053$ and $R_w = 0{\cdot}061$ for (II). Final difference Fourier excursions $\Delta\rho$ 0·4 (I) and 0·6 (II) e Å^{-3}. $(\Delta/\sigma)_{max} = 0{\cdot}5$ for (I) and 0·9 (II). Atomic scattering factors from *SHELX*. Programs *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell, 1976) for geometrical calculations.

Discussion. The atomic coordinates for the non-H atoms with isotropic or equivalent isotropic thermal factors and bond geometrical values are given in Tables 1 and 2 respectively.*

* Lists of structure factors, anisotropic temperature factors and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39792 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å$^2 \times 10^3$)

$U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}/U_{iso}
Compound (I)				
S(1)	2511 (1)	472 (1)	7323 (1)	40*
C(2)	1340 (2)	296 (2)	6636 (5)	34*
N(3)	1007 (1)	679 (1)	4473 (4)	36*
N(4)	1678 (1)	1118 (1)	3221 (4)	36*
C(5)	2482 (2)	1066 (2)	4444 (5)	32*
C(6)	3321 (2)	1450 (2)	3438 (5)	34*
C(7)	4056 (2)	871 (2)	3081 (6)	48*
C(8)	4822 (2)	1201 (3)	1971 (7)	61*
C(9)	4860 (2)	2094 (3)	1182 (8)	66*
C(10)	4154 (2)	2681 (2)	1555 (6)	52*
C(11)	3387 (2)	2367 (2)	2690 (5)	35*
N(12)	826 (2)	−190 (2)	8153 (5)	53*
S(13)	2503 (1)	3170 (1)	3167 (1)	36*
O(14)	2182 (1)	3004 (1)	5651 (3)	45*
O(15)	2859 (2)	4057 (1)	2645 (4)	53*
N(16)	1660 (2)	2977 (2)	1051 (5)	44*
Compound (II)				
S(1*A*)	751 (1)	2400 (1)	5400 (1)	46*
C(2*A*)	401 (2)	3564 (3)	5362 (4)	37*
N(3*A*)	720 (1)	4253 (2)	4664 (4)	42*
N(4*A*)	1285 (2)	3884 (2)	4143 (4)	43*
C(5*A*)	1366 (2)	2951 (3)	4460 (4)	35*
C(6*A*)	1947 (2)	2376 (3)	4188 (5)	37
C(7*A*)	2235 (2)	1862 (3)	5524 (5)	42
C(8*A*)	2804 (2)	1364 (3)	5395 (5)	49
C(9*A*)	3077 (2)	1349 (3)	3945 (5)	53
C(10*A*)	2794 (2)	1832 (3)	2577 (5)	50
C(11*A*)	2231 (2)	2349 (3)	2701 (5)	40
N(12*A*)	−144 (2)	3746 (2)	6051 (5)	52*
S(13*A*)	1909 (1)	2972 (1)	899 (1)	45*
O(14*A*)	1239 (2)	2838 (2)	768 (4)	56*
O(15*A*)	2267 (2)	2652 (2)	−418 (4)	67*
N(16*A*)	2021 (2)	4153 (3)	1166 (4)	48
C(17*A*)	2662 (3)	4552 (4)	1354 (7)	70
S(1*B*)	−390 (1)	3245 (1)	1441 (1)	53*
C(2*B*)	−774 (2)	4222 (3)	378 (5)	45*
N(3*B*)	−1164 (2)	3935 (2)	−842 (4)	46*
N(4*B*)	−1188 (2)	2904 (2)	−975 (4)	43*
C(5*B*)	−821 (2)	2443 (3)	111 (4)	36*
C(6*B*)	−781 (2)	1355 (3)	337 (4)	34
C(7*B*)	−681 (2)	995 (3)	1940 (5)	43
C(8*B*)	−665 (2)	−22 (3)	2286 (5)	47
C(9*B*)	−753 (2)	−702 (3)	1020 (5)	46
C(10*B*)	−849 (2)	−369 (3)	−584 (5)	40
C(11*B*)	−858 (2)	644 (3)	−943 (4)	34
N(12*B*)	−676 (2)	5179 (3)	821 (6)	71*
S(13*B*)	−963 (1)	954 (1)	−3059 (1)	43*
O(14*B*)	−523 (2)	1717 (2)	−3388 (4)	58*
O(15*B*)	−951 (2)	34 (2)	−3953 (3)	63*
N(16*B*)	−1655 (2)	1417 (3)	−3389 (4)	50
C(17*B*)	−2198 (3)	752 (4)	−3356 (6)	65

* U_{eq} values.

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

	Compound (I)	Compound (II) Molecule *A*	Compound (II) Molecule *B*
S(1)–C(2)	1·737 (2)	1·731 (3)	1·738 (3)
S(1)–C(5)	1·730 (2)	1·737 (3)	1·736 (3)
C(2)–N(3)	1·314 (3)	1·305 (4)	1·300 (4)
C(2)–N(12)	1·338 (3)	1·354 (4)	1·346 (4)
N(3)–N(4)	1·380 (2)	1·400 (4)	1·389 (3)
N(4)–C(5)	1·290 (3)	1·287 (4)	1·289 (4)
C(5)–C(6)	1·482 (3)	1·491 (4)	1·473 (4)
C(6)–C(7)	1·391 (3)	1·389 (4)	1·393 (4)
C(6)–C(11)	1·401 (3)	1·401 (4)	1·414 (4)
C(7)–C(8)	1·388 (4)	1·395 (5)	1·394 (4)
C(8)–C(9)	1·369 (5)	1·360 (5)	1·378 (4)
C(9)–C(10)	1·367 (4)	1·385 (5)	1·381 (4)
C(10)–C(11)	1·387 (3)	1·396 (5)	1·391 (4)
C(11)–S(13)	1·777 (2)	1·778 (3)	1·771 (3)
S(13)–O(14)	1·433 (2)	1·434 (3)	1·431 (2)
S(13)–O(15)	1·430 (2)	1·434 (2)	1·435 (2)
S(13)–N(16)	1·607 (2)	1·615 (3)	1·601 (3)
N(16)–C(17)		1·463 (5)	1·464 (5)
C(2)–S(1)–C(5)	86·7 (1)	87·0 (1)	87·2 (1)
S(1)–C(2)–N(3)	113·7 (2)	114·1 (2)	113·7 (2)
S(1)–C(2)–N(12)	123·2 (2)	122·6 (2)	122·0 (3)
N(3)–C(2)–N(12)	123·1 (2)	123·3 (3)	124·3 (3)
C(2)–N(3)–N(4)	112·1 (2)	111·9 (2)	111·8 (2)
N(3)–N(4)–C(5)	113·1 (2)	112·8 (2)	114·1 (2)
S(1)–C(5)–N(4)	114·4 (2)	114·2 (2)	113·0 (2)
S(1)–C(5)–C(6)	122·3 (2)	120·8 (2)	120·9 (2)
N(4)–C(5)–C(6)	123·3 (2)	124·9 (3)	125·9 (3)
C(5)–C(6)–C(7)	119·2 (2)	117·3 (3)	117·6 (3)
C(5)–C(6)–C(11)	122·6 (2)	124·5 (3)	125·0 (3)
C(7)–C(6)–C(11)	118·1 (2)	118·2 (3)	117·3 (3)
C(6)–C(7)–C(8)	120·2 (3)	120·6 (3)	121·9 (3)
C(7)–C(8)–C(9)	120·7 (3)	120·6 (3)	119·8 (3)
C(8)–C(9)–C(10)	120·3 (3)	120·3 (3)	119·7 (3)
C(9)–C(10)–C(11)	120·0 (3)	119·5 (3)	120·9 (3)
C(6)–C(11)–C(10)	120·7 (2)	120·7 (3)	120·4 (3)
C(6)–C(11)–S(13)	121·6 (2)	122·6 (3)	124·0 (3)
C(10)–C(11)–S(13)	117·6 (2)	116·7 (2)	115·6 (2)
C(11)–S(13)–O(14)	108·1 (1)	108·4 (2)	108·6 (1)
C(11)–S(13)–O(15)	106·9 (1)	106·6 (1)	106·7 (1)
C(11)–S(13)–N(16)	108·2 (1)	107·9 (1)	107·1 (1)
O(14)–S(13)–O(15)	118·5 (1)	119·6 (2)	118·7 (2)
O(14)–S(13)–N(16)	107·4 (1)	105·6 (1)	107·5 (1)
O(15)–S(13)–N(16)	107·4 (1)	108·3 (2)	107·7 (2)
S(13)–N(16)–C(17)		120·0 (3)	118·6 (2)

Fig. 1 is a projection of the molecules of both compounds showing the atomic numbering and Fig. 2 shows the molecular packings.

The results of these investigations are in close agreement with those of related compounds: the thiadiazole ring is planar as in other 1,3,4-thiadiazole derivatives (Mathew & Palenik, 1974; Kornis, Marks & Chidester, 1980); similarly the C–S distances of the same ring are shorter than the usual single bond and longer than a double bond, owing to the high conjugation of the system (Mathew & Palenik, 1974; Flippen, 1972; Downie, Harrison, Raper & Hepworth, 1972; Kornis, Marks & Chidester, 1980).

The S endocyclic angles, 86·7 (1)° in (I) and 87·0 (1) and 87·2 (1)° in (II), are similar to the values found in other 1,3,4-thiadiazole rings. By comparison with other sulphonamides (Mathew & Palenik, 1974, and references therein) the S–C distances are the longest observed up to now, with the exception of acetazolamide, while the S–N and S–O distances fall within the observed range in analogous systems.

The dihedral angle between the thiadiazole and the phenyl ring is 55·7 (1)° for (I) and 52·3 (1) and 33·8 (1)° for (II); the significantly smaller value is

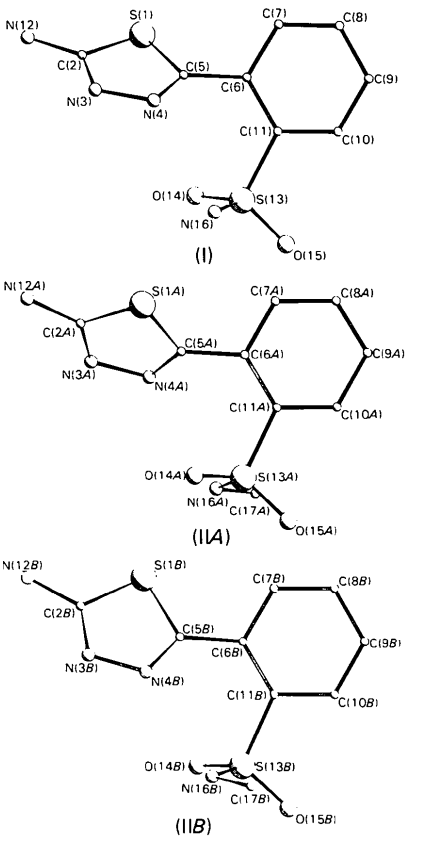

Fig. 1. Projections of the molecules of compounds (I) and (II) perpendicular to the phenyl-ring plane.

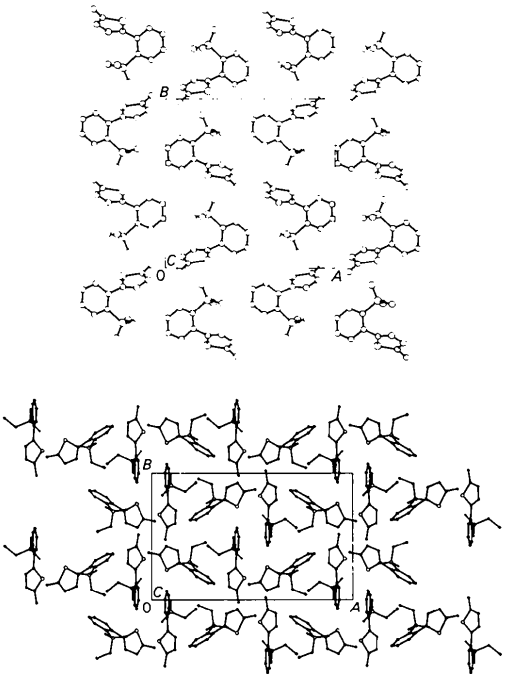

Fig. 2. Molecular packing of compounds (I) (top) and (II) (bottom) viewed down the *c* axis.

Table 3. *Hydrogen bonds (the translation indicates intra- or intermolecular contacts)*

Compound	Bond			Translation
(I)	N(16)–H···N(4)	2·940 (3)Å	154°	—
(II)	N(16*A*)–H···N(4*A*)	3·013 (5)	142	—
(II)	N(16*B*)–H···N(4*B*)	2·923 (5)	99	—
(I)	N(12)–H···N(3)	2·989 (3)	166	$-x,-y,1-z$
(I)	N(12)–H···O(15)	2·997 (4)	154	$0{\cdot}5-x,y-0{\cdot}5,1{\cdot}5-z$
(I)	N(16)–H···O(14)	2·974 (4)	154	$x,y,1+z$
(II)	N(12*A*)–H···N(3*A*)	2·991 (4)	173	$-x,1-y,1-z$
(II)	N(12*A*)–H···O(14*B*)	2·887 (4)	145	$x,y,1+z$

attributed here to packing effects. The increasing deformation of the C(6)–C(11)–S(13) angle, 121·6 (2)° for (I) and 122·6 (3) and 124·0 (3)° for (II), is a logical consequence of this effect, to keep the planarity of the system, while the C(6)–C(11) and C(11)–S(13) bond lengths are not significantly different in all three molecules. The geometry around C(6) is influenced by the same effect.

Table 3 lists the most relevant hydrogen-bond contacts (< 3·05 Å): it is possible to distinguish a different pattern, which we correlate with the more pronounced lipophilic character of compound (II), determined by liquid chromatography.

We thank Professor Giovanni Orzalesi, Istituto di Chimica Farmaceutica, Florence University, for supplying samples of the two compounds.

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Molecular Structure Analysis of Monoamine Oxidase Inhibitors. VII. *cis* and *trans* Isomers of 3-[4-(5-Methoxymethyl-4-methyl-2-oxo-1,3-oxazolidin-3-yl)-phenoxymethyl]benzonitrile, $C_{20}H_{20}N_2O_4$

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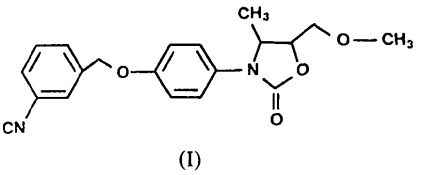
Abstract. $M_r = 352{\cdot}4$, $P2_1/c$, $Z = 4$, $F(000) = 744$, Cu $K\bar{\alpha}$, $\lambda = 1{\cdot}54178$ Å, $T = 293$ K. *cis*('*Z*') isomer: $a = 13{\cdot}491$ (2), $b = 14{\cdot}597$ (3), $c = 9{\cdot}187$ (3) Å, $\beta = 99{\cdot}85$ (2)°, $V = 1782{\cdot}5$ Å^3, $D_x = 1{\cdot}31$ Mg m^{-3}, $\mu = 0{\cdot}670$ mm^{-1}, $R = 0{\cdot}05$, 2010 significant reflections. *trans*('*E*') isomer: $a = 16{\cdot}961$ (2), $b = 14{\cdot}656$ (2), $c = 7{\cdot}525$ (1) Å, $\beta = 97{\cdot}40$ (1)°, $V = 1855{\cdot}0$ Å^3, $D_x = 1{\cdot}26$ Mg m^{-3}, $\mu = 0{\cdot}644$ mm^{-1}, $R = 0{\cdot}03$, 1137 significant reflections. Compared to the demethyl analogue previously studied, the oxazolidinone group of both *cis* and *trans* isomers is more distorted and markedly inclined with regard to the adjacent phenyl. Nevertheless the three O atoms of the 5-methoxymethyl-oxazolidin-2-one moieties remain close by.

Introduction. This work is part of a more general study on the conformational properties of a new series of monoamine oxidase inhibitors (MAOI's) belonging to an oxazolidinone family. Indeed, some of these have been reported as potent antidepressant drugs; their reversibility and their selectivity towards A and B forms of the enzyme depend on the nature of the substituents (Dostert, Strolin-Benedetti & Jalfre, 1982). The two stereoisomers here described have the 4-methyl and 5-methoxymethyl substituents in either *cis* ('*Z*') or *trans* ('*E*') positions.



(I)

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