

Structure of *N'*-(6-Methoxy-3-pyridazinyl)sulfanilamide (Sulfamethoxypyridazine)

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Abstract. $C_{11}H_{12}N_4O_3S$, $M_r = 280.3$, monoclinic, $P2_1/n$, $a = 8.724$ (2), $b = 11.291$ (2), $c = 26.872$ (9) Å, $\beta = 98.00$ (2)°, $V = 2621$ (1) Å³, $Z = 8$, $D_m = 1.434$, $D_x = 1.421$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.245$ mm⁻¹, $F(000) = 1168$, $T = 300$ K, final $R = 0.041$ for 2863 observed reflections. The rotation of the pyridazine rings about the sulfonamide–pyridazine N–C bonds in the two molecules in the asymmetric unit is different. The methoxy groups are coplanar with the pyridazine rings. The packing of the molecules is stabilized by N–H···O and N–H···N hydrogen bonds. The phenyl and pyridazine rings stack independently.

Introduction. Sulfonamides and their different substituted derivatives are well known drugs and are commonly used to control diseases caused by bacterial infections. The antibacterial action of this group of drugs is exerted by the complete inhibition of the dihydropteroate synthase enzyme towards the *p*-amino-benzoate (PAB) substrate. This enzyme catalyses the formation of dihydropteroate from PAB and hydroxymethyl-dihydropteridine pyrophosphate (Brown, 1971) so that its inhibition leads to bacteriostasis. The present compound also belongs to the same group of drugs with a methoxypyridazine ring as a substituent at the *amido* N(1) atom and has a half life of about 40 h. It belongs to the well absorbed and slowly excreted group of sulfa drugs which are heavily protein bound and undergo substantial renal tubular reabsorption leading to longer half lives. The major advantage of this drug is that the formation of crystalluria is very uncommon. This work was undertaken as part of our programme of systematic X-ray structural studies on substituted sulfonamides (Basak, Mazumdar & Chaudhuri, 1982, 1983, 1984; Basak, Chaudhuri & Mazumdar, 1984) with a view to study the effect of substitution on the molecular geometries and conformations of the molecules with the ultimate objective of having a better insight into their activity at the molecular level.

Experimental. Transparent, rectangular parallelepipeds grown from acetone at room temperature, density by

flotation (KI), crystal size: 0.40 × 0.35 × 0.15 mm, symmetry from oscillation and Weissenberg photographs, $P2_1/n$ (systematic absences: $0k0$, k odd; $h0l$, $h + l$ odd); Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, 25 high-angle reflections in the range $17 \leq \theta \leq 20^\circ$ used to measure and refine the cell parameters. 3647 unique reflections ($2 \leq \theta \leq 25^\circ$, $-9 \leq h \leq 9$, $0 \leq k \leq 12$, $0 \leq l \leq 29$) measured, 2863 observed with $I \geq 2.5\sigma(I)$, corrected for Lp; absorption correction not applied; three intensity control reflections ($\bar{2}73$, 536 and $\bar{4}, 5, 11$) monitored every hour of exposure, intensity variation (<2%) was corrected for. Structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) with 499 E values ≥ 1.475 ; phase set with highest combined figure of merit resulted in all but three of the non-H atoms being located from a subsequent ΔF map; all 24 H atoms were located from three successive ΔF maps; anisotropic full-matrix refinement based on F using *SHELX76* (Sheldrick, 1976) with H atoms refined isotropically resulted in a final $R = 0.041$, $wR = 0.052$, $R_{\text{all}} = 0.078$, $S = 1.963$, $w = 1/\sigma^2(|F_o|) + 0.018357 \times (|F_o|)^2$, where $\sigma(|F_o|)$'s were based on counting statistics; 439 parameters refined, max. shift/e.s.d. <0.02; $\Delta\rho$ excursions in final ΔF synthesis were -0.20 to $+0.25$ e Å⁻³; scattering factors of *SHELX76* used.*

Discussion. Fig. 1 is a perspective diagram of the two molecules, *A* and *B*, in the asymmetric unit together with the atomic numbering scheme. The final atomic parameters are listed in Table 1. The intramolecular bond lengths and bond angles together with some selected torsion angles are listed in Table 2.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, non-bonded contacts and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43465 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The S—O distances, except S(*B*)—O(2)*B*, which is slightly shorter than the others, indicate a π -bond character of over 60% (Cruickshank, 1961). The angular disposition of the bonds about the S atoms, in both molecules *A* and *B*, deviates significantly from that of a regular tetrahedron with the largest deviations in O—S—O and one of the O—S—N angles. The significant

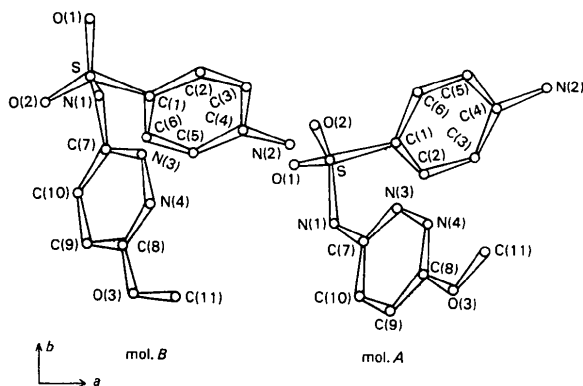


Fig. 1. Perspective view of the molecule down the *c* axis with atomic numbering scheme.

Table 1. Fractional atomic coordinates and equivalent isotropic values of the anisotropic thermal parameters for non-H atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{\AA}^2)$
S(<i>A</i>)	0.69471 (9)	0.81536 (7)	0.43439 (3)	0.0411 (3)
O(1) <i>A</i>	0.5928 (3)	0.8060 (2)	0.3873 (1)	0.050 (1)
O(2) <i>A</i>	0.6486 (3)	0.8920 (2)	0.4713 (1)	0.056 (1)
C(1) <i>A</i>	0.8784 (3)	0.8569 (3)	0.4221 (1)	0.037 (1)
C(2) <i>A</i>	0.9586 (4)	0.7871 (3)	0.3928 (1)	0.045 (1)
C(3) <i>A</i>	1.0997 (4)	0.8232 (3)	0.3809 (1)	0.051 (1)
C(4) <i>A</i>	1.1612 (4)	0.9331 (3)	0.3983 (1)	0.047 (1)
C(5) <i>A</i>	1.0776 (4)	1.0025 (3)	0.4275 (1)	0.053 (1)
C(6) <i>A</i>	0.9389 (4)	0.9651 (3)	0.4391 (1)	0.047 (1)
N(2) <i>A</i>	1.2990 (4)	0.9731 (5)	0.3850 (3)	0.074 (2)
N(1) <i>A</i>	0.7080 (4)	0.6786 (2)	0.4534 (1)	0.050 (1)
C(7) <i>A</i>	0.7938 (3)	0.6384 (3)	0.4985 (1)	0.043 (1)
N(3) <i>A</i>	0.8839 (4)	0.7141 (3)	0.5249 (1)	0.057 (1)
N(4) <i>A</i>	0.9696 (4)	0.6784 (3)	0.5687 (1)	0.059 (1)
C(8) <i>A</i>	0.9571 (5)	0.5693 (3)	0.5825 (1)	0.057 (1)
C(9) <i>A</i>	0.8643 (5)	0.4855 (3)	0.5557 (1)	0.065 (1)
C(10) <i>A</i>	0.7794 (4)	0.5192 (3)	0.5121 (1)	0.054 (1)
O(3) <i>A</i>	1.0393 (4)	0.5320 (3)	0.6264 (1)	0.082 (1)
C(11) <i>A</i>	1.1297 (8)	0.6198 (6)	0.6565 (2)	0.088 (2)
S(<i>B</i>)	0.36265 (9)	0.67361 (8)	0.27855 (3)	0.0483 (3)
O(1) <i>B</i>	0.3535 (3)	0.7996 (2)	0.2820 (1)	0.062 (1)
O(2) <i>B</i>	0.2363 (3)	0.6093 (3)	0.2522 (1)	0.065 (1)
C(1) <i>B</i>	0.5301 (4)	0.6327 (3)	0.2541 (1)	0.045 (1)
C(2) <i>B</i>	0.6694 (4)	0.6887 (3)	0.2702 (2)	0.060 (1)
C(3) <i>B</i>	0.8010 (4)	0.6569 (4)	0.2519 (1)	0.059 (1)
C(4) <i>B</i>	0.7978 (4)	0.5669 (3)	0.2161 (1)	0.052 (1)
C(5) <i>B</i>	0.6582 (4)	0.5114 (4)	0.2007 (1)	0.067 (1)
C(6) <i>B</i>	0.5249 (4)	0.5439 (4)	0.2191 (1)	0.061 (1)
N(2) <i>B</i>	0.9282 (4)	0.5370 (4)	0.1968 (2)	0.081 (2)
N(1) <i>B</i>	0.3838 (3)	0.6314 (3)	0.3377 (1)	0.047 (1)
C(7) <i>B</i>	0.4121 (4)	0.5132 (3)	0.3541 (1)	0.045 (1)
N(3) <i>B</i>	0.5124 (3)	0.5057 (2)	0.3954 (1)	0.049 (1)
N(4) <i>B</i>	0.5415 (4)	0.3988 (3)	0.4185 (1)	0.055 (1)
C(8) <i>B</i>	0.4713 (5)	0.3052 (3)	0.3982 (2)	0.059 (1)
C(9) <i>B</i>	0.3669 (6)	0.3091 (4)	0.3532 (2)	0.074 (2)
C(10) <i>B</i>	0.3353 (5)	0.4148 (4)	0.3312 (1)	0.063 (1)
O(3) <i>B</i>	0.5019 (4)	0.1997 (2)	0.4203 (1)	0.076 (1)
C(11) <i>B</i>	0.6160 (6)	0.1977 (4)	0.4649 (2)	0.077 (2)

Table 2. Bond distances (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$)

	<i>A</i>	<i>B</i>		<i>A</i>	<i>B</i>
S—O(1)	1.446 (3)	1.428 (2)	C(4)—N(2)	1.377 (6)	1.357 (5)
S—O(2)	1.416 (3)	1.423 (3)	N(1)—C(7)	1.408 (4)	1.416 (5)
S—C(1)	1.745 (3)	1.745 (4)	C(7)—N(3)	1.302 (4)	1.317 (4)
S—N(1)	1.625 (2)	1.645 (3)	C(7)—C(10)	1.405 (5)	1.395 (5)
C(1)—C(2)	1.373 (4)	1.385 (5)	N(3)—N(4)	1.364 (4)	1.365 (4)
C(2)—C(3)	1.376 (5)	1.359 (5)	N(4)—C(8)	1.295 (5)	1.302 (5)
C(3)—C(4)	1.406 (5)	1.397 (5)	C(8)—C(9)	1.381 (5)	1.410 (7)
C(4)—C(5)	1.386 (5)	1.381 (5)	C(9)—C(10)	1.351 (4)	1.343 (6)
C(5)—C(6)	1.358 (5)	1.375 (5)	C(8)—O(3)	1.359 (4)	1.341 (4)
C(6)—C(1)	1.383 (5)	1.371 (5)	O(3)—C(11)	1.443 (7)	1.448 (6)
C(1)—S—N(1)	106.7 (2)	107.4 (2)	C(3)—C(4)—N(2)	120.6 (3)	120.4 (3)
C(1)—S—O(1)	108.8 (2)	110.2 (2)	C(5)—C(4)—N(2)	120.6 (4)	121.6 (3)
C(1)—S—O(2)	109.0 (2)	108.0 (2)	S—N(1)—C(7)	125.6 (2)	124.4 (2)
O(1)—S—N(1)	102.3 (1)	103.0 (2)	N(1)—C(7)—C(10)	118.5 (3)	124.1 (3)
O(1)—S—O(2)	117.2 (2)	119.6 (2)	N(1)—C(7)—N(3)	117.7 (3)	112.9 (3)
O(2)—S—N(1)	112.0 (2)	107.9 (2)	N(3)—C(7)—C(10)	123.8 (3)	122.8 (3)
S—C(1)—C(6)	119.6 (2)	120.1 (3)	C(7)—N(3)—N(4)	119.5 (3)	120.0 (3)
S—C(1)—C(2)	120.6 (2)	120.4 (3)	N(3)—N(4)—C(8)	118.0 (3)	118.7 (3)
C(1)—C(2)—C(3)	120.5 (3)	121.0 (3)	N(4)—C(8)—C(9)	124.7 (3)	122.9 (3)
C(2)—C(3)—C(4)	119.8 (3)	120.3 (3)	C(8)—C(9)—C(10)	118.0 (9)	118.3 (4)
C(3)—C(4)—C(5)	118.7 (3)	117.9 (3)	C(9)—C(10)—C(7)	115.9 (3)	117.2 (4)
C(4)—C(5)—C(6)	120.7 (3)	121.7 (3)	C(9)—C(8)—O(3)	116.1 (3)	118.2 (4)
C(5)—C(6)—C(1)	120.7 (3)	119.5 (3)	N(4)—C(8)—O(3)	119.2 (3)	118.8 (4)
C(6)—C(1)—C(2)	119.7 (3)	119.5 (3)	C(8)—O(3)—C(11)	117.1 (4)	116.9 (3)
C(1)—S—N(1)—C(7)		66.5 (3)		<i>B</i>	−57.7 (3)
O(2)—S—N(1)—C(7)		−52.8 (3)			58.5 (3)
O(1)—S—N(1)—C(7)		−179.2 (3)			−174.1 (3)
O(2)—S—C(1)—C(2)		171.1 (3)			175.0 (3)
O(1)—S—C(1)—C(2)		−59.9 (3)			42.7 (4)
O(2)—S—C(1)—C(6)		−13.5 (3)			−5.7 (3)
O(1)—S—C(1)—C(6)		115.5 (3)			−137.9 (3)
N(1)—S—C(1)—C(6)		−134.7 (3)			110.5 (3)
N(1)—S—C(1)—C(2)		49.9 (3)			−68.9 (3)
S—N(1)—C(7)—N(3)		−7.9 (5)			140.3 (3)
S—N(1)—C(7)—C(10)		173.0 (3)			−43.6 (5)
N(3)—N(4)—C(8)—O(3)		−178.9 (3)			178.7 (3)
N(4)—C(8)—O(3)—C(11)		3.4 (6)			−1.8 (6)
C(9)—C(8)—O(3)—C(11)		−176.3 (4)			176.7 (4)

widening of the O—S—O angles from the ideal tetrahedral value is the result of the non-bonding interactions between the short S—O bonds (Cotton & Stokley, 1970). The deviations from ideal geometry of the aminophenyl rings can be attributed to the effects of substituents (Domenicano, Vaciago & Coulson, 1975).

The S—N and S—C bond distances in both molecules, *A* and *B*, are shorter than the expected single-bond distances; this shortening can be attributed to $d\pi-p\pi$ interactions involving the neighbouring atoms (Cotton & Stokley, 1970). The partial double-bond character of the S—N bond in molecule *A* is more significant than that in molecule *B*. This is evident from the shorter S—N bond length and larger differences in the two O—S—N angles in molecule *A* (Kálmán, Czugler & Argay, 1981).

The dimensions of the pyridazine rings of the two molecules *A* and *B* compare well amongst themselves. The N—N bond distances in the pyridazine rings show bond orders of less than 1.5 (Burke-Laing & Laing, 1976). This feature is common to those structures where either one or both N atoms of the pyridazine rings are two coordinated (Otterson, 1973, 1974, 1975; Otterson & Seff, 1973). The distribution of the other (N—C, C—C) bond distances shows that out of the two

possible resonating forms I and II (Burke-Laing & Laing, 1976) the second form is dominant in the present structure.



The phenyl and pyridazine rings do not deviate significantly from planarity; the maximum deviations are those of the N(3)*B* atom and the C(7)*B* and C(9)*B* atoms of the pyridazine ring of molecule *B* which deviate by 0.009 (3), -0.009 (3) and 0.017 (5) Å, respectively, from the least-squares plane of the ring. The S atom in molecule *B* is almost coplanar with [0.016 (1) Å] while in molecule *A* it is 0.099 (1) Å from the least-squares planes of the corresponding phenyl rings. The dihedral angles between the phenyl and pyridazine rings are 89.5 (1) and 77.5 (1)° in *A* and *B*, respectively. The planes defined by the S, N(1), C(7) atoms are almost perpendicular to the phenyl rings [the dihedral angles are 91.3 (2)° in *A* and 92.3 (2)° in *B*], similar to that observed in sulfamethazine (Basak *et al.*, 1983), sulfapyridine (Basak, Chaudhuri & Mazumdar, 1984) and sulfacetamide (Basak *et al.*, 1982).

The asymmetry in the exocyclic angles at the point of substitution, C(8), of the methoxy group is a consequence of the tendency of this group to be coplanar with the ring, owing to conjugation (Domiano, Nardelli, Balsamo, Macchia & Macchia, 1979).

The conformation of the molecules can be described by means of the torsion angles about the C(1)–S, S–N(1) and N(1)–C(7) central bonds. In each molecule one of the sulfonyl oxygens, O(1), is synclinal while the other, O(2), is antiperiplanar to the phenyl ring. Also, the O(2) atom, which is involved in the larger O–S–N angle, is synclinal to C(7). The C(1)–S–N(1)–C(7) torsion angles lie almost within the clustering range of $|\epsilon_2| = 60\text{--}90^\circ$ found for this torsion in *N*-substituted arylsulfonamides (Kálmán *et al.*, 1981). From the torsion angles it has been observed that the only significant conformational difference between the two crystallographically independent molecules is the difference in rotation about the C(1)–S and N(1)–C(7) bonds. The torsion angles $X\text{--}C(1)\text{--}S\text{--}N(1)$ [$X = C(2)$ or C(6)] for molecule *A* lie outside the clustering range of $|\epsilon_1| = 70\text{--}120^\circ$ found in *N*-substituted arylsulfonamides (Kálmán *et al.*, 1981) while those in molecule *B* are close to this range. Similarly, the conformational difference between the two molecules about the N(1)–C(7) bonds involves almost a half rotation about this bond. The methoxy groups in both molecules *A* and *B* have identical conformations about the C(8)–O(3) central bonds with the methyl C(11) atom turned towards the pyridazine N(4) atom.

The crystal structure projected down the *b* axis is illustrated in Fig. 2. As in the structures of sulfamethazine (Basak *et al.*, 1983) and sulfapyridine (Basak, Chaudhuri & Mazumdar, 1984), stacking of like rings is also observed in the present structure. The molecular packing is stabilized by a network of intermolecular N–H...N and N–H...O hydrogen bonds. The aryl amino and amido N atoms are the donor atoms while the pyridazine N and sulfonyl and methoxy O atoms are the acceptor atoms in these hydrogen bonds. One of the type *A* aryl amino H atoms, besides being involved in an N–H...O(sulfonyl) bond with another type *A* molecule, has a second weaker N–H...O(sulfonyl) contact with a type *B* molecule indicating the possibility of a bifurcated hydrogen bond; the angle subtended by

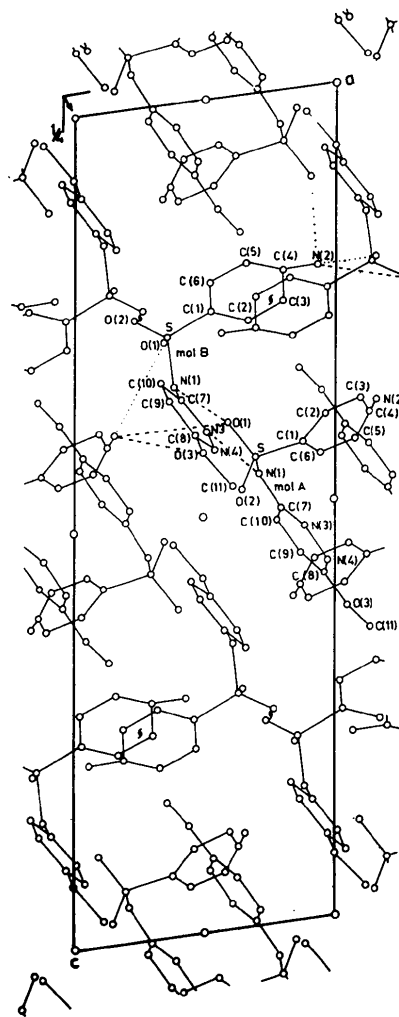


Fig. 2. The packing of the molecules as seen in projection down the *b* axis. Dashed lines indicate hydrogen bonds and dotted lines indicate hydrogen-bond-like contacts.

the two acceptor atoms, O(1)A and O(1)B, at the H atom is 76 (1)° (Jeffrey & Maluszynska, 1981). An N(aryl)—H...O(sulfonyl) contact between a type B aryl amino group and a type A sulfonyl O atom could also be a possible weak hydrogen-bond-like contact if allowance is made for the fact that the H atom appears to have refined to a position too close to the N atom. The geometrical details of the hydrogen bonds and the possible hydrogen-bond-like contacts and their symmetry codes are as follows:

A—H...B	A—H (Å)	A...B (Å)	H...B (Å)	∠A—H...B (°)
N(1)A—H(1)A...N(3)B ⁱ	0.90 (4)	2.900 (4)	2.01 (4)	170 (4)
N(2)A—H(2)A...O(1)A ⁱⁱ	0.83 (6)	3.176 (5)	2.59 (6)	129 (5)
N(2)A—H(2)A...O(1)B ^{ii*}	0.83 (6)	3.477 (8)	2.71 (6)	155 (5)
∠O(1)A ⁱⁱ ...H(2)A...O(1)B ⁱⁱ = 76 (1)°				
N(2)A—H(2)A...O(3)B ⁱⁱⁱ	0.93 (5)	3.180 (6)	2.34 (5)	149 (4)
N(1)B—H(1)B...O(1)A ⁱ	0.73 (4)	2.883 (4)	2.16 (4)	170 (4)
N(2)B—H(2)B...O(2)B ⁱⁱ	0.83 (5)	2.999 (5)	2.17 (5)	171 (4)
N(2)B—H(2)B...O(1)A ^{iv*}	0.64 (5)	3.439 (5)	2.80 (5)	172 (5)

Symmetry code: (i) x, y, z ; (ii) $x+1, y, z$; (iii) $x+1, y+1, z$; (iv) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

* Possible hydrogen-bond-like contacts.

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Structure of a Condensation Product of Isopropylidenemalononitrile under Basic Conditions, 5-Amino-3-methoxy-1,8,8-trimethyl-2-azabicyclo[2.2.2]octa-2,5-diene-4,6-dicarbonitrile

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Abstract. C₁₃H₁₆N₄O, $M_r = 244.3$, triclinic, $P\bar{1}$, $a = 12.541$ (2), $b = 13.404$ (3), $c = 8.733$ (1) Å, $\alpha = 93.93$ (2), $\beta = 90.44$ (3), $\gamma = 63.17$ (2)°, $V = 1306.5$ Å³, $Z = 4$, $D_m = 1.242$, $D_x = 1.241$ g cm⁻³, Mo K α , $\lambda = 0.71069$ Å, $\mu = 0.897$ cm⁻¹, $F(000) = 520$, room temperature, final $R = 0.052$ for 2487 reflections [$|F_o| > 2.5\sigma(|F_o|)$]. A condensation product obtained from isopropylidenemalononitrile was determined to be a 2-azabicyclo[2.2.2]octane derivative. There are two crystallographically independent molecules in the unit cell, which are very similar. The

main ring of the molecule has a bridged dihydropyridine skeleton with a short C=N bond and a long C—C(NH₂) bond. The molecules are held together by hydrogen bonding to form chains along the a axis.

Introduction. Alkylidenemalononitriles undergo anomalous self-condensation in the presence of methoxide ion to give a product as shown below (Igarashi, Nakano, Takezawa, Wantanabe & Sato, 1987); the products (except those obtained from cycloalkylidenemalononitriles) degrade to substituted pyridine