Table 2. *Bond lengths* (Å) *and bond angles* (°) *for* $C_{10}H_{11}F_3O_2S$

S–C(3)	1·804 (3)	S–C(4)	1·832 (4)
F(1)–C(1)	1·339 (3)	F(2)–C(1)	1·342 (4)
F(3)–C(1)	1·344 (4)	O(1)–C(2)	1·404 (4)
O(1)–H(1)	0·789 (34)	O(2)–C(2)	1·402 (4)
O(2)–H(2)	0·741 (26)	C(1)–C(2)	1·524 (4)
C(2)–C(3)	1·535 (4)	C(4)–C(5)	1·484 (5)
C(5)–C(6)	1·391 (4)	C(5)–C(10)	1·397 (4)
C(6)–C(7)	1·370 (6)	C(7)–C(8)	1·378 (7)
C(8)–C(9)	1·381 (5)	C(9)–C(10)	1·376 (6)

C(3)–S–C(4)	102·7 (2)	C(2)–O(1)–H(1)	101·6 (29)
C(2)–O(2)–H(2)	105·6 (24)	F(1)–C(1)–F(2)	107·2 (2)
F(1)–C(1)–F(3)	107·0 (3)	F(2)–C(1)–F(3)	106·9 (3)
F(1)–C(1)–C(2)	111·8 (3)	F(2)–C(1)–C(2)	111·2 (3)
F(3)–C(1)–C(2)	112·3 (2)	O(1)–C(2)–O(2)	112·5 (2)
O(1)–C(2)–C(1)	105·2 (3)	O(2)–C(2)–C(1)	108·1 (2)
O(1)–C(2)–C(3)	112·2 (2)	O(2)–C(2)–C(3)	108·3 (3)
C(1)–C(2)–C(3)	110·5 (2)	S–C(3)–C(2)	112·4 (2)
S–C(4)–C(5)	114·7 (2)	C(4)–C(5)–C(6)	120·8 (3)
C(4)–C(5)–C(10)	120·6 (3)	C(6)–C(5)–C(10)	118·5 (3)
C(5)–C(6)–C(7)	120·9 (3)	C(6)–C(7)–C(8)	120·1 (3)
C(7)–C(8)–C(9)	120·1 (4)	C(8)–C(9)–C(10)	120·0 (4)
C(5)–C(10)–C(9)	120·4 (3)		

Hydrogen-bonding dimensions

O(1)···O(2^i)	2·851 (4)	O(1)···S	2·981 (3)
O(2^i)–H(2^i)···O(1)	172 (3)	O(1)–H(1)···S	135 (2)
H(2^i)···O(1)	2·11 (3)	H(1)···S	2·37 (2)

Symmetry code: (i) 1–*x*, –*y*, 2–*z*.

thioether hydrogen bonds with an amino acid in juvenile hormone esterase.

The inability to isolate a ketone structure provides further evidence that these compounds exist predominantly in the hydrated state. Although the X-ray structure presented here is likely to approximate the ultimate structure of the inhibitor in the catalytic site, it is not known if the inhibitor approaches the enzyme as the abundant hydrated form or the more substrate-like but rare carbonyl compound.

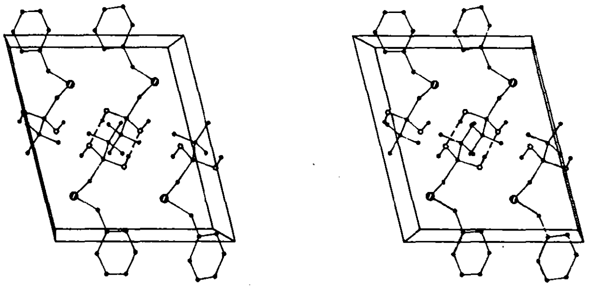

Fig. 2. Stereoview of the molecular packing as viewed down **b**. S atoms are shown as shaded circles, O atoms as open circles, and the remaining atoms as solid circles.

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Heterocyclic Tautomerism. III.* The Structure of the Product of Dimerization of 2-Pyridylacetonitrile

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Abstract. (*E*)-3-Amino-2,4-di(2-pyridyl)-2-butenenitrile, $C_{14}H_{12}N_4$, $M_r = 236·3$, orthorhombic, *F*2*dd*, $a = 4·693\ (1)$, $b = 20·023\ (5)$, $c = 49·636\ (21)$ Å, $V = 4664$ Å^3, $Z = 16$, $D_m = 1·33$, $D_x = 1·34$ Mg m^{-3}, Mo *Kα*, $\lambda = 0·71069$ Å, $\mu = 0·079$ mm^{-1}, $F(000) = 1984$, $T = 140$ K, $R = 0·037$ for 1195

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* Part II. O'Connell, Ramsay & Steel (1985).

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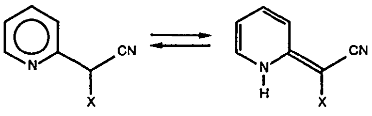
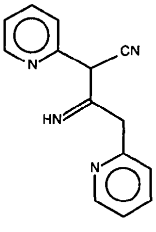
independent observed reflections. The molecule exists as the enamino tautomer and possesses an intramolecular hydrogen bond between an amino proton and pyridyl nitrogen and an intermolecular hydrogen bond between the other amino proton and the other pyridyl nitrogen of an adjacent molecule. The C=C bond is significantly lengthened [1·382 (3) Å] due to through-conjugation, but there is very little twisting about this bond, which is held planar by the intramolecular hydrogen bond.

Introduction. The tautomerism of 2-cyanomethylpyridine derivatives has been the subject of a number of studies (Elguero, Marzin, Katritzky & Linda, 1976). Whereas 2-pyridylacetonitrile (1) itself exists as the CH tautomer (1*A*), 2-pyridylmalononitrile (2) and 2-pyridylcyanoacetamide (3) and derivatives exist as the NH tautomers (*B*) (Ghosh & Ternai, 1972; Junetk, Wolfbeis, Sprintschnik & Wolny, 1977; Sharanin, Baskakov, Abramenko, Putsykin, Nazarova & Vasilev, 1984).

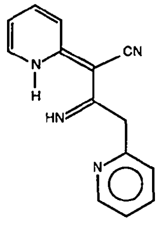


(*A*) (*B*)

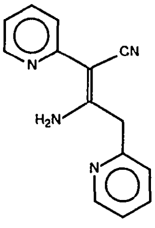
(1) X = H
(2) X = CN
(3) X = CONH$_2$



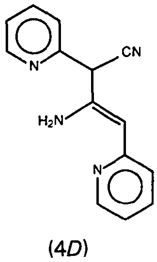
(4*A*)



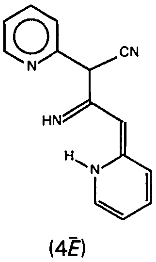
(4*B*)



(4*C*)



(4*D*)



(4*E*)

2-Pyridylacetonitrile (1) has been reported to dimerize in the presence of sodium ethoxide to a product which was assigned structure (4*C*) on the basis of limited spectroscopic data (Gutsche & Voges, 1967). Such a molecule could exist in a number of tautomeric forms (4*A*–4*E*), each of which could exist as more than one geometrical isomer. In order to determine the exact structure of (4) and to examine the hydrogen bonding indicated by infrared spectroscopy, a single-crystal X-ray structure determination was carried out.

Experimental. 2-Pyridylacetonitrile (Aldrich) was dimerized according to the literature procedure (Gutsche & Voges, 1967) and recrystallized from methanol to give (4) as colourless needles, m.p. 399–400 K (lit. m.p. 397–399 K), ^{1}H NMR (300 MHz) d_6-Me$_2$SO δ 4·14, CH$_2$; 7·44, H3′; 7·88, H4′; 7·19, H5′; 8·57, H6′; 7·51, H3″; 7·91, H4″; 7·41, H5″; 8·65, H6″; 8·32 and 10·71, NH$_2$. ^{13}C NMR d_6-Me$_2$SO δ 121·42, C1; 76·29, C2; 162·72, C3; 43·50, C4; 156·37 and 156·23, C2′ and C2″; 118·56, C3′; 136·97, C4′; 118·27, C5′; 147·02, C6′; 122·85, C3″; 136·89, C4″; 122·08, C5″; 149·09, C6″.

Crystal size 0·54 × 0·16 × 0·15 mm, D_m by flotation in aqueous potassium iodide solution. Nicolet *R*3*m* diffractometer; lattice parameters from 25 reflections with $2\theta > 20°$; ω data collection for $3 < 2\theta < 55°$, index ranges: *h* 0/6, *k* 0/26, *l* 0/64. Standard reflections: $20\bar{2}$, 080, 0,0,20 (2% intensity variation) measured every 100 reflections. 1499 unique reflections measured, 1195 observed reflections $[I > 3\sigma(I)]$. Corrections for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods and refined on $|F|$ by blocked-cascade least-squares procedures. All non-hydrogen atoms anisotropic, H atoms in calculated positions with isotropic thermal parameters equal to the isotropic equivalent of the carrier atoms (C—H = 0·96 Å) except for the NH$_2$ hydrogens which were located from a difference Fourier synthesis and their positions refined. $w^{-1} = [\sigma^2(F) + g(F)^2]$. $R = 0·037$, $wR = 0·048$, $g = 0·0012$, $S = 1·00$, 168 parameters, $(\Delta/\sigma)_{\max}$ 0·059, $(\Delta\rho)_{\max} = 0·15$, $(\Delta\rho)_{\min} = -0·18$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations, including diagrams, on a Nova 4X computer using *SHELXTL* (Sheldrick, 1983).

Discussion. Full assignments for the ^{1}H and ^{13}C NMR spectra of (4) are given in the *Experimental* section, with the atom labelling the same as for the crystal structure described below. The ^{1}H NMR spectrum was assigned with the aid of homonuclear decoupling experiments, with the pyridine rings distinguished by NOE difference spectroscopy by means of mutual NOE enhancements between the CH$_2$ protons and H3″. The ^{13}C NMR spectrum was unambiguously assigned by ^{1}H–^{13}C heteronuclear two-dimensional correlation spectroscopy (Bax & Morris, 1981). These spectra support the previously proposed (Gutsche & Voges, 1967) structure (4*C*) for this compound in solution.

The crystal structure of (4) is shown in Fig. 1 along with the atom labelling. Tables 1 and 2† list final atom coordinates, bond lengths and bond angles, with estimated standard deviations in parentheses. The structure in the solid state is thus confirmed as the enamino tautomer (4*C*), *viz.* (*E*)-3-amino-2,4-di(2-pyridyl)-2-butenenitrile. However, in contrast to the previously proposed (Gutsche & Voges, 1967) hydrogen-bonding scheme involving two intramolecular hydrogen bonds, the structure actually possesses one strong intramolecular hydrogen bond between one amino proton and the nitrogen of a pyridine ring [N(3)—N(1′) = 2·715 (3); H(3*B*)—N(1′) = 1·96 (3) Å; N(3)—H(3*B*)—N(1′) = 137 (2)°] and a weaker intermolecular hydrogen bond between the other amino proton and the other pyridine nitrogen of a molecule in the adjacent (1 + *x*, *y*, *z*) unit cell [N(3)—N(1″)* = 3·054 (3); H(3*A*)—N(1″)* = 2·16 (4) Å; N(3)—H(3*A*)—N(1″)* = 165 (2)°]. This hydrogen-bonding scheme is more consistent with the observed spectroscopic (infrared and ^{1}H NMR) data than that previously proposed. The intermolecular hydrogen bond results in the molecules being linked in infinite chains as depicted in Fig. 2. All other intermolecular contacts between non-hydrogen atoms are >3·24 Å.

The two pyridine rings are each planar [maximum deviation from the mean planes 0·005 (3) Å]. As a consequence of the intramolecular hydrogen bond the C(2) pyridine ring is approximately coplanar with the plane of the double bond [angle between the pyridine mean plane and the mean plane described by the olefinic carbons and their four substituent atoms 1·1 (3)°]. In contrast the other pyridine ring is approximately orthogonal to the plane of the double bond [angle between mean planes 84·7 (3)°].

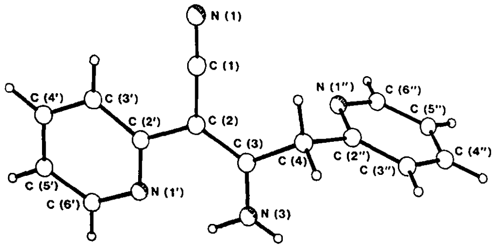


Fig. 1. Perspective view and atom labelling of the structure of (4).

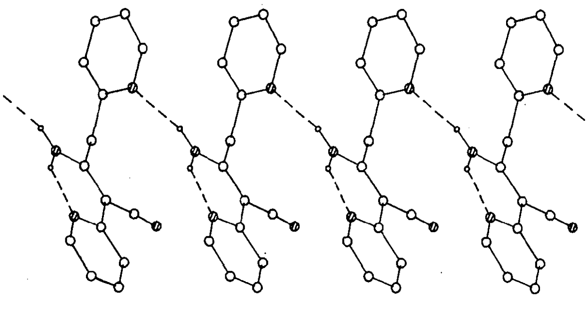


Fig. 2. Inter- and intramolecular hydrogen bonding (broken lines). *a* axis horizontal, *b* axis vertical. Methylene and pyridyl hydrogens omitted for clarity.

Table 1. *Atom coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^3) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*
N(1)	0†	5857 (1)	253 (1)	29 (1)
C(1)	1612 (6)	5661 (1)	411 (1)	22 (1)
C(2)	3630 (6)	5443 (1)	606 (1)	20 (1)
C(3)	5218 (6)	4878 (1)	551 (1)	20 (1)
N(3)	7252 (6)	4647 (1)	712 (1)	23 (1)
C(4)	4704 (7)	4477 (1)	297 (1)	24 (1)
N(1′)	5907 (6)	5697 (1)	1034 (1)	25 (1)
C(2′)	3974 (6)	5875 (1)	845 (1)	20 (1)
C(3′)	2318 (7)	6450 (1)	876 (1)	25 (1)
C(4′)	2663 (7)	6847 (1)	1101 (1)	30 (1)
C(5′)	4644 (7)	6667 (1)	1293 (1)	30 (1)
C(6′)	6198 (7)	6095 (1)	1250 (1)	29 (1)
N(1″)	1802 (6)	3651 (1)	533 (1)	25 (1)
C(2″)	3921 (6)	3756 (1)	354 (1)	20 (1)
C(3″)	5304 (7)	3238 (1)	223 (1)	24 (1)
C(4″)	4499 (7)	2587 (1)	278 (1)	26 (1)
C(5″)	2365 (6)	2471 (1)	462 (1)	27 (1)
C(6″)	1093 (7)	3016 (1)	583 (1)	28 (1)
H(3*A*)	8355 (70)	4289 (12)	661 (5)	21‡
H(3*B*)	7633 (63)	4914 (11)	862 (5)	21‡

* $U_{eq} = \frac{1}{3}$ (trace of the orthogonalized U_{ij} tensor).
† Origin-defining coordinate.
‡ Isotropic; fixed.

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

N(1)—C(1)	1·156 (3)	C(1)—C(2)	1·425 (4)
C(2)—C(3)	1·382 (3)	C(2)—C(2′)	1·475 (3)
C(3)—N(3)	1·331 (3)	C(3)—C(4)	1·511 (3)
C(4)—C(2″)	1·516 (3)	N(1′)—C(2′)	1·351 (3)
N(1′)—C(6′)	1·343 (3)	C(2′)—C(3′)	1·399 (3)
C(3′)—C(4′)	1·384 (3)	C(4′)—C(5′)	1·377 (4)
C(5′)—C(6′)	1·374 (4)	N(1″)—C(2″)	1·350 (4)
N(1″)—C(6″)	1·338 (3)	C(2″)—C(3″)	1·385 (3)
C(3″)—C(4″)	1·385 (3)	C(4″)—C(5″)	1·375 (4)
C(5″)—C(6″)	1·381 (4)		
N(1)—C(1)—C(2)	177·9 (2)	C(1)—C(2)—C(3)	118·2 (2)
C(1)—C(2)—C(2′)	116·2 (2)	C(3)—C(2)—C(2′)	125·5 (2)
C(2)—C(3)—N(3)	123·4 (2)	C(2)—C(3)—C(4)	121·0 (2)
N(3)—C(3)—C(4)	115·5 (2)	C(3)—C(4)—C(2″)	113·0 (2)
C(2′)—N(1′)—C(6′)	117·8 (2)	C(2)—C(2′)—N(1′)	118·4 (2)
C(2)—C(2′)—C(3′)	120·6 (2)	N(1′)—C(2′)—C(3′)	121·0 (2)
C(2′)—C(3′)—C(4′)	119·7 (2)	C(3′)—C(4′)—C(5′)	119·1 (2)
C(4′)—C(5′)—C(6′)	118·1 (2)	N(1′)—C(6′)—C(5′)	124·3 (3)
C(2″)—N(1″)—C(6″)	117·0 (2)	C(4)—C(2″)—N(1″)	116·7 (2)
C(4)—C(2″)—C(3″)	120·9 (2)	N(1″)—C(2″)—C(3″)	122·5 (2)
C(2″)—C(3″)—C(4″)	119·1 (2)	C(3″)—C(4″)—C(5″)	119·1 (2)
C(4″)—C(5″)—C(6″)	118·2 (2)	N(1″)—C(6″)—C(5″)	124·1 (3)

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43981 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Another interesting feature of the structure is the significant elongation of the C—C double bond [C(2)—C(3) = 1·382 (3) Å] relative to that in ethylene [1·314 (6) Å (van Nes & Vos, 1977)]. This can be attributed to through-conjugation from the electron-donating amino substituent to the electron-withdrawing cyano (and pyridyl) substituent. This is also reflected in the shortening of the N(3)—C(3) bond [1·331 (3) Å] relative to the value [1·452 (2) Å] for a pure $\ddot{N}$—C(sp^2) single bond (Ammon, Mazzocchi, Regan & Colicelli, 1979) and a slight shortening of the C(1)—C(2) bond [1·425 (4) Å] relative to the C(sp^2)—C(sp) bond length [1·437 (2) Å] in ethylenetetracarbonitrile (Little, Pautler & Coppens, 1971), indicating some double-bond character in these bonds, as has been previously observed in other 'push–pull' olefins (Hazell & Mukhopadhyay, 1980; Adhikesavalu & Venkatesan, 1981; Sen & Venkatesan, 1984; Sen, Venkatesan, Acharya & Guru Row, 1984; and references therein). Normally such C—C bond elongation is accompanied by significant bond twisting resulting from a combination of steric and conjugative effects. In the present case, however, there is very little twisting of the double bond as measured by the twist angle [3·6 (3)°] between the mean planes defined by C(2), C(1), C(2′) and by C(3), N(3), C(4). This lack of twisting is attributed to the intramolecular hydrogen bond which maintains one side of the double bond planar. A similar situation was reported for 3-(2-imidazolidinylidene)-2,4-pentanedione (Adhikesavalu & Venkatesan, 1983) wherein bond elongation without twisting was explained by intramolecular hydrogen bonding. The polarization of the double bond observed in the present structure is also reflected in the large difference in ^{13}C NMR chemical shifts of the two olefinic carbons.

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Structure of a Modified Cytosine: An Antiviral Nucleoside Analog

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Abstract. 5′-Azido-5′-deoxy-1-β-D-arabinofuranosylcytosine sesquihydrate, $C_9H_{12}N_6O_4.\frac{3}{2}H_2O$, $M_r = 295$, monoclinic, $C2$, $a = 15·835$ (7), $b = 7·286$ (4), $c = 12·039$ (6) Å, $\beta = 108·75$ (6)°, $V = 1316·5$ Å^3, $Z = 4$, $D_x = 1·488$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5·90$ cm^{-1}, $F(000) = 620$, $T = 288$ K, final $R = 0·056$ for 960 observed reflections. Conformational features of the nucleoside include a glycosidic bond conformation in the *anti* range, a ribose moiety in the ^2E [C(2′)-*endo*] form and a C(5′)—N(5′) bond that is *trans*

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