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Structure of Thermochromic Schiff Bases. II. Structures of *N*-Salicylidene-3-aminopyridine and *N*-(5-Methoxysalicylidene)-3-aminopyridine

BY I. MOUSTAKALI-MAVRIDIS AND E. HADJOUDIS

Nuclear Research Center 'Demokritos', Chemistry Department, Aghia Paraskevi Attikis, Athens, Greece

AND A. MAVRIDIS

University of Athens, Physical Chemistry Department, 13a Navarinou Str., Athens 144, Greece

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Abstract

The structures of the weakly thermochromic compounds *N*-salicylidene-3-aminopyridine (I) and *N*-(5-methoxysalicylidene)-3-aminopyridine (II) were determined by X-ray crystallographic methods. The crystal structure of (II) is disordered, the molecules having two orientations of the pyridine ring in a statistical sense. Bond distances and the packing arrangement of (I) are similar to those of *N*-salicylidene-2-aminopyridines, but the pyridine ring is tilted by 14·8° with respect to the rest of the molecule. [Crystal data: (I) $C_{12}H_{10}N_2O$, space group $P2_1/n$, $a = 15{\cdot}233\ (8)$, $b = 4{\cdot}692\ (2)$, $c = 14{\cdot}316\ (7)$ Å, $\beta = 98{\cdot}19\ (4)°$, $Z = 4$; (II) $C_{13}H_{12}N_2O_2$, space group $P2_1/n$, $a = 4{\cdot}649\ (2)$, $b = 20{\cdot}288\ (11)$, $c = 12{\cdot}068\ (5)$ Å, $\beta = 97{\cdot}04\ (3)°$, $Z = 4$.]

Introduction

In a previous study (Moustakali-Mavridis, Hadjoudis & Mavridis, 1978) we determined the crystal structures of the Schiff base *N*-salicylidene-2-aminopyridine and three of its derivatives. All four molecules are planar in the crystalline state, stacked along the shortest axis with similar interplanar distances (~3·45 Å), and exhibit strong thermochromic behaviour, in agreement with an earlier proposed classification (Bregman, Leiserowitz & Ozaki, 1964, and references therein). In this classification, planar geometry is associated with thermochromism, non-planar with photochromism.

Assuming that the phenomenon of thermochromism and/or photochromism is a monotonic function of the molecular geometry, *i.e.* of the angle variable which defines the orientation of one ring with respect to the other, we are exploring whether certain geometries can be allotted on the basis of their response towards heat or light. *N*-Salicylidene-3-aminopyridine (I) and *N*-(5-methoxysalicylidene)-3-aminopyridine (II) exhibit only weak thermochromism in the crystalline state. Their structure analyses were undertaken to shed more light on the relation between geometry in the crystalline state and chromo behaviour.

Experimental

The title compounds were synthesized by known methods (Vogel, 1966). Single crystals were obtained by cooling solutions in cyclohexane. Suitable crystals 0·7 × 0·25 × 0·15 mm mounted along the longest axis were used for data collection. The diffraction conditions determined by photographic and diffractometric methods ($h0l$: $h + l = 2n$; $0k0$: $k = 2n$) and the monoclinic symmetry indicate the space group $P2_1/n$ for both compounds. The densities were measured by flotation in silver nitrate solution.

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Table 1. *Crystal data*

	(I)	(II)
Empirical formula	$C_{12}H_{10}N_2O$	$C_{13}H_{12}N_2O_2$
M_r	198·23	228·25
Space group	$P2_1/n$	$P2_1/n$
a (Å)	15·233 (8)	4·649 (2)
b (Å)	4·692 (2)	20·288 (11)
c (Å)	14·316 (7)	12·068 (5)
β (°)	98·19 (4)	97·04 (3)
U (Å^3)	1012·9	1129·8
$D_m^{296\,K}$ (Mg m^{-3})	1·31	1·33
$D_m^{298\,K}$ (Mg m^{-3})	1·30	1·34
Z	4	4
F(000)	416	480
$\mu_{Mo\,K\alpha}$ (mm^{-1})	0·092	0·100
Number of reflections measured	1329	1978
Number of systematically absent reflections	160	283
Number of reflections used	965	1009

Table 2. *Summary of the structure determination and refinement*

	(I)	(II)
Minimum value of E used	1·40	1·60
Number of signs determined	186	206
Consistency index	0·89	0·87
R factor based on coordinates of E map	0·244	0·256
R factor at the introduction of anisotropic refinement	0·118	0·135
Final R	0·059	0·092
Final R_w	0·052	0·082
Data/parameter ratio (H atoms not included)	7·1	6·6
Maximum residual density (e Å^{-3})	0·17	0·22
Minimum residual density (e Å^{-3})	−0·20	−0·23

Diffraction data were measured at 293 K on a Picker FACS-I automatic diffractometer with Zr-filtered Mo $K\alpha$ radiation. The lattice parameters were determined by least squares from the setting angles 2θ, ω, χ and φ of 12 reflections in the range $35 < 2\theta < 41°$ for which the $\alpha_1\alpha_2$ doublet of Mo $K\alpha$ radiation was clearly resolved. Crystal data are summarized in Table 1.

Intensities of reflections were measured by the θ–2θ scan method with a scan speed of 1° (2θ) min^{-1}, a scan range 1·4° (2θ) for (I) and 1·6° (2θ) for (II) plus the α_1–α_2 divergence and a 20 s background at the start and end of each scan. The alignment and X-ray damage of the crystals were monitored every 100 reflections; there was no evidence of radiation damage to the crystals. Intensities were measured in the regions $\pm h + k + l$ up to $2\theta \leq 45°$ for (I) and $2\theta \leq 50°$ for (II). Attenuation filters were used to keep the intensities within the linearity range of the photon counter.

The intensities were converted to relative structure amplitudes but no corrections for absorption or extinction were made. E.s.d.'s for the structure factors were calculated as a function of counting statistics (Wei & Ward, 1976). The observable limits for the accidentally absent reflections were $I < \sigma(I)$ and $I < 3\sigma(I)$ for (I) and (II) respectively.

Structure determination and refinement

The structure amplitudes were converted to normalized values with approximate scale and temperature factors (Wilson, 1942). A summary of the structure determination and refinement appears in Table 2. The procedure was the same for both structures. They were solved by iterative application of Sayre's equation with Long's (1965) program. E maps based on the determined signs revealed the positions of all non-hydrogen atoms. After unit-weight, full-matrix least-squares refinement (Busing, Martin & Levy, 1962) of the initial positional parameters, isotropic temperature factors and scale factors, difference maps were calculated which revealed the positions of all H atoms. H atoms were assigned isotropic temperature factors 1·25 Å^2 greater than those of the C or O atoms to which they are bonded. Anisotropic thermal parameters were introduced and the refinement was continued until the parameter shifts were insignificant compared to their e.s.d.'s. The discrepancy indices are given by: $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum(w||F_o| - |F_c||)^2]^{1/2}/[\sum(w|F_o|)^2]^{1/2}$, where $w = 1/\sigma(F)$.

The bond distances and thermal parameters of the pyridine ring of (II) indicate disorder for that part of the molecule involving occupancy of two ring orientations, one with the hetero N atom *trans* to the exocyclic H(C7) and the other *cis*. Therefore, an additional full-matrix refinement was carried out where C(9), C(10), C(11), N(2) and C(12) at two positions

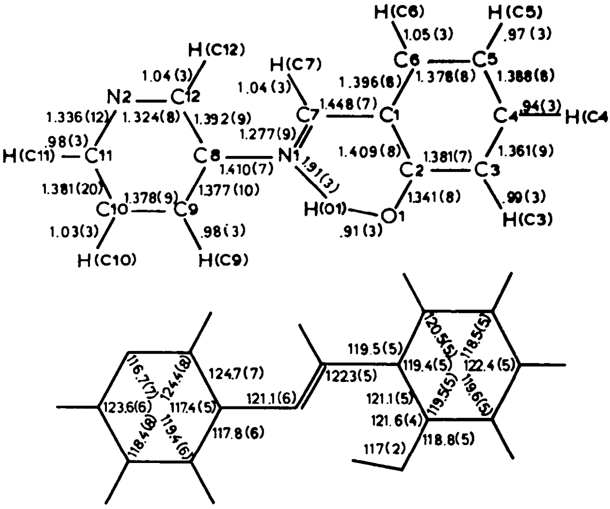

Fig. 1. Bond distances (Å), bond angles (°) and atom-numbering system for (I). E.s.d.'s are in parentheses.

Table 3. *Positional parameters and peak heights for* (I) *with e.s.d.'s in parentheses*

	x	y	z	Peak height (e Å^{-3})
C(1)	0·2253 (2)	0·2363 (9)	0·4967 (2)	5·8
C(2)	0·2612 (3)	0·2914 (9)	0·4131 (3)	5·5
C(3)	0·2204 (3)	0·4872 (10)	0·3492 (3)	5·0
C(4)	0·1462 (3)	0·6251 (11)	0·3678 (3)	4·4
C(5)	0·1096 (3)	0·5784 (11)	0·4498 (3)	4·9
C(6)	0·1491 (3)	0·3813 (10)	0·5137 (3)	5·3
C(7)	0·2661 (2)	0·0320 (9)	0·5654 (2)	5·7
C(8)	0·3757 (2)	−0·2983 (8)	0·6231 (2)	6·2
C(9)	0·4602 (3)	−0·3930 (10)	0·6166 (3)	5·6
C(10)	0·4998 (3)	−0·5874 (10)	0·6815 (3)	4·8
C(11)	0·4527 (3)	−0·6812 (10)	0·7512 (3)	5·0
C(12)	0·3337 (2)	0·4106 (10)	0·6951 (3)	5·9
N(1)	0·3371 (2)	−0·1016 (7)	0·5549 (2)	7·2
N(2)	0·3704 (2)	−0·5955 (8)	0·7588 (2)	6·5
O(1)	0·3344 (2)	0·1585 (7)	0·3938 (2)	7·0
H(C3)	0·252 (2)	0·513 (7)	0·294 (2)	0·34
H(C4)	0·119 (2)	0·760 (7)	0·324 (2)	0·42
H(C5)	0·056 (2)	0·665 (6)	0·466 (2)	0·47
H(C6)	0·124 (2)	0·337 (6)	0·577 (2)	0·45
H(C7)	0·229 (2)	−0·019 (6)	0·619 (2)	0·47
H(C9)	0·496 (2)	−0·310 (6)	0·572 (2)	0·44
H(C10)	0·566 (2)	−0·631 (6)	0·683 (2)	0·39
H(C11)	0·482 (2)	−0·814 (6)	0·798 (2)	0·36
H(C12)	0·268 (2)	−0·357 (6)	0·698 (2)	0·52
H(O1)	0·368 (2)	0·069 (6)	0·443 (2)	0·36

Table 4. *Positional parameters and peak heights for* (II) *with e.s.d.'s in parentheses*

	x	y	z	Peak height (e Å^{-3})
C(1)	0·3391 (14)	0·2321 (3)	0·3125 (5)	6·6
C(2)	0·2217 (14)	0·2215 (3)	0·2025 (5)	5·6
C(3)	0·0108 (17)	0·1725 (4)	0·1795 (6)	4·7
C(4)	−0·0806 (16)	0·1347 (4)	0·2645 (6)	5·3
C(5)	0·0354 (16)	0·1457 (3)	0·3739 (6)	5·1
C(6)	0·2455 (16)	0·1944 (3)	0·3986 (6)	5·4
C(7)	0·5579 (15)	0·2810 (3)	0·3436 (6)	5·6
C(8)	0·8615 (14)	0·3687 (3)	0·3046 (6)	6·3
C(9)	0·9773 (17)	0·3822 (4)	0·4110 (6)	5·0
C(10)	1·1722 (18)	0·4317 (4)	0·4342 (7)	4·3
C(11)	1·2476 (19)	0·4685 (4)	0·3484 (9)	4·2
C(12)	0·9458 (19)	0·4064 (4)	0·2203 (7)	4·8
C(13)	−0·2439 (20)	0·0605 (4)	0·4447 (8)	4·2
N(1)	0·6504 (12)	0·3202 (3)	0·2716 (4)	7·1
N(2)	1·1397 (18)	0·4563 (4)	0·2396 (7)	4·4
O(1)	0·2999 (11)	0·2576 (3)	0·1163 (4)	6·5
O(2)	−0·0377 (12)	0·1109 (3)	0·4643 (4)	6·6
H(C3)	−0·090 (14)	0·170 (3)	0·099 (5)	0·58
H(C4)	−0·233 (13)	0·102 (3)	0·247 (5)	0·40
H(C6)	0·366 (13)	0·198 (3)	0·483 (5)	0·51
H(C7)	0·647 (12)	0·278 (3)	0·428 (5)	0·52
H(C9)	0·957 (14)	0·357 (3)	0·464 (5)	0·33
H(C10)	1·265 (14)	0·443 (3)	0·511 (5)	0·41
H(C11)	1·430 (15)	0·503 (4)	0·364 (6)	0·34
H(C12)	0·837 (14)	0·405 (3)	0·133 (5)	0·47
H(O1)	0·441 (14)	0·297 (3)	0·152 (5)	0·36
H1(C13)	−0·231 (15)	0·035 (4)	0·514 (6)	0·27
H2(C13)	−0·369 (15)	0·067 (4)	0·392 (6)	0·38
H3(C13)	−0·142 (16)	0·020 (4)	0·395 (6)	0·36

Table 5. *Deviations* (Å) *from least-squares planes*

E.s.d.'s are 0·12 Å for (I) and 0·02 Å for (II).

	(I)	(II)		(I)	(II)
C(1)	0·02	0·02	C(9)	0·15	0·01
C(2)	−0·13	0·00	C(10)	0·17	−0·02
C(3)	−0·15	−0·02	C(11)	0·02	−0·05
C(4)	−0·02	−0·03	C(12)	−0·18	0·02
C(5)	0·15	−0·02	N(1)	−0·04	0·02
C(6)	0·15	0·00	N(2)	−0·15	−0·02
C(7)	0·04	0·06	O(1)	−0·26	−0·01
C(8)	−0·02	0·03			

with half occupancies according to the assumed disorder were refined separately with isotropic thermal parameters, with the other atoms anisotropic. The best agreement was obtained for a 3:1 ratio of the *trans* to *cis* orientation ($R = 0{\cdot}108$, $R_w = 0{\cdot}092$). Continuation of the refinement with anisotropic thermal parameters for the disordered atoms did not change the bond distances and angles and led virtually to the same discrepancy index as the previous refinement ($R = 0{\cdot}093$, $R_w = 0{\cdot}083$).

The scattering factors of Doyle & Turner (1968) were used for the non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for H.

Results and discussion

The final atomic parameters and peak heights are listed in Tables 3 and 4 for (I) and (II) respectively.* Figs. 1 and 2 show atom notation, bond distances and bond angles. Deviations from best least-squares planes are in Table 5. Best least-squares planes were also computed for the atoms of three separate parts of the molecules: the phenyl ring (plane *A*), the pyridine ring (plane *B*) and the plane through C(1), C(2), C(7), N(1), O(1) (plane *C*), as shown in Table 6. Table 7 lists the angles between the normals to *A*, *B* and *C*.

It was mentioned earlier that the pyridine moiety of (II) shows a statistical disorder in which N(2) occupies two positions corresponding to a rotation by 180° of the ring around N(1)–C(8). Indications for this are the equality of the bond lengths to the mean length of the C–C and C–N bonds of a pyridine ring, a weak electron density (peak height = 0·2 e Å^{-3}) at ~1·1 Å

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* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35069 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 6. *Deviations* (Å) *from least-squares planes A, B and C*

Plane *A*

E.s.d.'s are 0·004 Å for (I) and 0·002 Å for (II).

	(I)	(II)		(I)	(II)
C(1)	−0·001	0·003	C(4)	−0·004	0·004
C(2)	0·003	−0·001	C(5)	0·006	−0·001
C(3)	−0·001	−0·003	C(6)	−0·003	−0·002

Plane *B*

E.s.d.'s are 0·007 Å for (I) and 0·006 Å for (II).

	(I)	(II)		(I)	(II)
C(8)	0·007	−0·003	C(11)	0·003	−0·008
C(9)	−0·002	0·000	C(12)	−0·008	0·000
C(10)	−0·003	0·006	N(2)	0·002	0·006

Plane *C*

E.s.d.'s are 0·009 Å for (I) and 0·008 Å for (II).

	(I)	(II)		(I)	(II)
O(1)	−0·006	0·004	C(7)	−0·010	0·014
C(2)	0·004	0·001	N(1)	0·008	−0·009
C(1)	0·004	−0·010			

Table 7. *Dihedral angles* (°)

E.s.d.'s are 2° for (I) and 1° for (II).

	(I)	(II)
Between *A* and *B*	14·8	2·8
Between *A* and *C*	0·9	1·2
Between *B* and *C*	14·2	2·4

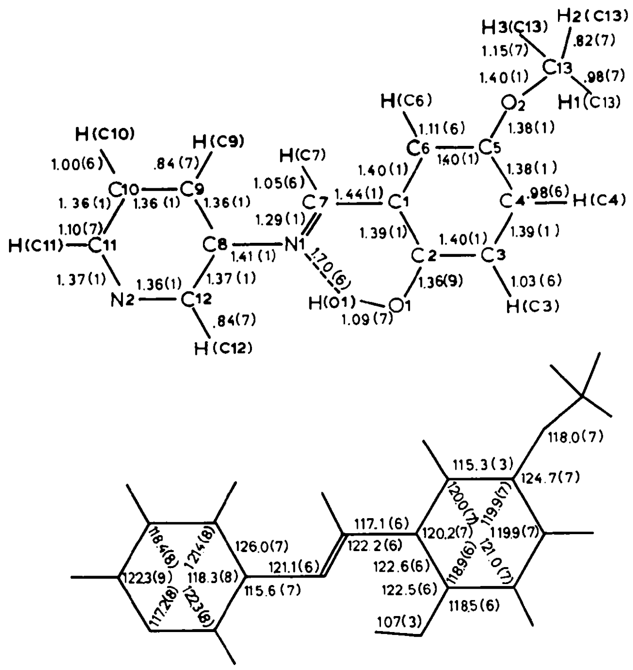

Fig. 2. Bond distances (Å), bond angles (°) and atom-numbering system for (II). E.s.d.'s are in parentheses.

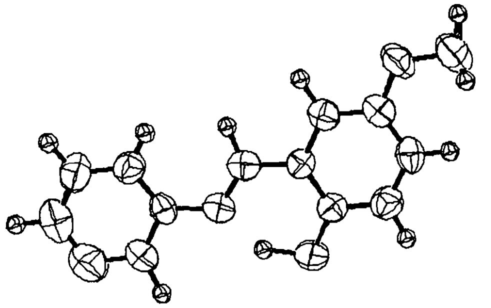

Fig. 3. Vibrational ellipsoids [50% probability level (Johnson, 1965)] of (II) projected on the mean plane of the molecule.

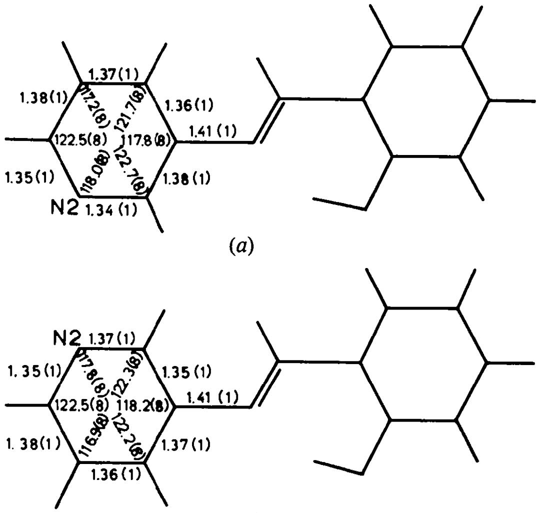

Fig. 4. Result of the refinement of (II) in terms of two orientations with partial occupancy for the pyridine ring. (*a*) Bond distances (Å) and angles (°) of the *trans* orientation. (*b*) Bond distances (Å) and angles (°) of the *cis* orientation.

from N(2) and the thermal parameters of C(10), C(11) and N(2), as depicted in Fig. 3. The bond lengths were differentiated towards the correct directions when disorder was taken into account (Fig. 4), while the level of agreement remained essentially the same (R = 0·093). However, the disorder of the crystal and the subsequent high discrepancy index make comparison of (II) with (I) and with other relevant crystal molecular structures unreliable.

The bond distances and angles of the pyridine ring for (I) compare well with those of salicylidene-2-aminopyridine (Moustakali-Mavridis, Hadjoudis & Mavridis, 1978). The hetero N(2) atom is *cis* with respect to H(C7), as opposed to N(2) of (II) which is mainly (75%) *trans*. Apparently, there is no appreciable energy difference between the two orientations due to the symmetry of interaction of both H atoms *ortho* to the imino group with H(C7). This is in contrast to salicylidene-2-aminopyridines, where the observed

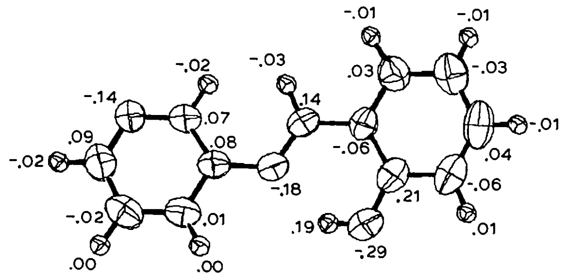

Fig. 5. Charge densities of (I) computed by the CNDO/2 method. Vibrational ellipsoids are at the 50% probability level (Johnson, 1965).

unique conformation does not involve such an interaction. As a result of this repulsive interaction, a rotation of the pyridine plane around N(1)—C(8) by 14·8° (Table 7) and an in-plane deformation [N(1)C(8)C(12) = 124·7°] occur to give a separation of 2·0 Å for H(C7)···H(C12). However, the small deviation from planarity does not seem to prevent the close parallel packing of the molecules along the shortest axis with an interplanar distance of 3·44 Å.

The rest of (I) presents the same features as salicylidene-2-aminopyridines: short C(3)—C(4), C(5)—C(6), C(2)—O(1) bond lengths, due to a quinoid resonance structure, and essentially identical distances for the imino C(7)—N(1) bond as well as C(1)—C(7). The distance 1·448 Å for the latter is in agreement with the partial double-bond character of a formal single bond between an aromatic and a double or a triple bond (Mavridis & Moustakali-Mavridis, 1977, and references therein).

Fig. 5 shows the charge distribution of (I) calculated by the CNDO/2 method (Pople & Beveridge, 1970). The geometry used is that of the present analysis. As has been observed in our previous studies of salicylidene-2-aminopyridines, there is a strong intramolecular hydrogen bond from the hydroxylic H(O1) to the imino N(1) atom. Assuming that the main cause of the hydrogen bond is electrostatic in origin, a value of ~25 kJ mol^{-1} is obtained from the CNDO/2 charges.

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Neutron Structural Refinement for Pyridoxinium Chloride, a Component $C_8H_{12}ClNO_3$ of the Vitamin B_6

By G. E. Bacon and J. S. Plant*

Department of Physics, The University, Sheffield S10 2TN, England

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Abstract

The structure of pyridoxinium chloride, a constituent of the vitamin B_6, has been re-investigated using high-flux measurements of neutron intensity diffracted by a small single crystal. Re-determined triclinic $P\bar{1}$ cell ($Z = 2$) constants, $a = 9{\cdot}68$ (2), $b = 5{\cdot}83$ (1), $c = 9{\cdot}54$ (2) Å, $\alpha = 93{\cdot}88$ (8), $\beta = 115{\cdot}06$ (5), $\gamma = 98{\cdot}53$ (7)°, differ from reported values by 1·7% for a. Least-squares refinement ($R = 3{\cdot}6\%$) of the structure, using neutron data, produces 1·012 (9) Å for the O(2)—H(12) bond

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* Latterly at the Computer Services Department, Sheffield City Polytechnic, but now at the Computer Centre, The University, Keele.

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