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Formation of 2,4,5-triaryl-4,5-dihydro-1*H*-imidazoles, (**1**), from aryl aldehydes. Crystal structures of *cis*-(**1**: aryl = pyridin-2-yl), {*trans*-[(**1**: aryl = pyridin-2-yl)H]$^+$[OAc]$^-$·3H$_2$O}, {*cis*-[**1**: aryl = thien-2-yl]·0.5H$_2$O} and *trans*-(**1**: aryl = thien-2-yl)

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Abstract

The preparations of *cis*-2,4,5-triaryl-4,5-dihydro-1*H*-imidazoles, (aryl = thien-2-yl or pyridin-2-yl) from aryl aldehydes, ammonium chloride and triethylamine in methanol, and their conversions to the *trans*-isomers are reported. Crystal structures of *cis*-(**1**: aryl = pyridin-2-yl), *cis*-[**1**: aryl = thien-2-yl·0.5H$_2$O], *trans*-(**1**: aryl = thien-2-yl), and *trans*-{[(**1**: aryl = pyridin-2-yl)H]$^+$[OAc]$^-$·3H$_2$O}, have been determined and compared with related structures.

Keywords: 2,4,5-Triaryl-4,5-dihydro-1*H*-imidazoles; Crystal structures; *cis–trans*-isomerisation

1. Introduction

The reaction of an aryl aldehyde with a source of ammonia, which provides 2,4,5-triaryl-4,5-dihydro-1*H*-imidazoles, **1**, has been known for many decades. The history of the reaction provides a fascinating example of how knowledge and confirmation of the structure of an organic compound slowly developed over time in the 19th and 20th centuries.

It was noted as early as 1837 that PhCHO reacted with NH_3 to give a compound now known to be 1,3,5-triphenyl-2,4-diaza-pentadiene (**2**: Ar = Ph) [1]. A little later, in 1844, it was reported that heating (**2**: Ar = Ph) resulted in cyclisation and formation of *cis*-2,4,5-triphenyl-4,5-dihydro-1*H*-imidazole, *cis*-(**1**: Ar = Ph), (amarine) [2], see Scheme 1. Other researchers, in the 19th century, found that *cis*-(**1**: Ar = Ph) rearranges under strong basic conditions, e.g., using KOBu^t/HOBu^t, to the isomeric isoamarine, *trans*-2,4,5-triphenyl-4,5-dihydro-1*H*-imidazole *trans*-(**1**: Ar = Ph) [3]. Confirmations of these now accepted structures came somewhat later in 1900 [4,5]. During the early period, various other authors, including the composer-chemist Borodin, showed that these reactions occur for various aryl aldehydes.

The mechanism of the formation of **1** from starting reagents, NH_3 and ArCHO, was fully established by Hunter and Sim in 1972 [6]. Reaction of NH_3 and PhCHO gives initially 1,3,5-triphenyl-2,4-diaza-pentadiene, (**2**: Ar = Ph), which rearranges in the presence of a base, under kinetic control, mainly to *cis*-(**1**: Ar = Ph) [ca. 96%], but also to a little *trans*-(**1**: Ar = Ph). Under more strongly basic conditions, *cis*-(**1**: Ar = Ph) rearranges to the *trans*-(**1**: Ar = Ph)

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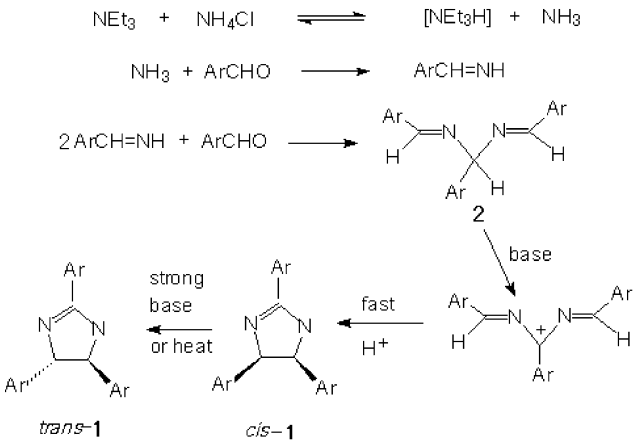


Scheme 1.

[thermodynamic control]. The pathway of the formation of *cis*-1 from **2** proceeds *via* a "W"-shaped carbanion, derived from 1,3,5-aryl-2,4-diaza-pentadiene. From orbital symmetry considerations, a concerted cyclisation of this carbanion will occur in a disrotatory manner to give the *cis*-product, as found [6].

Reactive aldehydes, e.g., furfuryl aldehyde and *p*-chlorobenzaldehyde, react with liquid ammonia to give compounds *cis*-**1** directly [7]. For less reactive aldehydes, as well as addition of a strong base such as PhLi [8,9], KNH_2 [8] or hexamethyldisilazane [10], controlled heating of the intermediate 1,3,5-triarylphenyl-2,4-diaza-pentadiene **2** [9,11,12] has been reported to be necessary to convert **2** to **1**. One-pot syntheses of **1** include the microwave radiation of solvent-free mixtures of an aldehyde, NH_4OAc and alumina [13].

Conversions of *cis*-**1**, to *trans*-**1**, have been achieved either using stronger bases, at higher temperatures or longer heating times than required initially to produce the cis compounds.

Different carbonyl-containing reagents or analogues have also been used for the formation of **1**. Among these reactions are those between RCO–COR, ArCHO and NH_4OAc in AcOH, [14–16], and between ArCH═NOH and $NaNH_2$ in refluxing xylene [17], as well as reduction of ArCN trimers with Zn/AcOH [18].

A few crystal structures of **1** have been reported. These include *cis*-[(**1**: Ar = phenyl)·H]$^+$·Cl$^-$ [11], *cis*-[(**1**: Ar = 4-tolyl)·H]$^+$·Br$^-$ [19], *cis*-(**1**: Ar = pyridin-2-yl) [9] and *trans*-(**1**: Ar = pyridin-2-yl) [9]. While structural data are available for the first two compounds, this is not, unfortunately, the case for the other two for which only drawings of the molecules are accessible.

We were especially interested in preparing heteroaromatic derivatives of **1**, in particular the pyridin-2-yl and thien-2-yl derivatives, both for use as ligands in coordination chemistry and for our studies in supermolecular arrangements. An earlier report had indicated the use of 2,4,5-tri(pyridin-2yl)imidazoline, as ligands for Ni(II), Cu(II), and Zn(II) [20].

We now wish to report the structures of *cis*-(**1**: Ar = pyridin-2-yl), *trans*-{[(**1**: Ar = pyridin-2-yl)H]$^+$[OAc] $^-$·3H_2O}, *cis*-[**1**: Ar = thien-2-yl·0.5H_2O] and *trans*-(**1**: Ar = thien-2-yl). Comparisons are made with related structures, reported earlier.

2. Experimental

2.1. General

Ir spectra were recorded on a Nicolet FT-IR 760 instrument either in KBr disks or as films. NMR spectra were recorded on a Jeol Eclipse instrument. C, H, N elemental analyses were carried out on a Perkin-Elmer 2400 analyser. Tlcs were carried out using Merck-Kieselgel 60 F_{254} and were visualized using iodine. Column chromatography used Merck-Kieselgel silica gel.

2.2. Synthesis of 1

2.2.1. cis-2,4,5-Tri(thien-2-yl)-4,5-dihydro-1H-imidazole, cis-(1: Ar = thien-2-yl)

A solution of thiene-2-carboxaldehyde (3 ml, 0.03 mol), ammonium chloride (3 g, 0.06 mol) and triethylamine (8.1 ml, 0.06 mol) in MeOH (30 ml) was refluxed for 26 h. The solvent was removed in vacuo, the residue was extracted into $CHCl_3$ and washed successively with brine and a little isopropanol. The pale yellow solid was recrystallised from EtOH.

Anal. Calc. for $C_{15}H_{15}N_2S_3$. C, 56.93; H, 3.82; N, 8.84. Found: C, 56.3; H, 3.94; N, 8.42%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.50 (d, J = 3.6 Hz, 1H), 7.49 (d, J = 3.6 Hz,1H), 7.12 (dd, J = 3.6, 5.1 Hz, 1H), 7.06 (dd, J = 1.0 Hz, 5.0 Hz, 2H), 6.80 (dd, J = 3.5 Hz, 5.0 Hz, 2H), 6.74 (s.br, 2H), 5.7 (s.br, 1H), 5.5 (s.br, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ: 159.4, 142.0, 132.9, 129.5, 128.2, 127.5, 126.3, 125.3, 124.8, 99.7, 62.8.

Further recrystallisations from ethanol were required to give suitable crystals for crystallography. The crystals used in the structure determination were found to be the hemihydrate.

2.2.2. trans-2,4,5-Tri(thien-2-yl)-4,5-dihydro-1H-imidazole, trans-(1: Ar = thien-2-yl)

cis-2,4,5-Tri(thien-2-yl)-4,5-dihydro-I*H*-imidazole,(20 mg) was dissolved in a solution of Bu^{t}OK (30 mg in Bu^{t}OH (5 ml). After stirring the reaction solution for 2 h at room temperature, water (1 ml) and CH_2Cl_2 (1 ml) were added, the organic layer was collected, dried over $MgSO_4$and rotary evaporated. The residue was dissolved in EtOH and left at room temperature. Crystals of anhydrous *trans*-2,4,5-tri(thien-2-yl)-4,5-dihydro-I*H*-imidazole, *trans*-(**1**:Ar = thien-2-yl) slowly were deposited. m.p. 130–133 °C.

^{1}H NMR ($CDCl_3$, 200 MHz) for *trans*-(**1**: Ar = thien-2-yl): δ: 8.61(m, 3H), 8.31 (d, J = 7.9 Hz), 7.79 (dt, J = 1.6, 7.7 Hz, 1H), 7.68 (dt, J = 1.8 Hz, 6.5 Hz, 2H), 7.49 (d, J = 7.7 Hz, 2H), 7.38 (m, 1H), 7.22 (m, 2H), 6.80 (s.br, 1H), 5.54 (s, 2H) [9] ^{13}C NMR ($CDCl_3$, 50 MHz) *trans*-

(**1**: Ar = thien-2-yl): δ: 163.2, 161.7, 149.6, 148.8, 136.6, 125.5, 123.1, 122.4, 121.5, 73.5 [9].

*2.2.3. cis-2,4,5-Tri(pyridin-2-yl)-4,5-dihydro-1H-imidazole, cis-(**1**: Ar = pyridin-2-yl)*

A solution of pyridine-2-carboxaldehyde (10 ml, 0.093 mol), ammonium chloride (5.0 g, 0.093 mol) and triethylamine (13 ml, 0.093 mol) in MeOH (30 ml) was stirred at room temperature for 24 h. The solvent was removed in vacuo, extracted into $CHCl_3$, washed with water, dried over $MgSO_4$ and rotary evaporated. The residue was recrystallised from EtOH, m.p 145 °C; lit m.p. 141–143 °C for *cis*-2,4,5-tri(pyridin-2-yl)-4,5-dihydro-1*H*-imidazole [9]. Spectral data agreed with those reported by Larter et al. [9].

Suitable crystals of anhydrous *cis*-2,4,5-tri(pyridin-2-yl)-4,5-dihydro-1*H*-imidazole for X-ray study were grown from MeCN solution.

*2.2.4. trans-2,4,5-Tri(pyridin-2-yl)-4,5-dihydro-1H-imidazole, trans-(**1**: Ar = pyridin-2-yl)*

This was obtained similarly to *trans*-2,4,5-tri(thien-2-yl)-4,5-dihydro-1*H*-imidazole, (**1**: Ar = thien-2-yl), but at the 1 mmol scale, m.p. 130–132 °C; lit m.p. 129–131 °C [9].

*2.2.5. trans-2,4,5-Tri(pyridin-2-yl)-4,5-dihydro-1H,3H-imidazolium acetate.trihydrate, [trans-(**1**: Ar = pyridin-2-yl)H]$^+$[OAc]$^-$·3H$_2$O*

cis-2,4,5-Tri(pyridin-2-yl)-4,5-dihydro-1*H*-imidazole, *cis*-(**1**: Ar = pyridin-2-yl) (0.20 g), was added to ethyl acetate (15 ml) and the solution heated to cause dissolution. On leaving the solution at room temperature, pale yellow crystals of *rac-trans*-2,4,5-tri(pyridin-2-yl)-4,5-dihydro-1*H*,3*H*-imidazolium acetate·trihydrate were slowly deposited.

^{1}H NMR (DMSO-d_6, 400 MHz) for *trans*-[(**1**: aryl = pyridin -2-yl)H·AcOH·3H$_2$O]: δ: 8.68 (d, J = 1.6 Hz,

Table 1
Crystal data and structure refinement[a]

Compound	*cis*-(**1**: R = Py)	*trans*-(**1**: R = Py)H	*cis*-(**1**: R = Tp)	*trans*-(**1**: R = Tp)	*trans*-(**1**: R = Tp)
Empirical formula	$C_{18}H_{15}N_5$	$(C_{18}H_{16}N_5)^+(C_2H_3O_2)^-\cdot 3H_2O$	$2(C_{15}H_{12}N_2S_3)\cdot H_2O$	$C_{15}H_{12}N_2S_3$	$C_{15}H_{12}N_2S_3$
Temperature (K)	120(2)	120(2)	120(2)	120(2)	291(2)
Formula weight	301.35	415.45	650.91	316.45	316.45
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Triclinic, P-1	Orthorhombic, $Pbca$	Orthorhombic, $Pbca$
Unit cell dimensions					
a (Å)	8.9544(3)	15.1297(5)	9.9207(3)	9.6867(2)	9.8305(5)
b (Å)	15.1425(5)	9.2230(1)	12.3200(3)	29.4008(6)	9.9464(5)
c (Å)	11.4455(3)	15.1308(4)	14.0979(4)	31.5991(7)	31.9543(16)
α (°)	90	90	104.0955(16)	90	90
β (°)	101.594(2)	93.9585(10)	110.4382(12)	90	90
γ (°)	90	90	95.5952(17)	90	90
Volume (Å^3)	1520.25(8)	2106.33(9)	1534.09(7)	8999.3(3)	3124.4(3)
Z, D_{calc} (Mg/m^3)	4, 1.317	4, 1.310	2, 1.409	24, 1.401	8, 1.345
Absorption coefficient (mm^{-1})	0.083	0.096	0.478	0.484	0.465
F(000)	632	880	676	3936	1312
Crystal size (mm)	0.36 × 0.18 × 0.05	0.50 × 0.30 × 0.14	0.30 × 0.20 × 0.10	0.40 × 0.20 × 0.10	0.30 × 0.25 × 0.20
θ range for data collection (°)	2.97–27.69	2.96–27.47	3.10–27.56	2.93–27.51	2.43–23.24
Index ranges	$-11 \leqslant h \leqslant 11$ $-19 \leqslant k \leqslant 19$ $-14 \leqslant l \leqslant 14$	$-19 \leqslant h \leqslant 19$ $-10 \leqslant k \leqslant 11$ $-19 \leqslant l \leqslant 19$	$-12 \leqslant h \leqslant 12$ $-15 \leqslant k \leqslant 16$ $-18 \leqslant l \leqslant 17$	$-12 \leqslant h \leqslant 12$ $-38 \leqslant k \leqslant 38$ $-40 \leqslant l \leqslant 40$	$-10 \leqslant h \leqslant 10$ $-10 \leqslant k \leqslant 11$ $-29 \leqslant l \leqslant 35$
Reflections collected/ unique	19901/3493 [R(int) = 0.0541]	23623/4767 [R(int) = 0.0447]	28688/7007 [R(int) = 0.0642]	65725/10255 [R(int) = 0.0605]	13916/2238 [R(int) = 0.0327]
Reflections observed [I > 2sigma(I)]	2698	3631	5303	6505	1582
Max. and min. transmission	1.0000 and 0.7892	1.000 and 0.8947	0.9867 and 0.9323	1.0000 and 0.6641	0.9280 and 0.7351
Data/restraints/ parameters	3493/0/268	4767/0/305	7007/280/497	10255/36/590	2238/30/218
Goodness-of-fit on F^2	1.089	1.022	1.011	1.062	1.043
Final R indices [I > 2sigma(I)]	$\boldsymbol{R}_1 = 0.0470$ $w\boldsymbol{R}_2 = 0.1067$	$\boldsymbol{R}_1 = 0.0413$ $w\boldsymbol{R}_2 = 0.1031$	$\boldsymbol{R}_1 = 0.0433$ $w\boldsymbol{R}_2 = 0.1082$	$\boldsymbol{R}_1 = 0.0561$ $w\boldsymbol{R}_2 = 0.1305$	$\boldsymbol{R}_1 = 0.0619$ $w\boldsymbol{R}_2 = 0.1767$
R indices (all data)	$\boldsymbol{R}_1 = 0.0664$ $w\boldsymbol{R}_2 = 0.1148$	$\boldsymbol{R}_1 = 0.0619$ $w\boldsymbol{R}_2 = 0.1135$	$\boldsymbol{R}_1 = 0.0646$ $w\boldsymbol{R}_2 = 0.1188$	$\boldsymbol{R}_1 = 0.1078$ $w\boldsymbol{R}_2 = 0.1535$	$\boldsymbol{R}_1 = 0.0839$ $w\boldsymbol{R}_2 = 0.1951$
Extinction coefficient		0.0122(15)			
Largest diff. peak and hole (e/Å^3)	0.214 and −0.231	0.296 and −0.232	0.604 and −0.613	0.513 and −0.498	0.341 and −0.402

[a] In all cases the X-ray wavelength was 0.71073 Å, correction for absorption was semi-empirical from equivalent reflections and the refinement method was full-matrix least-squares on F^2.

1H), 8.54 (m, 2H), 8.14 (d, $J = 7.6$ Hz), 7.95 (t, $J = 7.6$ Hz, 1H), 7.78 (t, 7.6 Hz, 2H), 7.56 (m, 1H), 7.45 (d, $J = 7.6$ Hz, 2H), 7.30 (m, 2H), 5.25 (s, 2H), 3.4 (s.br, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) *trans*-[(**1**: Ar = pyridin -2-yl). AcOH·3H$_2$O]: δ: 172.0, 162.4, 162.0, 149.0, 148.8, 148.2, 136.9, 136.8, 125.6, 122.5. 122.4, 121.5, 21.0.

2.3. X-ray crystallography

2.3.1. Data collection

In a preliminary experiment intensity data were obtained for *trans*-(**1**: Ar = thien-2-yl) with Mo Kα radiation at 291(2) K by means of a Bruker SMART area detector diffractometer under the control of the programs SMART [21] and, for data reduction and cell refinement, SAINT [22]. Thereafter intensity data for all four compounds were obtained at 120(2) K with Mo Kα radiation by means of the Enraf-Nonius KappaCCD area detector diffractometer of the EPSRC National crystallographic service at the University of Southampton. Data collection was carried out under the control of the program COLLECT [23] and data reduction and unit cell refinement were achieved with the COLLECT and DENZO [24] programs. Correction for absorption, in all cases by comparison of the intensities of equivalent reflections, was applied using the program SADABS version 2.10 [25] in the case of *cis*-(**1**: Ar = pyridin-2-yl), SADABS version 2.03 [26] in the case of *trans*-(**1**: Ar = thien-2-yl) at 291(2) K and the program SORTAV [27] in the other cases. In the case of [*trans*-(**1**: Ar = thien-2-yl)H]$^+$[OAc]$^-$·3H$_2$O, correction for extinction was applied in the standard SHELXL-97 [28] manner. The program ORTEP-3 for Windows [29] has been used in the preparation of the Figures and programs SHELXL-97 and PLATON [30] in the calculation of molecular geometry and intermolecular contacts.

2.3.2. Structure solution and refinement

All structures were solved by direct methods using SHELXS-97 [31] and completed and fully refined by means of the program SHELXL-97 [28]. In the final stages of refinement hydrogen atoms were introduced into the structural models. Except for *trans*-(**1**: Ar = thien-2-yl) at 291 K when they were treated in the same manner as hydrogen attached to carbon, hydrogen atoms attached to nitrogen

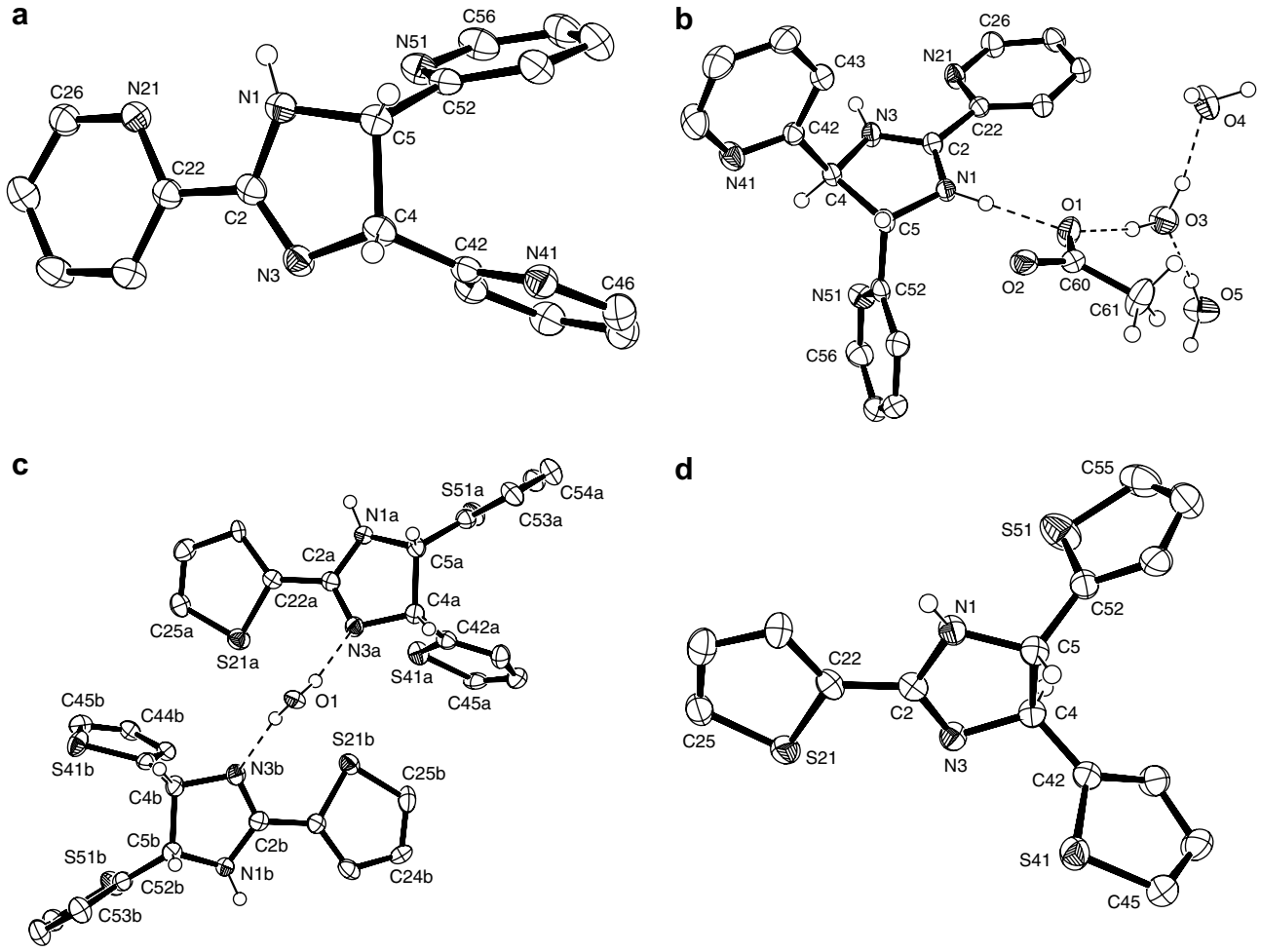


Fig. 1. (a) The molecule of *cis*-(**1**: Ar = pyridin-2-yl). (b) The asymmetric unit in the structure of [*trans*-(**1**: Ar = pyridin-2-yl)H]$^+$[OAc]$^-$·3H$_2$O. (c) The asymmetric unit in the structure of *cis*-(**1**: Ar = thien-2-yl)·0.5H$_2$O. (d) Molecule A of *trans*-(**1**: Ar = thien-2-yl). Ellipsoids are shown at the 50% probability level. Hydrogen atoms, where shown, are drawn as small spheres of arbitrary radii. For clarity selected non-hydrogen atoms of aryl groups are labelled.

or oxygen atoms were placed initially in positions determined by peaks in difference maps and then their coordinates and isotropic displacement parameters were refined in the usual manner. This same procedure was applied to the hydrogen atoms attached to carbon in the case of *cis*-(**1**: Ar = pyridin-2-yl). Otherwise hydrogen atoms attached to carbon were placed in calculated positions and refined with a riding model. The asymmetric unit of [*trans*-(**1**: Ar = pyridin-2-yl)H]$^+$[OAc]$^-\cdot 3H_2O$ comprises, in addition to the cationic imidazole, an acetate anion [C(60), C(61), O(1) and O(2)] and three water molecules [O(3)–O(5)]. The asymmetric unit of *cis*-(**1**: Ar = thien-2-yl) contains, in addition to a molecule of water [O(1)], two imidazole molecules which are distinguished by suffix A and B. The asymmetric unit of *trans*-(**1**: Ar = thien-2-yl) at 291(2) K is a single molecule but at 120(2) K comprises three imidazole molecules distinguished by suffix A, B and C. Three thiophenyl groups in *cis*-(**1**: Ar = thien-2-yl) and at both 120(2) K and 291(2) K one in *trans*-(**1**: Ar = thien-2-yl) are disordered over two positions related to one another by rotation through 180° about the bond connecting them to the imidazole ring. In such cases all of the ring atoms except that which bonds directly to the imidazole ring occur in the structural models in pairs as, for *cis*-(**1**: Ar = thien-2-yl), S41A/S41C, S21B/S21D and S41B/S41D with occupancies within each pair as 0.681(4)/0.329(4), 0.550(4)/0.450(4) and 0.670(4)/0.330(4), respectively. In *trans*-(**1**: Ar = thien-2-yl) at 120(2) K the disordered pair is of the form S51C/S51D with occupancies 0.700(4)/0.300(4) while at 291(2) K it is of the form S51/S51A with occupancies 0.647(11)/0.353(11). Successful refinement of the disordered rings required their bond lengths and bond angles to be restrained to match those of an ordered thienyl ring. The minor components of the disorder have been ignored in the preparation of the Figures and Tables.

Crystal data and structure refinement details are listed in Table 1.

3. Results and discussion

3.1. Synthesis

Our synthesis involved reaction of an aryl aldehyde, NH_4Cl and NEt_3 in methanol for ca. 24 h. The combination of NH_4Cl and NEt_3 provided both the ammonia for the reaction and a sufficiently strong basic media for the conversion of the aldehyde to *cis*-(**1**: Ar = 2-pyridinyl, 2-thienyl or Ph) in a one-pot reaction. Isomerisation of *cis*-**1** to *trans*-**1** were generally achieved by heating in Bu^{t}OH solution in the presence of KOBu^t, while, in addition, for *trans*-(**1**: aryl = 2-pyridinyl), isomerisation was achieved on heating an ethyl acetate solution. The product isolated from the

Table 2
Selected geometric parameters (Å, °) for various **1**

	cis-(**1**: R = py)	*trans*-(**1**: R = Py)H	*cis*-(**1**: R = Tp)		*trans*-(**1**: R = Tp) at 120(2) K			*trans*- (**1**: R = Tp) at 291(2) K	*cis*- (**1**: R = Ph)H[a,b]	*cis*-(**1**: R = p-tolyl) H[a,c]
			Mol. A	Mol. B	Mol. A	Mol .B	Mol.C			
N(1)–C(2)	1.369(2)	1.3142(17)	1.376(3)	1.369(3)	1.359(4)	1.369(4)	1.368(4)	1.357(5)	1.3135	1.3575
N(1)–C(5)	1.457(2)	1.4784(16)	1.470(3)	1.476(3)	1.463(4)	1.470(4)	1.458(4)	1.443(5)	1.4707	1.4824
C(2)–N(3)	1.287(2)	1.3211(17)	1.288(3)	1.299(3)	1.299(4)	1.292(4)	1.281(4)	1.285(5)	1.3168	1.3308
N(3)–C(4)	1.471(2)	1.4671(17)	1.479(3)	1.480(3)	1.477(4)	1.491(4)	1.482(4)	1.479(5)	1.4751	1.4859
C(4)–C(5)	1.584(2)	1.5676(18)	1.569(3)	1.569(3)	1.570(4)	1.554(4)	1.568(4)	1.572(6)	1.5638	1.5782
C(2)–C(22)	1.482(2)	1.4754(18)	1.460(3)	1.457(3)	1.456(4)	1.465(4)	1.452(4)	1.466(6)	1.4750	1.4775
C(4)–C(42)	1.501(2)	1.5181(18)	1.498(3)	1.500(3)	1.486(4)	1.493(4)	1.492(4)	1.496(6)	1.5110	1.5154
C(5)–C(52)	1.515(2)	1.5150(19)	1.495(3)	1.495(3)	1.494(4)	1.497(4)	1.499(4)	1.488(6)	1.5131	1.5320
C(2)–N(1)–C(5)	107.98(13)	110.80(11)	105.68(17)	105.70(17)	108.4(2)	107.0(2)	108.3(2)	109.1(3)	111.86	107.64
N(1)–C(2)–N(3)	117.18(14)	112.88(12)	116.93(19)	116.84(19)	116.6(3)	116.7(3)	116.7(3)	116.6(4)	111.21	108.82
C(2)–N(3)–C(4)	106.25(13)	111.21(11)	106.64(17)	106.74(17)	106.0(2)	105.9(2)	107.2(2)	106.4(3)	110.88	114.48
N(3)–C(4)–C(5)	105.59(12)	102.00(10)	103.55(16)	103.08(16)	105.3(2)	104.6(2)	104.8(2)	104.9(3)	100.97	101.27
N(1)–C(5)–C(4)	100.10(12)	102.17(10)	100.88(16)	101.16(16)	100.0(2)	100.6(2)	101.4(2)	100.5(3)	100.43	102.69
C(42)–C(4)–C(5)–C(52)	16.77(18)	129.38(12)	−26.8(3)	−30.0(3)	94.6(3)	−92.6(3)	−102.8(3)	99.1(5)	−23.49	−26.19
Q(2)[d] (Å)	0.166(2)	0.095(1)	0.246(2)	0.252(2)	0.186(3)	0.220(3)	0.125(3)	0.154(4)	0.211	0.223
ϕ(2)[d] (°)	144.5(6)	118.9(8)	318.9(5)	314.7(5)	313.7(9)	136.9(8)	138.6(14)	313.8(16)	301.63	300.53
Closest descriptor	Envelope On C(5)	Twist on C(4)–C(5)	Envelope On C(5)	Twist on C(4)–C(5)	Twist on C(4)–C(5)	Envelope on C(5)	Envelope on C(5)	Twist on C(4)-C(5)	Twist on C(4)–C(5)	Twist on C(4)–C(5)
Dihedral(2)[e] (°)	9.53(9)	16.54(8)	13.86(4)	11.7(9)	4.8(2)	14.6(2)	6.9(2)	8.2(4)	22.68	21.36
Dihedral(4)[e] (°)	66.40(4)	82.49(4)	74.9(3)	78.0(4)	76.64(11)	83.80(10)	85.59(11)	87.1(2)	81.41	49.35
Dihedral(5)[e] (°)	77.09(5)	80.80(5)	72.53(9)	77.45(8)	84.35(11)	73.91(10)	62.0(4)	84.8(7)	58.23	80.67

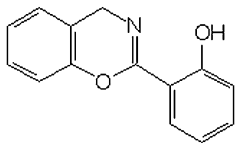
[a] Su's are lacking in the cif format coordinate data extracted from the Cambridge Structural Database [33], through the agency of the EPSRC Chemical Database Service at Daresbury [34], and also, therefore, in quantities derived from them.
[b] Ref. [11].
[c] Ref. [19].
[d] Pucker parameters as defined by Cremer and Pople [32].
[e] Dihedral(*n*) is the angle between the least-squares planes of the imidazole nucleus and the aryl substituent at C(*n*).

latter was found to be a hydrated acetic acid salt. The formation of the acetate salt clearly results from either acetic acid contamination of the solvent or, less probably, from hydrolysis of the ethyl acetate.

While solid **1** had localised structures, with distinct NH and N sites in the imidazole ring (see below) NMR spectra in solution indicated 2-fold symmetrical rings as a result of delocalisation of the hydrogen over the two ring nitrogen sites.

To obtain sufficiently good crystals for X-ray structure determinations, samples were recrystallised from different solutions. Thus obtained and used in the X-ray analyses were *cis*-(**1**: Ar = pyridin-2-yl), from MeCN solution, *cis*-[**1**: Ar = thien-2-yl·0.5H_2O] and *trans*-(**1**: Ar = thien-2-yl) both from EtOH and *trans*-{[(**1**: Ar = pyridin-2-yl)H]$^+$[OAc]$^-$·3H_2O} which was isolated from EtOAc.

A limitation in this being a general reaction for arylaldehydes was provided by 2-hydroxybenzaldehyde, which gave **3** on reaction with ammonium chloride and triethylamine in methanol solution.. This will be reported on elsewhere.



When $NaBH_4$ was added as an additional reagent to the thien-2-ylcarboxaldehyde, NH_4Cl. NEt_3, $NaBH_4$ reaction mixture, other products, in addition to *cis*-(**1**: Ar = thien-2-yl), were indicated. The major one of these was isolated by chromatography and shown to be tris(thien-2-ylmethyl)amine.

3.2. Crystal structures

The atom arrangements and numbering schemes for *cis*-(**1**: Ar = pyridin-2-yl), [*trans*-(**1**: Ar = pyridin-2-yl)H]$^+$[OAc]$^-$·3H_2O, *trans*-(**1**: Ar = thien-2-yl)·0.5H_2O and molecule A of *trans*-(**1**: Ar = thien-2-yl), all at 120 K, are shown in Fig. 1. The labelling of only selected atoms of the aryl substituents is possible because their carbon atoms are labelled in strict cyclic order. These examples indicate just how similar, apart from the disposition of the hydrogen atoms attached to C(4) and C(5), the *cis* and *trans* molecules are. All of the imidazoles in the structures whose refinements are reported in this paper are asymmetric and can exist as enantiomeric pairs. For the *cis* species the enantiomers differ with regard to which of the two nitrogen atoms in the imidazole ring is protonated and the 4R, 5S or 4S, 5R configurations at C(4) and C(5) are irrelevant. For the *trans* species the converse is true. Now it is the 4R, 5R or 4S, 5S configurations at C(4) and C(5)

Table 3
Hydrogen-bond parameters (Å, °) for various **1**

	D–H	H···A	D···A	D–H···A
a. *cis*-(**1**: Ar = pyridin-2-yl)				
N(1)–H(1)···N(41^{i})	0.90(2)	2.37(2)	3.1526(19)	145.1(16)
C(4)–H(4)···N(21^{ii})	0.984(16)	2.525(16)	3.331(2)	139.0(12)
Symmetry codes (i) $x, -y + 1/2, z - 1/2$; (ii) $x, -y + 1/2; z + 1/2$				
b. [*trans*-(**1**: Ar = pyridin-2-yl)H]$^+$[OAc]$^-$·3H_2O				
N(1)–H(1)···O(1)	0.894(19)	1.82(2)	2.7140(15)	178.9(18)
N(3)–H(3)···O(2^{i})	0.886(19)	1.84(2)	2.7111(16)	166.0(17)
O(3)–H(3A)···O(4)	0.92(2)	1.84(2)	2.7548(17)	170(2)
O(3)–H(3B)···O(1)	0.93(3)	1.85(3)	2.7666(15)	169(2)
O(4)–H(4A)···O(5^{ii})	0.89(2)	1.80(2)	2.6928(16)	175(2)
O(4)–H(4B)···N(41^{iii})	0.90(3)	2.09(3)	2.9832(17)	172(2)
O(5)–H(5A)···O(2^{iv})	0.89(3)	1.88(3)	2.7684(16)	173(2)
O(5)–H(5B)···O(3)	0.87(3)	1.84(3)	2.7060(17)	176(2)
Symmetry codes (i) $-x + 1/2, y - 1/2, -z + 1/2$; (ii) $-x + 1/2, y + 1/2, -z - 1/2$; (iii) $-x + 1/2, y + 1/2, -z + 1/2$; (iv) $-x + 1, -y + 2, -z$				
c. *cis*-(**1**: Ar = thien-2-yl)·0.5H_2O				
O(1)–H(1W)···N(3A)	0.80(3)	2.00(3)	2.791(2)	170(3)
O(1)–H(2W)···(N3B)	0.79(3)	2.01(3)	2.793(2)	171(3)
N(1A)–H(1A)···O(1^{i})	0.88(3)	2.06(3)	2.892(2)	158(2)
N(1B)–H(1B)···O(1^{ii})	0.88(3)	1.99(3)	2.845(2)	163(3)
C(5A)–H(5A)···S(21A^{i})	1.00	2.87	3.852(2)	169
Symmetry codes (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, -y, -z$				
d. *trans*-(**1**: Ar = thien-2-yl) at 120(2) K				
N(1A)–H(1A)···N(3B)	0.906(10)	2.020(17)	2.859(3)	153(3)
N(1B)–H(1B)···N(3C^{i})	0.907(10)	1.989(13)	2.876(3)	166(3)
N(1C)–H(1C)···N(3A)	0.901(10)	2.036(14)	2.913(3)	164(3)
Symmetry code (i) $-x + 3/2, y - 1/2, z$				
e. *trans*-(**1**: Ar = thien-2-yl) at 291(2) K				
N(1)–H1···N(3^{i})	0.90	2.07	2.918(5)	156
Symmetry code (i) $-x + 1/2, y - 1/2, z$				

which distinguish between the enantiomers and the protonation of the imidazole nitrogen atoms is now irrelevant. As a consequence the structures described in this paper, all of which are centrosymmetric, must be racemic. The known structures of *cis*-[(**1**: Ar = phenyl)·H]$^+$·Cl$^-$ [11] and *cis*-[(**1**: Ar = 4-tolyl)·H]$^+$·Br$^-$ [19], which are also centrosymmetric, are not racemic on this basis because, in both cases, both nitrogen atoms of the imidazole nucleus of the cation are protonated.

Selected geometric parameters for all of the structures whose structure determinations are described in this paper, and for two related structures, are given in Table 2. No bond length or bond angle data is given for the aryl substituents, which are not discussed in detail in this paper, because they are not unusual in any way, are comparatively poorly determined and, for some of the thienyl groups, subject to the effects of severe disorder. For the neutral molecules the N(1)–C(2) bond distances are in the range

Table 4
Parameters (Å, °) for selected π···π interactions in various **1**

Cg(I)···Cg(J)	Cg···Cg	α	β	γ	CgI_{perp}	CgJ_{perp}
a. *cis*-(**1**: Ar = pyridin-2-yl)						
Cg(3)···Cg(4)	3.814	39.75	24.70	27.36	3.387	3.465
Ring(3) with Cg(3) defined by N(41)/C(42)–C(46); ring(4) with Cg(4) defined by N(51)/C(52)–C(56)						
Intramolecular contact						
b. [*trans*-(**1**: Ar = pyridin-2-yl)H]$^+$[OAc]$^-$·3H$_2$O						
Cg(2)···Cg(3^i)	3.822	15.81	17.50	10.74	3.755	3.645
Ring(2) with Cg(2) defined by N(21)/C(22)–C(26); ring(3) with Cg(3) defined by N(41)/C(42)–C(46)						
Symmetry code (i) $-x+1/2, y-1/2, -z+1/2$						
c. *cis*-(**1**: Ar = thien-2-yl)·0.5H$_2$O						
Cg(2)···Cg(2^{iii})	3.999	0.0	20.61	20.61	3.743	3.743
Ring(2) defined by S(21B)/C(22B)–C(25B)						
Symmetry code (iii) $-x, -y, -z$						
d. *trans*-(**1**: Ar = thien-2-yl) at 120(2) K – no significant π···π interaction observed						
e. *trans*-(**1**: Ar = thien-2-yl) at 291(2) K – no significant π···π interaction observed						

Note. Cg···Cg is the distance between ring centroids (Å), CgI_{perp} is the perpendicular distance of Cg(I) from ring J (Å) and CgJ_{perp} the perpendicular distance of Cg(J) from ring I (Å). The angles in (°) are α – the dihedral angle between the planes, β – the angle between vectors Cg···Cg and CgI_{perp}, and γ – the angle between vectors Cg···Cg and CgJ_{perp}.

Table 5
Parameters (Å, °) for selected C–H···π interactions in various **1**

C–H···Cg	H···Cg	H_{perp}	γ[a]	C–H···Cg	C···Cg
a. *cis*-(**1**: Ar = pyridin-2-yl)					
C(24)–H(24)···Cg(3^{iii})	3.046	2.736	26.10	140.00	3.869
C(46)–H(46)···Cg(4^{ii})	3.297	2.953	26.38	131.26	4.029
Ring(3) with Cg(3) defined by N(41)/C(42)–C(46); ring(4) with Cg(4) defined by N(51)/C(52)–C(56)					
Symmetry codes (ii) $x, -y+1/2, z+1/2$; (iii) $-x, -y, -z+2$					
b. [*trans*-(**1**: Ar = pyridin-2-yl)H]$^+$[OAc]$^-$·3H$_2$O					
C(24)–H(24)···Cg(4^v)	3.166	2.902	23.58	118.70	3.717
C(25)–H(25)···Cg(4^v)	3.147	2.870	24.18	119.49	3.707
Ring(4) with Cg(4) defined by N(51)/C(52)–C(56)					
Symmetry code (v) $x-1/2, -y+3/2, z-1/2$					
c. *cis*-(**1**: Ar = thien-2-yl)·0.5H$_2$O					
C(5A)–H(5A)···Cg(1^i)	2.643	2.622	7.17	152.51	3.560
C(5B)–H(5B)···Cg(2^{ii})	2.751	2.705	10.57	153.44	3.673
Ring(1) with Cg(1) defined by S(21A)/C(22A)–C(25A); ring(2) with Cg(2) defined by S(21B)/C(22B)–C(25B)					
Symmetry codes (i) $-x+1, -y+1, -z$; (ii) $-x+1, -y, -z$					
d. *trans*-(**1**: Ar = thien-2-yl) at 120(2) K					
C(45A)–H(45A)···Cg(1^{ii})	2.683	2.670	5.53	139.15	3.457
C(45B)–H(45B)···Cg(2^{iii})	2.796	2.794	2.22	136.65	3.547
C(45C)–H(45C)···Cg(3^{iii})	2.727	2.714	5.60	148.77	3.573
Ring(1) defined by S(21A)/C(22A)–C(25A); ring(2) defined by S(21B)/C(22B)–C(25B) and ring(3) defined by S(21C)/C(22C)–C(25C). Symmetry codes (ii) $x-1, y, z$; (iii) $x+1, y, z$.					
e. *trans*-(**1**: Ar = thien-2-yl) at 291(2) K					
C(45)–H(45)···Cg(1^i)	2.856	2.856	0.34	145.33	3.658
Symmetry code (i) $x+1, y, z$					

[a] γ is the angle at the hydrogen atom between the vectors H···Cg and H_{perp}.

1.359(4)–1.376(3) Å and always significantly greater than the C(2)–N(3) bond distances which are in the range 1.281(4)–1.299(3) Å. In the cations the N(1)–C(2) and C(2)–N(3) distances are very similar within each cation and fall in the range 1.3142(17)–1.3575 Å. Otherwise the bond distances are very similar throughout the series with the C(4)–C(5) bond distances, in the range 1.554(4)–1.584(2) Å, always the longest.

The intra-ring bond angles are largely consistent throughout the entire series. The N(1)–C(2)–N(3) angle, however, in the range 116.6(3)–117.18(4)° is larger in the neutral molecules than in the cations where the corresponding range is 108.82–112.88(12)°. The converse is true for the C(2)–N(3)–C(4) angle which falls in the ranges 105.9(2)–107.2(2)° and 110.88–114.48° for the neutral molecules and the cations, respectively. None of the parameters discussed so far correlate with the *cis* or *trans* disposition of the hydrogen atoms attached to C(4) and C(5). The values of the C(42)–C4–C(5)–C(52) torsional angle clearly do, being in the ranges, in terms of magnitude, of 16.77(18)–30.0(3)° and 92.6(3)–129.38(12)° for the *cis* and *trans* cases, respectively. As expected the imidazole rings are non-planar and this is expressed in terms of the Cremer and Pople [32] pucker parameters. The departure from planarity is always one or other of two closely related types. Despite this, calculation of dihedral angles between least-squares planes provides a convenient, if somewhat approximate, means of assessing the disposition of the aryl substituents relative to the imidazole ring. The values for the substituent on C(2) occur in two ranges, in the range 4.8(2)–14.6(2)° for the neutral molecules where the aryl group is conjugated with the C(2)–N(3) double bond and 16.54(8)–22.68° for the cations where conjugation is absent. For the substituents on C(4) or C(5) the values, determined by the steric requirements of the substituents and the packing of the molecules, are greater and in the much wider range of 49.35–85.59(11)°. The dihedral angles provide the most obvious differences between molecules A and B and molecules A, B and C in the asymmetric units of *cis*-(**1**: Ar = thien-2-yl)·0.5H_2O and *trans*-(**1**: Ar = thien-2-yl) at 120(2), respectively.

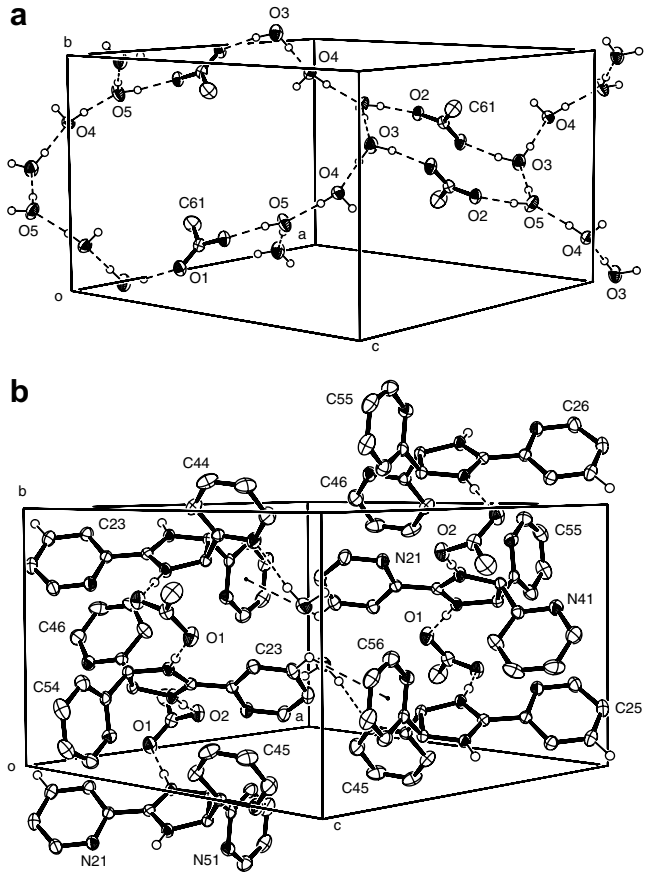


Fig. 3. Hydrogen bonds (dashed lines) in (a) the layer of acetate anions and water molecules and (b), along with C–H···π contacts, in the layer of imidazole cations in [*trans*-(**1**: Ar = pyridin-2-yl)H]$^+$[OAc]$^-$·3H_2O. Ellipsoids are drawn at the 50% probability level and the hydrogen atoms involved in the intermolecular contacts are shown as small spheres of arbitrary radii. Selected atoms are labelled.

Hydrogen-bonds (Table 3), π···π contacts (Table 4) and C–H···π interactions (Table 5) all contribute to the intermolecular connectivity in the structures whose refinements are

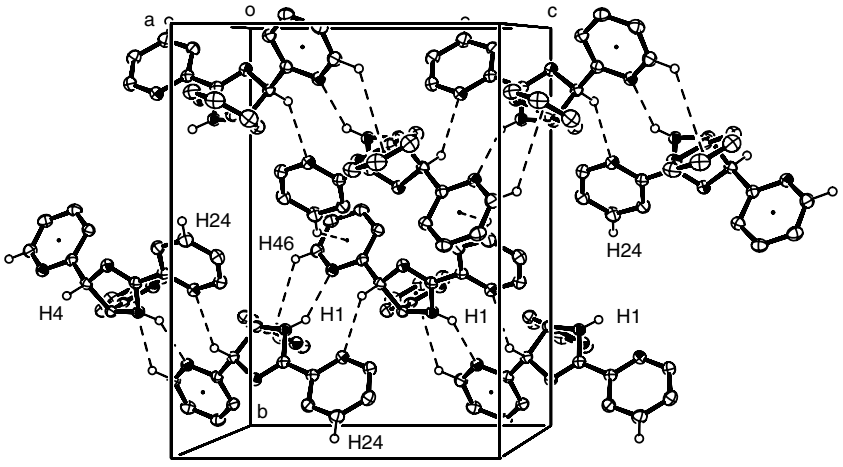


Fig. 2. Intermolecular connectivity (dashed lines) within a layer of molecules of *cis*-(**1**: Ar = pyridin-2-yl). Ellipsoids are drawn at the 50% probability level and the hydrogen atoms involved in the intermolecular contacts are shown as small spheres of arbitrary radii. Selected atoms are labelled.

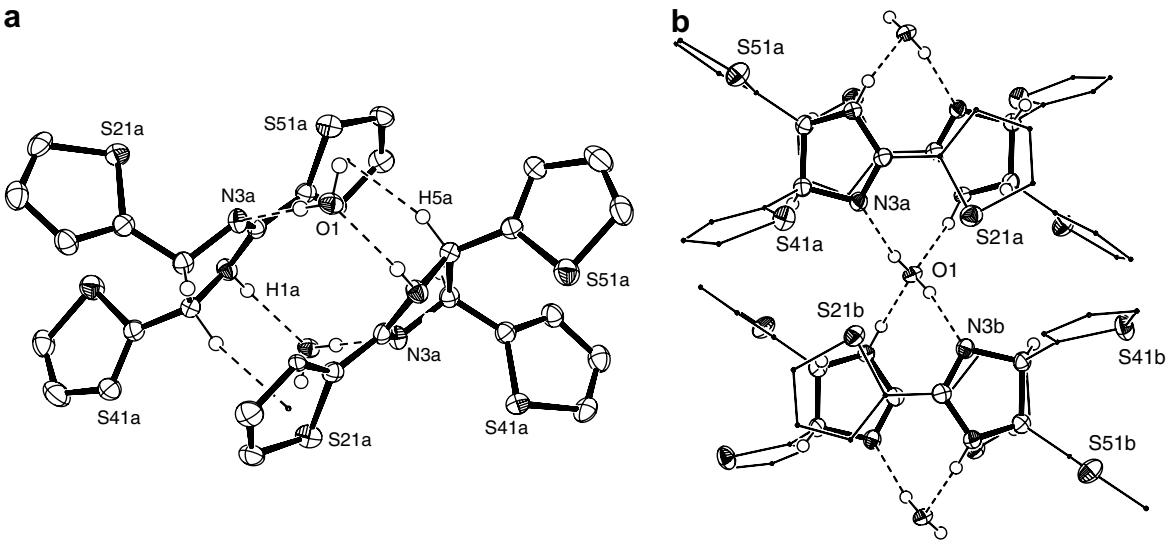


Fig. 4. Hydrogen-bonding in *cis*-(**1**: Ar = thien-2-yl)·0.5H_2O showing (a) the formation of centrosymmetric dimers exemplified for the case of molecule A and (b) type B and type A dimers alternating in a hydrpgen bonded chain propagated in the direction of b. In (b), for clarity, the carbon atoms of the thienyl groups are shown as point atoms and the bonds as thin lines. Selected atoms are labelled and in (b) they apply to the molecules at the front of the image. Ellipsoids are drawn at the 50% probability level and the hydrogen atoms which are present are shown as small spheres of arbitrary radii.

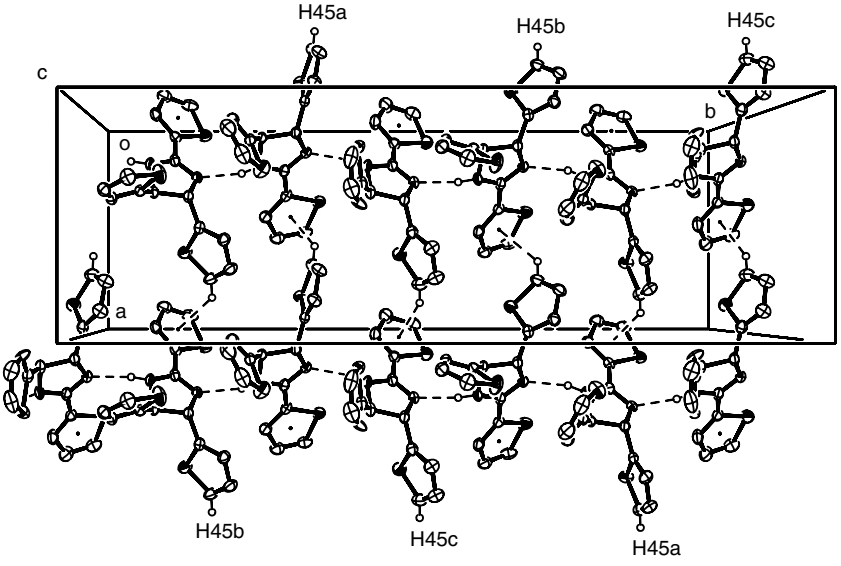


Fig. 5. A layer of molecules in *trans*-(**1**: Ar = thien-2-yl). Dashed lines running across the page represent hydrogen-bonds while those running up and down represent C–H···π contacts. Ellipsoids are drawn at the 50% probability level and the hydrogen atoms which are present are shown as small spheres of arbitrary radii.

described in this paper. In *cis*-(**1**: Ar = pyridin-2-yl), Fig. 2, the hydrogen-bonds of the form N(1)–H(1)···N(41) and C(4)–H(4)···N(21) and the C–H···π contact of the form C(46)–H(46)···Cg(4) interconnect the molecules to form zigzag chains propagated in the direction of *c*. Two of these, one each centred on $y = 1/4$ and 3/4, are shown in Fig. 2. The C–H···π contact of the form C(24)–H(24)···Cg(3) interconnects the chains to form layers, one unit cell thick, parallel to (1 0 0). There is no significant connectivity between the layers.

In [*trans*-(**1**: Ar = pyridin-2-yl)H]$^+$[OAc]$^-$·3H_2O the acetate anions and the water molecules are connected by hydrogen-bonds to form a two dimensional network in a layers parallel to (−1 0 1) (Fig. 3a). These layers alternate with layers of imidazole cations (Fig. 3b). Connectivity between the layers of anions and cations, which completes the three dimensional connectivity of the structure, is achieved by hydrogen bonds of the form N(1)–H(1)···O(1) and N(3)–H(3)···O(2) with the imidazole as donor and acetate as acceptor and O(4)–H(4B)···N(41) where water molecule O(4) is the donor species. The imidazole/acetate hydrogen-bonding creates chains propagated in the direct of b examples of which appear on either side of Fig. 3b. Connectivity between the chains within the imidazole layer, as distinct from that provided through the anion layer by

hydrogen-bonding, is provided by contacts of the form C(24)–H(24)···Cg(4) and C(25)–H(25)···Cg(4).

The water molecule has a particularly significant role in the structure of *cis*-(**1**: Ar = thien-2-yl)·0.5H_2O. First it participates in hydrogen-bonds which create centrosymmetric dimers comprising pairs of type A molecules (Fig. 4a) and, separately, virtually identical dimers of type B molecules. Second it links the dimers, alternating in type, to form chains propagated in the direction of b (vertically up the page in Fig. 4b). There is no significant intermolecular contact between the chains formed in this way.

In the structure of *trans*-(**1**: Ar = thien-2-yl) at both 120(2) K and 291(2) K the molecules occur in well defined layers parallel to (0 0 1) (Fig. 5) within which hydrogen-bonds of the form N(1)–H(1)···N(3) (Table 3d and e) connect the molecules to form chains propagated in the direction of b and the C–H···π contacts given in Table 5d and e connect the chains, related to one another by cell translation, in the direction of a and complete the connectivity within the layer. In neither case is there significant interaction between molecules in adjacent layers. The single molecule in the asymmetric unit of the structure of *trans*-(**1**: Ar = thien-2-yl) at 291 K is simply the average over the three molecules in the asymmetric unit of the structure of the same compound at 120 K. The 291 K structure has a number of deficiencies including an impossibly short intermolecular C–C contact and is clearly somewhat approximate.

These four examples reveal a remarkable variation in the packing and intermolecular connectivity between molecules which are not, in many respects as noted earlier, dramatically different from one compound to another.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2006.11.010.

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