Crystal structure and thermochromic behavior of the inclusion compounds of 4,5-diphenyl-2-(4-nitrophenyl)-1*H*-imidazole and of 4,5-diphenyl-2-(2-hydroxy-5-nitrophenyl)-1*H*-imidazole

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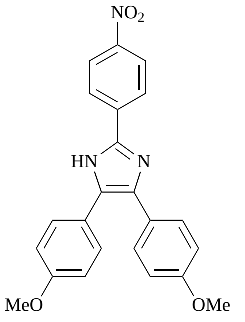
Menahem Kaftory,* Helena Taycher and Mark Botoshansky

Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

4,5-Diphenyl-2-(4-nitrophenyl)-1*H*-imidazole 2 and 4,5-diphenyl-2-(2-hydroxy-5-nitrophenyl)-1*H*-imidazole 3 form inclusion compounds with various guest molecules that possess hydrogen donor or hydrogen acceptor groups. The guest molecules play a crucial role in building up the three-dimensional structure. The guest molecules link host molecules through hydrogen bonds. The colors of the solid compounds vary from light yellow to dark red. The thermochromic properties have been determined by the removal of the guest molecules. The crystal structure and the thermal behavior are described and discussed.

Introduction

Dimers of 2,4,5-triarylimidazolyl radicals, that are obtained by the oxidation of 2,4,5-triarylimidazoles, have chromotropic properties.[1] The dimers dissociate to the radicals upon irradiation, heating and trituration. Similar properties have been detected[2] in crystals of 4,5-bis-(4-methoxyphenyl)-2-(4-nitrophenyl)imidazolium acetate dihydrate that show rapid color change upon drying, trituration or heating. The color change is found to be reversible below 70 °C. It was found that 4,5-bis(methoxyphenyl)-2-(4-nitrophenyl)-1*H*-imidazole **1** react with a wide variety of organic compounds to form inclusion compounds of various colors,[3] ranging from yellow to black. Some of the inclusion compounds have thermochromic properties. We have recently prepared new derivatives of imidazole that crystallize with guest molecules in various colors. Some of them show thermochromic properties. We describe here the crystal structure and thermal behavior of inclusion compounds of 4,5-diphenyl-2-(4-nitrophenyl)-1*H*-imidazole **2** with water **2a**, with acetic acid **2b** and dimethyl sulfoxide **2c**, and of 4,5-diphenyl-2-(2-hydroxy-5-nitrophenyl)-1*H*-imidazole **3** with dioxane **3a** and with picric acid **3b**. 4,5-Diphenyl-2-(4-nitrophenyl)-1*H*-imidazole is found to crystallize in four different polymorphs whose colors are yellow, lemon, orange and red. A detailed description of the polymorphs will be published elsewhere.



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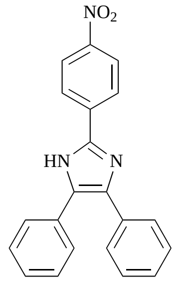

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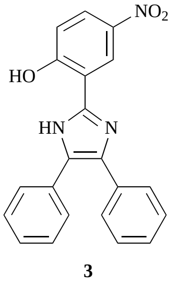

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Results and discussion

Crystal structure and thermal properties

4,5-Diphenyl-2-(4-nitrophenyl)-1*H*-imidazole–water, 2a. Selected bond lengths and angles are listed in Table 1. The hydrogen pattern and the molecular packing are shown in Fig. 1. The imidazole ring is planar, with a maximum out of plane displacement of 0.005 Å. The nitrophenyl is practically coplanar with the imidazole ring and the dihedral angle between the two planes is only 3.1(2)°. The other two phenyl rings are rotated by 22.3(2) and 43.3(1)° with respect to the imidazole ring. The molecular packing can best be described as being made up of sheets of molecules running parallel to the (2 0 2) plane (see Fig. 2). The distances between the sheets are 3.5–3.7 Å. The water molecules form the link between the parallel sheets of host molecules by hydrogen bonding. The water oxygen atom is hydrogen bonded to the HN of the imidazole (N1–H···O3). One of the two hydrogen atoms of the water molecule is hydrogen bonded to the nitrogen atom of a second host molecule (N2···H–O3), while the other hydrogen atom is hydrogen bonded to an oxygen of a nitro group of a third host molecule (O3–H···O2). The hydrogen bond distances between the heavy atoms are 2.888(3), 2.901(4) and 2.997(4) Å respectively. The thermal behavior of **2a** is shown by the differential scanning calorimeter (DSC) thermograph given in Fig. 3. The shallow endotherm between 110–158 °C is assigned to the removal of the water molecules ($\Delta H = 21.8$ kJ mol^{-1}). Upon removal of water the red crystals turned partially yellow, and at 237 °C the crystals turn completely red. This abrupt change in color is shown in the thermograph as a sharp endothermic peak ($\Delta H = 7.9$ kJ mol^{-1}). The endotherm is attributed to the phase change from the yellow to the red polymorph of the pure host compound.[4] The endotherm at 241 °C is assigned to the melting of the red polymorph ($\Delta H = 27.2$ kJ mol^{-1}).

4,5-Diphenyl-2-(4-nitrophenyl)-1*H*-imidazole–acetic acid, 2b. Selected bond lengths and angles are listed in Table 1. The molecular arrangement is shown in Fig. 4. The host compound crystallizes from acetic acid as orange plates. There are two crystallographically independent pairs of host–guest molecules in the asymmetric unit. One of the two molecules of acetic acid

Table 1 Comparison of selected bond lengths, *d*/Å

Bond	**2a**	**2b** (A)	**2b** (B)	**2c**	**3a**	**3b**
O(1)–N(3)	1.212(4)	1.201(4)	1.229(4)	1.210(5)	1.226(4)	1.230(4)
O(2)–N(3)	1.223(4)	1.223(4)	1.219(4)	1.218(5)	1.224(4)	1.224(4)
N(1)–C(7)	1.362(3)	1.343(3)	1.357(4)	1.348(5)	1.352(4)	1.341(4)
N(1)–C(8)	1.381(3)	1.374(4)	1.382(4)	1.376(4)	1.378(4)	1.377(4)
N(2)–C(7)	1.323(3)	1.332(4)	1.327(4)	1.319(4)	1.329(4)	1.339(4)
N(2)–C(9)	1.376(3)	1.386(4)	1.392(4)	1.378(4)	1.387(4)	1.391(4)
N(3)–C(4,5)[a]	1.464(4)	1.466(4)	1.470(5)	1.467(5)	1.458(4)	1.458(4)
C(1)–C(6)	1.390(4)	1.390(4)	1.389(4)	1.362(6)	1.388(4)	1.392(4)
C(1)–C(2)	1.395(4)	1.393(4)	1.397(4)	1.388(5)	1.405(4)	1.401(4)
C(1)–C(7)	1.460(3)	1.471(4)	1.467(4)	1.466(5)	1.458(4)	1.459(4)
C(2)–C(3)	1.379(4)	1.370(5)	1.383(5)	1.388(5)	1.393(5)	1.398(4)
C(3)–C(4)	1.365(4)	1.383(5)	1.364(5)	1.360(6)	1.367(5)	1.368(5)
C(4)–C(5)	1.366(4)	1.375(4)	1.379(5)	1.351(6)	1.376(5)	1.384(4)
C(5)–C(6)	1.381(4)	1.384(5)	1.382(5)	1.408(6)	1.370(4)	1.378(4)
C(8)–C(9)	1.384(4)	1.375(4)	1.379(4)	1.378(5)	1.378(4)	1.365(4)
O(3)–C(2)					1.339(4)	1.335(3)

[a] For **2a**, **2b** and **2c** read N(3)–C(4) and for **3a** and **3b** read N(3)–C(5).

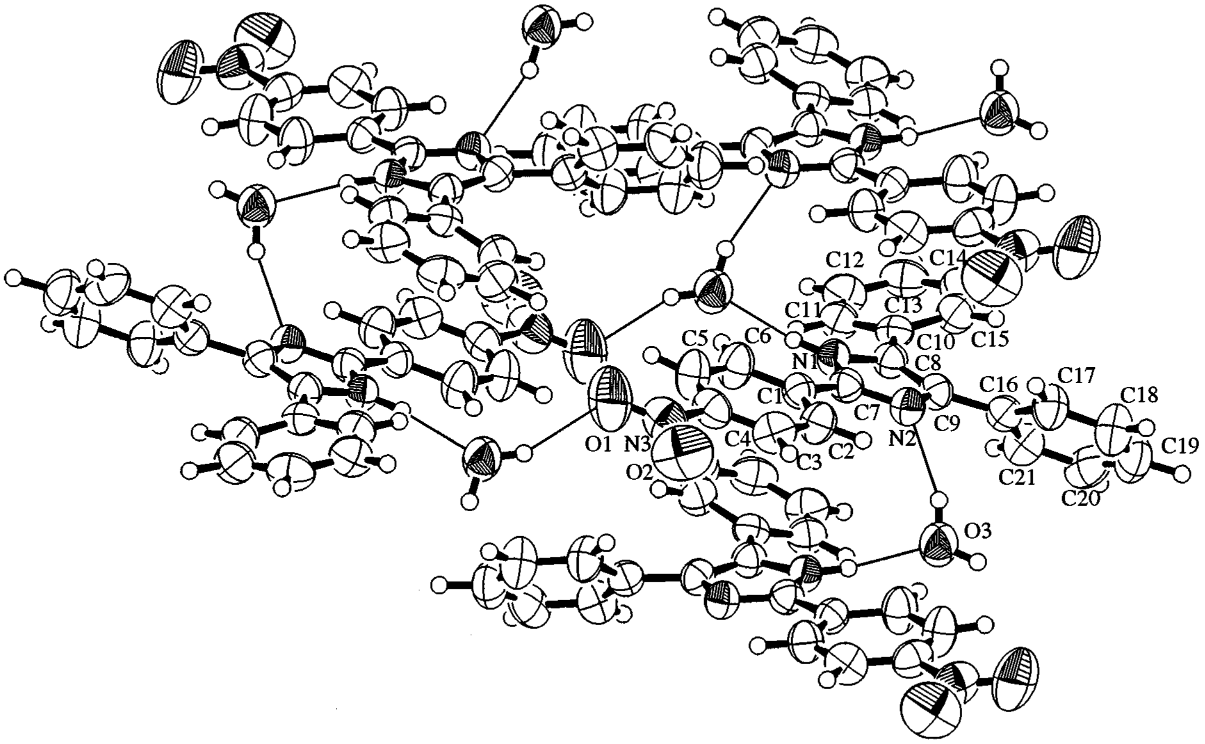

Fig. 1 Perspective diagram showing the hydrogen bonding between host–guest molecules of **2a**. The ellipsoids are drawn at the 50% probability level.

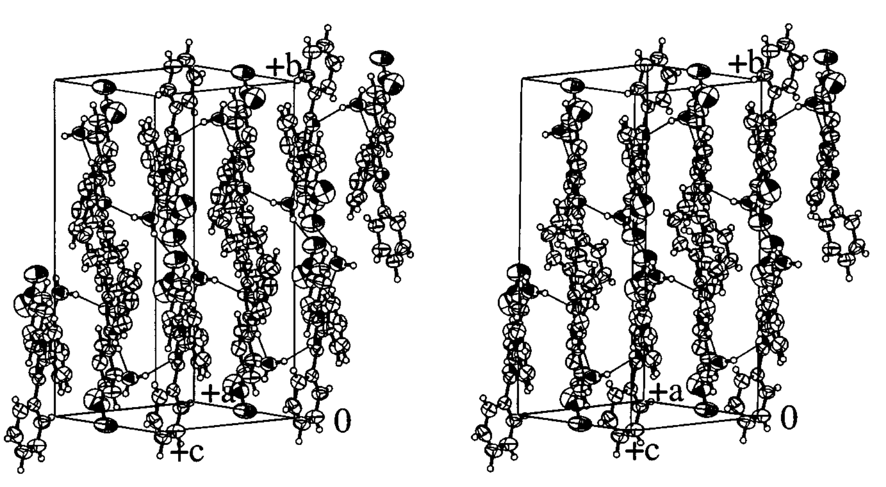

Fig. 2 Stereoscopic drawing showing packing arrangement parallel to (2 0 2). The ellipsoids are drawn at the 50% probability level.

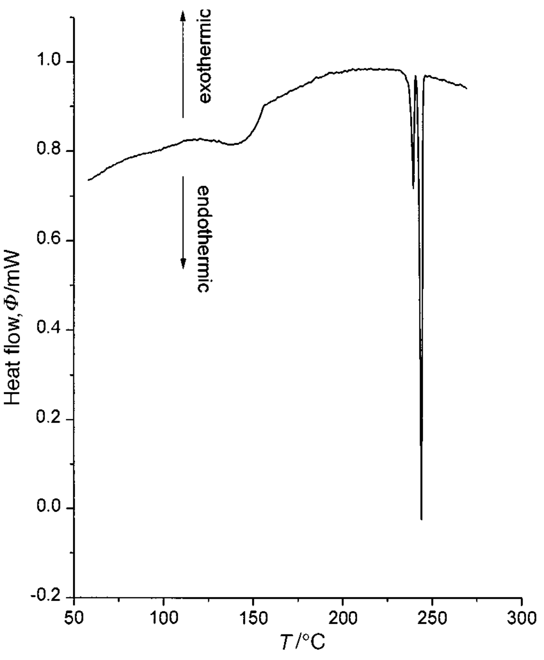

Fig. 3 DSC thermograph of **2a**

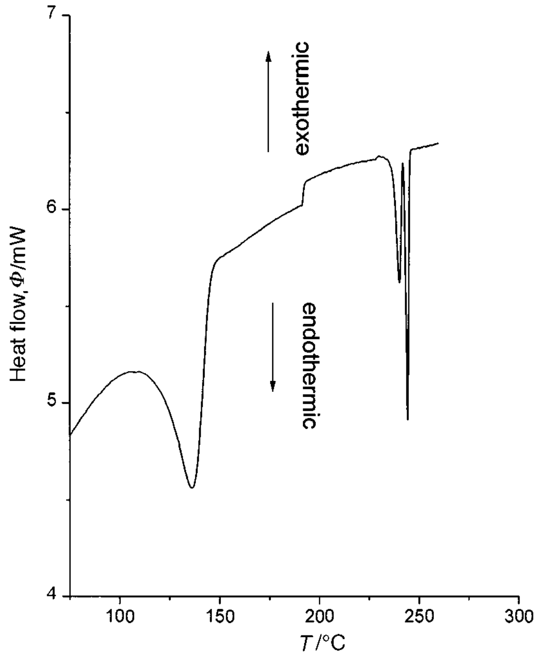

Fig. 5 DSC thermograph of **2b**

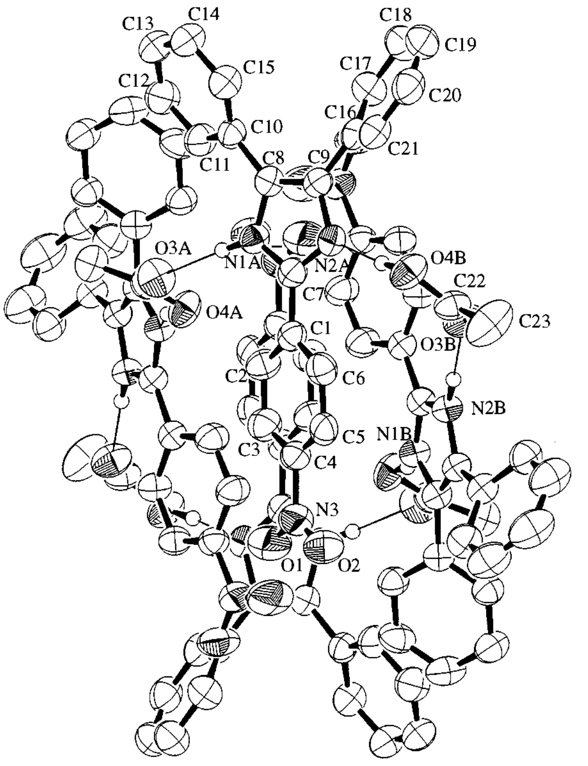

Fig. 4 Perspective diagram showing the hydrogen bonding between host–guest molecules of **2b**. The ellipsoids are drawn at the 50% probability level.

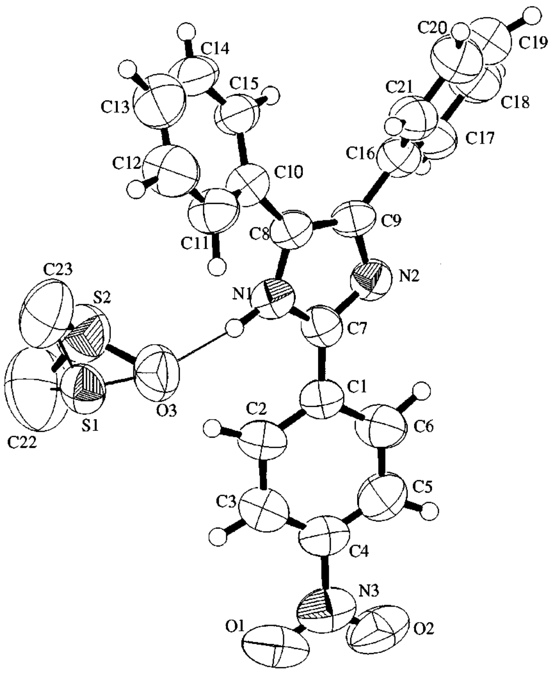

Fig. 6 Perspective diagram showing the hydrogen bonding between host–guest molecules of **2c**. The ellipsoids are drawn at the 50% probability level.

is *syn* and the other is *anti* with respect to the OCOH fragment. The two pairs of host–guest molecules form a ring with two other pairs related by an inversion center. The eight molecules that form the ring are connected to each other by hydrogen bonds between successive guest and host molecules (see Fig. 4). The carbonyl oxygen of the acetic acid molecule is hydrogen bonded to the HN group of imidazole (N1–H · · · O3). The OH group of acetic acid is hydrogen bonded to the nitrogen atom of the imidazole (O4–H · · · N2). The range of hydrogen bond distances is 2.681(3)–2.872(4) Å between the heavy atoms. The crystals are unstable in air and turn orange–red in a few days, but revert to their original color when the sample is exposed to acetic acid vapor. The loss and regain of acetic acid is also observed by using ^{1}H NMR spectra. The thermal behavior of **2b** is similar to that of **2a**. The DSC thermograph given in Fig. 5 shows an endotherm from 105 to 148 °C, which is assigned to loss of acetic acid ($\Delta H = 32.3$ kJ mol^{-1}) and followed by the phase transition from the yellow to the red polymorph of the pure host compound at 235 °C and melt at 242 °C. The enthalpies of the two last endotherms depends on the experimental conditions.

4,5-Diphenyl-2-(4-nitrophenyl)-1*H*-imidazole–dimethyl sulfoxide, 2c. Selected bond lengths and angles are listed in Table 1. While in the two compounds mentioned above the guest molecules form links between the host molecules, the guest molecule, dimethyl sulfoxide (DMSO), has no such role in determining the three-dimensional structure of **2c**. The DMSO is disordered between two equally distributed orientations, determined by the position of the sulfur atom (see Fig. 6). The

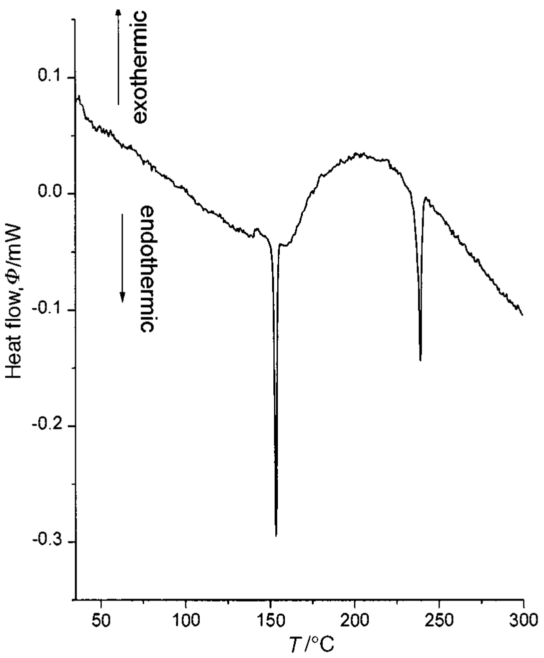

Fig. 7 DSC thermograph of **2c**

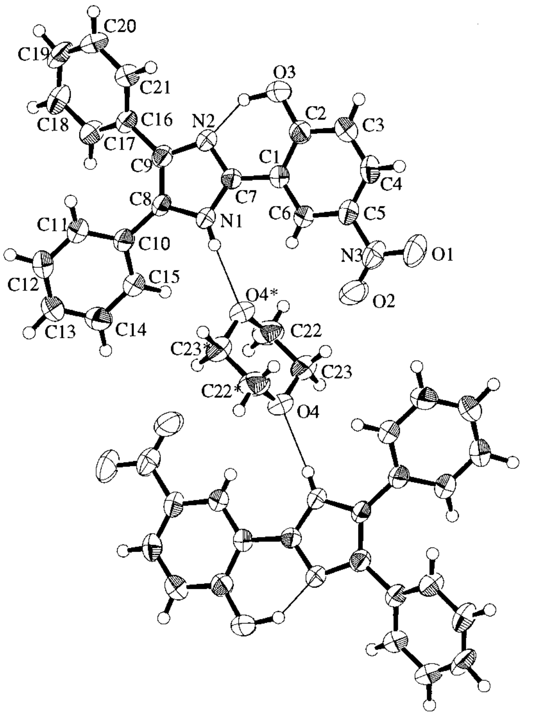

Fig. 8 Perspective diagram showing the hydrogen bonding between host–guest molecules of **3a**. The ellipsoids are drawn at the 50% probability level.

thermal behavior of a single crystal of (**2c**) is shown in Fig. 7. The endotherm at 148 °C ($\Delta H = 10.5$ kJ mol^{-1}) is assigned to the removal of the guest molecule while the endotherm at 235 °C ($\Delta H = 9.7$ kJ mol^{-1}) is assigned to the melting of the pure host compound. The yellow polymorph of the pure host compound was not observed.

4,5-Diphenyl-2-(2-hydroxy-5-nitrophenyl)-1*H*-imidazole–dioxane (1/2), 3a. Selected bond lengths and angles are listed in Table 1. When the host compound is crystallized from dioxane, silky, yellow plate crystals are formed. The imidazole and the 2-hydroxy-5-nitrophenyl rings are nearly coplanar, making a dihedral angle of 4.6(2)°. The coplanarity is attributed to the intramolecular hydrogen bond between the hydroxy and the nitrogen atom of the imidazole. The dioxane molecule lies on an inversion center and links two host molecules by hydrogen

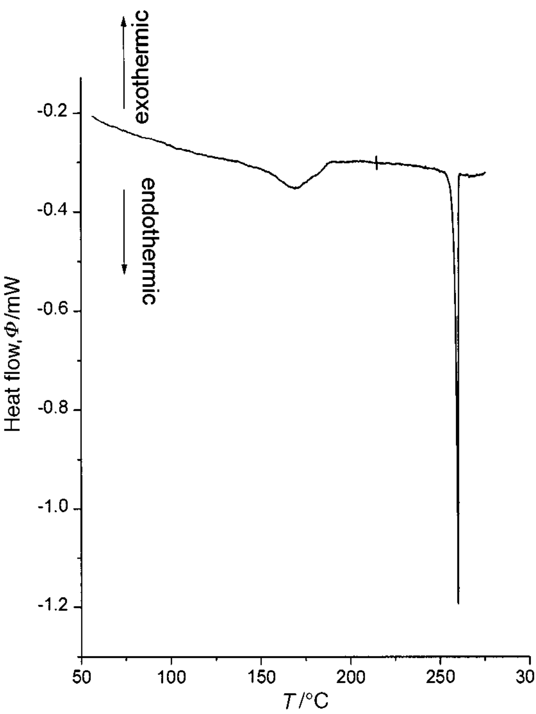

Fig. 9 DSC thermograph of **3a**

bonds with HN of the imidazole (see Fig. 8). The intramolecular hydrogen bond distance is 2.564(4) Å and the intermolecular hydrogen bond distance is 2.876(3) Å. 4,5-Bis(4-methoxyphenyl)-2-(4-nitrophenyl)-1*H*-imidazole which forms an inclusion compound with dioxane[3] is shown to have different packing; one molecule of dioxane is hydrogen bonded to the HN of the imidazole, while a second dioxane molecule in a disordered state, lies in a cavity encircled by four methoxyphenyl groups. The thermal behavior of **3a** is shown by the DSC thermograph in Fig. 9. Between 151–180 °C the dioxane is removed ($\Delta H = 20.8$ kJ mol^{-1}) and the crystal becomes orange. The second endotherm at 256 °C is assigned to the melting temperature of the host compound ($\Delta H = 19.8$ kJ mol^{-1}).

4,5-Diphenyl-2-(2-hydroxy-5-nitrophenyl)-1*H*-imidazolium–picrate, 3b. Crystallization of the host compound and picric acid from ethanol forms orange–yellow crystals with the shape of distorted hexagonal prisms. Selected bond lengths and angles are listed in Table 1. The packing arrangement showing the hydrogen bonds in **3b** is given in Fig. 10. The imidazole ring is protonated by the acid proton of picric acid. However there is no effect on the bond lengths involved with the nitrogen atoms. The bond lengths are 1.327(4) and 1.345(4) Å for the formally HN=C double bond and for the HN–C formally single bond, respectively. Similar bond lengths have been observed in the crystal structure of 4,5-bis(4-methoxyphenyl)-2-(4-nitrophenyl)-1*H*-imidazolium acetate dihydrate[2] where the equivalent bond lengths are 1.336(6) and 1.346(10) Å. The same bond lengths in imidazolium picrate,[5] on the other hand, are 1.305 and 1.318 Å.

The dihedral angle between the imidazole ring and the 2-hydroxy-5-nitrophenyl is 17.4(1)°, slightly larger than the dihedral angle found in **3a**. The difference is explained by the loss of the OH · · · N(imidazole) intramolecular hydrogen bond that is replaced by the less favorable HO · · · HN(imidazole) hydrogen bond. The O · · · N distances are 2.564(4) and 2.744(4) Å, respectively. Two molecules of the host that are related by an inversion center are interlinked by a picrate molecule through hydrogen bonds thus forming a ring (see Fig. 10).

The thermochromic properties of the imidazolium picrate are not fully understood. The crystal color changes twice while the crystals are heated. At first, there is a loss of the shiny crystal faces, which takes place between 140–180 °C. In the

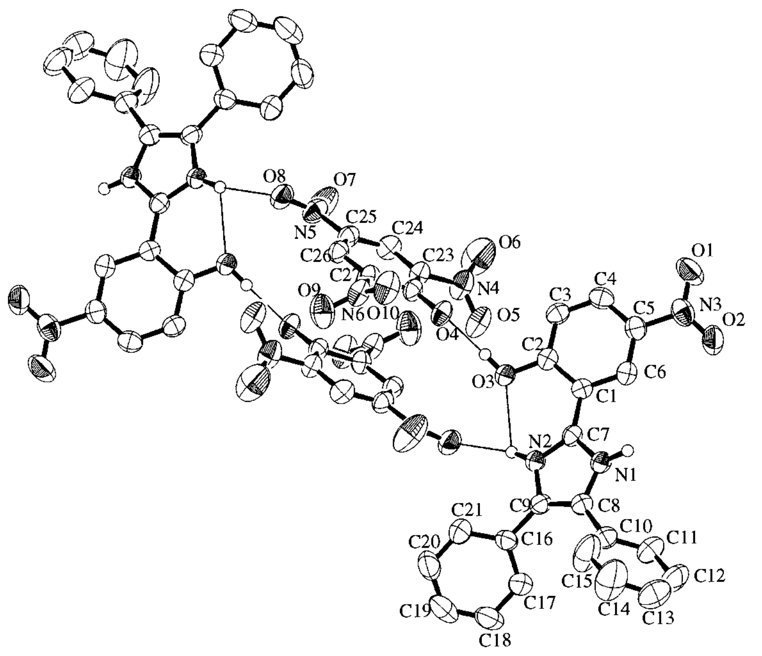

Fig. 10 Perspective diagram showing the hydrogen bonding between host–guest molecules of **3b**. The ellipsoids are drawn at the 50% probability level.

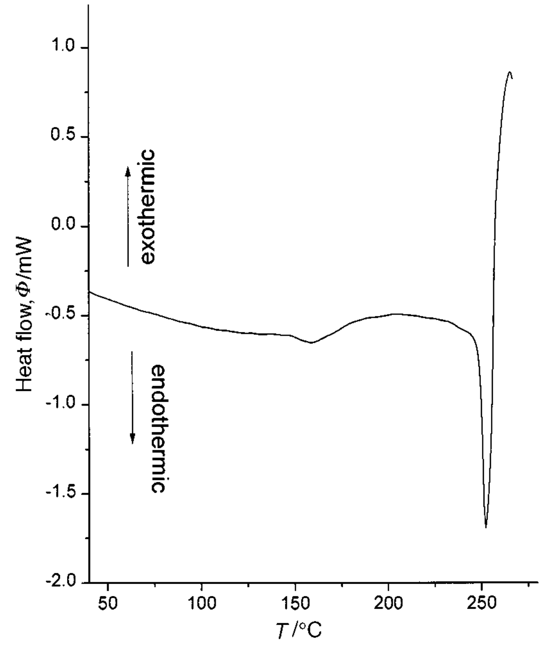

Fig. 11 DSC thermograph of **3b**

second stage, there is a color change from orange to yellow between 220–240 °C. High temperature X-ray diffraction did not show any significant change of the diffraction pattern, nor was a significant change in the ^1H NMR spectra observed. The DSC thermograph (see Fig. 11) shows two endotherms. The first at the range of 147–173 °C which was found to be reversible ($\Delta H = 10.9$ kJ mol^{-1}) and may be attributed to a proton transfer from imidazolium to the picrate to form imidazole and picric acid. Such a process was also observed by heating bis(4-methoxyphenyl)-2-(4-nitrophenyl)-1*H*-imidazolium acetate dihydrate.[2] The second endotherm at 241 °C ($\Delta H = 99.6$ kJ mol^{-1}) is assigned to the melting of the imidazole–picric acid compound. The thermal behavior is under study.

Geometry of the imidazole ring

The average HN–C bond length in imidazole was calculated using 134 values obtained from the Cambridge Structural Database (CSD)[6] to be 1.345(1) Å. The average of the N=C double bonds was calculated to be 1.324(1) Å. The calculated average bond lengths are in excellent agreement with those observed by neutron diffraction of the unsubstituted imidazole,[7] 1.347 and 1.322 Å for HN–C and N=C bond lengths, respectively. The range of the equivalent bond lengths observed in **2a**, **2b**, **2c**, **3a** are 1.343–1.362 Å and 1.319–1.332 Å for the HN–C and N=C bond lengths, respectively. In imidazole the N=C double bond is localized, however it is delocalized in imidazolium. This effect can be observed by comparing the bond lengths discussed above. Of 69 observations extracted from the CSD, only nine examples of the differences between the two N–C bond lengths are larger than 3σ of a bond length (0.2 Å). The average HN–C bond length, omitting the nine exceptions, was found to be 1.335(1) Å. In the exceptional example the double bonds seem to be localized as in imidazole. In the most extreme cases the differences between the bond lengths are even more pronounced than in imidazole. These bond lengths were observed in guanine hydrobromide monohydrate,[8] 1.310 and 1.340 Å, in guanine hydrochloride monohydrate[9] 1.316 and 1.348 Å, and in 6-thioguanine picrate monohydrate[10] 1.300 and 1.335 Å.

Experimental

The host molecules **2** and **3** were synthesized according to the Davidson method,[11] and were characterized by ^1H NMR. The inclusion compounds **2a**–**2c**, and **3a** were obtained by crystallization from the guest solvent; **3b** was obtained by grinding equimolar amounts of the guest and the host compounds and recrystallization from ethanol solution. The host : guest stoichiometric ratios were based on the accurate determination of the crystal structures of single crystals. Since the guest molecules are hydrogen bonded to the host molecules and in all cases the temperatures at which they leave the solid material are above 100 °C, it is assumed that the host : guest stoichiometric ratio is the same as that of the single crystal.

Thermal analyses were carried out using a DSC PL (Polymer Laboratories). The temperatures mentioned in the paper are the onset and not the peak temperatures.

Data collection, structure analysis and refinement

Data collection for all crystals was done on a Phillips PW 11000 diffractometer, $\omega/2\theta$ mode, graphite monochromator, Mo-Kα radiation. The crystal structures were solved by direct methods and refined by a full-matrix least-squares procedure using F^2. All non-hydrogen atoms were refined with anisotropic hydrogen atoms with isotropic atomic displacement parameters. Final agreement factors and other refinement details are given below for each crystal structure. A list of computer programs used and sources of data are given in ref. 12.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC Web pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/110.

Crystal data

2a, $C_{21}H_{15}N_3O_2\cdot H_2O$, $M = 359.38$. Monoclinic, $a = 9.332(4)$, $b = 19.053(9)$, $c = 10.127(5)$ Å, $\beta = 91.92(5)°$, $V = 1799.6(9)$ Å^3, $\lambda = 0.710\,69$ Å, space group $P2_1/c$, $Z = 4$, $D_c = 1.326$ g cm^{-3}. Red rhombic crystal of size 0.4 × 0.2 × 0.1 mm, μ(Mo-Kα) = 0.091 mm^{-1}. 3366 reflections measured ($2.1 < \theta < 25.0°$), 3028 used for refinement of 312 parameters. Final agreement factors are: $R = 0.068$, $wR = 0.136$, for reflections with $[I > 2\sigma(I)]$, $R = 0.121$, $wR = 0.159$ for all the data.

2b, $C_{21}H_{15}N_3O_2\cdot C_2H_4O_2$, $M = 401.41$. Monoclinic, $a = 10.849(4)$, $b = 28.71(1)$, $c = 13.839(5)$ Å, $\beta = 110.50(4)°$, $V = 4038.1(9)$ Å^3, $\lambda = 0.710\,69$ Å, space group $P2_1/c$, $Z = 8$, $D_c = 1.321$ g cm^{-3}. Orange plate crystal of size 0.6 × 0.4 × 0.2 mm, μ(Mo-Kα) = 0.092 mm^{-1}. 8050 reflections measured ($2.5 < \theta < 27.0°$), 7189 used for refinement of 693 parameters. Final agreement factors are: $R = 0.062$, $wR = 0.133$, for reflections with $[I > 2\sigma(I)]$, $R = 0.125$, $wR = 0.184$ for all the data.

2c, $C_{21}H_{15}N_3O_2\cdot C_2H_6SO$, $M = 419.50$. Monoclinic, $a = 7.753(3)$, $b = 28.413(10)$, $c = 10.337(4)$ Å, $\beta = 110.97(3)°$, $V = 2126.1(14)$ Å^3, $\lambda = 0.710\,69$ Å, space group $P2_1/n$, $Z = 4$, $D_c = 1.311$ g cm^{-3}. Orange–yellow prism crystal of size 0.4 × 0.1 × 0.1 mm, μ(Mo-Kα) = 0.182 mm^{-1}. 3959 reflections measured ($2.2 < \theta < 25.0°$), 2300 used for refinement of 382 parameters. Final agreement factors are: $R = 0.077$, $wR = 0.170$, for reflections with $[I > 2\sigma(I)]$, $R = 0.248$, $wR = 0.344$ for all the data.

3a, $C_{21}H_{15}N_3O_3\cdot 1/2C_4H_8O_2$, $M = 401.41$. Triclinic, $a = 13.652(4)$, $b = 10.220(3)$, $c = 7.774(2)$ Å, $\alpha = 109.21(3)$, $\beta = 82.96(3)$, $\gamma = 108.89(3)°$, $V = 968.9(4)$ Å^3, $\lambda = 0.710\,69$ Å, space group $P\bar{1}$ (No. 2), $Z = 2$, $D_c = 1.376$ g cm^{-3}. Silky yellow plate crystal of size 0.4 × 0.2 × 0.1 mm, μ(Mo-Kα) = 0.096 mm^{-1}. 3680 reflections measured ($2.2 < \theta < 25.0°$), 3212 used for refinement of 347 parameters. Final agreement factors are: $R = 0.066$, $wR = 0.118$, for reflections with $[I > 2\sigma(I)]$, $R = 0.119$, $wR = 0.141$ for all the data.

3b, $C_{21}H_{16}N_3O_3\cdot C_6H_2N_3O_7$, $M = 586.47$. Triclinic, $a = 13.119(4)$, $b = 13.988(4)$, $c = 8.171(2)$ Å, $\alpha = 91.83(3)$, $\beta = 108.03(3)$, $\gamma = 64.80(2)°$, $V = 1281.4(6)$ Å^3, $\lambda = 0.710\,69$ Å, space group $P\bar{1}$ (No. 2), $Z = 2$, $D_c = 1.520$ g cm^{-3}. Orange–yellow distorted hexagonal crystal of size 0.4 × 0.2 × 0.1 mm, μ(Mo-Kα) = 0.119 mm^{-1}. 4856 reflections measured ($2.6 < \theta < 25.0°$), 4356 used for refinement of 460 parameters. Final agreement factors are: $R = 0.056$, $wR = 0.115$, for reflections with $[I > 2\sigma(I)]$, $R = 0.118$, $wR = 0.131$ for all the data.

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