Solid–gas reactions between 1,3-dimethylbarbituric acid and amines. A structural and spectroscopic study

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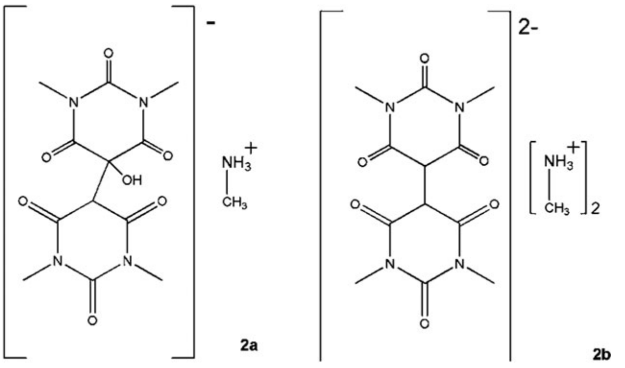
The reactions of solid 1,3-dimethylbarbituric acid (DMBA) with vapours of NH_3 and of the volatile amines $NH_2(CH_3)$ and $NH(CH_3)_2$ have been investigated. The barbiturate salts (DMB) $[NH_4]$DMB (**1**), $[NH_3(CH_3)]$DMB (**2**) and $[NH_2(CH_3)_2]$DMB (**3**) have been characterized by X-ray powder diffraction, differential scanning calorimetry and thermogravimetric analysis. The solid–gas reactions were monitored by UV–Vis spectroscopy in the solid state. Single crystal X-ray diffraction was used to characterize compounds **1**, obtained by recrystallization from methanol, and **3**, obtained by direct reaction of DMBA with aqueous $NH(CH_3)_2$. In the case of **3**, recrystallization from methanol yields the salt $[NH_2(CH_3)_2][DMB]\cdot 2[DMBA]$ (**3a**), while recrystallization of **2** yields both the dimerization product $[NH_3(CH_3)][(C_6O_3N_2H_6)_2\text{-}OH]\cdot 2H_2O$ (**2a**) and the hydurilate salt $[NH_3(CH_3)]_2[(C_6O_3N_2H_6)_2]$ (**2b**), *i.e.* the product **2** is only accessible *via* the solid–gas reaction.

Introduction

Solvent-free reactions, such as those occurring in the solid state[1–4] between a crystalline solid and a vapour, have many advantages and are important from the environmental viewpoint.[5] Even though solid–gas chemistry has been the subject of investigations in the past decades,[6] there is a rapidly growing literature on recent applications of solid–gas reactions[2] to the preparation of novel systems,[7,8] including supramolecular ones with important implications in host–guest chemistry[9] and gas-trapping[10,11] as well as in the investigation of crystal polymorphism.[12] Solid–gas and solid–solid reactions involving organometallic acids and organic bases as well as organometallic bases and volatile acids have been studied by our group.[13–17]

More recently, we have reported the investigation of the reactions between barbituric acid and volatile amines,[18] with a focus on the reactivity of the different crystal forms of barbituric acid. Based on this experience we have extended the investigation of solid–gas reactions to the interactions between 1,3-dimethylbarbituric acid (DMBA) and the volatile amines NH_3, $NH_2(CH_3)$, and $NH(CH_3)_2$. In contrast to barbituric acid, the crystal structure of DMBA does not contain any traditional H-donor group that would enable formation of strong hydrogen bonding interactions. The structure of DMBA[19] is composed of molecular chains linked by C–H···O interactions.[20] Gilli *et al.* have reported the preparation of co-crystals of DMBA with aromatic amines as H-bond donors.[19]

The gas–solid reactions between DMBA and the volatile amines yield the polycrystalline dimethylbarbiturate (DMB) salts: $[NH_4]$DMB (**1**), $[NH_3(CH_3)]$DMB (**2**) and $[NH_2(CH_3)_2]$DMB (**3**), which have been investigated by powder diffraction, DSC, TGA as well as UV–Vis spectroscopy. Single crystal growth was attempted *via* recrystallization of polycrystalline **1**, **2** and **3** from methanol, but it was successful only for **1** and **3**. The powder diffraction patterns computed on the basis of the single-crystal structures were compared with the ones measured on the polycrystalline materials. The structure of $[NH_3(CH_3)]$DMB (**2**) has been determined from powder diffraction data with the DASH software (see below).[21] Recrystallization of **2** from methanol yields the dimerization product $[NH_3(CH_3)][(C_6O_3N_2H_6)_2\text{-}OH]\cdot 2H_2O$ (**2a**) and the hydurilate salt $[NH_3(CH_3)]_2[(C_6O_3N_2H_6)_2]$ (**2b**) (see Scheme 1) while recrystallization of $[NH_2(CH_3)_2]$DMB (**3**) yields the salt $[(CH_3)_2NH_4][DMB]\cdot 2[DMBA]$ (**3a**). It had



Scheme 1

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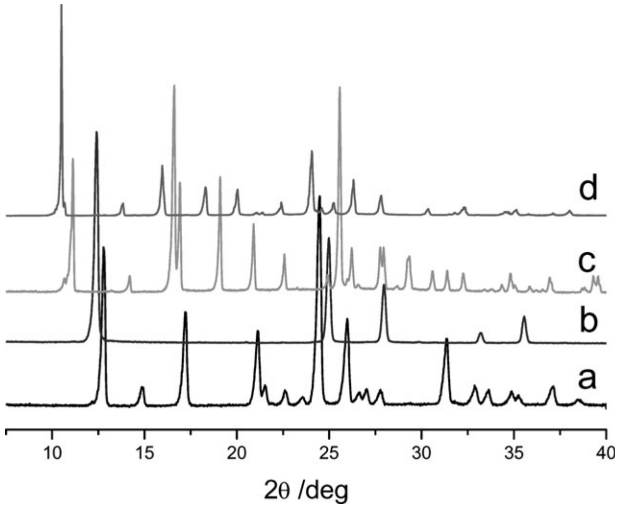

Fig. 1 Comparison between the powder diffraction patterns of unreacted 1,3-dimethylbarbituric acid (a) and those measured after exposure to vapours of NH_3 (b), $NH_2(CH_3)$ (c), $NH(CH_3)_2$ (d).

previously been observed that a basic environment promotes the diketone enolization of DMBA.[22]

Results and discussion

Solid–gas reactions of dimethylbarbituric acid with amines

The X-ray powder diffraction (XRPD) analysis of the products obtained by solid–gas reaction of 1,3-dimethylbarbituric acid with the amines is reported in Fig. 1. The reaction processes were monitored in all cases after two days of exposure to the base vapours. The XRPD patterns reveal that all products are crystalline; no trace of unreacted DMBA was detected. All reaction products were also characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The TGA measurements show that the release of the amines is followed by evaporation of DMBA at 200 °C. The DSC of DMBA shows the melting of the acid at 121 °C, while DSC measurements of **1**, **2** and **3** all show a broad endothermic peak with onset at *ca.* 144 °C; this might be due to release of base vapours, as heating these salts under vacuum at 100 °C partially results in the formation of the starting DMBA. Removal of base by vacuum treatment is never complete, because of sublimation of part of the sample and its recondensation on the internal walls of the flask.

The solid state structure of $[NH_4]$DMB (1) as obtained *via* recrystallization of polycrystalline 1 from methanol

Well shaped crystals of **1**, suitable for single-crystal X-ray diffraction, were obtained by recrystallization in methanol of the powder obtained *via* the heterogeneous reaction of DMBA with NH_3. The structural analysis revealed formation of the dimethylbarbiturate salt $[NH_4]$DMB, **1**. The dimethylbarbiturate anion is disordered over three orientations, thus generating a crystallographic ternary axis. As a matter of fact, the structure has been solved in the trigonal crystal system *P*3*c*1. The dimethylbarbiturate anions are organized in layers (one of these is shown in Fig. 2), which are then stacked on top of each other at the interplanar distance of 3.58 Å. The ammonium cations act as bridges between the anions *via* charge assisted $N–H^{(+)}\cdots O^{(-)}$ hydrogen bonds (Fig. 2, N···O distances 2.872(6) and 2.886(7) Å). The powder diffraction pattern calculated on the basis of the crystal structure was compared with that obtained by the solid–gas reaction, and both correspond to the same crystal structure (Fig. 3).

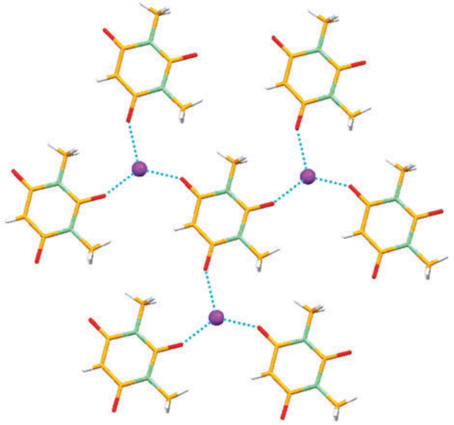

Fig. 2 One of the layers formed by the dimethylbarbiturate anions in crystalline **1**, with the ammonium cations acting as bridges between the anions *via* charge assisted $N–H^{(+)}\cdots O^{(-)}$ hydrogen bonds (N···O distances 2.872(6) and 2.886(7) Å). Only one of the three disordered images is shown; $H_{N–H}$ atoms not shown for clarity).

The solid state structure of the condensation products $[NH_3(CH_3)][(C_6O_3N_2H_6)_2\text{-}OH]\cdot 2H_2O$ (2a) and $[NH_3(CH_3)]_2[(C_6O_3N_2H_6)_2]$ (2b), obtained *via* recrystallization of polycrystalline 2 from methanol

Attempts to obtain single crystals of **2** by recrystallization from solution succeeded in two cases, but the single crystals obtained were found to be condensation products, due to the diketone enolization promoted by the basic environment, as observed previously.[19,22] In the first case recrystallization of a diluted solution of **2** yielded the salt of formula

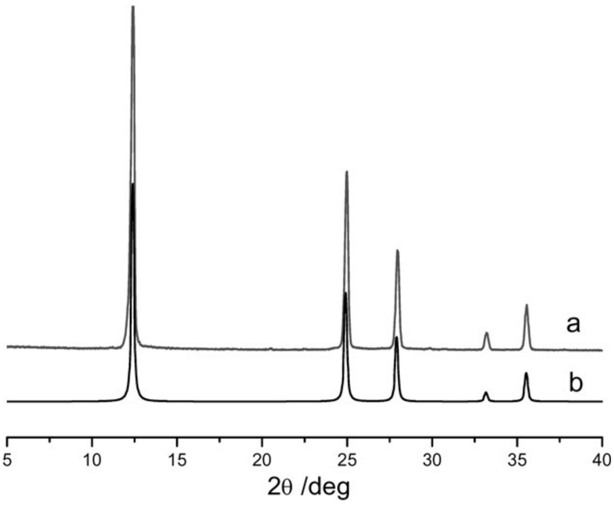

Fig. 3 Comparison between the powder pattern calculated on the basis of the single-crystal structure (b) and that measured on the powder of the dimethylbarbiturate salt **1** (a).

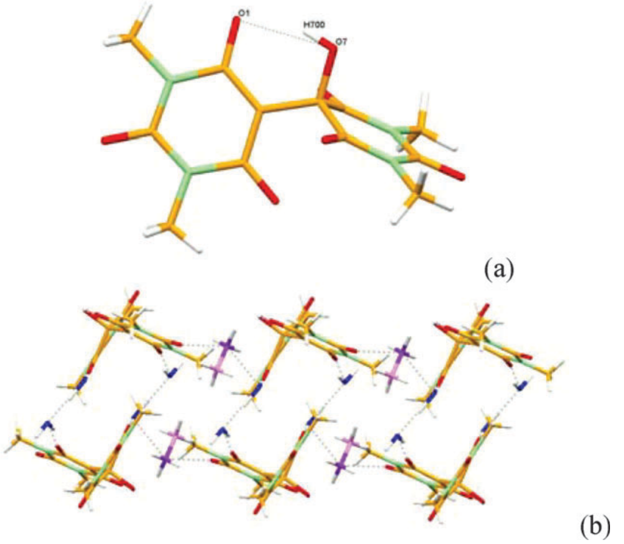

Fig. 4 The conformation of the $[(C_6O_3N_2H_6)_2\text{-OH}]^-$ anion fixed by the intramolecular hydrogen bond (a) and the packing of the salt of formula $[NH_3(CH_3)][(C_6O_3N_2H_6)_2\text{-OH}]\cdot 2H_2O$ **2a** (b).

$[NH_3(CH_3)][(C_6O_3N_2H_6)_2\text{-OH}]\cdot 2H_2O$ (**2a**). The unexpected formation of the [5′-hydroxy-5,5′-bis-dimethylbarbituric acid]$^-$ had been observed before by Bertolasi *et al.*[19] during the preparation of co-crystals with amines. The anionic unit in **2a** is in a conformation fixed by the intramolecular hydrogen bond $[O(H)\cdots O_{CO}$ 2.592(4) Å], while the remaining carboxyl groups form a plethora of hydrogen bonds with the water molecules and the methylammonium cation (see Fig. 4). The diffraction pattern calculated on the basis of the crystal structure differs from the one measured on the product of the solid–gas reaction, indicating that the heterogeneous process does not lead to the condensation product **2a**.

Recrystallization of the solid–gas reaction product from a supersaturated solution yielded the methylammonium 1,1′–3,3′ hydurilate salt $[NH_3(CH_3)]_2[(C_6O_3N_2H_6)_2]$ (**2b**). No crystal structure of the hyduric acid or the conjugated base is available in the CSD.[23] In crystalline **2b** the 1,1′–3,3′ tetramethyl hydurilate dianion lies on a binary axis, which comprises the carbon–carbon bond connecting the two aromatic rings, with the ring planes forming a dihedral angle of *ca.* 66° (see Fig. 5a). The methylammonium cation acts as a bridge between the anions (Fig. 5b), forming two-dimensional networks that are stacked on top of each other (Fig. 5c). Again, the powder pattern calculated on the basis of the crystal structure differs from the one measured on the product of the solid–gas reaction, indicating that the heterogeneous process does not lead to the condensation product **2b**.

The solid state structure of $[NH_3(CH_3)]$DMB (2) as determined from powder diffraction data

We have been able to establish the exact nature of the solid–gas reaction product by solving the crystal structure of compound **2**, $[NH_3(CH_3)]$DMB, from powder diffraction data. This was possible with the program DASH.[21] The powder pattern was indexed by DICVOL91 and the best Pawley fit to the measured XRPD data is achieved by a $P2_1$ unit cell with a = 8.4227(1), b = 6.97215(6), c = 8.0631(11) Å, β = 98.685(1)° and a volume of 468.07(1) Å^3 with Z = 2. The crystal structure was successfully determined with DASH and Rietveld refinement with TOPAS[24] produced the fit shown in Fig. 6 with χ^2 = 1.527, R_{wp} = 4.714 and R_p = 3.618; after background correction R_{wp}' = 8.656 and R_p' = 8.251. Each methylammonium cation forms hydrogen bonds with three dimethylbarbiturate anions (N···O distances in the range

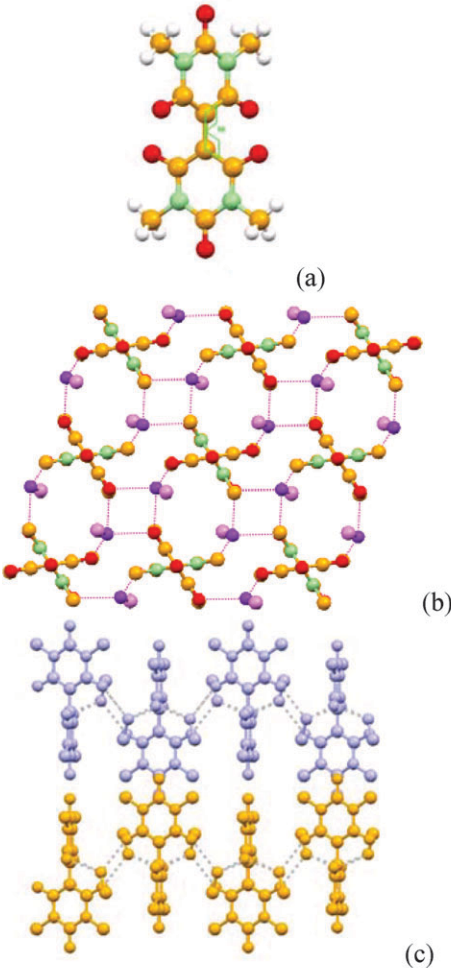

Fig. 5 The 1,1′–3,3′ hydurilate dianion (a); the two-dimensional network in the $[NH_3(CH_3)]_2[(C_6O_3N_2H_6)_2]$ (**2b**) salt (b) and two planes stacked on top of each other (c) (H atoms not shown for clarity.)

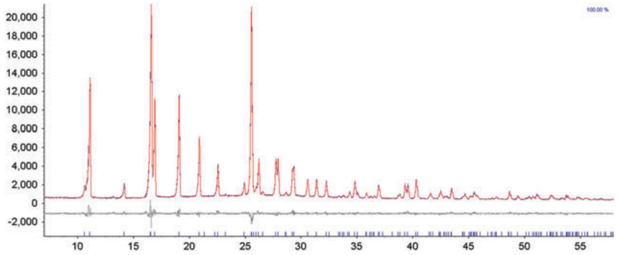

Fig. 6 The Rietveld refinement of the crystal structure of salt **2** (x-axis: 2θ/deg). Experimental (blue), calculated (red) and difference (black) profiles are shown. Allowed peak positions are indicated by blue tick marks.

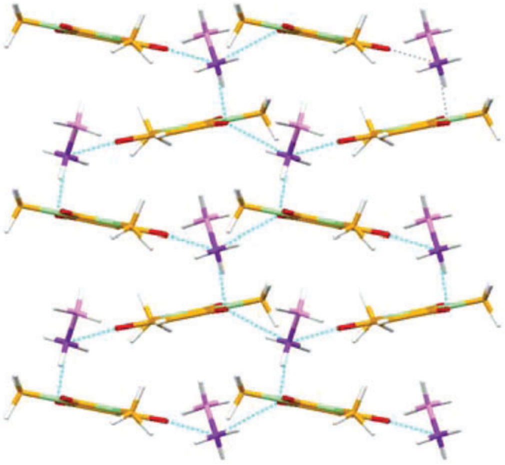

Fig. 7 The crystal structure of the salt **2** as determined from powder diffraction data.

2.737(6) to 2.825(6) Å); the resulting packing pattern can be seen as a stacking of corrugated layers (see Fig. 7).

The solid state structure of [$NH_2(CH_3)_2$][DMB] (3) and the solid state structure of [$NH_2(CH_3)_2$][DMB]·2[DMBA] (3a), as obtained *via* recrystallization of polycrystalline 3 from methanol

Several attempts to obtain single crystals of [$NH_2(CH_3)_2$][DMB] (**3**) *via* recrystallization of polycrystalline **3** from methanol failed, and gave the salt [$NH_2(CH_3)_2$][DMB]·2[DMBA] (**3a**), which contains both the neutral dimethylbarbituric acid and its conjugated base.

Interestingly, though, if the product of the solid–gas reaction of DMBA with aqueous $NH_2(CH_3)$ was left in the glass holder for a prolonged time (more than one week), the clearly hygroscopic powder product became slowly soaked with the aqueous base solution, and a concentrated solution formed, from which single crystals of **3** were recovered.

In crystalline **3** the DMB anions form hydrogen bonds with the dimethylammonium cations (N(H)···O distances 2.671(2) and 2.714(2) Å), thus establishing a chain motif (Fig. 8). The same chain motif can be observed in crystalline **3a** (Fig. 9a) (N(H)···O distances 2.683(2) and 2.766(2) Å); the chains are then surrounded by the neutral DMBA molecules (Fig. 9b).

UV–Vis in the solid state

The gas–solid reactions between DMBA and the volatile bases were studied also by UV–Vis spectroscopy, both in solution and in the solid state. In order to perform measurements in the solid state, DMBA was deposited as a thin film on a quartz plate, and a UV–Vis absorption spectrum was recorded that is consistent with the UV–Vis spectrum of DMBA in solution (see Fig. 10, curves a).

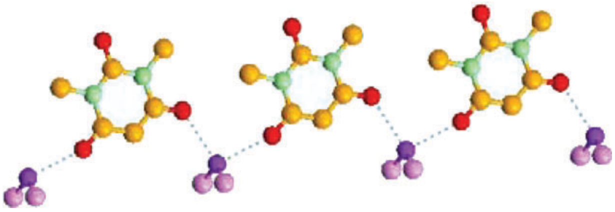

Fig. 8 In crystalline **3** the DMB anions form hydrogen bonds with the dimethylammonium cations [N(H)···O distances 2.671(2) and 2.714(2) Å], thus establishing a chain motif. H atoms not shown for clarity.

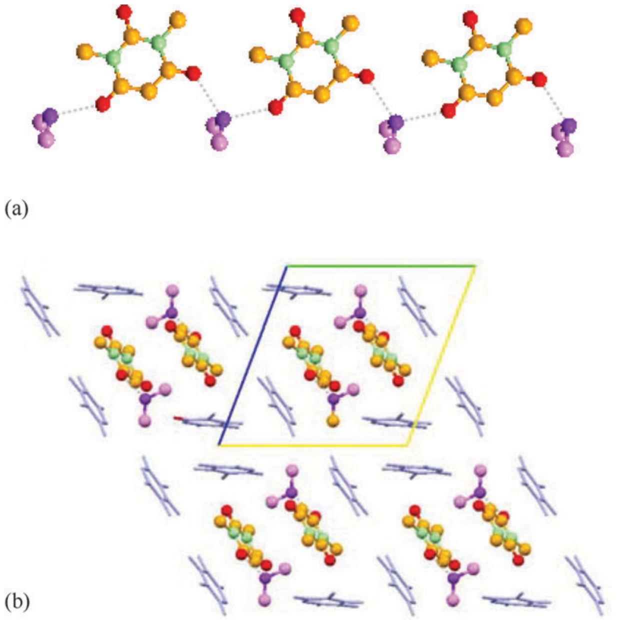

Fig. 9 The same chain motif observed in **3** is also present in crystalline [$NH_2(CH_3)_2$][DMB]·2[DMBA], **3a** (a) [N(H)···O distances 2.683(2) and 2.766(2) Å]. A projection along the chains shows how pairs of chains are surrounded by the neutral DMBA molecules (b). H atoms not shown for clarity.

The UV spectrum of DMBA is characterised by two bands, centred at 223 nm and at 259 nm. The first band is ascribed to a π–π* transition from the NHOMO (Next to the Highest Occupied MO), which is distributed on the heteroatoms and mostly on the C=O groups adjacent to the CH_2 group, to the LUMO (Lowest Unoccupied MO), mainly localised on the carbonyl groups.[25] The band at 259 nm is attributed to a keto–enol equilibrium, since the band is not present in the spectrum of 5,5′-disubstituted barbituric acids.[25] Upon addition of the amines the UV spectra of DMBA change: the band at 259 nm increases in intensity, while the one at 223 nm disappears (see Fig. 10, curves b).

Conclusions

In this paper we have reported the results of the investigation of a series of solid–gas reactions between the dimethylbarbituric acid and vapours of ammonia, methylamine and dimethylamine. In all cases it has been possible to ascertain reaction between acid and bases with formation of anhydrous salts recovered in the form of polycrystalline powders. In contrast to the case of barbituric acid,[18,26] no polymorphic transformation has been observed in the case of DMBA upon removal of the amine. The structures of these salts have been investigated by a combination of single-crystal and powder diffraction and calorimetric measurements (DSC and TGA). It has been shown that recrystallization of the polycrystalline

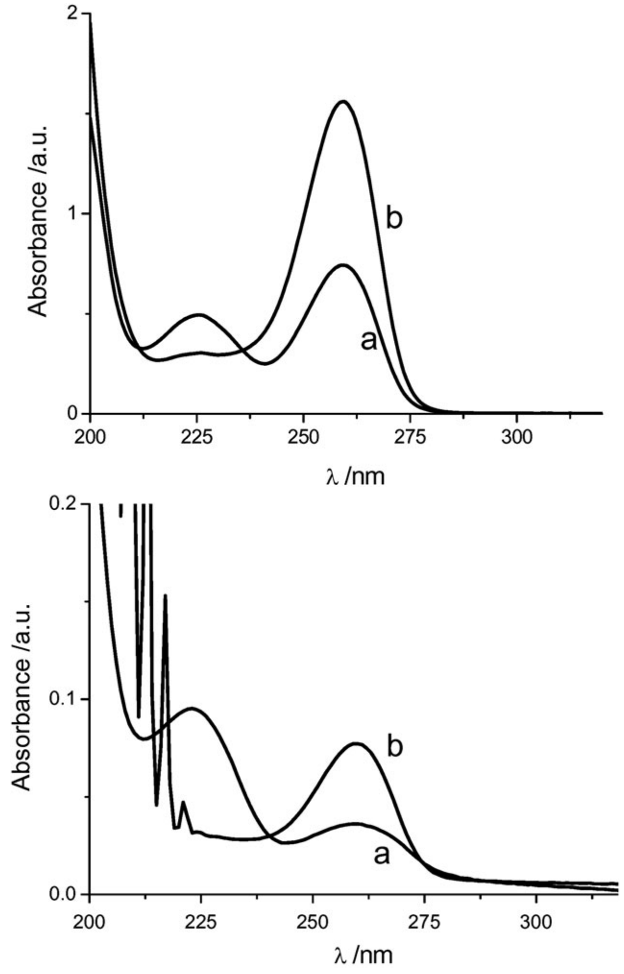

Fig. 10 UV–Vis spectra of DMBA in aqueous solution (top) and as a film deposited from an EtOH solution on a quartz plate (bottom), measured before (a) and after (b) reaction with ammonia.

products leads, with the notable exception of the ammonia salt, to different chemical products and/or different stoichiometries. The structure of the ammonium salt **1** has been established by single-crystal diffraction and confirmed by powder diffraction to correspond to the solid–gas products. The structure of the methylammonium salt **2**, on the other hand, has been established by *ab initio* powder diffraction solution and refinement.

Experimental

All reagents were purchased from Aldrich and used without further purification.

Gas–solid reactions

Exposure to the base vapours was attained by placing a glass sample holder, containing the powder sample of DMBA, in a cylindrical weighing bottle containing 5 mL of the base aqueous solution (NH_3 30%, NH_2CH_3 40%, $NH(CH_3)_2$ 40%). In this way the powder and the solution were not in contact; the reaction took place in a closed system.

Single crystals preparation from solution

Single crystals of compound **1** were obtained by dissolving the polycrystalline product **1** in methanol. The solution was left to stand at room temperature and crystals started to appear after *ca.* three days.

Single crystals of compounds **2a** and **2b** were obtained from different crystallization batches, prepared by dissolving polycrystalline **2** in methanol.

Single crystals of compound **3** were obtained by prolonged exposure to the vapours of aqueous $NH(CH_3)_2$ of the powder product obtained from the solid–gas reaction.

Single crystals of compound **3a** were obtained by dissolving polycrystalline **3** in methanol.

UV measurements

Measurements were carried out on a Varian Cary 50 Scan. An aqueous solution of DMBA (0.5×10^{-4} M) was used to record

Table 1 Crystal data and details of measurements for **1**, **2**, **2a**, **2b**, **3** and **3a**

	1	**2**[a]	**2a**	**2b**	**3**	**3a**
Formula	$C_6H_{11}N_3O_3$	$C_7H_{13}N_3O_3$	$C_{13}H_{23}N_5O_9$	$C_{14}H_{24}N_6O_6$	$C_8H_{15}N_3O_3$	$C_{20}H_{31}N_7O_9$
M_r	173.18	187.20	393.36	372.39	201.23	513.52
Crystal system	Trigonal[b]	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P3c1$	$P2_1$	$P\bar{1}$	$C2/c$	$P2_1/m$	$P\bar{1}$
a/Å	8.250(1)	8.4227(1)	8.500(2)	11.290(5)	8.4110(9)	8.495(1)
b/Å	8.250(1)	6.97215(6)	10.560(3)	19.761(6)	7.3972(8)	12.416(2)
c/Å	7.150(1)	8.0631(1)	11.412(2)	8.300(3)	8.532(1)	12.697(2)
α/°	90	90	65.84(2)	90	90	110.082(2)
β/°	90	98.685(1)	88.12(2)	95.17(2)	98.474(2)	95.887(2)
γ/°	120	90	71.47(2)	90	90	95.181(2)
V/Å^3	421.5(1)	468.07(1)	880.6(4)	1844.2(12)	525.0(1)	1239.8(3)
Z	2	2	2	4	2	2
$\mu(\mathrm{Mo}_{K\alpha})$/mm^{-1}	0.110	—	0.126	0.106	0.098	0.110
Measured reflns	1432	—	3258	1747	6071	10652
Unique reflns	272	—	3089	1626	1356	5575
Ref. parameters	48	—	249	125	92	341
GOF on F^2	1.103	—	0.918	0.957	1.073	0.834
$R1$ [on F, $I > 2\sigma(I)$]	0.0355	—	0.0468	0.0583	0.0432	0.0457
$wR2$ (on F^2, all data)	0.1007	—	0.1610	0.2106	0.1471	0.1453

[a] Solution from powder diffraction data. [b] Refinement was performed also in the hexagonal space group P-6c2, but it proved to be unstable.

the UV–Vis spectra. The UV–Vis measurements in the solid state were performed on a film of 1,3-dimethylbarbituric acid, obtained by deposition of 200 μL of an ethanol solution (5×10^{-3} M) on a quartz plate. Measurements were carried on a Varian Cary 50 Scan.

X-Ray powder diffraction

X-Ray powder diffractograms were collected on a Panalytical X'Pert PRO automated diffractometer with Cu-Kα radiation and an X'Celerator detector without a monochromator. In the case of compound **2** powder data were obtained with a spinner capillary stage. The program Mercury[27] was used for calculation of X-ray powder patterns.

Crystal structure determination

Crystal data for **1**, **2a** and **2b** were collected on a Nonius CAD4 diffractometer; crystal data for **3** and **3a** were collected on a Bruker Smart Apex II CCD. Crystal data and details of measurements are summarized in Table 1. Common to all compounds: Mo-Kα radiation, λ = 0.71073 Å, monochromator graphite, T = 298 K. SHELX97[28] was used for structure solution and refinement based on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were added in calculated positions. Mercury[27] was used for the graphical representation of the results. The program PLATON[29] was used to calculate hydrogen bonding interactions. CCDC reference numbers 654148–654152. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704772j

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