The crystal structure and evidence of the phase transition in D-amphetamine sulfate, as studied by X-ray crystallography, DSC and NMR spectroscopy†

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X-Ray crystallography, DSC and NMR spectroscopy methods have been used to study the phase transition of D-amphetamine sulfate. The phase transition temperature occurs at about 325 K, and belongs to the discontinuous type with a large temperature hysteresis. A change in the space group is observed from monoclinic $P2_1$ in the low temperature phase to monoclinic $C2$ in the high temperature phase. The transformation from phase I to phase II is a result of the ordering of the SO_4^{2-} groups, allowing a T-shape interaction between D-amphetamine molecules. Proton relaxation rate data obtained for the studied compound have been analysed by assuming two dynamically-inequivalent methyl groups below the phase transition and only one type of ammonium group above the phase transition. The activation energies for the C_3 reorientation of the methyl groups have been determined to be 7.31 and 11.89 kJ mol^{-1}, whereas for the ammonium group it is 27.29 kJ mol^{-1}.

1. Introduction

Amphetamine is one of the most popular synthetic drugs, with strong stimulant effects. This compound traditionally comes in the form of sulfate or phosphate salts, usually composed of 50% L- and 50% D-amphetamine. The basic skeleton of D-amphetamine is a β-phenyl amine arrangement characteristic of the sympathomimetic amines, *e.g.* the neurotransmitters noradrenaline, dopamine and other biologically-active catecholamines. Biochemically, D-amphetamine releases catecholamines from their neuronal storage sites, and it has a variety of pharmacological effects.

Amphetamine is a member of a group of at least eight β-substituted ethylamines that are either neurotransmitters or central nervous system-active species. The biological activation of D-amphetamine is related to the conformation of the amphetamine molecule, and inter- and intramolecular interactions. In earlier papers, the structures of crystals of the amphetamine molecules D-amphetamine sulfate,[1] amphetamine dihydrogen phosphate[2] and (±)-*N*-ethyl-*m*-(trifluoromethyl)-amphetamine hydrochloride[3] were reported.

The crystal structure of D-amphetamine sulfate $[(C_9H_{13}N)_2{\cdot}H_2SO_4]$ was determined for the first time by Bergin and Carlström[1] at the room temperature. D-Amphetamine sulfate crystallized in the monoclinic space group $P2_1$ with $Z = 4$ in the unit cell, with $a = 10.51$ Å, $b = 6.35$ Å and $c = 31.34$ Å, and $\beta = 95.0°$.[1] However, the poor quality and low accuracy of the X-ray data made impossible the determination of the hydrogen atom positions. For amphetamine dihydrogen phosphate, the *S*-configuration was ascribed, and it corresponds to a *trans* conformation of the molecule.[2,15]

To the best of our knowledge, the detailed crystal structure of D-amphetamine sulfate has not been studied to date. Therefore, we decided to repeat the determination of the crystal structure at 298 and 337 K (sample I), and at 120 K and 336 K (sample II). The motivation for the high temperature investigations resulted from our DSC and NMR measurements on a polycrystalline sample of D-amphetamine sulfate, which showed that the material undergoes a structural phase transition above 325 K.

2. Experimental

Materials and physical measurements

The starting material was commercial D-amphetamine sulfate purchased from Sigma-Aldrich Ltd. The crystalline product was twice re-crystallized. Single crystals not of good quality but sufficient for X-ray crystallography analysis were grown by the slow evaporation of an aqueous solution. Differential scanning calorimetry (DSC) data were recorded using a Perkin-Elmer DSC-7 instrument in the temperature range 100 to 450 K. The measurements were carried out on both heating and cooling runs with a scanning rate of 10 K per minute. For NMR measurements, the powder sample was stored in a glass tube, evacuated at room temperature at 6×10^{-6} hPa for 4 h to remove oxygen and then sealed under vacuum. The NMR proton spin–lattice relaxation time, T_1, was measured using an SXP 4/100 Bruker pulse spectrometer operating at 90 MHz, corresponding to a magnetic field, B_0, of

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2.1 T. The relaxation time was determined by an inverse recovery method using a $180^\circ - \tau - 90^\circ$ pulse sequence for 45 variable time intervals, τ, in the temperature range 86.4 to 440 K. Eight FIDs were acquired with a repeat delay equal to at least $5T_1$ to provide an acceptable signal-to-noise ratio. The temperature of the sample was controlled by means of a continuous nitrogen gas flow system and determined with an accuracy of 1 K. Recovery of the magnetization exhibited an exponential character within experimental error at all temperatures. The errors in the measurements of T_1 were estimated to be about 5 to 10% (at the lowest temperature).

Crystal structure determination

The single crystal diffraction data were collected using an automatic X-ray four-circle KUMACCD diffractometer and an XCALIBUR diffractometer with CCD area detectors. X-Ray studies were performed in the temperature range 110 to 380 K using a temperature attachment (Oxford Cryo-system).

The temperature dependence of the lattice parameters was determined from 40 frames (measured in a special regime) for every temperature point. Data reduction was performed using the CrysAlis program version 170.32.06 (Oxford Diffraction) with an analytical absorption correction. Structure refinement was carried out using the SHELXL-97 program system.[4] The crystallographic data for the structures presented in this paper have been deposited with the CCDC(sample II).† The obtained single crystals grew in the form of thin plates and contained any number of defects.

For this reason, the range of executed 2Θ angles of measurable reflexes for measured samples was small, and the standard deviations of the measured intensities were comparatively high. In connection with the above, in the refinement of the structure at 120 K, constraints on the length of hydrogen bonds of type N–H and C–H were applied to the amphetamine molecules.

3. Results and discussion

DSC measurements

Fig. 1 shows the heat flow measurements performed for D-amphetamine sulfate by the DSC method in the temperature range 315 to 355 K for the heating run and then the cooling run. Above room temperature, one solid–solid reversible phase transition is disclosed. A strong heat anomaly (342.36/325.07 K, heating–cooling) of the discontinuous (the first order) transition is coupled with an order–disorder mechanism, and with quite a large transition entropy of about 9.32/8.52 J g^{-1}.

Crystal structure

The phase transition at 325 K observed by DSC for the cooling process corresponds to a discontinuous transition at about 325(2) K observed in the temperature dependence of the lattice parameters and the unit cell volume during cooling. The data for the lattice parameters a, b, c, the monoclinic angle and the volume of the unit cell are shown in Fig. 2a–c, respectively.

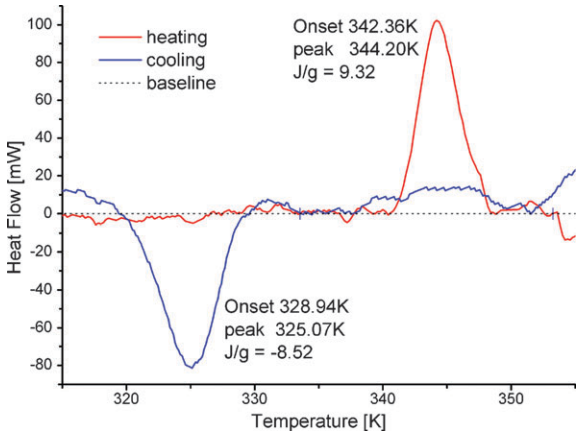

Fig. 1 A DSC curve of a D-amphetamine sulfate single crystal measured on both heating and cooling the sample.

The X-ray crystallographic measurements reveal that the crystal structure of the D-amphetamine sulfate in both phases belongs to the monoclinic system, and after transformation from the high temperature phase I to the room temperature phase II, the unit cell is doubled along the c axis. In the high temperature phase I, the crystal structure is described by space group $C2$, whereas at room temperature (phase II) it is described by monoclinic space group $P2_1$.

Details of the crystal data, diffraction experiments and structure refinement of D-amphetamine sulfate in both phases are shown in Table 1.

Low temperature phase II (120 K)

The crystal structures of D-amphetamine sulfate at room temperature[1] and at 120 K are isostructural. Our X-ray diffraction experiments at 120 K revealed the positions of the hydrogen atoms from the Fourier difference maps. The geometry of the hydrogen atoms is in good agreement with those of other amphetamine analogues, for example amphetamine dihydrogen phosphate.[2]

The chemical unit consists of two protonated molecules of D-amphetamine $(C_9H_{14}N)^+$ and one sulfate SO_4^{2-} anion, which interact to form $[(C_9H_{14}N)^+_2{\cdot}SO_4^{2-}]$. The asymmetric unit of phase II consists of four non-equivalent D-amphetamine molecules, A, B, C and D, and two SO_4^{2-} groups, A and B (Fig. 3). Thus, the unit cell of phase II contains eight D-amphetamine molecules (four D-amphetamine sulfate chemical units).

Each D-amphetamine molecule consists of two almost planar, mutually perpendicular, parts: the phenyl ring and the 2-aminopropane side chain. The crystal packing of phase II shown in Fig. 4a and b clearly demonstrates that the crystal structure is formed with the sequence of layers parallel to the a–b plane:

(i) layer AB (BA) contains the D-amphetamine molecules A and B,

(ii) layer SO with SO_4^{2-} anions and

(iii) layer CD (DC) with D-amphetamine molecules C and D.

These layers form a sequence: AB_BA–SO–CD_DC–SO–AB_BA–SO–CD_DC... along the c axis. A geometrical

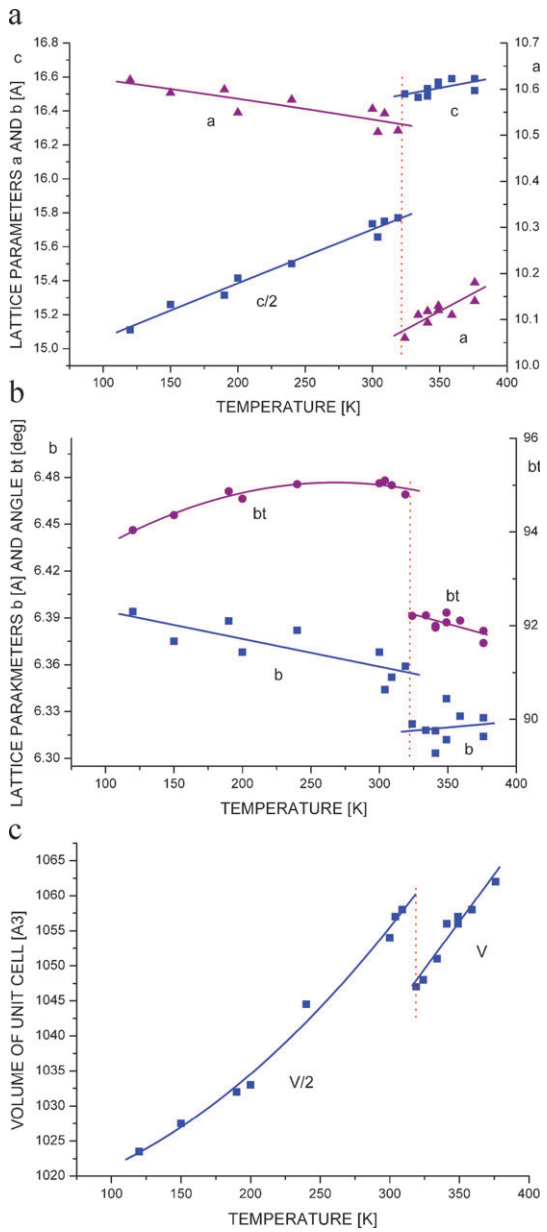

Fig. 2 The temperature dependence of lattice parameters: on the cooling run from 372 K (a) *a* and *c* axis, (b) the monoclinic angle and *b* axis, and (c) the crystal volume.

analysis of the aromatic interactions of the phenyl rings in the crystal structure of phase II shows two different arrangements: deformed parallel displaced and T-shaped (edge-phase).[5,6] In the layers AB_BA, the D-amphetamine molecules are held together by electrostatic interactions of the type C–H···π (Fig. 5). The phenyl rings in the layers form columns along the b axis with a parallel orientation, but the distance between the phenyl rings is about 6.334 Å. The layers AB_BA and CD_DC are bonded to the SO layer by N–H···O hydrogen bonds between the nitrogen atoms belonging to 2-aminopropane side chains and oxygen atoms of the SO_4^{2-} groups. In the layer CD_DC, the aromatic part of D-amphetamine molecule D, which is almost perpendicular to the phenyl ring of D-amphetamine molecule C, creates a typical T-shaped arrangement. The distance from the center of the ring of D-amphetamine molecule D to the H1C hydrogen atom of D-amphetamine molecule C is about 2.527(6) Å (Fig. 5). The dihedral angles between the aromatic rings of the D-amphetamine molecules are as follows: ring amphetamine-A in layer AB–ring amphetamine-A′ in layer BA = 43.70°, ring-B–ring-B′ = 45.39° and ring-C–ring-D = 69.85°. The details of the N–H···O hydrogen bonds and C–H···π interactions are summarized in Tables 1–4 in the ESI.†

High temperature phase I (336 K)

In D-amphetamine sulfate, the phase transition from room temperature phase II to high temperature phase I is of the first order-type, with a temperature hysteresis of about 20 K. As a result of the large distortion to the structure in this phase, the quality of the samples became worse and therefore the standard deviations of the refined parameters were higher than in phase II.

The unit cell is reduced two-fold along the c axis and the asymmetric unit contains one symmetrically-independent D-amphetamine molecule and one SO_4^{2-} anion, as shown in Fig. 6. The oxygen atoms of the SO_4^{2-} groups in phase I are disordered and located in general positions with an occupancy factor of 0.5. The sulfur atom occupies a site with the point symmetry 2.

Fig. 7a and b show that the crystal structure of the high temperature phase belongs to a layered structure-type with a similar layer to that in phase II, but the sequence of the layers is simpler: AA_AA–SO–AA_AA–SO–AA_AA. The T-shaped arrangement characteristic of the CD_DC layers in phase II transforms into C–H···π-type interactions in phase I. The dihedral angle between the phenyl rings of the AA and AA′ stacks is about 30.45°. The disordered oxygen atoms of the SO_4^{2-} groups are bonded to the nitrogen atoms of the 2-aminopropane side chain by hydrogen bonds of the type N–H···O. The bond distances and valence angles (see the tables in the ESI†) of the aromatic ring and the amine chain are close to expected values and in reasonable agreement with those reported earlier for the other amphetamine compounds[2,3]

Hydrogen bonds

D-Amphetamine sulfate aggregates into moieties interconnected by N–H···O hydrogen bonds, with N···O distances in the ranges 2.718(8)–2.825(9) and 2.668(9)–3.202(10) Å for phase II and phase I, respectively (Table 3 in the ESI†). The intermolecular electrostatic interactions of the C–H···π hydrogen bonds also play a role in the structure's stability. The C–H···π interactions in phase I and II could be analyzed using the description reported by Malone *et al.*,[7] where the π_o is the center of the ring, π_o–H is the distance to the hydrogen atom, and θ is the angle between the ring plane and the π_o–H axis. In phase I and phase II, almost all interactions of the C–H···π-type are classed as very weak interactions of the V-type in Malone's notation, with the exception of the C1C–H1C···ring-molecule D hydrogen bond in phase II (Table 4 in the ESI†). The hydrogen bond C1C–H1C···ring-molecule D in phase II forms a T-shape

Table 1 Crystal data, X-ray diffraction experiment data, and structure refinement at 120 and 336 K for low and high temperature phases of D-amphetamine sulfate

Data	Low temperature phase	High temperature phase
Empirical formula	$C_{18}H_{28}N_2O_4S$	$C_{18}H_{28}N_2O_4S$
Formula weight	368.48	368.48
Temperature/K	120(2)	336(2)
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)	*C*2
a/Å	10.6090(12)	10.1020(19)
b/Å	6.3820(6)	6.3180(12)
c/Å	30.133(4)	16.512(6)
β (°)	94.370(10)	92.07(2)
Volume/Å^3	2034.3(4)	1053.2(5)
Z	4	2
Calculated density/Mg m^{-3}	1.203	1.162
Absorption coefficient/mm^{-1}	0.182	0.176
F(000)	792	396
Crystal size/mm	0.29 × 0.21 × 0.12	0.32 × 0.24 × 0.15
2*Θ* range (°)	2.39–28.28	3.70–27.74
Limiting indices	$-13 \leftarrow h \leftarrow 13$ $-8 \leftarrow k \leftarrow 6$ $-39 \leftarrow l \leftarrow 39$	$-10 \leftarrow h \leftarrow 13$ $-8 \leftarrow k \leftarrow 7$ $-21 \leftarrow l \leftarrow 21$
Reflections collected	24 561	5278
Reflections unique	7997	2251
R_{int}	0.0344	0.0375
Completeness to *Θ* (%)	97.9%	95.0
Absorption correction	None	Numerical-CrysAlis v171.32.18
Restraints	49	1
Parameters	675	145
Goodness-of-fit on F^2	1.190	1.023
*R*1	0.0491	0.0512
w*R*2	0.0886	0.0856
Absolute structure parameter	0.10(5)	−0.11(08)
Largest differential peak/hole/e Å^{-3}	0.410/−0.415	0.200/−0.103

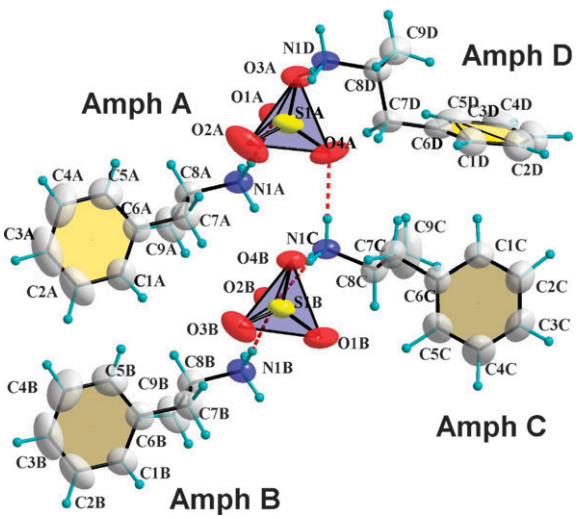

Fig. 3 The asymmetric unit of the structure of D-amphetamine sulfate showing four non-equivalent D-amphetamine ions, A, B, C and D, at 120 K (displacement ellipsoids are shown at the 90% probability level).

arrangement, which is the strongest interaction in Malone's notation.

The transformation from phase I to phase II is a result of the ordering of SO_4^{2-} groups, allowing the T-shape interaction in CD_DC layers.

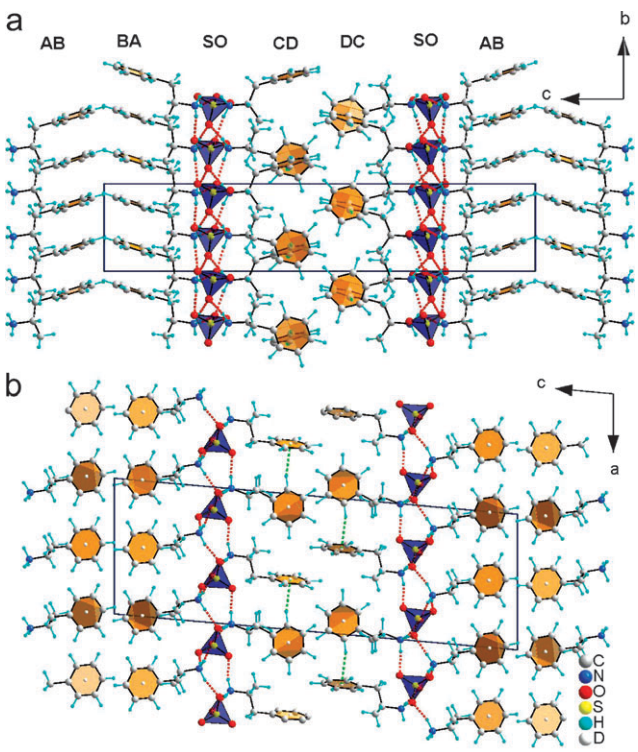

Fig. 4 a: The projection of the crystal structure along the a axis with the layers marked. b: The projection along the b axis at room temperature.

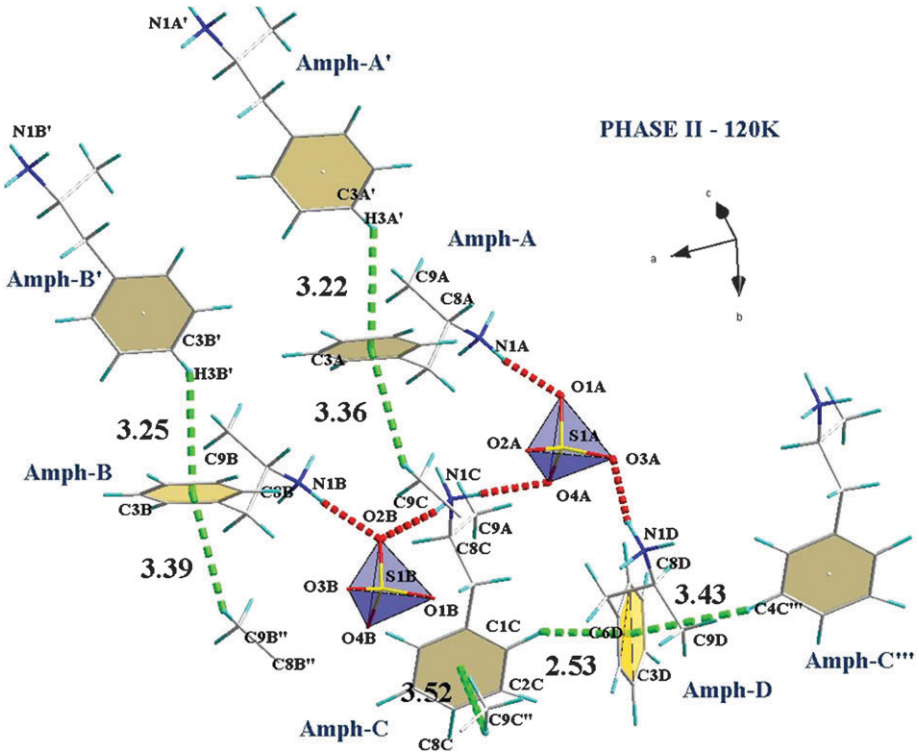

Fig. 5 Selected details of N–H···O-type hydrogen bonds (red dashed lines) and weak C–H···π interactions (green dashed lines) between the D-amphetamine molecules at 120 K. Bold digits show the distance between hydrogen atoms and the centroid for C–H···π interactions. Symmetry transformations used to generate equivalent atoms: Amph-A(B,C,D) ≡ x, y, z; Amph-A′ ≡ $-3 - x$, $-0.5 + y$, $2 - z$; Amph-A″ ≡ x, $1 + y$, z; Amph-Ai‴ ≡ $-1 + x$, y, z.

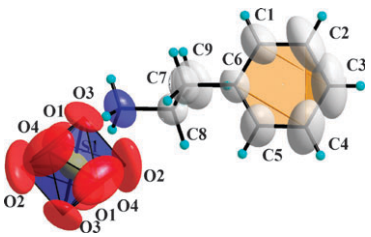

Fig. 6 The arrangement of the D-amphetamine cation and disordered sulfate anion in phase I at 336 K (displacement ellipsoids are shown at the 50% probability level).

D-Amphetamine molecules A, B, C and D in phase II and D-amphetamine molecule A in phase I exhibit a "*trans*" conformation and an *S*-configuration (Fig. 8).

Proton NMR relaxation

Nuclear spin relaxation experiments have been used to probe the dynamics of the intramolecular reorientation of substituent groups in solid powders of D-amphetamine sulfate and also to detect the phase transition. Data of the Zeeman spin–lattice relaxation rate, R_1 (where $R_1^{-1} = T_1$—the proton spin–lattice relaxation time), *vs.* the inverse of temperature are shown in Fig. 9. The main features of the temperature dependence of the relaxation rate are the two maxima: a broad, slightly asymmetrical maximum that occurs at 191.5 K and the other, much narrower, maximum at about 356.8 K. The low temperature side of the second minimum is not well pronounced because of a sudden discontinuity in the temperature dependence of R_1, which occurs at about 325 K. Such behaviour of R_1 is characteristic of a compound undergoing a phase transition. The temperature of the phase transition observed from the relaxation data for D-amphetamine sulfate corresponds very well to the DSC data (Fig. 1) and to a discontinuous transition at about 325 K, which was observed in the temperature dependence of the lattice parameters and unit cell volume studied by X-ray crystallography (Fig. 2).

From the structure of D-amphetamine sulfate presented in Fig. 4 and Fig. 6, it can be assumed that the main sources of the proton spin–lattice relaxation rate are the proton–proton dipole–dipole interactions within the CH_3 and NH_3^+ groups modulated by reorientation about their C_3 axes. The D-amphetamine sulfate chemical unit is sufficiently large that whole-molecule translation and reorientation does not occur on the Larmor frequency scale (90 MHz in our experiment). Therefore, the CH_3 and NH_3^+ group reorientations are the only motions that contribute significantly to the observed nuclear spin relaxation. The low temperature maximum, which is broad and slightly asymmetric, corresponds to the methyl groups in the crystal structure of D-amphetamine sulfate in the low temperature phase. In this phase, the unit cell of the crystal contains four D-amphetamine sulfate chemical units with eight D-amphetamine molecules, which gives a network of equivalent and inequivalent sites, in which the methyl groups are placed. As a consequence of the two different environments of the methyl groups in the low temperature phase, there are two such sites. Two of the eight

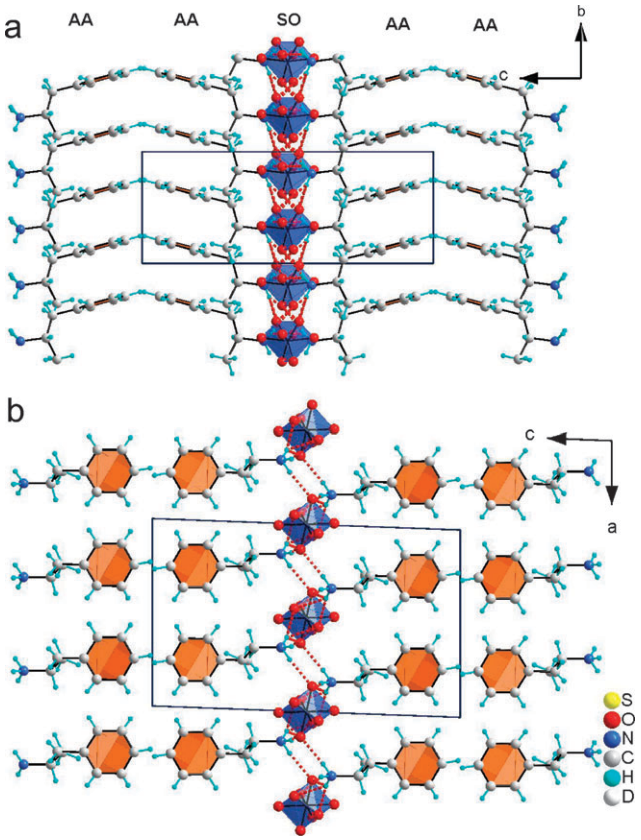

Fig. 7 (a) A projection of the crystal structure along the a axis with the layers marked. (b) A projection along the b axis at 336 K.

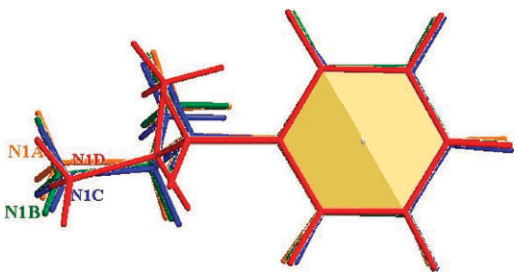

Fig. 8 A comparison of the conformation of D-amphetamine molecules A, B, C and D at 298 K.

methyl groups (CH_3') belong to D-amphetamine molecules with phenyl rings almost perpendicular to the ac plane (Fig. 4b) and six others (CH_3') belong to D-amphetamine molecules A, B and C with phenyl rings almost in the ac plane. The CH_3 rotors within each of the groups are dynamically-equivalent, but the CH_3's of the first group are dynamically-inequivalent to the CH_3''s of the second. The dynamic inequivalence of the methyl groups is responsible for the asymmetry of the observed low temperature maximum presented in Fig. 9, and is also used to interpret the spin–lattice relaxation time in other molecular solids.[8–10]

The general theory of proton spin–lattice relaxation has been discussed by Abragam[11] and Slichter.[12] We have presented only the minimum summary needed to introduce the fitting parameters. The observed Zeeman spin–lattice

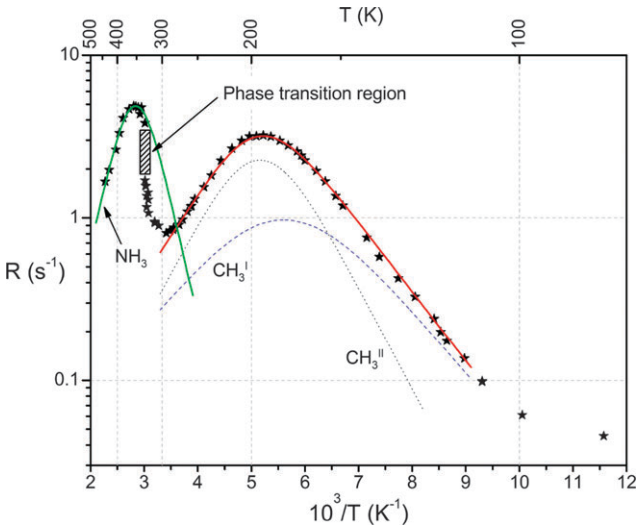

Fig. 9 The proton spin–lattice relaxation rate, R_1, *vs.* the inverse of temperature, T^{-1}, in polycrystalline D-amphetamine sulfate at 90 MHz. The contributions to R_1 from the two inequivalent CH_3' and CH_3'' groups are indicated (dashed lines) below the phase transition, whereas the contribution from the NH_3^+ group (green line) is seen above the phase transition.

relaxation rate, R_1, below the phase transition in Fig. 9 results from the modulation of proton dipole–dipole interactions due to the reorientation of methyl groups about their three-fold axes. R_1 is given by refs. 11 and 12 as

$$R_1 = \sum_{i=1}^{2} R_i, \qquad (1)$$

where i is the number of dynamically-inequivalent methyl groups. In the amphetamine unit cell of the low temperature phase, $i = 2$. The relaxation rate for each of the dynamically-equivalent methyl groups is given as

$$R_i = A_i\left(\frac{\tau_{ci}}{1+(\omega_0\tau_{ci})^2} + \frac{4\tau_{ci}}{1+(2\omega_0\tau_{ci})^2}\right), \qquad (2)$$

where τ_{ci} is the correlation time of this group described by the Arrhenius law

$$\tau = \tau_0 \exp(E_a/kT), \qquad (3)$$

with activation energy E_a and a pre-exponential factor τ_0.

The parameter A_i takes the form

$$A_i = \frac{n}{N}\frac{9}{20}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\gamma^4\hbar^2}{r_i^6}, \qquad (4)$$

where r_i is the proton–proton distance in a methyl group, γ is the magnetogyric ratio and μ_0 is the permeability of free space. A_i is interpreted as the strength of the spin–lattice coupling due to intramethyl proton dipole–dipole interactions, diluted by n/N, which is the ratio of the number of protons in equivalent methyl groups (n) to the total number of protons in a unit cell of the crystal (N). For CH_3' and CH_3'' in a D-amphetamine sulphate powder in the low temperature phase, $n = 6$ and 18, respectively, and $N = 112$, as obtained from the crystal structure.

Eqn (1) (after inserting eqn (2) and eqn (3)) was used to fit the experimental R_1 data of the low temperature phase of D-amphetamine. The solid line in Fig. 9 represents the best six-parameter fit, with the following parameters for the CH_3' group: E_a = 7.31 kJ mol^{-1}, τ_0 = 7.93 × 10^{-12} s and r = 1.81 × 10^{-10} m, and for the CH_3'' group: E_a = 11.89 kJ mol^{-1}, τ_0 = 6.82 × 10^{-13} s and r = 1.89 × 10^{-10} m. The contributions to R_1 from the two dynamically-inequivalent types of methyl group are also indicated (broken and dotted lines in Fig. 9). As seen from the fitting procedure, the inequivalent methyl groups differ in their dynamic parameters. As a general rule, more-hindered rotors (associated with larger E_a barriers) give rise to an R_1 maximum *vs.* the inverse of T at higher temperatures. In this way, we were able to assign the obtained parameters E_a, τ_0 and r to the appropriate types of methyl group, CH_3' and CH_3''.

The high temperature (above the phase transition) maximum was ascribed to C_3 rotation of the NH_3^+ groups. In the high temperature phase, as shown from our X-ray crystallography studies, all of the D-amphetamine molecules in the unit cell of the crystal are equivalent. Therefore, it is reasonable to assume that the NH_3^+ groups are also identical in this phase. To fit the experimental data above the phase temperature, we used eqn (1), eqn (2) and eqn (3) for i = 1 with the following parameters: E_a = 27.29 kJ mol^{-1}, τ_0 = 9.81 × 10^{-12} s and proton–proton distance r = 1.74 × 10^{-10} m. The values determined in D-amphetamine sulfate for the C_3 reorientation of CH_3 and NH_3^+ groups are in a good agreement with those for similar compounds reported in the literature.[13,14]

4. Conclusions

The combined methods of X-ray crystallography, DSC and NMR spectroscopy were used to observe the phase transition of D-amphetamine sulfate. The temperature of the phase transition was determined to be: 325/345 K (from the cooling/heating process) by DSC, about 325 K based on NMR spectroscopy, and 325(2) K from the temperature dependence of the lattice parameters and unit cell volume detected by X-ray crystallography. The crystallographic data show that in D-amphetamine sulfate, the phase transition from the low temperature to the high temperature phase is of a first order-type, with a temperature hysteresis of about 20°, and is accompanied by a change in the space group from monoclinic $P2_1$ to monoclinic $C2$. The transformation from phase I to phase II is the result of the ordering of the SO_4^{2-} groups, allowing T-shape interactions in the D-amphetamine CD_DC layers. Such changes in arrangement explain the drastic increase of unit cell volume during the transformation from phase I to phase II. On the basis of the crystal structure, we were able to analyze the proton relaxation rate data we obtained for the studied compound. The simple dynamic model, assuming two inequivalent methyl groups below the phase transition and only one type of NH_3^+ group above the phase transition, agreed very well with the experimental data.

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