Evidence of low temperature phase transition in 2,6-dimethylpyrazine - picric acid cocrystal by means of temperature dependent investigations: X-ray, DSC and IR.

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PII:	S0022-2860(20)31747-6
DOI:	https://doi.org/10.1016/j.molstruc.2020.129432
Reference:	MOLSTR 129432

To appear in: Journal of Molecular Structure

Received date:	22 July 2020
Revised date:	7 October 2020
Accepted date:	8 October 2020

Please cite this article as: A. Pawlukojć Conceptualization;Methodology;Investigation;Writing–Oryginal Draft;Project J. Hetmańczyk Investigation;Formal analysis;Writing–Review and Editing;Visualization,

L. Hetmańczyk Investigation;Formal analysis;Writing–Review and Editing, J. Nowicka-Scheibe Concepualization; Jan K. Maurin Investigation;Formal analysis, W. Schilf Investigation;Formal analysis, D. Trzybiński Investigation;Formal analysis, K. Woźniak Investigation;Formal analysis, Evidence of low temperature phase transition in 2,6-dimethylpyrazine - picric acid cocrystal by means of temperature dependent investigations: X-ray, DSC and IR., *Journal of Molecular Structure* (2020), doi: https://doi.org/10.1016/j.molstruc.2020.129432

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Highlights

- New 2,6-dimethylpyrazine picric acid cocrystal was synthezed and investigated. •
- DFT calculation for solids state model was performed. •
- Low temperature phase transition was observed. •
- Full vibrational analysis was performed. •
- Activation energy for reorientation of C-CH₃bending vibration was obtained. •

Evidence of low temperature phase transition in 2,6-dimethylpyrazine - picric acid cocrystal by means of temperature dependent investigations: X-ray, DSC and IR.

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Abstract

In the present paper the structural and dynamical properties of crystalline 2,6- dimethylpyrazine - picric acid cocrystal are described. The title cocrystal crystallizes in centrosymmetric monoclinic P2₁/c space group. The X-ray diffraction and NMR spectroscopy show the presence of protonated form of 2,6-dimethypyrazine and deprotonated form of picric acid molecules. The Hirshfeld surface analysis for determine of intermolecular contacts was performed. Low temperature phase transition was observed and described by temperature dependent investigations: X-ray diffraction, different scanning calorimetry (DSC) and IR spectroscopy. The vibrational properties of cocrystal were investigated by use of IR and Raman spectroscopies, as well as density functional theory (DFT) with periodic boundary conditions. Activation energy for reorientational motion of CH₃ group was determined from the band shape analysis of C-CH₃ bending vibration.

Keywords: 2,6-dimethylpyrazine-picric acid cocrystal; X-ray diffraction; Raman spectroscopy; temperature dependent IR spectroscopy, DFT calculation; phase transition.

1.Introduction

In this report a synthesis and investigation of 2,6-dimethylpyrazine with picric acid cocrystal was presented. Picric acid forms crystalline picrate through ionic, hydrogen bonding and π - π interactions, favors the formation of the salts with various organic bases. In recent years the studies on growth and nonlinear optical properties cocrystals of picric acid with amino acids [1-9] were presented. They were investigated by structural, spectroscopic, thermal, optical and theoretical calculation methods. All of them show SHG (second harmonic generation) effect more than for KDP (potassium dideuterium phosphate) crystal. Picrate salts crystallize with other organic bases in the non-centrosymmetric space groups and show nonlinear optical properties (second harmonic generation, third harmonic generation) also [10-14]. In these crystals picric acid appears in the form of anion and forms intermolecular hydrogen bonds type of O-H···O or N-H…O with cation molecules. Another class of the picric acid cocrystals is centrosymmetric crystals characterized by intermolecular hydrogen bonds and weak π - π stacking interaction between symmetry related picric benzene ring and aromatic ring of charge donors [15-21]. The distance of $\pi - \pi$ interaction is observed in the range of 3.4Å - 3.9Å. The picric acid as well as 2,6-dimethylpyrazine are interesting compounds for materials engineering [22-26]. Their organometallic complexes show luminescence, fluorescence and magnetic properties. As all pyrazine methyl derivatives, 2,6-dimethylpyrazine is interesting molecule for investigation of methyl group's dynamics [27, 28] performed by IR, Raman, inelastic neutron scattering and theoretical DFT methods.

The main goal of this work is determination and description of structural and dynamical properties as well as low temperature phase transition of 2,6-dimethylpyrazine - picric acid cocrystal. Crystallography studies by X-ray diffraction at several temperatures, DSC and infrared temperature dependent spectroscopy were performed. Additionally, NMR spectroscopies in solid states, CDCl₃ and acetone solution, Raman spectroscopy as well as DFT calculation with periodic boundary conditions for an experimental data analysis were used.

2.Experimental

2.1. Sample preparation

Picric acid (moistened with water) and 2,6-dimethylpyrazine were purchased from Sigma-Aldrich Chemical Companies and were used without further purification. Methanol, chloroform and ethyl alcohol of HPLC grade were also from Aldrich. Two mmol of 2,6-dimethylpyrazine (20 ml) were added to 20 ml of methanol solutions containing picric acid (2 mmol) and mixture was stirred at 40°C temperature for 1 h. The resulting solution was allowed

to stand at room temperature. The formed complex was isolated, filtered off and washed with minimum amounts of chloroform to obtain the pure product and dried under vacuum over anhydrous CaCl₂. Cocrystal in a molar ratio 1:1 was synthesized and needle yellow crystals were obtained.

2.2. X-Ray diffraction

Good quality single crystal of investigated system was selected for the X-ray diffraction experiments at T = 100, 120, 140, 160, 200, 250 and 295 K. Diffraction data were collected on the Agilent Technologies SuperNova Dual Source diffractometer with CuKa radiation ($\lambda =$ 1.54184 Å) using CrysAlis RED software [29]. The multi-scan empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm, was applied [29]. The structural determination procedure was carried out using the SHELX package [30]. The structures were solved with direct methods and then successive least-square refinement was carried out based on the full-matrix least-squares method on F^2 using the SHELXL program [30]. The H-atoms linked to the N-atom in all cases were located on Fourier difference maps and refined as riding on heavy atoms with $U_{iso}(H) = 1.2U_{eq}(N)$. Other H-atoms were positioned geometrically, with C–H equal to 0.93 and 0.96 Å for the aromatic and methyl H-atoms, respectively, and constrained to ride on their parent atoms with $U_{iso}(H) = xU_{eq}(C)$, where x = 1.2 for the aromatic and 1.5 for the methyl-H-atoms.

2.3. NMR spectroscopy

The solid state CPMAS spectra were run on a Bruker Avance 500 MHz spectrometer using 4 mm CPMAS Bruker probehead. The typical spectral condition for natural abundance nitrogen CPMAS NMR spectra were: spectral width 28 kHz, acquisition time 40ms, spin rate 6-12 kHz, contact time for spin-lock 5ms, relaxation delay 10 to 120 s depending on relaxation condition for particular sample, estimated from carbon measurement. The typical experimental condition for carbon CPMAS were: spectral width 31 kHz, acquisition time 20 ms, contact time 2 ms, spin rate 12 kHz. For differentiation of protonated and quaternary carbon atoms, the short contact time spectra with contact time 40µs were done. In SCT (semi constant time) experiments only protonated carbon signals are displayed. Originally, the solid-state spectra were referenced to the solid glycine sample and then the obtained chemical shifts of appropriate signals were recalculated to TMS (tetramethylsilane) scale for carbon, and nitromethane for nitrogen measurements, respectively.

All solution state NMR experiments were performed on Varian-Agilent 600 MHz VNMRS instrument using 5 mm inverse probehead equipped with Z-gradient coil. The nitrogen chemical shifts were obtained from 2D GHMBC experiments. For data acquisition and spectra processing standard Varian-Agilent software was used. The proton and carbon spectra were

referenced with respect to internal TMS as a standard. For nitrogen-15 external nitromethane was applied as a standard.

2.4. Differential scanning calorimetry (DSC)

DSC measurement below room temperature was performed using a *Mettler-Toledo* 822^e calorimeter. The sample weighing 6.40 mg was placed in standard alumina 40 µl crucibles (closed by compression) and heated at a rate of 10 K min⁻¹ under a dry N₂ atmosphere at a constant flow (50 ml min⁻¹). The DSC measurements were made both during heating and cooling of the sample. Transition temperatures were taken as the onset temperature (T_{onset}).

2.5. Raman spectroscopy

The Raman spectrum was recorded on the Horiba LabRam HR Evolution Raman microscope with 633 nm HeNe laser (17mW power) as an excitation source. The resolution was set up to 2 cm⁻¹. An Olympus microscope objective lens SLWD with a focus x50 and a numerical aperture of NA = 0.35 were used to focus the laser beam on the sample surface. The spectrum was obtained using 20 scans (50-4000 cm⁻¹ wavenumber) with an acquisition time of 72 s of each.

2.6. Infrared spectroscopy

Fourier transforms far and middle infrared (FT-FIR, FT-MIR) absorption measurements were performed using a *Bruker Vertex 70v* vacuum Fourier Transform spectrometer. The transmission spectra were collected with a resolution of 2 cm⁻¹ and with 32 scans per each spectrum for FIR and MIR, respectively. The FT-FIR spectra (600-50 cm⁻¹ wavenumber range) were collected for sample suspended in Apiezon N grease and placed on polyethylene (PE) disc. The FT-MIR spectra were collected for sample suspended in Nujol between KBr pellets. The Nujol and Apiezon additionally preserve the sample from decomposition and the influence of atmospheric conditions. Temperature measurements were carried out using *Advanced Research System cryostat DE-202A* and water-cooled helium compressor *ARS-2HW* working in a closed cycle manner. The sample was loaded at room temperature and measurements were performed on cooling down to *ca*. 9 K. The desired temperature was measured with accuracy of ± 0.1 K and stabilized for *ca*. 3 minutes before the measurements were taken. The *LakeShore 331S* temperature controller equipped with silicon diode sensor was used to control the temperature. The cooling rate between desired temperatures was *ca*. 3 Kmin⁻¹. The *PE* and *KRS5* windows were used in a cryostat in the case of FT-FIR and FT-MIR measurements, respectively.

2.7. Quantum chemical calculations

The total energy optimization and the frequency calculations were performed using the density functional theory (DFT) [31,32] as implemented in the CASTEP [33] program. The unit cell parameters were held constant, only atomic coordinates were optimized using the BFGS

minimizer installed within CASTEP [34]. The results were obtained for the crystalline state within the generalized gradient approximation (GGA) at PBE (Perdew–Burke–Ernzerhof correlation) functional [35]. An essentially semiempirical dispersion correction introduced by Tkatchenko and Scheffler (TS) [36] was used to include the van der Waals interactions in the molecular crystal. Calculations were performed using on the fly generated norm-conserving pseudopotentials as implemented in CASTEP. The density functional perturbation theory (DFPT) [37] was used to calculate the vibrational properties at Gamma point. The plane-wave cut-off energy was 1012 eV. Brillouin zone sampling of electronic states was performed on a $1\times3\times1$ Monkhorst-Pack grid where k-point grip was kept to maintain a spacing of ca. 0.07 Å⁻¹. The convergence threshold for self-consistent iterations was set at 5×10^{-10} eV/atom. The optimization parameters were set as follows: total energy convergence tolerance: 5×10^{-7} eV/atom, maximum force tolerance: 0.01 eV/Å, and maximum displacement tolerance: 5×10^{-4} Å [38]. The IR and Raman spectra were generated from the CASTEP frequency calculation results. As initial data for calculated properties the crystal structure determined at 100 K was applied.

3. Results and discussion

3.1. X-ray diffraction studies

Crystal data, data collection and structure refinements details for cocrystal of 2,6dimethylpyrazine with picric acid for different temperatures are collected in Table 1. The crystals structures have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers CCDC 1968087, 1968088, 1968089, 1968090, 1968091, 1968092 and 1968382). These data can be obtained free of charge via http://www.ccdc.cam ac uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

The cocrystal of 2,6-dimethylpyrazine – picric acid in the temperature 295 K crystallizes in monoclinic P2₁/c space group with a=15.3303(5)Å, b=5.70917(19)Å, c=16.8234(6)Å, β =101.2704(7)° and Z=4. The asymmetric part of the unit cell contains one 2,6dimethylpyrazinium(+) cation and one picrate(-) anion as shown in Fig 1. The arrangement of the molecules in the unit cell is depicted in Fig 2. The bond lengths, bond and torsion angles for cocrystal observed in the room temperature and calculated for PBE + vdW level are presented in Table 2. In the 2,6-dimethylpyrazine – picric acid cocrystal the pyrazine N4 atom forms bifurcated hydrogen bonds, N5-H5A····O1 and N5-H5A····O7, with the picrate anion. The corresponding distances are equal to 2.628Å and 2.925 Å (see Table 3). The nitro group in position 1, being in the vicinity of the acidic oxygen acid, is twisting by ca. 47° around C-N bond, while nitro groups in positions 2 and 3 are twisting by 0.45° and 4.63° respectively (see Table 2). In the crystalline lattice ions form a columnar packing along c-axis with the motif \cdots ADADAD \cdots , where A - denote picric acid anion and D - 2,6-dimethylpyrazine cation. 2,6dimethylpyrazine and picric acid ions forms charge transfer (CT) complex with distance between center of rings 3.849 Å and angle between ring planes 1.1°. The angle between pair of CT complexes is equal to 66.11°. The temperature dependence of unit cell parameters as well as volume of unit cell and hydrogen bond length (N5-H5A \cdots O1) during heating cycle are presented in Fig.3. It can be seen that the nonlinear temperature dependence for a, b, c and β parameter of unit cell can suggest the existence of phase transition at about 160 K. The temperature dependence of hydrogen bond N5-H5A \cdots O1 length show the same behavior.

3.2. Hirshfeld surface analysis

Fig.4 shows Hirshfeld surface generated with the aim of CrystalExplorer program [39] for crystal packing determined at 295 K. Hirshfeld surface is an excellent tool and provides valuable information on molecular interactions presented in the studied system. A crystallographic data file (CIF) is needed in order to calculate this surface. Many properties can be mapped on such surface. Similar analyses were performed for many molecular systems, for example see Ref [40] where reader can find additional explanations. The hydrogen interactions in Fig. 4 were marked as green dashed lines. The so called d_{norm} parameter, which gives information about intermolecular contacts between atoms, was mapped on the surfaces. For the contacts closer than the sum of van der Waals radii of atoms the red spot appears on surface. These regions correspond to hydrogen bonds. Surface colored in blue means no close contact between atoms enclosed by the surface and outside atoms occur. This additionally proofs the assumption made earlier that picric acid and 2,6-dimethylpyrazine molecules do not interact strongly in the discussed cocrystal besides of the hydrogen bonds. Very similar results were obtained for d_i and d_e parameters mapped onto surface. Parameter d_i denotes distance from the surface to the nearest atom inside the surface whereas d_e is the distance from the surface to the nearest external atom. In the Figure 5 fingerprints plots (de versus di) for investigated cocrystal are shown. Namely, Fig 5a displays all the intercontact presented in the discussed system. Fig 5 b-d depicts the most important interactions found in the studied cocrystal. Only contributions higher than 10% were shown in this figure. The main contribution to the fingerprint gives the O-H interactions (43.1%, Fig. 5b). Two characteristic sharp spikes are clearly visible. The H-H, C-O and N-O interactions contribute to the fingerprint in the following amounts: 20.8%, 10.2% and 5.3%, respectively. It is worth noting that H-H interactions occupy the second position among the highest contribution. The contribution of the remaining intermolecular contacts was found to be less than 5% of the total surface (C-C 2.3%, C-H 4.8%, C-N 4.8%, H-N 3.1%, N-N 1%, O-O 4.7%). It can be concluded that hydrogen bonds are the most important interaction found in the 26DMP-PA cocrystal. The π - π interactions are rather small.

3.3. NMR spectroscopy

The structure of 2,6-dimethylpyrazine - picric acid cocrystal was investigated in CDCl₃ solution, acetone solution and the solid state. The results of this study are collected in Table 4. Due to intermolecular interaction with chloroform some signals for cocrystal were severe broadened or missed, therefore the measurements were repeated in acetone solution. The signal assignments for aromatic carbon atoms were done on the base of signal intensity comparing (intensity of protonated carbon atoms are few times more intensive than those of quaternary atoms). For picric acid anion the C1, C2, C3 and C4 atoms signals were distinguished by intensity as well. In CPMAS ¹³C spectra the protonated and quaternary carbon atoms signals were assigned using SCT experiments, where only protonated carbon signals are present. The chemical shift observed on the C1 carbon atom in picric acid, at the CPMAS investigation, is about 161 ppm, while for solutions is 154 ppm. On the other hand, the chemical shift on N5 shows -160.4 ppm in the CPMAS, it is lower than for solutions. Those both effects, upfield on carbon and downfield on nitrogen signals, indicate that some proton transfer from picric acid to pyrazine nitrogen sites can take place [41]. Since this process does not change symmetry of the compounds it should be considered as fast on NMR time scale dynamic exchange of protons. In investigated cocrystal this effect is different on both nonequivalent nitrogen atoms, which means that position N5 (stronger upfield effect detected) is preferred in protonation reaction.

3.4. DSC investigation

The phase situation for the 2,6–dimethylopyrazine - picric acid cocrystal was probed using differential scanning calorimetry (DSC) method in the temperature range 120–295 K. Investigations were performed on heating and cooling of sample. Fig.6 shows the temperature dependencies of the heat flow obtained on heating (pink curve) and on cooling (blue curve) of the titled compound. The heating/cooling rate for the sample was 10 K min⁻¹. One distinct anomaly on each of these two DSC curves was registered at: $T_c^h = 163.5$ K (onset on heating) and $T_c^c = 153.1$ K (onset on cooling). Thus, the title compound has two solid phases. The thermal hysteresis of the phase transition temperature T_c equal to ca. 10.4 K and the heat flow anomaly sharpness suggest that the detected phase transition is a first-order one. The relatively high entropy change ($\Delta S = 3.95$ J·mol⁻¹·K⁻¹) connected with observed phase transition indicates high degree of dynamical disorder of high temperature phase.

3.5. Vibrational spectral studies

The investigated 2,6-dimethylopyrazine - picric acid cocrystal contains 140 atoms in a crystallographic unit cell. It's implying that 420 normal modes are expected where 372 of them described normal vibration modes, 45 described translation and rotation modes and 3 are non-active acoustic modes. Due to selection rules in the C_{2h} crystallographic symmetry group the

number of modes equals to $\Gamma_{vib} = 105A_g + 104A_u + 105B_g + 103B_u$, where modes with symmetry A_g and A_u are active only in IR while B_u and B_g modes are active only in Raman spectra for $\mathbf{k} = 0$. Details are described in Table 5.

IR spectra collected at 9.8K and 290K, Raman spectrum at 290K as well as IR and Raman spectra calculated in periodic boundary conditions in far infra-red region are presented in Fig. 7. These same spectra in the energy range 3600-600 cm⁻¹ are show on Fig. 8. Observed IR and Raman frequencies as well as calculated one and their tentative assignments are listed in Table 6. The assignment was done based on available literature data [28, 42-44] and visualization of particular modes in Jmol software [45]. For the high wavenumbers internal vibrations of both constituting building blocks i.e. picric acid (PA⁻) anion and 2,6dimethylpyrazine (26DMP⁺) cation can be treated independently, so the total spectrum can be obtained as a sum coming from particular molecular parts. For far infrared region the vibrations origin from PA⁻ and 26DMP⁺ are mixed. In the 3300 - 3000 cm⁻¹ range C-H stretching vibration from aromatic hydrogen are visible. The calculated IR spectrum describes well this region. In the Raman experimental spectrum only one low intensity peak is presented at 2934 cm⁻¹ (CH₃ str. sym. 26DMP⁺). This peak is visible at 2978 cm⁻¹ in the calculated spectrum. In the IR spectra hydrogen bonds vibrations, overlapping with continuous absorption and Fermi resonance, are represented by the very broad maximum between 1700 and 2700 cm⁻¹. Peaks at 2199, 2173, 1989 and 1961 cm⁻¹ at 9.8K in IR spectra are connected to overtone (2 x CH bend.) and summation (CH_{bend.}+ CH_{wagg.}) vibrations modes while at 290 K these peaks are observed at 2170 and 1972 cm⁻¹ respectively. In the Raman spectrum there is no visible bands in this region (see Fig. 8). In the calculated IR spectrum one can observe sharp very intensive peak at about 2800 cm⁻¹ which is connected with N-H stretching vibration. In the theoretical RS spectrum band of low intensity is observed (not visible in the experimental data). The ring stretching, CH₃ bending, CH₃ rocking of 2,6-dimethylpyrazine cation as well as C=O stretching, ring stretching, NO₂ stretching, C-N stretching of picric acid anion modes are observed in the wavenumber range 1700–850 cm⁻¹ in the IR and Raman spectra. In this range there is a good agreement between experimental and predicted IR and Raman spectra. The N-H bend (26DMP⁺) and N-H wagg (26DMP⁺) modes are observed at 1113 cm⁻¹ and 869 cm⁻¹ in the room temperature respectively. In the far infrared region C-CH₃ bending and wagging modes, CH₃ torsion modes as well as ring deformation and ring torsion modes for 2,6-dimethylpyrazine cation are observed. In this same region for the picric acid anion the NO₂ bending, rocking, wagging and torsion modes and C-NO₂ bending and wagging modes as well as ring deformation and ring torsion modes are observed. The region 600 -200 cm^{-1} (both IR and Raman) is very well reproduced by computations. Below 200 cm⁻¹ the

predicted bands are slightly shifted toward higher wavenumber range relative to experimental spectra.

3.6. Temperature-dependent IR spectroscopy

Figures 9 and 10a show the selected IR spectra of the 2,6-dimethylopyrazine-picric acid cocrystal, within the wavenumber range 1700–850 cm⁻¹ and 2250–1900 cm⁻¹respectively, registered during the cooling of the sample from 290K to 9.8K. In the middle infrared spectra, some evident changes can be noticed. The narrowing of the peaks and the appearing of some new bands can be observed. The narrowing of bands with lowering of temperature indicates slowing of their fast reorientational motions. Fig. 10b presents contour plot of bands connected to overtone (2 x CH_{bend.}) and summation (CH_{bend.} + CH_{wagg.}) vibrations modes. In the vicinity of phase transition the changes of intensity as well as splitting of broad bands into two components are visible. Moreover, the maxima of emerging doublets in particular peaks are moving away from each other. Fig. 11 presents the temperature dependence of the bands position in a 1680-840 cm⁻¹ region. As can be seen in Figs. 9 and 11, some bands (at 1635 cm⁻¹, 1464 cm⁻¹, 1113 cm⁻¹ and 869 cm⁻¹) start to split in the spectra at temperature close to $T_c = 153.1$ K. The band at 1635 cm⁻¹ is assigned to C=O stretching mode of picric acid anion. During cooling a new band emerges and two well distinguishable bands are observed at 1639 and 1632 cm⁻¹ in the lowest temperature. The band at 1464 cm⁻¹ which relates to stretching asymmetric N-O mode of picric acid anion, splits into two components. Interesting features can be noticed for hydrogen bond at 1113 cm⁻¹ (N-H in-plane deformation) and at 869 cm⁻¹ (N-H out-of-plane deformation) for 26DMP⁺ cation. For both bands a splitting in the vicinity of phase transition is visible. This may mean that the dynamics of hydrogen bonds is changing in the phase transition. The and shape analysis contain information concerning molecular reorientational motions of molecules in condensed phases, when the reorientational correlation time τ_R is of an order $10^{\text{-13}}$ - $10^{\text{-11}}$ seconds. For this, the analysis of FWHM which is based on the formula used for the damping associated with the order-disorder transition [46, 47] was performed. The reorientational correlation time τ_c is the mean time between instantaneous jumps from one potential well to the other, and it is defined by the following formula:

$$\tau_{\rm c} = \tau_{\infty} \cdot \exp(\frac{E_a}{RT}), \tag{1}$$

where: τ_{∞} is the relaxation time at an infinite temperature *T*, E_a is the potential barrier height for reorienting group, $R = N_A \cdot k_B = 8.314472 \text{ JK}^{-1} \text{mol}^{-1}$ is the gas constant, and N_A and k_B are Avogadro's and Boltzmann's constants, respectively. When $\omega^2 \cdot \tau_R^2 \gg 1$, where $\omega = 2\pi v$ and v is the frequency of a particular phonon mode, the temperature dependence of the FWHM of the infrared bands connected with this mode is determined by following expression [46-48]:

$$FWHM(T) = (a + bT) + c \cdot exp(-\frac{E_a}{RT}), \qquad (2)$$

where: a, b, c and E_a are fitting parameters. Here the E_a is activation energy of the reorientation process. The linear part of equation (2) is associated with the vibrational relaxation and the exponential term is associated with rotational relaxation and corresponds to the thermal reorientational motions of a diffusion nature.

In the studied system two groups belonging to different molecules, namely the methyl CH₃ from 2,6-dimethylpyrazine and nitro NO₂ from picric acid may potentially reorientate. However, the rotation of NO₂ is less probable. These groups take part in the formation of hydrogen bonds network and are rather immobilized due to this effect. On the other hand, CH₃ groups are not engaged in the formation of such bonds and moreover there is no steric effect. The rotation of methyl groups is not strongly hindered and affected by the environmental effects such as close contact. This is the reason why the rotation of methyl group is much more probable and can be responsible for the narrowing of particular bands.

Analysis of the temperature dependency of the full-width-at-half-maximum (FWHM) was carried out for the band at 294 cm⁻¹ associated with C-CH₃ bending mode. In order to perform analysis of FWHM a few conditions must be fulfilled. Firstly, the analyzed peak should be well isolated from others (energy separated). Secondly, it should be connected with only one mode. In other words, it should describe only one process i.e. motion of particular group whereas the remaining atoms should not be involved (engaged) in this vibration. The third condition states that intensity of analyzed peak should not be very small; it means that investigated transition should be connected with noticeable change of dipole moment. Figure 12 presents the temperature dependence of the FWHM of the analyzed infrared band at 294 cm⁻¹. The shape of the analyzed peak was approximated by a Lorentz function. It can be seen that during the cooling of the sample from the room temperature, FWHM of this band decreases exponentially down to the temperature 150 K. Below T_c the changes of FWHM are small and it can be said that this temperature dependency reaches plateau. This indicates that below ~150 K, reorientational motion of the C-CH₃ groups is slowed down. The fitting Eq. (2) to FWHM vs. T dependence was done to all experimental points in the temperature range 290-9.8 K. The fitted parameters are listed in Table 7. The mean value of activation energy $E_a(I/II)$ obtained from the analysis of this band is equal to 5.2 kJmol⁻¹. The obtained E_a is characteristic for methyl groups which exhibit tunneling behavior. It is interesting to notice that very similar value ($E_a \sim 3.5 \text{ kJmol}^{-1}$) was obtained for 2,6-dimethylpyrazine (DMP) and chloranilic acid (CLA) complex [27] from the analysis of neutron scattering data. FT-IR analysis for the 2,6-dimethylopyrazine-picric acid

cocrystal, suggests that the rapid C-CH₃ group reorientation is slowing down below 150 K (correlation time $\tau > 10^{-12}$ s).

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4. Conclusion

The new molecular cocrystal 2,6–dimethylopyrazine - picric acid crystallizes in P2₁/c space group with Z=4, a=15.3303(5)Å, b=5.70917(19)Å, c=16.8234(6)Å and β =101.2704(7)°. From NMR and X-ray investigations it was found that 2,6–dimethylopyrazine exists in the cation form and picric acid exists in anion form. They are bonded to each other by hydrogen bonds N-H⁺···O⁻ with the length 2.628Å and 2.925Å. Hirshfeld surface analysis shows that intermolecular contacts are performed mainly by hydrogen bonds (43.1% contribution). On the base of temperature dependent measurements (DSC, X-ray and IR) low temperature phase transition at 153.1K on cooling and at 163.5K on heating was observed. The temperature dependent overtone (2 x CH _{bend.}), summation (CH _{bend.} + CH _{wagg}), C=O _{str.}, NO_{2 str.}, N-H _{bend.} and N-H _{wagg}, vibrational modes were observed. IR, Raman and DFT calculation for periodic boundary condition were used for determination of cocrystal dynamic structure. The normal modes were described and analyzed as a function of temperature. Activation energy for C-CH₃ group bending reorientation was obtained to be equal 5.2 ± 0.5kJmol⁻¹.

5. Acknowledgements

The infrared absorption (FT-FIR and FT-MIR) researches were carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

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Figure captions



Fig.1. The molecular structure and the atom numbering scheme in the 2,6–dimethylopyrazinepicric acid cocrystal.



Fig.2. The packing of 2,6–dimethylopyrazine-picric acid cocrystal in the crystalline lattice.



Fig.3. Temperature dependence for a, b, c and β parameters of unit cell, volume of unit cell and N5-H5A···O1hydrogen bond length for 2,6–dimethylopyrazine-picric acid cocrystal.

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Fig.4. Hirshfeld surfaces analysis for 2,6-dimethylpyrazine-picric acid cocrystal. Parameters mapped onto the surface, a) d_{norm} b) d_i and c) d_e .



Fig.5. Fingerprint generated for 2,6-dimethylpyrazine-picric acid cocrystal with relative percentage contributions of particular intermolecular contacts to Hirshfeld surface area: a) all interactions (100%), b) O-H (43.1%), c) H-H (20.8%) d) C-O (10.2%).



Fig.6. DSC curves for 2,6-dimethylopyrazine-picric acid cocrystal.

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Fig.7. Comparison of Raman, IR and calculated IR spectra in the far infra-red region for 2,6-

dimethylopyrazine-picric acid cocrystal.



Fig.8. Comparison of Raman, IR and calculated IR spectra in the middle infra-red region for 2,6– dimethylopyrazine-picric acid cocrystal.



Fig.9. IR spectra in the wavenumber range of 1700–850 cm⁻¹ during cooling of the 2,6– dimethylopyrazine-picric acid cocrystal from 290 K to 9.8 K with the step 10 K.



Fig.10. IR spectra in the wavenumber range of 2250–1900 cm⁻¹ during cooling of the 2,6– dimethylopyrazine-picric acid cocrystal a), contour plots of IR spectra in the H-bonding region b).



Fig.11. The temperature dependence of peak positions in the wavenumber range 1670–850 cm⁻¹.



Fig.12. Temperature evolutions of FWHM of the band at 294 cm⁻¹ associated with C-CH₃ bending mode. Solid line represents fitting of equation (2) to the experimental data.

Graphical abstract





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Temperature	295K	250K	200K
Empirical formula	$C_{12}H_{11}N_5O_7$	$C_{12}H_{11}N_5O_7$	$C_{12}H_{11}N_5O_7$
Formula weight	337.26	337.26	337.26
Wavelength	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_{1}/c$
	a=15.33636(12) Å,	a=15.3239(2) Å,	a=15.3064(4) Å,
Unit cell dimensions	α=90°	α=90°	α=90°
	b=5.71358(4) Å,	b=5.7014(2) Å,	b=5.68891(19) Å,
	β=101.2704(7)°	$\beta = 101.612(3)^{\circ}$	β=101.998(3)°
	c=16.83224(12) Å,	c=16.7488(5) Å,	c=16.6552(5) Å,
	γ=90°	γ=90°	γ=90°
Volume	, 1446.491(18)Å ³	$1433.36(8)\text{\AA}^3$	1418.59(7)Å ³
Z	4	4	4
Density (calculated)	1.549 Mg/m^3	1.563 Mg/m^3	1.579 Mg/m^3
Absorption coefficient	1.128 mm^{-1}	1.138 mm^{-1}	1.150 mm^{-1}
F(000)	696	696	696
Crystal size	0.33 x 0.19 x 0.14	0.222 x 0.183 x 0.15	0.222 x 0.183 x 0.15
	mm ³	mm^3	mm ³
θ range for data	2.94 to 71.09°	2.94 to 67.06°	2.95 to 67.07°
collection			
Index ranges	-18≤h≤18, -6≤k≤6, -	-18≦h≦18, -6≦k≦6, -	-18≦h≦18, -6≦k≦6, -
	20≤l≤20	20≤l≤20	20 <u>≤</u> 1 <u>≤</u> 20
Reflections collected	21504	19547	19357
Independent reflections	2781[R(int)=0.0363]	2558[R(int)=0.0213]	2530[R(int)=0.0209]
Completeness to	99.6%	100%	100%
$\theta = 71.16^{\circ}$	\sim		
Refinement method	Full-matrix least-	Full-matrix least-	Full-matrix least-
	squares on F ²	squares on F ²	squares on F ²
Data/restrains/parameters	2781/0/223	2558/0/223	2530/0/223
Goodness-of-fit on F^2	1.032	1.04	1.051
Final R indices [I>2o(I)]	R1=0.0406,	R1=0.0388,	R1=0.0367,
	wR2=0.1154	wR2=0.1061	wR2=0.0994
R indices (all data)	R1=0.0431,	R1=0.0422,	R1=0.0397,
	wR2=0.1191	wR2=0.1100	wR2=0.1029
Extinction coefficient	0.0096(7)	none	none
Largest diff. peak and	0.228 and -0.302	0.249 and -0.253	0.266 and -0.273
hole	e·A ⁻³	e·A ⁻³	e·A ⁻³

 Table 1. Crystal data and structure refinement for 2,6-dimethylpyrazine – picric acid cocrystal in the temperature function.

Temperature	160K	140K	120K
Empirical formula	$C_{12}H_{11}N_5O_7$	$C_{12}H_{11}N_5O_7$	$C_{12}H_{11}N_5O_7$
Formula weight	337.26	337.26	337.26
Wavelength	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_{1}/c$	$P2_{1}/c$
	a=15.1897(4) Å,	a=15.1790(4) Å,	a=15.1709(4) Å,

Unit cell dimensions	α=90°	α=90°	α=90°
	b=5.8517(2) Å,	b=5.85307(19) Å,	b=5.85340(19) Å,
	$\beta = 101.903(3)^{\circ}$	β=101.973(3)°	$\beta = 102.057(3)^{\circ}$
	c=16.1037(5) Å,	c=16.0540(5) Å,	c=16.0137(5) Å,
	v=90°	ν=90°	ν=90°
Volume	$1400.62(18)\text{Å}^3$	1395.27(7)Å ³	1390.67(7)Å ³
Z	4	4	4
Density (calculated)	1.599 Mg/m^3	1.606 Mg/m^3	1.611 Mg/m^3
Absorption coefficient	1.165 mm^{-1}	1.169 mm^{-1}	1.173 mm^{-1}
F(000)	696	696	696
Crystal size	0.222 x 0.183 x 0.15	0.222 x 0.183 x 0.15	0.222 x 0.183 x 0.15
	mm ³	mm^3	mm ³
θ range for data	2.97 to 67.08°	2.98 to 67.06°	2.98 to 67.06°
collection			
Index ranges	-18≤h≤18, -6≤k≤6, -	-18≤h≤18, -6≤k≤6, -	-18≤h≤18, -6≤k≤6, -
	19 <u>≤</u> 1 <u>≤</u> 19	19 <u>≤</u> 1 <u>≤</u> 19	19 <u>≤</u> 1≤19
Reflections collected	18967	18915	18867
Independent reflections	2488[R(int)=0.0203]	2479[R(int)=0.0200]	2473[R(int)=0.0199]
Completeness	100%	100%	100%
Refinement method	Full-matrix least-	Full-matrix least-	Full-matrix least-
	squares on F ²	squares on F ²	squares on F ²
Data/restrains/parameters	2488/0/223	2478/0/222	2473/0/222
Goodness-of-fit on F^2	1.057	1.072	1.050
Final R indices $[I>2\sigma(I)]$	R1=0.0363,	R1=0.0341,	R1=0.0331,
	wR2=0.0935	wR2=0.0887	wR2=0.0859
R indices (all data)	R1=0.0386,	R1=0.0362,	R1=0.0348,
	wR2=0.0958	wR2=0.0909	wR2=0.0.876
Extinction coefficient	none	none	none
Largest diff. peak and	0.190 and -0.254	0.200 and -0.251	0.199 and -0.256
hole	e·Å ⁻³	e·Å⁻³	e∙Å ⁻³

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Jour			
Temperature		100K	
Empirical formula		$C_{12}H_{11}N_5O_7$	
Formula weight		337.26	
Wavelength		1.54184 Å	
Crystal system		Monoclinic	
Space group		$P2_1/c$	
Unit cell dimensions		a=15.1638(4) Å, α =90° b=5.85420(19) Å, β =102.131(2)° c=15.9784(5) Å, γ =90°	þ
Volume		$1386.76(18)\text{\AA}^3$	
Z		4	
Density (calculated)		1.615 Mg/m^3	
Absorption coefficient		1.177 mm^{-1}	
F(000)		696	

Crystal size	0.222 x 0.183 x 0.15 mm ³
θ range for data collection	2.98 to 67.08°
Index ranges	-18≤h≤18, -6≤k≤6, -19≤l≤19
Reflections collected	18819
Independent reflections	2469[R(int)=0.0201]
Completeness	100%
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	2469/0/222
Goodness-of-fit on F^2	1.056
Final R indices $[I>2\sigma(I)]$	R1=0.0320, wR2=0.0853
R indices (all data)	R1=0.0338, wR2=0.0873
Extinction coefficient	none
Largest diff. peak and hole	0.217 and -0.282 $e \cdot Å^{-3}$

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Table 2. The bond lengths, bond and torsion angles for 2,6-dimethylpyrazine – picric acid cocrystal at
the room temperature.

Coordinates	Experimental	Calculated	Coordinates	Experimental	Calculated
	X-ray	CASTEP/PBE+vdW		X-ray	CASTEP/PBE+vdW
	Bond lengt	hs	C7-C8-N5	118.9(1)	118.8
C1-C2	1.452(2)	1.465	C8-N5-C9	121.7(1)	122.1
C2-C3	1.358(2)	1.373	N5-C9-C10	118.7(1)	118.4
C3-C4	1.391(2)	1.397	C9-C10-N4	120.8(1)	120.8
C4-C5	1.373(2)	1.386	C10-N4-C7	119.0(1)	119.5
C5-C6	1.384(2)	1.385	N4-C7-C8	120.9(1)	120.5
C6-C1	1.442(2)	1.464	C9-C10-C12	120.8(2)	120.4
C1-O1	1.248(2)	1.251	N4-C10-C12	118.5(1)	118.8
C2-N1	1.458(2)	1.461	N4-C7-C11	118.1(2)	118.8
C4-N2	1.447(2)	1.446	C8-C7-C11	121.1(2)	120.7
C6-N3	1.448(2)	1.451		Torsion angles	5
N1-O2	1.212(2)	1.234	C6-C1-C2-C3	0.1(2)	-2.7
N1-O3	1.222(2)	1.243	C6-C1-C2-N1	177.8(1)	173.6
N2-O4	1.225(2)	1.242	01-C1-C2-C3	-178.5(2)	179.5
N2-O5	1.229(2)	1.244	01-C1-C2-N1	-0.7(2)	-4.2
N3-06	1.212(2)	1.245	C2-C1-C6-C5	0.6(2)	2.7
N3-07	1.213(2)	1.242	C2-C1-C6-N3	-179.0(1)	-176.3
C7-C8	1.388(2)	1.399	01-C1-C6-C5	179.0(2)	-179.6
C8-N5	1.327(2)	1.342	01-C1-C6-N3	-0.5(3)	1.4
N5-C9	1.332(2)	1.341	C1-C2-C3-C4	-0.5(3)	1.2
C9-C10	1.390(2)	1.400	N1-C2-C3-C4	-178.3(1)	-175.2
C10-N4	1 339(2)	1 347	C1-C2-N1-O2	49 5(2)	32.8
N4-C7	1.337(2)	1 348	C1-C2-N1-O3	-132.2(2)	-146.9
C7-C11	1.337(2) 1 494(2)	1 494	C3-C2-N1-O2	-132.5(2)	-150.7
C10-C12	1.191(2) 1.490(2)	1 494	C3-C2-N1-O3	457(2)	29.6
010 012	Rond angl	2.1.2	$C^{2}-C^{3}-C^{4}-C^{5}$	0.3(2)	07
C2-C1-C6	111 4(1)	112.4	C2-C3-C4-N2	179.6(2)	177 7
C2-C1-O1	121 6(1)	122.1	C3-C4-C5-C6	0.3(2)	-0.7
C6-C1-O1	127.0(1)	125.5	N2-C4-C5-C6	-1790(2)	-177 7
C1-C2-C3	1254(1)	123.3	C3-C4-N2-O4	0.4(2)	39
C1-C2-N1	117.6(1)	119.5	C3-C4-N2-O5	-1792(2)	-175.8
C3-C2-N1	117.0(1)	116.3	C5-C4-N2-O4	179.2(2)	-179.0
$C_{2}-C_{3}-C_{4}$	117.0(1) 118.6(1)	110.5	C5-C4-N2-O5	0.1(2)	14
$C_{3}-C_{4}-C_{5}$	1211(2)	121.2	C4-C5-C6-C1	-0.8(2)	-1.2
C3-C4-N2	119.5(1)	119.6	C4-C5-C6-N3	178.8(1)	-177.9
C5-C4-N2	119.3(1)	119.0	C1-C6-N3-O6	-175.0(1)	179.9
C4-C5-C6	119.6(1)	120.0	C1-C6-N3-O7	43(2)	0.13
C1-C6-C5	123.9(1)	123.0	C5-C6-N3-O6	53(2)	0.15
C1-C6-N3	120.1(1)	121.3	C5-C6-N3-O7	-175 2(2)	-178.9
C5-C6-N3	120.1(1) 1160(1)	115 7	C10-N4-C7-C8	-1.6(2)	21
C2-N1-O2	118.9(1)	119.3	C10-N4-C7-C11	1784(2)	-179 3
C2-N1-O3	110.9(1) 117.1(1)	117.0	C11-C7-C8-N5	-179.1(2)	-179.0
02-N1-03	1240(2)	123.7	N4-C7-C8-N5	10(2)	-0.5
C4-N2-O4	124.0(2) 118 1(2)	118.2	C7-C8-N5-C9	0.7(2)	-1 2
C4-N2-O4	118.1(2) 118.6(2)	118.2	$C_{8}N_{5}C_{9}C_{10}$	-1.5(2)	1 2
04-N2 05	173 2(2)	173.6	$N5_C0_C10 N1$	-1.3(2) 0.8(2)	0.5
C6-N3 O6	123.2(2) 118 6(2)	117 8	$N5_C0_C10_C12$	-170 6(2)	170 5
C6-N3-07	120.0(2) 120.5(2)	110 8	$C9_C10_N/_C7$	-177.0(2)	_2 1
06-N3-07	120.3(2) 120.9(2)	122 4	C12-C10-N4-C7	-1783(2)	178 9
001001	120.7(2)	1 <i>22</i> , T		1,0.3(2)	110.7

Table 3. Hydrogen bonds geometry for 2,6-dimethylpyrazine – picric acid cocrystal at room temperature.

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N5-H5A…O1#1	0.92(2)	1.77(2)	2.628(2)	154(2)
N5-H5A…O7#1	0.92(2)	2.31(2)	2.925(2)	124(2)

Symmetry transformations used to generate equivalent atoms: #1 x, -y+5/2, z-1/2

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Atom	2,6-dimethylpyrazine	2,6-dimethylpyrazine – picric acid		
	CDCl ₃	CDCl ₃	acetone	CPMAS
C7	152.7	#	152.4	145.8
C10	152.7	#	152.4	145.8
C8	141.4	#	141.1	~129.8
C9	141.4	#	141.1	~129.8
Methyl groups	21.45	#	25.2	21.8
				21.1
N4	-51.6	-63.5	-63.8	-49.0 \$
N5	&	-57.3	-53.4	-160.4 \$
C1		154.3	153.4	162.2 %
				160.9 %
				159.8 %
C2/C6		137.9	136.7	~134.7
C3/C5		126.2	125.5	126.2
C4		137.0	138.8	~134.7
$C2-NO_2$		-21.2	-18.0	-13.6
				-14.5
				-15.9
$C4-NO_2$		-18.8	-16.3	

Table 4. NMR data for 2,6-dimethylpyrazine - picric acid cocrystal (ppm).

- in carbon spectrum only picric acid signals are observed, the other signals are too broad to be detected in the reasonable time.

& - in $CDCl_3$ only N4 signal was detected (correlated with Methyl groups) whereas in acetone two signals were found.

\$ - nitrogen signal assignment done on the base of analysis of carbon CPMAS spectra. The large up field shift of C8 and C9 signals suggests protonation on N5 nitrogen atom [41].

% - three quaternary carbon signals indicating unsymmetrical molecular structure.

~ - overlapped signals.

Table 5. Classification of the fundamental modes (k=0) for 2,6-dimethylpyrazine - picric ac	cid
cocrystal.	

UCG	Lattice modes		Internal modes		Selection rules		
C_{2h}	Ac.	Trans.	Rot.	26DMP^+	PA^{-}	IR	Raman
Ag		6	6	45	48		x^{2}, y^{2}, z^{2}, xy
\mathbf{B}_{g}		6	6	45	48		xz, yz
A_u	1	5	6	45	48	Z	
$\mathbf{B}_{\mathbf{u}}$	2	4	6	45	48	х, у	

UCG - unit cell (factor) group, Ac. - acoustic modes, Trans. - translation modes, Rot. - rotation modes,

s ournal provide states of the second states of the

Table 6. Observed and calculated frequencies for 2,6–dimethylpyrazine-picric acid cocrystal (cm⁻¹). The structure is centrosymmetric so vibrations active in IR are not active in Raman and vice versa.

	Experimental		Calculated	Approximate
IR(9K)	IR(290K)	Raman	CASTEP/PBE + vdW	assignments
3210	3202	Itumun	3175(IR) 3175(R)	$C-H_{\text{str}}$ (PA ⁻)
3143	3139		3173(IR) 3173(R)	$C-H_{\text{str.}}(PA^{-})$
			3157(IR) 3156(R)	$C-H_{str}$ (26DMP ⁺)
			3150(IR) 3150(R)	$C-H_{str}$ (26DMP ⁺)
3102	3091		3091(IR) 3091(R)	$CH_{3 \text{ str. asym.}}(26DMP^{+})$
3066	3071		3085(IR) 3084(R)	$CH_{3 \text{ str. asym.}}(26DMP^+)$
			3048(IR) 3048(R)	CH _{3 str. asym} (26DMP ⁺)
			3035(IR) 3035(R)	CH _{3 str. asym} (26DMP ⁺)
		2934	2978(IR) 2978(R)	$CH_{3 \text{ str. sym.}}(26DMP^+)$
			2969(IR) 2969(R)	$CH_{3 \text{ str. sym.}}(26DMP^{+})$
			2825(IR) 2833(R)	$N-H_{str.}(26DMP^+)$
2199 2173	2170			C-H _{bend.} overtone
1989 1961	1972		C .	$C-H_{bend.} + C-H_{wagg.}$ summation
1639 1632	1635	1636	1609(IR) 1613(R)	$C=O_{str.}(PA^{-})$
1616	1616	1615	1607(IR) 1607(R)	Ring str. $(26DMP^+)$
1591	1589	1587	1583(IR) 1587(R)	Ring str. $(26DMP^+)$
1576 1570	1571	1562	1556(IR) 1559(R)	Ring str. (PA ⁻)
			1553(IR) 1557(R)	
1552	1550	1546	1548(IR) 1551(R)	Ring str. $(26DMP^+)$
1511 1506	1508	1489	1500(IR) 1499(R)	$NO_{2str.}(PA^{-})$
1468 1461	1464		1480(IR) 1483(R)	$NO_{2str.}(PA^{-})$
			1461(IR) 1461(R)	$NO_{2str.}(PA^{-})$
1445	1458		1460(IR) 1460(R)	CH _{3 bend. asym.} (26DMP ⁺)
			1454(IR) 1454(R)	$CH_{3 \text{ bend. asym.}}$ (26DMP ⁺)
1437 1432	1432	1431	1439(IR) 1441(R)	$CH_{3 \text{ bend. asym.}}$ (26DMP ⁺)
			1432(IR) 1431(R)	CH _{3 bend. asym.} (26DMP ⁺)
			1429(IR) 1425(R)	Ring str. $(26DMP^+)$
1401			1417(IR) 1420(R)	Ring str. (PA ⁻)
1385		1382	1381(IR) 1382(R)	Ring str. $(26DMP^+)$
1375	1376		1370(IR) 1374(R)	$CH_{3 \text{ bend. sym.}}$ (26DMP ⁺)
1366 1353	1365	1364	1364(IR) 1365(R)	$CH_{3 \text{ bend. sym.}}$ (26DMP ⁺)
1344 1339	1340	1341	1343(IR) 1345(R)	Ring str. (PA ⁻)
1321	1320	1318	1319(IR) 1321(R)	Ring str. $(26DMP^+)$
1304	1301	1302	1298(IR) 1298(R)	$NO_{2str.}(PA^{-})$
1287			1290(IR) 1291(R)	Ring str. (PA ⁻)
1281	1285	1284	1284(IR) 1283(R)	Ring str. (PA ⁻)
1276	1274	1277	1273(IR) 1280(R)	Ring str. $(26DMP^+)$
1268 1262	1264	1261	1263(IR) 1263(R)	$NO_{2str.}(PA^{-})$
1249 1242	1244		1251(IR) 1252(R)	NO _{2str.} (PA ⁻)
1201 1185	1194	1196	1227(IR) 1226(R)	$C-H_{bend.}$ (26DMP ⁺)
1167 1163	1163	1166	1152(IR) 1152(R)	$C-H_{bend.}$ (26DMP ⁺)
1144 1132	1140		1140(IR) 1136(R)	$C-N_{str.}$ (26DMP ⁺)
1123 1103	1113	1114	1129(IR) 1128(R)	$N-H_{bend.}$ (26DMP ⁺)
1091 1082	1081	1083	1110(IR) 1110(R)	C-H _{bend} .(PA ⁻)
1065 1053	1062		1055(IR) 1052(R)	C-H _{bend} .(PA ⁻)
1048 1034	1035	1035	1042(IR) 1042(R)	$CH_{3rock.}$ (26DMP ⁺)
1019	1029		1024(IR) 1023(R)	$CH_{3 \text{ rock.}}$ (26DMP ⁺)
1014		1015	1014(IR) 1013(R)	$CH_{3rock.}$ (26DMP ⁺)
			1002(IR) 1001(R)	$C-H_{wagg}$ (26DMP ⁺)
985	980	980	970(IR) 967(R)	$CH_{3rock.}$ (26DMP ⁺)
947	944	945	937(IR) 936(R)	$C-CH_{3str.}$ (26DMP ⁺)
933	928		934(IR) 935(R)	C-N _{str.} (PA ⁻)
	~ • • •	926	930(IR) 930(R)	C-N _{str.} (PA ⁻)
923 915	918	922	923(IR) 923(R)	C-H wagg. (PA ⁻)
000 055	0.40	0.45	915(IR) 915(R)	$C-H_{wagg}$ (26DMP ⁺)
880 870	869	869	902(IR) 902(R)	N-H wagg. $(26DMP^+)$

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842 834	841		865(IR) 865(R)	C-H (PA ⁻)	
824	822	822	822(IR) 822(R)	Ring def(PA-)	
793	790	791	806(IR) 806(R)	NO_{2} hand (PA^{-})	
757	756	//1	783(IR) 783(R)	NO_2 (PA ⁻)	
744 733	744	745	744(IR) 744(R)	Ring def (PA ⁻)	
/ 11 / 55	,	727	730(IR) 730(R)	$NO_2 \text{ waves} (PA^-)$	
	724		725(IR) $725(R)$	$C-CH_{2male}$ (26DMP ⁺)	
	, <u> </u>		712(IR) 714(R)	$NO_2 \text{ waves} (PA^-)$	
712	711	713	710(IR) 710(R)	$C-CH_{2star}$ (26DMP ⁺)	
/	,	, 10	701(IR) 701(R)	NO_2 hand (PA^-)	
673			694(IR) 694(R)	NO_2 bend (PA^-)	
			663(IR) 663(R)	NO_{2} bend (PA ⁻)	
560	557		554(IR) 556(R)	Ring def. $(26DMP^+)$	
551	550	553	547(IR) 548(R)	$C-CH_{3wagg}$ (26DMP ⁺)	
545	543	544	541(IR) 541(R)	Ring def. (26DMP ⁺)	
532 525	530		534(IR) 535(R)	Ring def. $(26DMP^+)$	
518	516		517(IR) 517(R)	Ring tors. (PA ⁻)	
509	510		487(IR) 487(R)	Ring tors. (PA ⁻)	
456	455		454(IR) 454(R)	Ring def. $(26DMP^+)$	
428 421	420	422	419(IR) 420(R)	$NO_{2 \text{ rock}}$ (PA ⁻)	
409	410		404(IR) 405(R)	$C-CH_{3hend}$ (26DMP ⁺)	
388			403(IR) 402(R)	$C-CH_{3bend}$ (26DMP ⁺)	
374	372	373	375(IR) 375(R)	$C=O_{bend}(PA^{-})$	
364	363	365	359(IR) 359(R)	Ring def. (PA ⁻)	
336	335	336	338(IR) 338(R)	$NO_{2 \text{ bend.}}(PA^{-})$	
322	320	322	325(IR) 324(R)	Ring def. (PA ⁻)	
310	311	300	307 (IR) 307(R)	$C-NO_{2 \text{ bend.}}(PA^{-})$	
295 276	294	293	299(IR) 298(R)	$C-CH_{3bend.}$ (26DMP ⁺)	
234	228		245(IR) 244(R)	Ring tors. $(26DMP^+)$	
214		218	224(IR) 221(R)	Ring tors. $(26DMP^+)$	
201		208	215(IR) 215(R)	Ring tors. $(26DMP^+)$	
189		185	194(IR) 195(R)	$C-NO_{2 \text{ wagg.}}(PA^{-})$	
			185(IR) 184(R)	$CH_{3tors.}$ (26 DMP^+)	
165	160	163	174(IR) 173(R)	$CH_{3tors.}$ (26 DMP^+)	
155	151	150	165(IR) 161(R)	$CH_{3tors.}$ (26 DMP^+)	
141	138		143(IR) 145(R)	$CH_{3tors.}$ (26DMP ⁺)	
			127(IR) 127(R)	$NO_{2 \text{ tors.}} (PA^{-})$	
93	91	90	90(IR) 90(R)	$NO_{2 \text{ tors.}} (PA^{-})$	
			84(IR) 83(R)	Ring tors. (PA ⁻)	
			67(IR) 67(R)	$NO_{2 \text{ tors.}} (PA^{-})$	
123	104 117	106 115	28–163, 45 modes	Lattice vibrations	

str. – stretching,asym. – asymmetric, sym. – symmetric, bend. – bending, wagg. – wagging, rock. – rocking, def. – *deformation, tors. – torsion modes*

Table7. The fitted parameters: a, b, c and E_a for the temperature dependence of FWHM of the infrared band at 294 cm⁻¹ associated with C–CH₃ bending mode obtained in the temperature range 290-9.8 K for 2,6–dimethylopyrazine - picric acid cocrystal.

Parameter	Value
a [cm ⁻¹]	5.75 ± 0.17
$b [cm^{-1} \cdot K]$	$-2.58 \cdot 10^{-3} \pm 1.3 \cdot 10^{-4}$
c [cm ⁻¹]	54.36 ± 8.70
$E_a [kJ \cdot mol^{-1}]$	5.2 ± 0.5

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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