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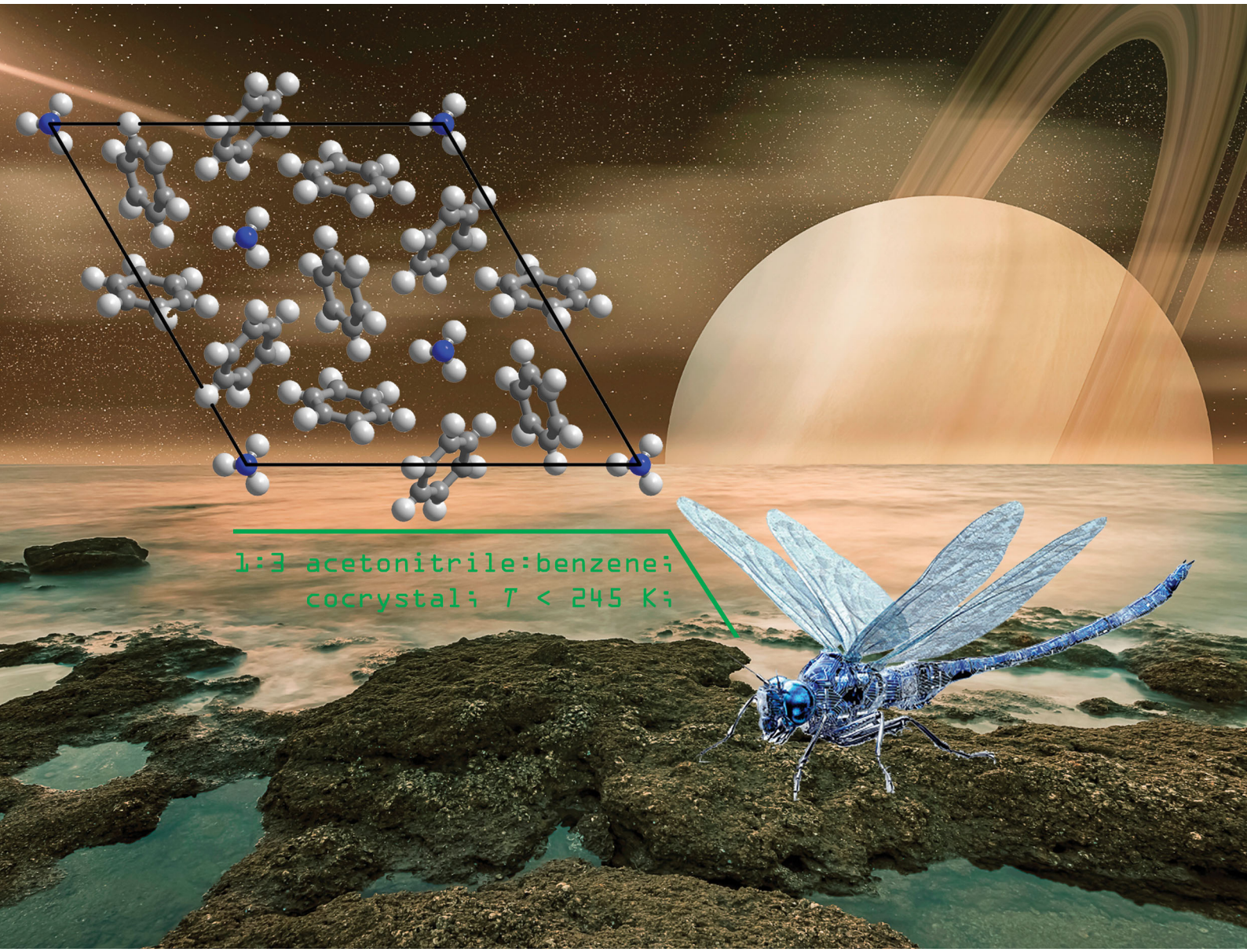

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Peritectic phase transition of benzene and acetonitrile into a cocrystal relevant to Titan, Saturn's moon†

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Benzene and acetonitrile are two of the most commonly used solvents found in almost every chemical laboratory. Titan is one other place in the solar system that has large amounts of these compounds. On Titan, organic molecules are produced in the atmosphere and carried to the surface where they can mineralize. Here, we report the phase diagram of mixtures of acetonitrile and benzene, and provide an account of the structure and composition of the phases. To mimic the environment on Titan more accurately, we tested the stability of the structure under liquid ethane. The results provide new insights into the structure and stability of potential extraterrestrial minerals. In light of Dragonfly, NASA's upcoming mission to Titan, revisiting the fundamental chemistry of the smallest molecules with modern methods and techniques can have significant contributions to this epochal mission and can open new research directions in chemistry.

Research on benzene[1a] and acetonitrile[1b] dates back to the earliest days of modern chemistry. The determination of the crystal structure of hexamethylbenzene[2a] in 1928 was one of the earliest milestones in crystallography, with reports on the crystal structures of pure benzene and acetonitrile following in 1958[2b,c] and 1981,[2d,e] respectively. The phase diagram of these compounds was first studied in 1934,[3a] and later revisited in 1961.[3b] These early and incomplete studies suggest the formation of a cocrystal with unknown stoichiometry. To the best of our knowledge, the structure of the cocrystal, as well as the nature of the molecular interactions of acetonitrile and benzene in its solid state, remain unknown. In fact, cryogenic research on solvents and room-temperature liquids is relatively scarce. However, this research field has now become increasingly relevant with the advances in space exploration, where these molecules play a crucial role. Last year, NASA announced the new frontiers mission to Titan, Saturn's icy moon.[4] A rotorcraft, aptly named Dragonfly, will launch in 2026 and is expected to arrive on the surface of Titan in 2034. Dragonfly will explore Titan's lakebeds, dunes and the floor of an impact crater, searching for signatures of extinct, extant, or future life. This endeavour is timely preceded by the Cassini–Huygens mission, which was critical to the characterization of Saturn and its moons.[5] The Cassini–Huygens mission confirmed that Titan possesses a dense and chemically active atmosphere composed mainly of N_2 and CH_4. Fuelled by radiation from the Sun and Saturn's magnetosphere, N_2 and CH_4 react to produce various organic molecules[6] including benzene and acetonitrile, which are then carried by methane rainfall and storms[7] to the surface, where they dissolve in the ethane lakes.[8] Additionally, aromatic hydrocarbons can be formed on Titan's surface ices and on airless bodies.[9] A seasonal cycling of evaporation and precipitation, a process notably similar to Earth's hydrological cycle, produces evaporite lakebeds and organic mineral deposits.[10] One theoretical model estimates constant precipitation fluxes of 1.08×10^6 and 1.27×10^7 molecules cm^{-2} s^{-1} for benzene and acetonitrile, respectively, among other organic compounds.[11] If we consider a scenario in which the precipitation cycle repeats for over 4 billion years (the age of Titan), the accumulated surface layer of aromatics could reach up to 3 m.[11b] Recently, a cocrystal of benzene and ethane, was thoroughly studied and characterized as a potential mineral on Titan.[12] Several other cocrystals relevant to Titan have recently been considered, including acetylene and ammonia,[13a] acetylene and butane,[13b] and a ternary phase cocrystal of benzene, acetylene and hydrogen cyanide,[13c] complementing previous studies of small-molecule binary phases, such as the cocrystal of acetylene and benzene.[13d]

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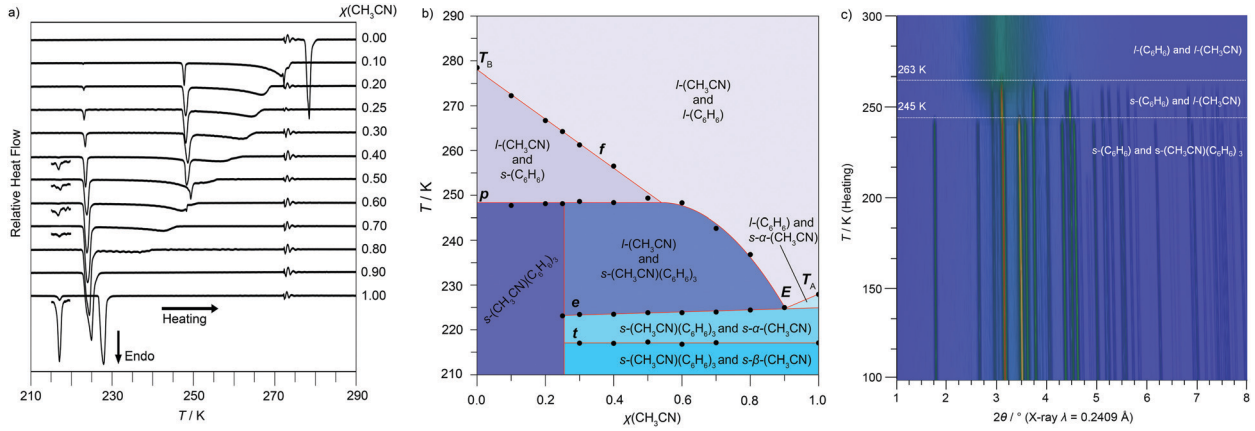

Fig. 1 (a) DSC curves of mixtures of benzene and acetonitrile and their (b) χ–T phase diagram. The composition of the condensed phase regions was determined from the (c) X-ray diffraction data collected upon heating of 1 : 3 sample of acetonitrile and benzene.

The early reports on the composition temperature (χ – T) phase diagram of benzene and acetonitrile were based on an observation of the melting point variations as a function of composition.[3] In order to provide a more accurate description, we revisited the system using DSC as a modern thermoanalytical technique (information provided in the ESI†). Considering the sensitivity of crystallization events to the experimental conditions, the binary phase diagram was constructed using the endothermic peak maxima of the heat flux in the DSC curves collected upon heating (Fig. 1a). Fig. 1b presents the χ–T binary phase diagram for the acetonitrile–benzene system, expressed as function of the mole fraction of acetonitrile, $\chi(CH_3CN)$. The presence of a secondary phase decreased the melting points of both pure benzene (T_B = 279 K) and acetonitrile (T_A = 230 K). The gradual decrease clearly outlines an upper fusion boundary line (f) converging to a eutectic halt (E) at T = 224 K and $\chi(CH_3CN)$ = 0.9. The upper fusion line, the eutectic line and the eutectic point are all in good agreement with previously reported data (E = 224.45[3a] and 224.82[3b] K). A comparison with the earlier binary phase diagrams is given in Fig. S2 in the ESI.† A peritectic reaction between solid benzene, s-C_6H_6, and liquid acetonitrile, l-CH_3CN, was observed at 248 K, establishing a peritectic‡ boundary line (p) extending to $\chi(CH_3CN)$ = 0.55. The DSC measurements revealed a previously unobserved region in the binary phase diagram, which is indicative of the phase change of acetonitrile from the low-temperature β form to the high-temperature α form.[2e] This phase transition was detected as a series of relatively weak endothermic events outlining a solid-to-solid transition (t) line at 217 K. The overall shape of the χ–T binary phase diagram of benzene and acetonitrile is typical for a solid–liquid binary phase diagram of two components featuring incongruent melting.

The calorimetric study of the χ–T binary phase diagram clearly outlined a region of incongruent melting and a peritectic phase transition, however, it did not provide structural information of the constituent phases. To investigate the solid state structures and composition in the regions below both the fusion and peritectic lines, we performed variable-temperature *in situ* PXRD measurements. Fig. 1c presents the PXRD data of a mixture of acetonitrile and benzene in a 1 : 3 ratio, shown as a 2D plot of scattered intensity as a function of temperature. A Rietveld refinement[14] analysis indicated that above the peritectic line, from 245 to 263 K, solid benzene (in the *Pbca* polymorphic modification) is the only crystalline phase present in the system (Fig. S3, ESI†). Below 245 K, additional reflections were observed in the measured patterns, corresponding to the formation of a secondary crystalline phase (Fig. S4, ESI†). The PXRD pattern collected at 100 K was used to solve and refine the crystal structure of this phase (further details are provided in the ESI†). The unit cell symmetry size indicated that the stoichiometry of the cocrystal is 1 : 3 acetonitrile : benzene (1 : 3 ACN : B), $\chi(CH_3CN)$ = 0.25. The crystal structure was solved in the trigonal space group $R3$ and was later confirmed and refined by the Rietveld method[14] (Fig. S4, ESI†).

The crystal packing diagram of the cocrystal is presented in Fig. 2a with selected structural and crystallographic information in Table S1 (ESI†). The structure is related to the structure of benzene[2b,c] and the 1 : 3 ethane : benzene cocrystal (Fig. S5, ESI†),[12c] adopting similar crystal packing. The packing features channels of benzene molecules, self-assembled along a $\bar{3}$ axis parallel to the c crystallographic direction. The channels are stabilized by weak C–H···π interactions. Acetonitrile molecules are positioned along the channels with a relatively short $CH_3CN\cdots CH_3CN$ distance of 3.18(1) Å. The ordered, linear arrangement or the asymmetric acetonitrile molecules reduces the symmetry of the crystal structure from the space group $R\bar{3}$ to $R3$. It should be noted that the crystal structure can also be described in the $R\bar{3}$ space group, with disordered acetonitrile molecules in the crystal packing. Due to intrinsic limitations of the powder diffraction method, the $R\bar{3}$ and $R3$ space groups cannot be distinguished based on the observed absences of reflections.

To validate the crystal packing, and to assess the possibility for a disordered structure, we performed energy optimization (further technical details are provided in the ESI†), on isolated $(CH_3CN)_2(C_6H_6)_{12}$ clusters. In one of the clusters, the starting relative atomic positions were taken from the crystallographic

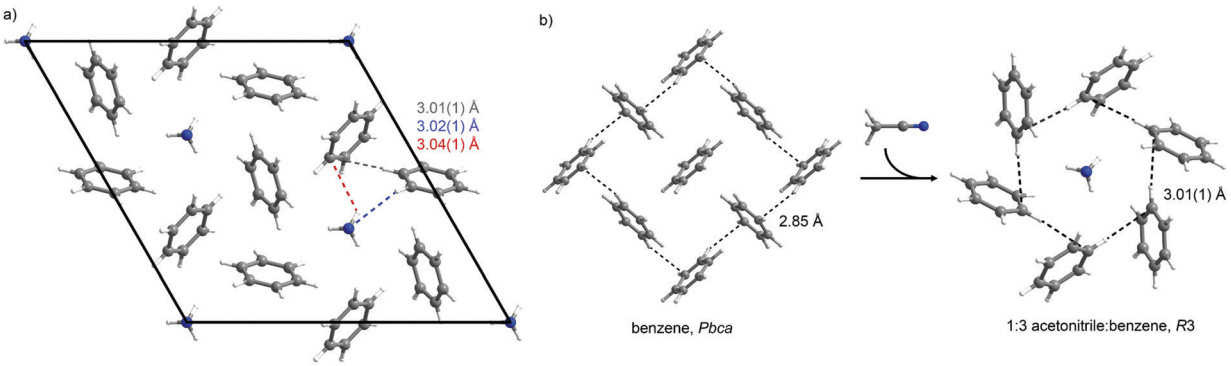

Fig. 2 (a) Crystal packing diagram of the 1 : 3 acetonitrile : benzene cocrystal. (b) Fragments of the crystal packing diagrams of benzene and the cocrystal schematically representing the peritectic phase transition. Legend: nitrogen in blue, carbon in grey, hydrogen in white.

analysis, representing the ordered, *R*3 structure. In the other cluster, the two CH_3CN molecules were related by a center of inversion. Upon relaxation of the atomic position, only the non-centrosymmetric cluster reached a local minimum on the potential energy surface, as confirmed by vibrational analysis. The centrosymmetric cluster was shown to be significantly less stable ($\sim$6 kcal mol^{-1}). These calculations support the model of the crystal structure in the *R*3 polar space group and the optimized structure was found to be in excellent agreement with the experimentally obtained crystal structure (see an overlay Fig. S6, ESI†).

Crystallization in a polar space group may have important implications on the physical properties. Acetonitrile is a highly polar molecule with a dipole moment of $\mu = 13.17 \times 10^{-30}$ C m. The alignment of polar molecules onto a 3-fold axis, in the absence of a center of inversion, gives a polar macroscopic crystal. Polar crystals are functional materials that can exhibit pyroelectric, piezoelectric, ferroelectric and/or electrooptic effects, second harmonic generation, triboluminescence and other useful properties.[15] The potential presence of polar structures on Titan is relevant to the development of improved astrobiological models.[16] Finally, it should be mentioned that with these crystal-packing features, 1 : 3 ACN : B can serve as a precursor in pressure-induced polymerization reactions toward functionalized graphene structure,[17a] and nitrogen-rich compounds,[17b] which is relevent for developing alternative solid-state synthetic routes. The similarity of the crystal structure of the 1 : 3 ACN : B cocrystal and the *Pbca* polymorphic modification of crystalline benzene explains the tendency of solid benzene to react with liquid acetonitrile and form a peritectic product. Fig. 2b shows the crystal packing before and after the peritectic phase transition, which can be envisaged as a replacement of a benzene molecule for acetonitrile, and subsequent reorganization of the lattice of benzene molecules while maintaining the network of close C–H$\cdots\pi$ interactions.

The *in situ* diffraction data were used to assess thermal stability of the cocrystal. Crystallographic analyses of the data collected upon cooling and heating of 1 : 3 mixture of acetonitrile and benzene indicate that the cocrystal forms upon cooling at 227 K (crystalizing in a phase mixture with benzene) and it is stable upon further decrease of the temperature (Fig. S9, ESI†). Upon heating, the cocrystal is stable up to a melting temperature of 245 K (Fig. S10, ESI†). Molecular solids respond to a decrease in temperature with decreases in atomic thermal vibrations, resulting in positive linear thermal expansion.[18a] The thermal expansion of the 1 : 3 ACN : B cocrystal was studied by observing the changes of the unit cell parameters (details are provided in the ESI†). The principal axes§ of linear expansion were calculated as orthogonal strains based on the variation of the unit cell parameters.[18b,c] The x_1 and x_2 principal axes were found to coincide with the *c* and *a* crystallographic axes, respectively. The third principal axis, x_3, was found to be approximately parallel to the [210] crystal axis, which aligns with the direction of the short benzene–benzene interactions between neighbouring benzene rings in the crystal packing. The axial linear thermal expansion coefficients, $a_1 = 95(3) \times 10^{-6}$ K^{-1} and $a_{2,3} = 131(3) \times 10^{-6}$ K^{-1}, result in a volumetric expansion coefficient of $366(9) \times 10^{-6}$ K^{-1}. These values are significantly higher than the typical expansion coefficients of molecular solids ($<20 \times 10^{-6}$ K^{-1}).[18a] This thermal expansion is a consequence of the crystal packing being based exclusively on weak supramolecular interactions (*e.g.* van der Waals forces), which are particularly sensitive to atomic thermal vibrations.

In order to test the stability of the 1 : 3 ACN : B cocrystal under conditions relevant to evaporite deposits on Titan, we performed *in situ* analyses of the cocrystal upon contact with liquid ethane. Acetonitrile and ethane have the same polar molecular diameter, and can fit within the channels formed by benzene molecules (Fig. S3, ESI†). In fact, the only structural difference between these cocrystals is in their symmetry; the ethane : benzene cocrystal forms in the space group $R\bar{3}$, while acetonitrile : benzene forms in a space group of lower symmetry, *R*3, as a result of the asymmetry of the acetonitrile molecule. To explore this ternary system, we filled a capillary with a 1 : 3 mixture of acetonitrile and benzene and we saturated the atmosphere in the capillary with gaseous ethane. After that, we slowly decreased the temperature to 100 K and collected diffraction data (Fig. 3). Diffraction data were also collected upon heating at 200 K and 240 K. Interestingly, the diffraction pattern does not correspond to either of the cocrystals in a phase-pure form. Further experiments and analyses are necessary to solve the crystal structure of this phase or potential mixture of phases.

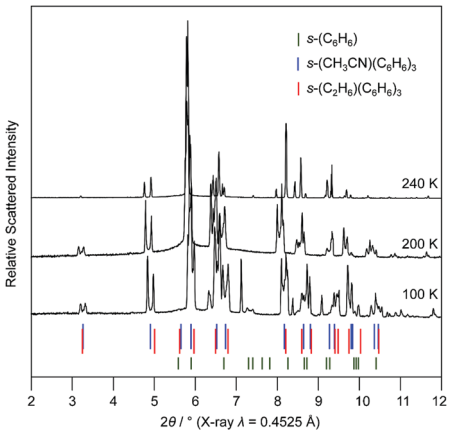

Fig. 3 Powder diffraction patterns of a system made of acetonitrile and benzene in a 1 : 3 ratio, crystallized in a environment saturated with liquid ethane.

This experimental observation hints at the possibility of mixed—and potentially non-stoichiometric—crystalline phases, which would have a significant impact on the approach to identifying potential minerals on Titan. This possibility draws yet another parallel between the mineralogy on Titan and the mineralogy on Earth, where non-stoichiometric phases frequently occur. Furthermore, these results indicate that the 1 : 3 ACN : B cocrystal may be used as an indicator for the past presence of ethane. This type of structural markers may become relevant for on-site analyses of the Titanean surface terrain by Dragonfly.

The recently concluded Cassini–Huygens mission to Titan and the forthcoming Dragonfly mission have reignited interest in the fundamental organic chemistry of small molecules. Here, we report the χ–T phase diagram of benzene and acetonitrile, which features incongruent melting and a peritectic phase transition of solid benzene and liquid acetonitrile into a 1 : 3 ACN : B cocrystal. The crystal structure of the cocrystal was solved and refined from *in situ* diffraction data collected using synchrotron radiation. The system crystalized in the polar space group $R3$ and is characterized by a trigonal structure of benzene molecules self-assembled into hexagonal channels; these channels surround the acetonitrile molecules, which are in a parallel alignment with the central 3-fold axis. Under conditions relevant to the surface around the lakes of Titan, benzene and acetonitrile react with ethane and produce complicated mixture of phases. These results highlight the pronounced structural and compositional diversity of potential minerals on Titan.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ In the early literature, peritectic transitions are sometimes referred to as meritectic transitions.

§ Due to the trigonal symmetry (space group $R3$) of the unit cell of 1 : 3 ACN : B cocrystal, the crystallographic axes do not coincide with the principal axes of linear expansion.

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