Can a Finite Chain of Hydrogen Cyanide Molecules Model a Crystal?

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Abstract: When calculating structural or spectroscopic properties of molecular crystals, the question arises whether it is sufficient to simulate only a single molecule or a small molecular cluster or whether the simulation of the entire crystal is indispensable. In this work we juxtapose calculations on the high-pressure structural properties of the (periodic) HCN crystal and chains of HCN molecules of finite length. We find that, in most cases, the behavior of the crystal can be reproduced by computational methods simulating only around 15 molecules. The pressure-induced lengthening of the C–H bond in HCN found in calculations on both the periodic and finite material are explained in terms of orbital interaction. Our results pave the way for a more thorough understanding of high-pressure structural properties of materials and give incentives for the design of materials that expand under pressure. In addition, they shed light on the complementarity between calculations on periodic materials and systems of finite size.

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TOC Graphic
Simulation methods in computational chemistry that focus on isolated molecules or small molecular clusters distinguish themselves by their ease of use and, depending on the applied electronic structure method, by their modest computational cost. Moreover, a plethora of observables can be calculated, e.g., molecular energies, geometries, reaction paths and various spectroscopic properties. In experiments, however, measurements are usually carried out on a large quantity of molecules, e.g., in the form of liquids or crystals. The question arises in how far the calculated properties of the simulated systems with a finite number of molecules can serve as a feasible model for the macroscopic material on which measurements are carried out.

In the case of water, for example, machine learning was applied to simulate structural and dynamical bulk properties based on atom-centered descriptors. In another computational work it was shown that a cluster of 21 water molecules exhibit the vibrational features of liquid water. Below this threshold, bulk behavior was not observed and the simulated system instead showed properties characteristic for smaller clusters. However, the number of water molecules required to reproduce bulk behavior depends on the investigated property. In an experimental study, at least 275 water molecules were required to form ice crystals.

In a broader context, such considerations touch upon the classical philosophical problem of emergence, which asks the question in how far the properties of a composed entity depend on the properties of its components. Transferred to chemistry, the question arises at what size of a molecular cluster the properties of the macroscopic material emerge.

In this contribution, we gain insight into this conundrum by simulating the high-pressure structural properties of hydrogen cyanide, which crystallizes in long chains. We answer the question how long a chain of HCN molecules needs to be in order to reproduce the pressure-induced structural changes shown by the crystal.

Simulation techniques are indispensable tools for this task, since only with computational methods
Table 1: Lattice parameters $a$, $b$ and $c$ and unit cell volume at $P = 0$ GPa obtained in previous experiments\(^6\) and in the calculations presented here.

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\begin{array}{cccc}
\text{Experiment} & 4.07 & 4.77 & 4.20 & 81.5 \\
\text{Calculation} & 4.53 & 4.63 & 4.17 & 87.2 \\
\end{array}
\]

It is possible to juxtapose the behavior of any desired finite number of molecules and the properties of the crystal. Many electronic structure methods for the simulation of chemical systems under pressure have been developed.\(^7,8\) Both periodic materials\(^7,9\) and systems with a finite number of atoms and molecules\(^10–18\) can be modeled under elevated pressure. Here, we simulate the HCN crystal under pressure using PBEsol,\(^19,20\) as implemented in Quantum Espresso 6.7,\(^21,22\) whereas finite numbers of HCN molecules are simulated using the recently introduced eXtended Hydrostatic Compression Force Field (X-HCFF)\(^16\) and Gaussians On Surface Tesserae Simulate HYdrostatic Pressure (GOSTSHYP)\(^17\) approaches at the PBE\(^23\)/cc-pVDZ\(^24\) level of theory, as implemented in Q-Chem 5.4.\(^25\) Further computational details can be found in the Supporting Information.

The HCN crystal comprises strong triple bonds (C≡N), single bonds with average strength (C−H) and weak intermolecular interactions (N⋯H). Since it is expected that these coordinates differ tremendously in their compressibilities, HCN lends itself particularly well for investigations of pressure-induced structural changes. Moreover, the structural complexity of the HCN crystal is low, which is another beneficial trait for a comparison between calculations on the crystal and on finite systems. Previous calculations on the high-pressure properties of HCN have revealed changes in its crystal structure under pressure as well as the generation of insulating, semiconducting or metallic behavior.\(^26,27\)

Focusing on the HCN crystal first, the applied methodology delivers pressure-free cell parameters that are remarkably close to the experiment (Table 1). As expected, the lattice parameters $a$, $b$ and $c$ decrease with increasing hydrostatic pressure (Figure 1, top). Interestingly, $a$ and $b$ assume the same values at
25 GPa, which is at a lower pressure than in previous calculations (between 45 and 50 GPa).\textsuperscript{26,27} The crystallographic angles $\alpha$, $\beta$ and $\gamma$ remain at 90° even at the highest simulated pressure.

When testing the performance of simulation methods for a finite number of HCN molecules under high pressure, one needs to take into account that HCN chains extend along the crystallographic c direction, whereas different chains are placed next to each other along the a and b directions (Figure 1, bottom). In this contribution, we limit ourselves to a discussion of structural changes along the c direction by simulating HCN chains of different length. For this purpose, we use both the straightforward, mechnano-chemical X-HCFF method\textsuperscript{16} and the more sophisticated GOSTSHYP approach,\textsuperscript{17} which simulates the...
influence of pressure on the electron density explicitly. Up to 100 HCN molecules were simulated with X-HCFF, whereas GOSTSHYP calculations were limited to a maximum of 40 HCN units due to the increased computational cost.

In a first test, we compare the percentage shortening of the lattice parameter \( c \), calculated for the crystal, to the decrease in the end-to-end distance between the H atom on one end of a HCN chain of variable length and the N atom on its other end (Figure 2). When applying a pressure of 50 GPa to HCN, \( c \) decreases by 10.9% in the periodic calculation. The smooth decrease of \( c \) upon increasing pressure is reproduced both by GOSTSHYP and X-HCFF, as long as at least four (GOSTSHYP) or two (X-HCFF) HCN molecules are simulated. Compressing only a single HCN shows qualitatively wrong behavior, since the long intermolecular N···H coordinate is not included. Increasing the number of HCN units in the chain causes the curve for the change in \( c \) to approach the one for the crystal. However, the observed pressure-induced changes in \( c \) converge rather quickly with the number of HCN molecules in the chain. At 50 GPa, for example, no tremendous changes are observed when growing the chains beyond 15 or 20 HCN molecules, both for GOSTSHYP and X-HCFF (Figure 3).

The remaining differences in the changes in \( c \) when comparing the periodic calculations and the simulations of a HCN chain with up to 100 molecules have two reasons. First, the simulation methods differ, both with regard to the applied density functional and the way the pressure is applied in the simulations (cf. also the Computational Details in the Supporting Information). Second, pressure-induced changes in the crystallographic \( a \) and \( b \) axes, which lead to closer packing of the HCN chains in the periodic calculations, are only modeled as an arbitrary medium exerting hydrostatic pressure, while other environmental effects are excluded. However, environmental effects resulting from shortening the distance between neighboring chains are expected to have an influence on the \( c \) axis as well. Despite these discrepancies, it is remarkable that, qualitatively, the pressure-induced changes in \( c \) are reproduced by calculations on chains with only a handful of HCN units and that the remaining differences are on the order of 1-2%.
Figure 2: Calculated changes in the lattice parameter $c$ for HCN chains of various lengths, calculated with the GOSTSHYP$^{17}$ (top) and X-HCFF$^{16}$ (bottom) models (circles). Reference values are provided by calculations on the crystal (black squares).
Figure 3: Change in the lattice parameter $c$ at 50 GPa when simulating HCN chains of up to 50 units with the GOSTSHYP (red) and X-HCFF (blue) models. Lines were included to guide the eye.

Turning to the interatomic distances within the HCN chains, the changes induced by pressure in the crystal and in the HCN chains of finite length can be compared directly. For the latter, the average values were recorded. A comparison between the results for the crystal and the finite chains, calculated with X-HCFF, are shown in Figure 4. GOSTSHYP produces analogous results (Supporting Information, Figure S1), demonstrating the usefulness of the computationally cheaper mechanochemical model X-HCFF when calculating geometric parameters under pressure.

Focusing on the C–H bond first, in the calculations on the periodic material it can be observed that the C–H distance initially increases up to around 35 GPa. The intuitive shortening of this bond under pressure can only be observed at higher pressures. In the case of finite chains, X-HCFF predicts a continuous shortening of the C–H bond under pressure up to a chain length of six HCN molecules. A lengthening of this bond is found only in longer chains. The transitions between these effects are fluent. Remarkably, even in the case of 20 HCN units, the C–H bonds at the ends of the chain are being shortened by pressure (Supporting Information, Figure S2), whereas those bonds in the middle
Figure 4: Average interatomic distances H–C (top), C–N (middle), and N–H (bottom) in HCN chains of different lengths at various pressures calculated with X-HCFF. Reference values are provided by calculations on the crystal (black squares).
are elongated, resulting in a net lengthening when calculating the average. The behavior of chains with more than 20 HCN units is remarkably close to the crystal, however, the switching from pressure-induced lengthening to shortening of the C–H bond is not found in the calculations on the finite systems.

The reason for the lengthening of the C–H bond under pressure in the middle region of longer chains can be explained by Natural Bond Orbital (NBO)\textsuperscript{28,29} analysis. With increasing pressure, the interaction energy between the lone electron pair of nitrogen and a neighboring C–H $\sigma^*$ orbital increases steadily, leading to a weakening of the C–H bond (Supporting Information, Figure S3). This interaction is weaker at the chain ends and converges quickly towards the middle of the chains, which explains why the pressure-induced lengthening of the C–H bond is not observed in very short HCN chains. This effect is also in line with the observed lengthening of the C–H bonds only in the middle of longer chains. Hence, the accommodation of the lone pair of nitrogen under pressure happens at the expense of the C–H bond.

Another remarkable observation is that the C≡N triple bond is stretched by pressure in the periodic calculations, although it must be noted that the observed changes are on the order of 0.01 Å per 50 GPa. In addition, the occurrence and magnitude of this effect in the calculations on the period material depends on the chosen functional, since PBE shows an initial decrease of the C≡N bond length under pressure (Supporting Information, Figure S4). This discrepancy between PBEsol and PBE in the periodic calculation calls the meaningfulness of the observed pressure-induced lengthening of the C≡N bond into question. The calculations on the finite system, by contrast, show a continuous shortening of the C≡N bond under pressure.

Finally, the intermolecular distance N⋯H decreases smoothly and significantly under pressure, both in the calculations on the crystal and on the finite chains. Depending on the interatomic distance, convergence of the results for the finite chains is reached at slightly different HCN chain lengths (Supporting information, Figure S5), but, generally, changes beyond 20 HCN units are insignificant.
In summary, we have compared high-pressure calculations on the HCN crystal with equivalent simulations on HCN chains of finite length. Despite the technical differences in the simulation approaches and the neglect of explicit environmental effects in the calculations on the isolated chains of finite size, we observe that around 15–20 HCN molecules are sufficient to reproduce the pressure-induced structural changes observed in the crystal. Our findings suggest that approaches simulating only a finite number of molecules can be suitable for describing bulk properties, as long as an appropriate model system is found. If this is not ensured, however, calculations on periodic and finite systems should be carried out synergistically. In the future, the calculations presented here will be extended to three-dimensional assemblies of HCN molecules, different crystalline systems and other observables, e.g., spectroscopic properties. Such studies will give important insights into the relation between calculation and experiment.

Supplementary Material

Computational details, average interatomic distances (H–C, C–N, H–N) in HCN calculated with the GOSTSHYP method, distances H–C in (HCN)$_{20}$. NBO analysis, distance C≡N in the HCN crystal calculated by PBE, convergence properties of interatomic distances at 50 GPa.

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