Superconductivity in solid benzene molecular crystal

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Abstract
Light-element compounds hold great promise of high critical temperature superconductivity judging from the theoretical perspective. A hydrogen-rich material, benzene, is such a kind of candidate but also an organic compound. A series of first-principles calculations are performed on the electronic structures, dynamics properties, and electron–phonon interactions of solid benzene at high pressures. Benzene is found to be dynamically stable in the pressure range of 180–200 GPa and to exhibit superconductivity with a maximum transition temperature of 20 K at 195 GPa. The phonon modes of carbon atoms are identified to mainly contribute to the electron–phonon interactions driving this superconductivity. The predicted superconductivity in this simplest pristine hydrocarbon shows a common feature in aromatic hydrocarbons and also makes it a bridge to organic and hydrogen-rich superconductors.

Keywords: benzene, superconductivity, pressure, hydride, hydrocarbon

(Some figures may appear in colour only in the online journal)
found in 1980 [12]. Since then, numerous organic superconductors have been reported including electron donor and electron acceptor molecules. Superconductivity with $T_c$ as high as 38 K was observed in cesium-doped fullerene [13], and more than 120 K was also found in potassium-doped $p$-terphenyl [14]. These findings highlight that organic compounds have potential to become high-$T_c$ superconductors. This is mainly because non phonon mechanisms were found to account for their superconductivity in these kinds of materials. Only electron–phonon coupling is not enough to produce such high-$T_c$ superconductivity in alkali metal doped fullerides [13] and aromatic hydrocarbons [15]. Meanwhile, the low dimensional feature of organic molecule was proposed to favor the strong electronic correlation effects in these materials such as doped fullerides [16] and aromatic hydrocarbons [17–19].

While pressure can greatly enhance superconductivity in aromatic hydrocarbons such as potassium-doped phenanthrene [20] and picene [21], the realization of superconductivity solely by applying pressure on pristine organic compounds has not been achieved yet.

In this work, we choose benzene ($C_6H_6$), a hybrid of the simplest aromatic hydrocarbon and a hydrogen-rich material, to explore superconductivity at high pressures. Solid $C_6H_6$ was previously predicted to enter a metallic state at pressures above 180 GPa [22], though the metalization had not been realized experimentally [23]. Through extensive calculations of electronic structures, dynamical properties and electron–phonon interactions, we find that $C_6H_6$ is in fact superconducting in the pressure range of 180 and 200 GPa with a maximum $T_c$ of 20 K. Within the framework of electron–phonon coupling, the superconductivity is examined to mainly come from the contribution of C element, differing from the H dominant materials. Based on our systematical investigations on the superconductivity of potassium-doped aromatic hydrocarbons in recent years [24], we conclude that the materials containing benzene rings must be superconducting, with $T_c \sim 5–7$ K, and the superconductivity is increased with the change of structure, electronic correlations and pressure.

2. Computational methods

To study the structural and electronic properties of solid $C_6H_6$, we employed the Vienna $ab$ initio simulation package (VASP) [25, 26] based on the projector augmented wave method. For the plane-wave basis-set expansion, an energy cutoff of 800 eV was adopted. Dense $k$-point meshes were used to sample the first Brillouin zone and ensured that energies converged to within 1 meV/atom. At the same time, lattice dynamics and electron–phonon interactions were calculated using density functional perturbation theory [27] and the Troullier–Martins norm-conserving potentials [28], as implemented in the QUANTUM-ESPRESSO (QE) code [29]. The cutoff energies of 80 and 600 Ry were used for wave functions and charge densities, respectively. $24 \times 24 \times 24$ Monkhorst–Pack $k$-point grid with Gaussian smearing of 0.003 Ry was used for the electron–phonon interaction matrix element calculation at $6 \times 6 \times 6$ $q$-point mesh. In both VASP and QE codes, the local density approximation (LDA) [30, 31] functional was selected. Forces and stresses for the converged structures were optimized and checked to be within the error allowance of the VASP and QE codes. The computational methods have been proved to be reliable in previous reports [6, 22].

3. Results and discussion

For solid $C_6H_6$, it has well-known that the pressure can change its morphology and structure and lead to a series of phase transitions [32–34]. At 1.4 GPa, the transition occurs from $Pbca$ phase to $P4_2_1_2$ phase. At 4 GPa, phase II transfers to $P2_1/c$ phase, and up to 11 GPa. However, at higher pressure above 11 GPa, the experimental results are still not perfect. Keeping the molecular characteristic of benzene, the previous theoretical study pointed out that [22], solid benzene transforms to $P2_1$ from $P2_1/c$ at 40 GPa and remains to 300 GPa. Noticeably, from the energy point of view, the graphane-like crystal possesses the lower enthalpy than molecular benzene crystal starting from about 10 GPa to 300 GPa. $P2_1$ and $P2_1/c$ are only two metastable phases in the high pressure region [22]. However, it is not easy to convert benzene to polymer or amorphization compound. Because there are likely significant barriers among these interconverting processes and the conversion reaction also involves temperature condition except for pressure [22, 35]. Thus, both $P2_1$ and $P2_1/c$ phases can keep the feature of benzene molecule instead of the amorphous structure of C and H at high pressure. Especially, $P2_1/c$ phase of $C_6H_6$ can behave as a metal in the pressure range of 180–200 GPa [22].

As a comparison and a check on accuracy, we start our investigation by looking at the first solid phase of benzene with $Pbca$ symmetry. Our optimized crystal constants are respectively $a = 7.041$ Å, $b = 8.903$ Å and $c = 6.357$ Å at zero temperature, which are 3%–6% less than experimental values at 78 K [36]. If the effect of temperature is considered, the error between theoretical prediction and experimental measurement is acceptable. Moreover, for $Pbca C_6H_6$, our calculated band gap of 4.1 eV is in a good agreement with previous results [22]. Based on the test, we have optimized the crystal structures of $P2_1/c$ $C_6H_6$ in the range of 180–200 GPa. Figure 1 shows the geometrical structure of $P2_1/c$ phase of $C_6H_6$ crystal. In the case of 190 GPa, the optimized lattice constants $a = 3.962$ Å, $b = 3.881$ Å and $c = 5.287$ Å as well as the angle $\beta = 100.3^\circ$.

The calculated band gap of 4.1 eV for $C_6H_6$ is far less than 7.5 eV of methane ($C_2H_4$) [37], which indicates $C_6H_6$ is more easily to become into metal under pressure comparing with $CH_4$. Indeed, the band gap of $C_6H_6$ with $P2_1/c$ structure has been closed when the pressure increases to 180 GPa, and keeping the metallic behavior up to 200 GPa. On the contrary, until 520 GPa, $CH_4$ is still a semiconductor [38]. In the case of 190 GPa, we show the electronic band structures, density of states (DOS) and Fermi surface sheets of $C_6H_6$ in figure 2. As shown in figure 2(a), similar to other hydrogen-rich materials, the metallization of $C_6H_6$ are mainly derived from the increase of covalent interaction under pressure. However, the nature
of energy bands of C\textsubscript{6}H\textsubscript{6} is different from those of doped aromatic hydrocarbons where the band structure possessed the typical charge transfer characteristics. Corresponding to band structure, a small amount of electronic states gathers at Fermi level in the DOS picture, which is mainly contributed by C-2 \textit{p} states (figure 2(b)). The DOS at Fermi level is about 0.32 states/eV, which is a small value comparing with those of doped aromatic hydrocarbons. But, we find that the DOS at Fermi level continuously increases with the increase of pressure in this range of 180–200 GPa. Checking the fine electronic feature near Fermi level, we find additionally that the VB1 and VB2 bands (marked in figure 2(a)) form the hole-like Fermi surfaces around \textit{B} \textit{k}-point, as shown in figure 2(c). The CB1 band with higher energy forms the electron-like Fermi surface around \textit{\Gamma} \textit{k}-point.

For this metallic phase of C\textsubscript{6}H\textsubscript{6}, our calculated phonon dispersion (figure 3(a)) has confirmed the dynamical stability of \textit{P}2\textsubscript{1}/\textit{c} structure due to the absence of imaginary frequency modes. The visible gaps in the phonon spectra divide phonon frequency into three parts, low-frequency below 22.7 THz, intermediate-frequency from 24.3 to 56.0 THz and high-frequency above 102.0 THz. Combining with the projected phonon density of states shown in figure 3(b), we can determine that low-frequency modes come mainly from the C atomic motions, the intermediate-frequency region is between 14 and 62 THz owing to the intermolecular H\textsubscript{2} coupling and the Ge-H stretching vibrations, while the high-frequency phonon from the intramolecular H\textsubscript{2} vibrations is in the range of 73–80 THz.

Comparing with GeH\textsubscript{4}, both phonon vibrations and intermolecular coupling in C\textsubscript{6}H\textsubscript{6} are stronger. In H\textsubscript{2}-containing compounds such as PbH\textsubscript{4}(H\textsubscript{2})\textsubscript{2}, the alloy like compound of Pb and quasi H\textsubscript{2} units is formed at 200 GPa [41]. The low-frequency phonon below 8.6 THz comes from heavier element Pb. But the region of intermediate-frequency vibrations in 8.6–56 THz arises from the intermolecular H\textsubscript{2} coupling. Two regions of high-frequency in ranges of 81–87 THz and 96–101 THz are induced by the intramolecular vibrations of two kinds of quasi H\textsubscript{2} molecules. Comparing with PbH\textsubscript{4}(H\textsubscript{2})\textsubscript{2}, C\textsubscript{6}H\textsubscript{6} has almost the same intermediate-frequency phonon coupling, but stronger low-frequency vibrations. For sulfur hydride, H\textsubscript{3}S is

![Figure 1. The geometrical structure of C\textsubscript{6}H\textsubscript{6} crystal in the high pressure range of 180–200 GPa. Red and white spheres represent C and H atoms, respectively.](image-url)
the main form at 200 GPa with $\text{Im}\overline{3}m$ space-group [6]. At this pressure, the vibration modes below 18 THz are due to the motions of S atom, the other phonon bands between 18 and 55 THz are formed by the S–H bond stretching vibrations. There is no higher phonon frequency than 55 THz in $\text{H}_3\text{S}$ system. In addition, for superconducting aromatic hydrocarbons, in the $\text{K}_3\text{picene}$ [42], below 9 THz, the vibration modes come from the motions of potassium as well as the coupling between it and organic molecules, the intermolecular coupling vibrations appear in the range of 9–47 THz, and the high-frequency C–H stretching modes is localized around 91 THz. From this comparison, there is stronger intermolecular coupling vibrations in $\text{C}_6\text{H}_6$ at pressures than $\text{K}_3\text{picene}$.

Based on electronic and phonon properties above, the electron–phonon coupling $\lambda(\omega)$, logarithmic average phonon frequency $\omega_{\text{log}}$ and the Eliashberg phonon spectral function $\alpha^2F(\omega)$ have been investigated to explore the possible superconductivity of $\text{C}_6\text{H}_6$. The Eliashberg function was calculated for each phonon mode $\nu$ with wavevector $q$ by the following equation

$$\alpha^2F(\omega) = \frac{1}{2\pi N(\varepsilon_F)} \sum_{q\nu} \frac{\gamma_{q\nu}}{\omega_{q\nu}^2} \delta(\omega - \omega_{q\nu}),$$  \hspace{1cm} (1)$$

where

$$\gamma_{q\nu} = 2\pi \omega_{q\nu}\Sigma_{mm'}\Sigma_k |\tilde{q}_{k+q\nu}|^2 \delta(\varepsilon_k + \varepsilon_{m'} - \varepsilon_F) \delta(\varepsilon_k - \varepsilon_F).$$  \hspace{1cm} (2)$$

Correspondingly, the electron–phonon coupling was also calculated by the following equation

$$\lambda_{q\nu} = \frac{\gamma_{q\nu}}{\pi N(\varepsilon_F)\omega_{q\nu}^2}.$$  \hspace{1cm} (3)$$

Referring to the report by Casula et al [42], we decomposed the $\alpha^2F(\omega)$ by projecting on C and H phonons, plotted in figure 3(c), and the correspondingly integral $\lambda(\omega) = 2 \int_0^\infty \omega \alpha^2 F(\omega)/\omega$, shown in figure 3(d), which gives the total $\lambda = \Sigma_{q\nu} \lambda_{q\nu}$ in the $\omega \to \infty$ limit. From the $\alpha^2F(\omega)$ and $\lambda(\omega)$ shown in figure 3, the total electron–phonon coupling $\lambda$ is mainly contributed by the low-frequency phonon from C atom, namely the motion of electrons on benzene-ring plane. The rest small account of total $\lambda$ comes from the organic intermolecular coupling. In the case of 190 GPa of $P2_1/c$ structure, the total $\lambda$ is 0.68, a moderate-intensity electron–phonon coupling. The low-frequency vibration modes from C atoms contribute 83% of total $\lambda$, while the organic intermolecular coupling has only 17% contribution to total

Figure 2. Electronic structures of $\text{C}_6\text{H}_6$ at 190 GPa: (a) energy band structure, (b) total and projected density of states (DOS) and (c) Fermi surfaces. Zero energy denotes the Fermi level.
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and the high-frequency phonon from C–H bond stretching hardly couples the electron. Additionally, we have examined the pressure effect for phonon frequency, phonon density of states, Eliashberg function and electron–phonon coupling, shown in figure 4. We can find the obvious softening of phonon around Λ point (figure 4(a)) and the wider phonon band (figure 4(b)) and Eliashberg spectrum (figure 4(c)) with the increase of pressure. Thus, the total λ changes big by increasing pressure, from 0.53 at 185 GPa to 0.85 at 195 GPa as shown in figure 4(d).

Adopting the modified McMillan equation by Allen and Dynes [43] and combining with the obtained λ and $\omega_{\log}$, we analyzed the dependence of the superconducting critical temperature of C6H6 on pressure, shown in figure 5. However, $\omega_{\log}$ decreases with increasing pressure. On the other hand, λ is enhanced by the applied pressure. As a result, we obtain a slight increase for $T_c$ in the pressure range of 180–200 GPa by using commonly accepted values of the Coulomb pseudo-potential $\mu^* = 0.1–0.13$. As shown in figure 5, at 195 GPa, $T_c$ reaches 19.2 K in C6H6 for $\mu^* = 0.1$. Thus, we theoretically suggest that benzene is superconducting at high pressure, with the $T_c$ close to 20 K.

By analyzing superconductivity, we find that the total λ of K3picene [42] is mainly due to the low-frequency phonon coupling to electron from potassium, and their λ values, 0.53–0.85 in the range of 185–195 GPa for C6H6 and 0.73 for K3picene, are comparable in quantity. The difference is that C6H6 has higher $\omega_{\log}$ of 360.3–720.4 K than K3C22H14. Hence, the predicted $T_c$ of C6H6 is higher than that of K3picene [42]. Comparing with hydrogen-rich materials, the same is that the pressure induced the metallization, but the difference is that the total λ of hydrogen dominate material is mainly contributed by the intermediate-frequency phonon coupling electron. The higher λ is often obtained in hydrogen-rich systems. Especially, the H3S results in the λ of 2.19 at 200 GPa. Except for the small λ value, the $\omega_{\log}$ of C6H6 is less than half of H3S. As a result, the $T_c$ of C6H6 is much less than that of H3S. Combining with the comparison of phonon frequency above, we know that the low and intermediate-frequency phonon coupling electron mainly contributes to the superconductivity. On one hand, the phonon softening in this region will be help for the improvement of the $T_c$ in C6H6. On the other hand, the DOS at Fermi level is only 0.12–0.17 states/ev/f.u. for C6H6 in the range of 185–195 GPa. This value is much less than 0.75 states/ev/f.u. for PbH2(H2)2 at 200 GPa [41] and ~0.4 states/ev/f.u. at 200 GPa [6] (or 0.51 states/ev/f.u. at 210 GPa [44]) for H3S. Therefore, more Cooper pairing electrons are

Figure 3. Calculated phonon dispersion curves (a), phonon density of states (b), Eliashberg spectral function $\alpha^2 F(\omega)$ (c) and electron–phonon coupling integral $\lambda(\omega)$ resolved by projections on C and H phonon (d) for $P_{21}/c$ structure of benzene at 190 GPa.
another key to achieve the stronger electron–phonon coupling in \( \text{C}_6\text{H}_6 \). For instance, pressure leads to the increase of DOS at Fermi level, \( T_c \) rises with increasing pressure in \( \text{C}_6\text{H}_6 \), accordingly.

4. Conclusions

In conclusion, with the aim of exploring superconductivity in a compound containing only carbon and hydrogen, we
have studied electronic structures, dynamics properties, and electron–phonon interactions of C₆H₆ at high pressures. We revealed that C₆H₆ is superconducting in the pressure range of 180–200 GPa, which is further evidence that the system containing benzene rings must be superconducting. Tc was found to gradually increase with the increase of pressure, reaching 20 K at 195 GPa. Differing from the H-dominated materials, the phonon vibrations of C atom mainly contribute to the electron–phonon coupling. The Tc higher than that of K-doped benzene, phenanthrene and picene mainly comes from the larger ωₜ₉₉ induced by pressure. The prediction of superconductivity in C₆H₆ under pressure will call for experimental testing and the comparison of effects from the electron–phonon coupling and the electronic correlation in such a light element material.

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