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***Ab initio* study of the compressibility and electronic properties of a molecular organic crystal $C_8H_{10}O_2$**

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The structure and electronic properties of a molecular organic crystal octa-3,5-diyn-2,7-diol ($C_8H_{10}O_2$) were studied in the pressure range from 0 to 1 GPa on the basis of *ab initio* calculations in the framework of the density functional theory taking into account the dispersion interaction. The compressibilities of $C_8H_{10}O_2$ were calculated and a significant negative linear compressibility ($-44\,\mathrm{TPa}^{-1}$) was established, which is caused by a change in the orientation and linear dimensions of molecular structural units relative to the crystallographic axes. Based on a topological analysis of the electron density, it is shown that hydrogen bonds are partially covalent in nature, and their energies are relatively high. It is shown that the upper valence and lower unoccupied electronic states correspond mainly to the states of carbon atoms. The band gap of $C_8H_{10}O_2$ is calculated and its decrease with increasing pressure is predicted.

Keywords: molecular crystal, negative compressibility, pressure, band gap, electron density, density functional theory.

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1. Introduction

Compressibility under pressure is a typical example of the influence of external factors on solids and can be explained at the molecular level [1–4]. Its mechanisms may not always be obvious. Indeed, positive compressibility is normal for most crystals, but some solids exhibit an anomalous effect (negative linear compressibility) [5].

Of particular interest are molecular organic crystals. In the study [6] the crystal structure of a molecular organic crystal of octa-3,5-diyn-2,7-diol ($C_8H_{10}O_2$) at temperatures in the range of $225-330\,\mathrm{K}$ was determined by X-ray diffraction. This crystal has a rhombic structure (space group $P2_12_12_1$) with the number of formula units $Z = 4$. Its molecule $C_8H_{10}O_2$ has no aromatic ring and contains an almost linear carbon chain $C{-}C{\equiv}C{-}C{\equiv}C{-}C$ (carbon skeleton). This chain forms an angle of 54.2° with an axis a at 225 K. All atoms in the $C_8H_{10}O_2$ molecule are crystallographically unequal.

A crystal of octa-3,5-diyn-2,7-diol is characterized by a strong negative thermal expansion in the plane bc, especially along the axis c [6]. Crystals with negative thermal expansion are promising objects for finding negative linear compressibility (NLC) [7–11]. Materials with negative linear compressibility are of scientific and practical interest, which stimulates their search and research [12–19]. Figuring out the mechanism of negative compressibility can make it easier to find NLC materials. To date, relatively few NLC crystals are known, especially among molecular organic compounds. However, the compressibility of the molecular organic crystal $C_8H_{10}O_2$ has not been investigated. Also, to date, its electronic properties and the effect of external pressure on them have not been studied.

Ab initio calculations allow us to predict the behavior of the structure and properties of materials under conditions of external pressure [20–29]. The purpose of this work is to study the compressibility and electronic properties of the molecular organic crystal octa-3,5-diyn-2,7-diol ($C_8H_{10}O_2$) based on first-principle calculations.

2. Calculation method

Dispersion forces play an important role in the formation of molecular crystals, so their accounting is necessary for the correct modeling of the structure and properties of such crystals. To account for the dispersion interactions, the DFT-D3(BJ) [30] method was used in this study. This scheme was used by us in the study of the structure and properties of various molecular and ion-molecular crystals [11,31–34]. The results were in good agreement with the available experimental data.

To determine the crystal structure, the Quantum ESPRESSO package was used [35]. At the same time, calculations were carried out using the pseudopotential method and the exchange-correlation functional PBE [36] as part of the density functional theory. Plane waves with a energy cutoff of 65 Ry were used as the basis functions. The Monkhorst–Pack method [37] was used with a grid consisting of $4 \times 3 \times 2$ **k**-points of the Brillouin zone. The error in calculating the total energy was less than 5 meV/atom. Optimized structural parameters were

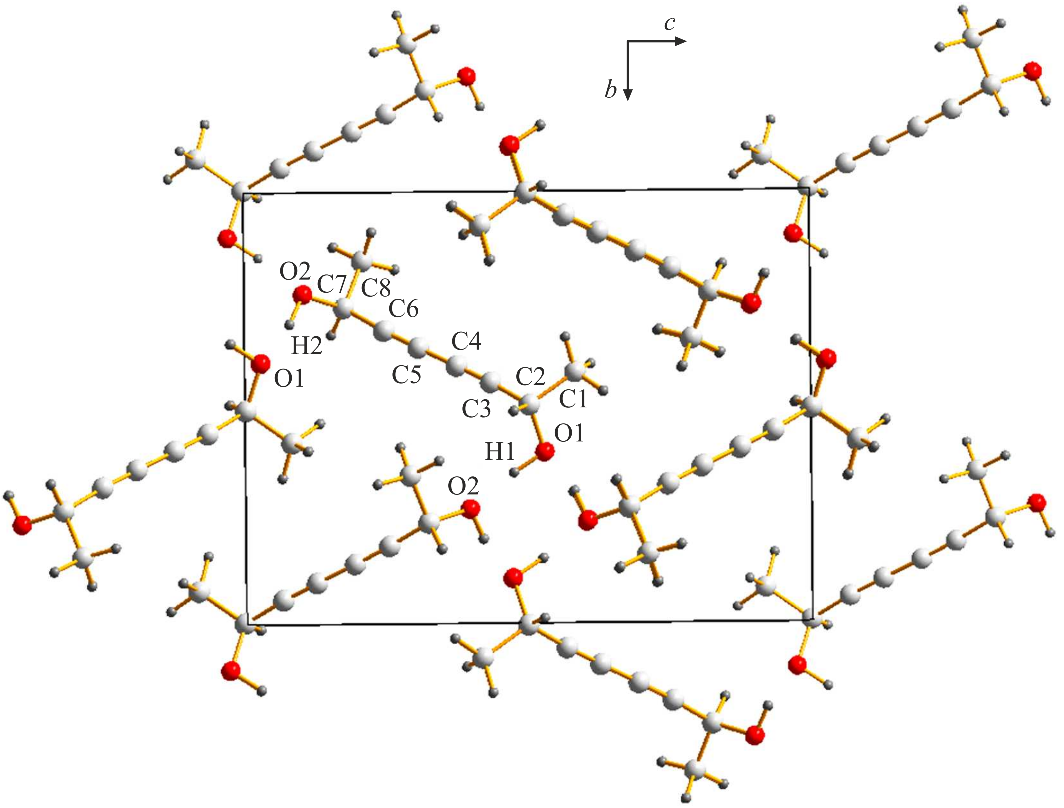

Figure 1. Projecting the structure of $C_8H_{10}O_2$ on the plane *bc*.

further used to study the electronic properties within the PBE0 hybrid functional and the basis of TZVP [38,39], implemented in CRYSTAL [40]. The code TOPOND [41] was used for topological analysis of electron density based on Bader's quantum theory of atoms in molecules (QTAIM) [42]. The energies of the hydrogen bonds were estimated using the potential energy density at bond critical points [43].

3. Results and discussion

The table presents the theoretical and experimental values of the parameters of the crystal cell octa-3,5-diyn-2,7-diol (ODD). In general, there is a good agreement between experimental and theoretical quantities. It should be noted that the calculated values correspond to a static lattice ($T = 0\,\mathrm{K}$), whereas experimental data were obtained at $T = 225\,\mathrm{K}$ [6]. This is manifested in the fact that the calculated value of the volume of the unit cell (see table) is 4% less than the one determined experimentally. The experimental value of the parameter *c* is slightly higher than the theoretical one, since the ODD crystal is characterized by negative thermal expansion. Thus, the computational scheme DFT-D3(BJ) correctly describes the structure of the ODD crystal.

The ODD molecular crystal has a structure in which the weak van der Waals interactions bind molecules in the direction of the axis *a*, whereas the intermolecular hydrogen bonds H1−O2 and H2−O1 are advantageous for the plane *bc* (Fig. 1). Thus, in the direction of the axis *a*, a relatively high compressibility of ODD can be expected, whereas in the plane *bc* — relatively low.

For the quantitative study of hydrogen bonds in ODD, a topological analysis of electron density, based on Bader's quantum theory [42] was conducted. The electron density ρ_c and Laplacian $\Delta\rho_c$ at the critical points of hydrogen bonds H1−O2 (H2−O1) were 0.056 (0.053) and 0.146 (0.137) a.u., respectively. At the same time, the energy density H_c for bonds H1−O2 (H2−O1) has a negative value of -0.011 (-0.010) a.u., which indicates the partially covalent nature of hydrogen bonds of ODD. It is known that when $H_c < 0$ interactions have a covalent component [44–48]. The length and energy of hydrogen bonds H1−O2 (H2−O1) is 1.621 (1.654)Å and 77 (71) kJ/mol, respectively.

Calculated and experimental lattice constants *a*, *b*, *c* (Å) and unit cell volume *V* (Å^3) for crystal $C_8H_{10}O_2$

Method	*a*	*b*	*c*	*V*
DFT-D3(BJ)	4.4337	11.6230	15.2226	784.47
exp. [6]	4.6159	11.6990	15.1910	820.34

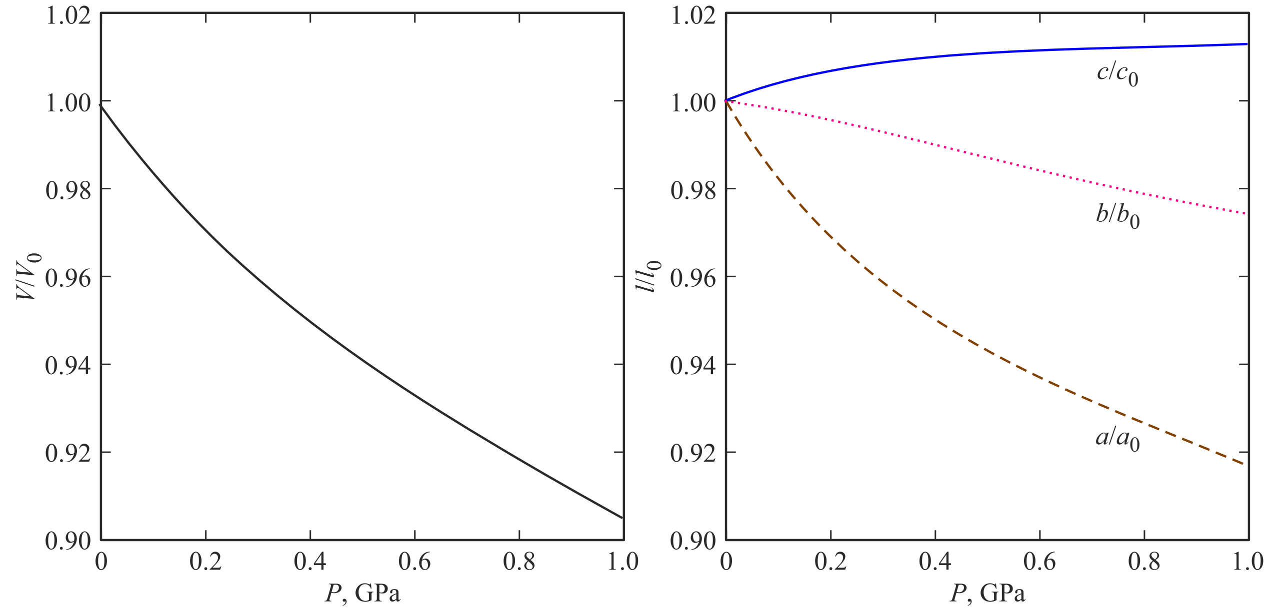

Figure 2. Calculated dependencies on the pressure of the relative volume V/V_0 and lattice parameters a/a_0 (dashed), b/b_0 (dotted), c/c_0 (solid) for octa-3,5-diyn-2,7-diol ($C_8H_{10}O_2$).

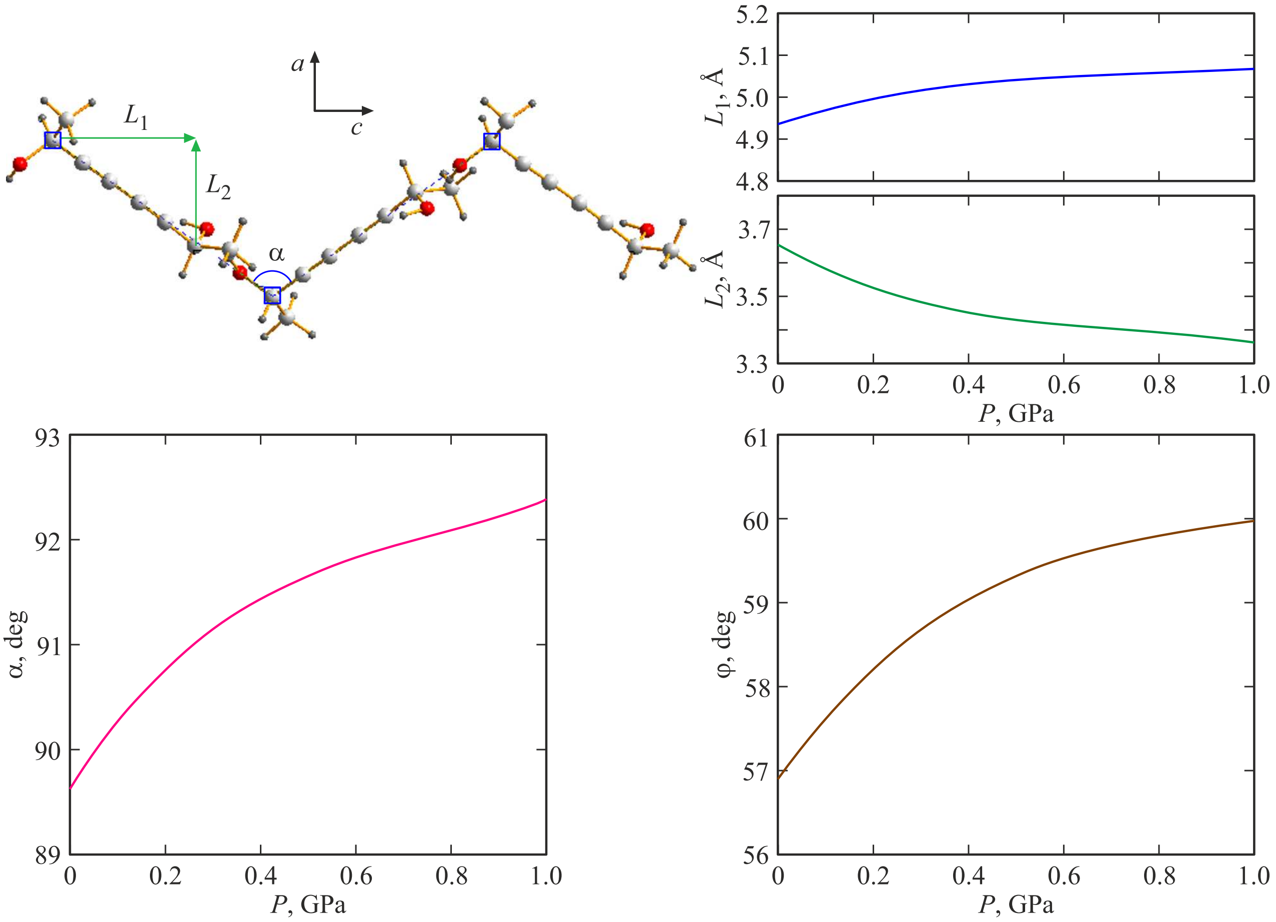

Figure 3. Projection of a fragment of the structure $C_8H_{10}O_2$, as well as calculated pressure dependencies for linear dimensions L_1, L_2 and angles α, φ.

Figure 2 shows the calculated volume and lattice parameters of the ODD crystal depending on the pressure. The values of the parameters a and b decrease under the influence of pressure. At a pressure of 1 GPa parameters a and b are reduced by ~ 8 and 2.5%, respectively. The response of the parameter c to external pressure is abnormal. The value of this parameter increases by 1.4% at a pressure of 1 GPa. Thus, the ODD crystal is characterized by a strong anisotropy of compressibility. The maximum linear compressibility (β_l) occurs along the a axis ($\beta_a = 182.5\,\mathrm{TPa}^{-1}$), which indicates relatively weak intermolecular interactions in this direction. The minimum compressibility for the ODD crystal is observed along the axis c and is negative ($\beta_c = -44.3\,\mathrm{TPa}^{-1}$). It is known that materials with negative linear compressibility are attractive for use in pressure sensors and incompressible composites [12].

Note that the values of negative linear compressibilities for known organic, inorganic and hybrid metal-organic framework (MOF) compounds have values up to -33, -76 and $-28\,\mathrm{TPa}^{-1}$, respectively [14,19]. Thus, the ODD crystal is in the series of NLC materials with the highest values of negative compressibility and, thus, is very promising for practical applications.

To interpret the negative linear compressibility of ODD at the microscopic (atomic) level, we calculated the pressure dependencies for the linear dimensions of the molecule L_1, L_2, for the angle α between the molecules, and for the angle φ between the molecule and the axis a (Fig. 3). From Fig. 3 it can be seen that with increasing pressure, the angles α and φ increase. This leads to the fact that the sizes of molecules in the direction of the axis c increase (L_1), while along the axis a decrease (L_2). Thus, along the axis c there is a negative compressibility and a positive — along the axis a (Fig. 2). It should be noted that the variation of the angle φ with a change in temperature leads to the occurrence of negative thermal expansion of ODD along the axis c [6]. The calculated volumetric compression module for ODD has a relatively small value. It is 6.3 GPa for static lattice ($T = 0\,\mathrm{K}$). Considering thermal effects (according to the work [29]), the bulk modulus is 4.9 GPa at $T = 225\,\mathrm{K}$.

Since crystals with negative linear compressibility are potential for use in highly sensitive optical pressure sensors, it is important to study their optical transparency. Thus, the study of the electronic properties of the ODD crystal is of interest, in particular the calculation of the band gap E_g. Figure 4 shows the total density of ODD electronic states and their partial contributions from hydrogen, carbon, and oxygen atoms.

The energy of the highest occupied states is set to zero. The main contribution to the formation of the upper valence and lower unoccupied states is made by carbon atoms. The ODD band gap is 5.41 eV at zero pressure Thus, the ODD crystal is optically transparent, since the optical (visible) range of photon energies lies in the range of 1.6–3.2 eV. External pressure causes a decrease in the band gap (Fig. 5). Thus, the band gap decreases by $\sim 5\%$ (up to 5.16 eV) with an increase in pressure to 1 GPa.

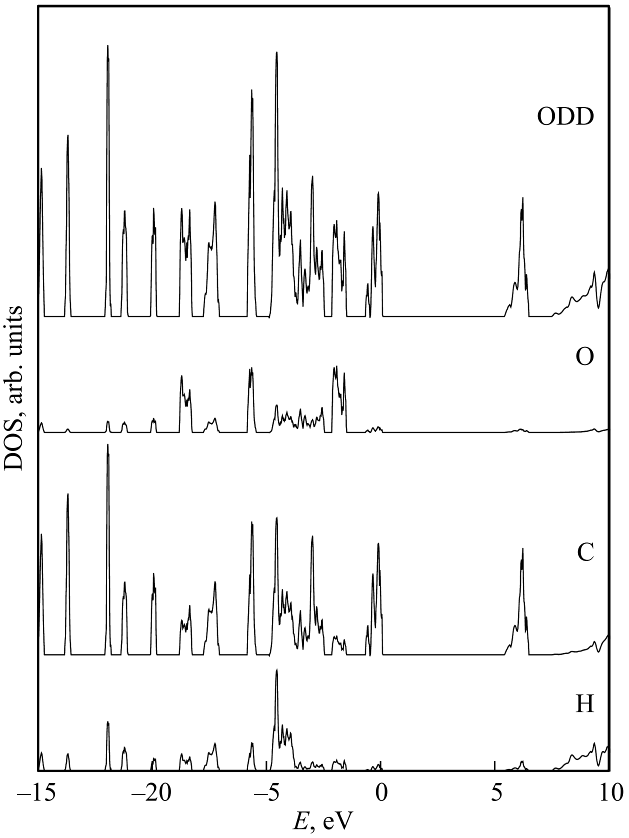

Figure 4. Total and partial densities of ODD electronic states.

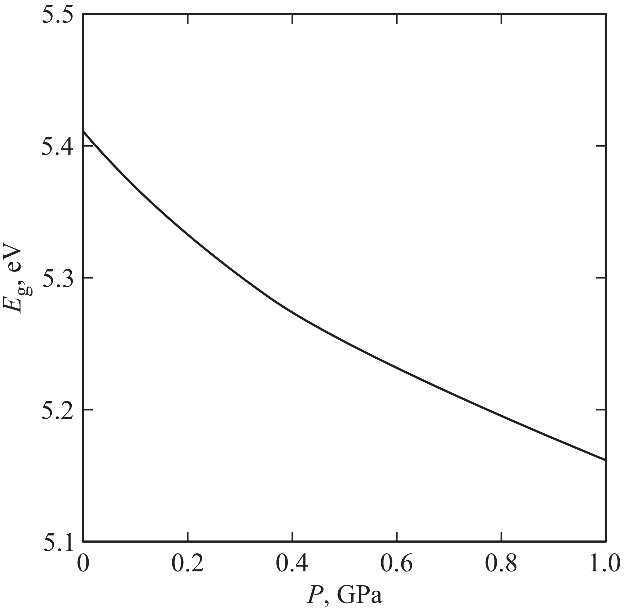

Figure 5. The dependence of the band gap on the pressure for the crystal $C_8H_{10}O_2$.

This indicates that when ODD is compressed, the intermolecular interactions in it are enhanced. At a pressure of 1 GPa, the energy of hydrogen bonds H1−O2 (H2−O1) and the electron density at their critical points increase by 11.7 (11.3) and 7.1 (7.5)%, respectively. In the linear approximation, the band gap of $C_8H_{10}O_2$ is reduced as 0.24 eV/GPa. Thus, according to our forecasts (in linear extrapolation) the optical transparency of ODD will be preserved up to ~ 9 GPa.

4. Conclusion

Ab initio study of the compressibility and electronic properties of an organic molecular crystal octa-3,5-diyn-2,7-diol ($C_8H_{10}O_2$) has been conducted. Pressure dependencies for the lattice parameters and linear compressibility of the crystal $C_8H_{10}O_2$, which made it possible to identify for it both a strong positive linear compressibility and a significant negative linear compressibility (NLC). For the crystal $C_8H_{10}O_2$ the value of the NLC ($-44\,\mathrm{TPa}^{-1}$) is one of the largest among NLC materials that are known to date, which makes it very promising for practical applications. It is shown that the negative linear compressibility of $C_8H_{10}O_2$ is caused by a change in the spatial orientation and linear dimensions of molecular structural units that are linked to each other by hydrogen bonds and van der Waals dispersion interactions. At the same time, the calculated volumetric compression module for $C_8H_{10}O_2$ has a relatively small value even for a static lattice.

A topological analysis of electron density was carried out to study the hydrogen bond in $C_8H_{10}O_2$. The topological parameters of the electron density were calculated and the partially covalent nature of hydrogen bonds of $C_8H_{10}O_2$ was established. It is shown that the energies of hydrogen bonds are relatively large. In addition, the total and partial densities of the electronic states were calculated and the band gap of $C_8H_{10}O_2$ depending on the pressure was determined. It is shown that the main contribution to the formation of upper valence and lower unoccupied electronic states is made by carbon atoms. External pressure leads to a decrease in the band gap. At the same time, the energy of hydrogen bonds and the electron density at their critical points increase with increasing pressure.

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Conflict of interest

The authors declare that they have no conflict of interest.

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