Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A predicted orthogonal semimetallic carbon with negative thermal expansion and compressibility

Zhen-Long Lv[1], Hong-Ling Cui[1], Cai Cheng[2,*]

[1]School of Physics and Engineering, Henan University of Science and Technology, Luoyang 471023, China

[2]School of Physics and Electronic Engineering, Sichuan Normal University, Chengdu 610101, China

Supplementary materials

Figures:

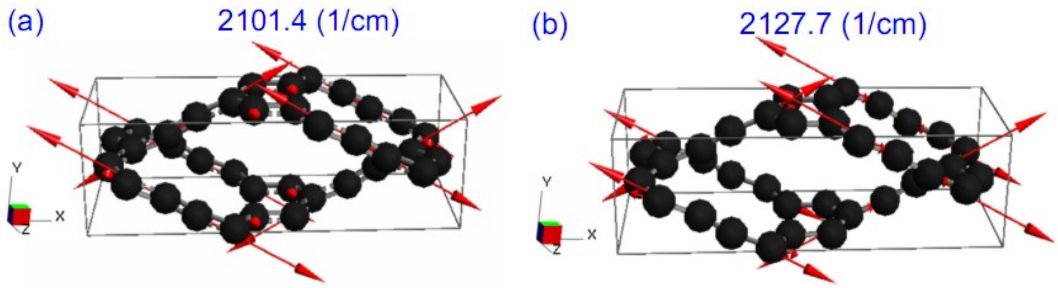


Fig. S1 Vibrational patterns of the two optical modes with the highest frequencies.

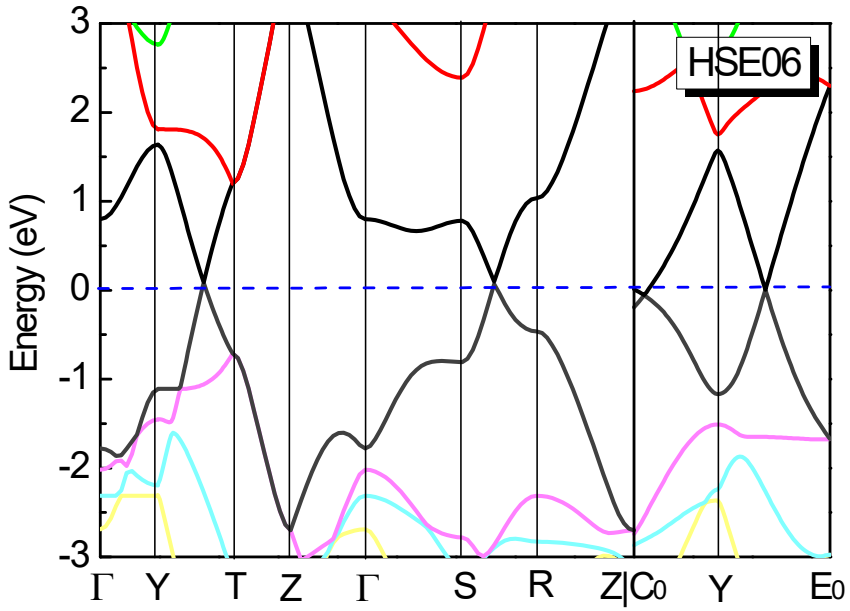


Fig. S2 Band structure of ort-C24 calculated by the HSE06 functional.

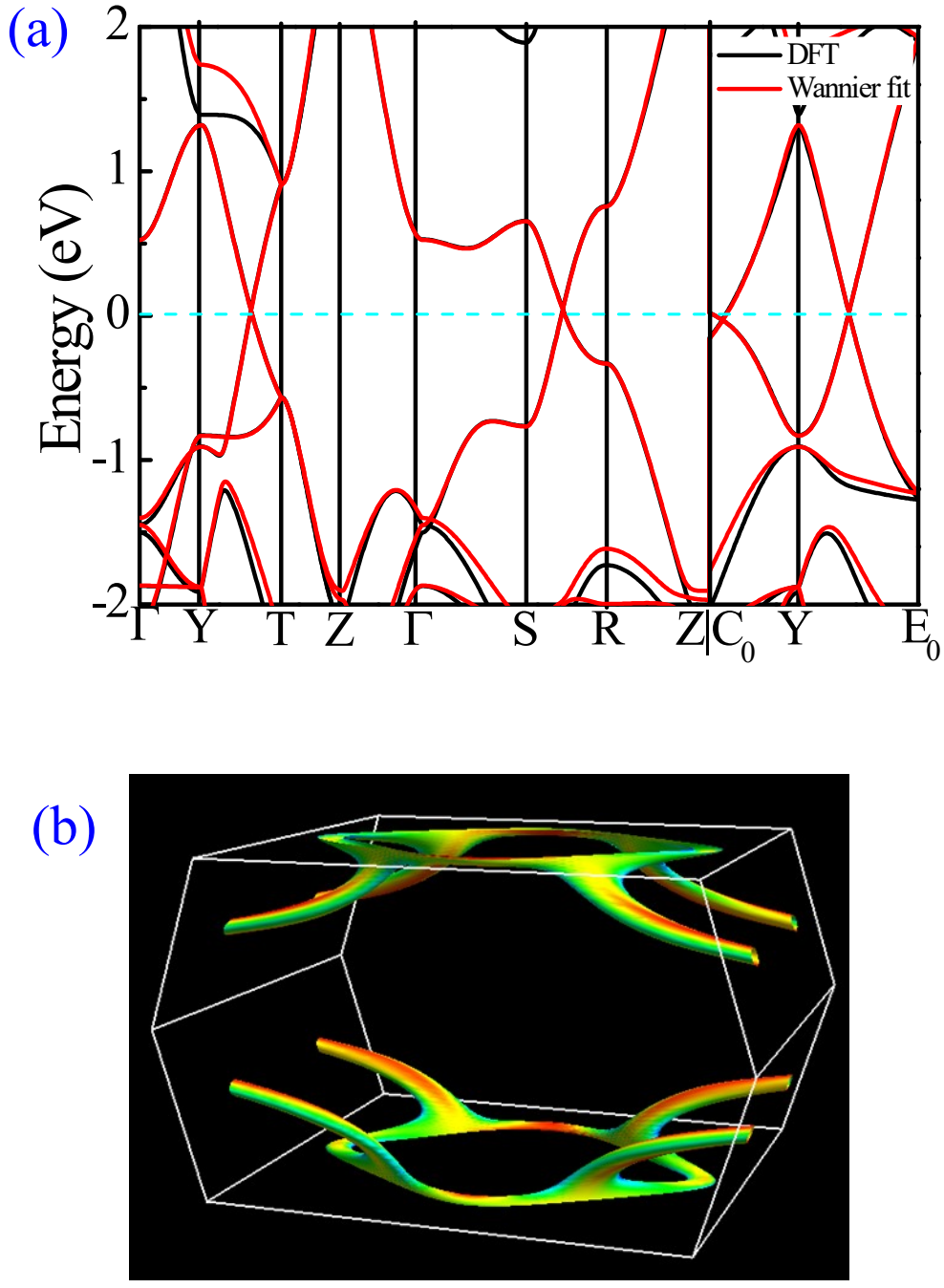


Fig. S3 (a) Fitted band structure (red) and (b) simulated Fermi surface of ort-C24 using the Wannier functions. For the possible calculation error, the energy for simulating is set to (E_F-0.06) eV to highlight the Fermi surface. A similar result can be obtained when it is set to (E_F+0.06) eV.

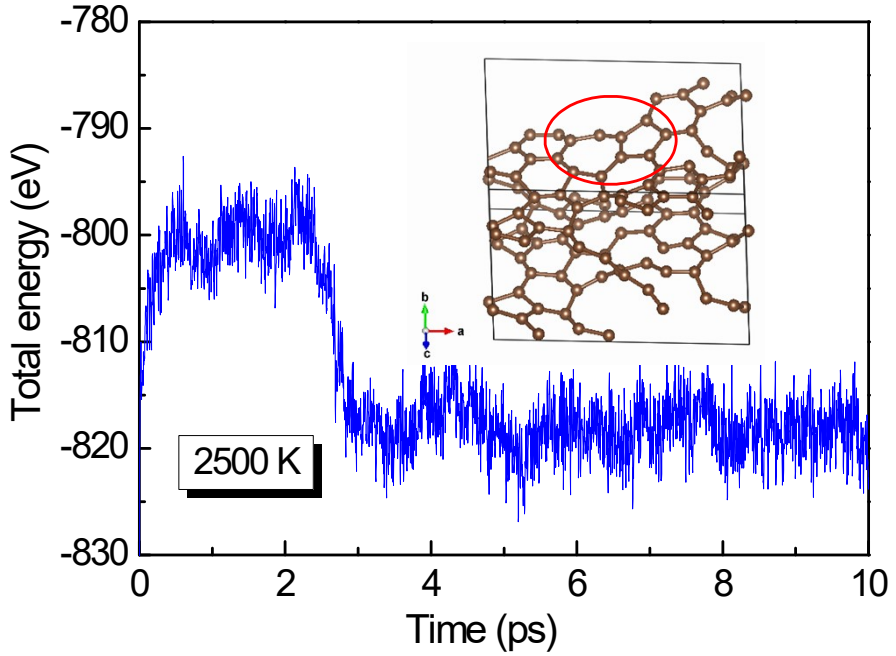


Fig. S4 Ab initio molecular dynamics simulated at 2500 K and 1 atmosphere for 10 ps using the Parrinello-Rahman dynamics with Langevin thermostat (NPT ensemble).

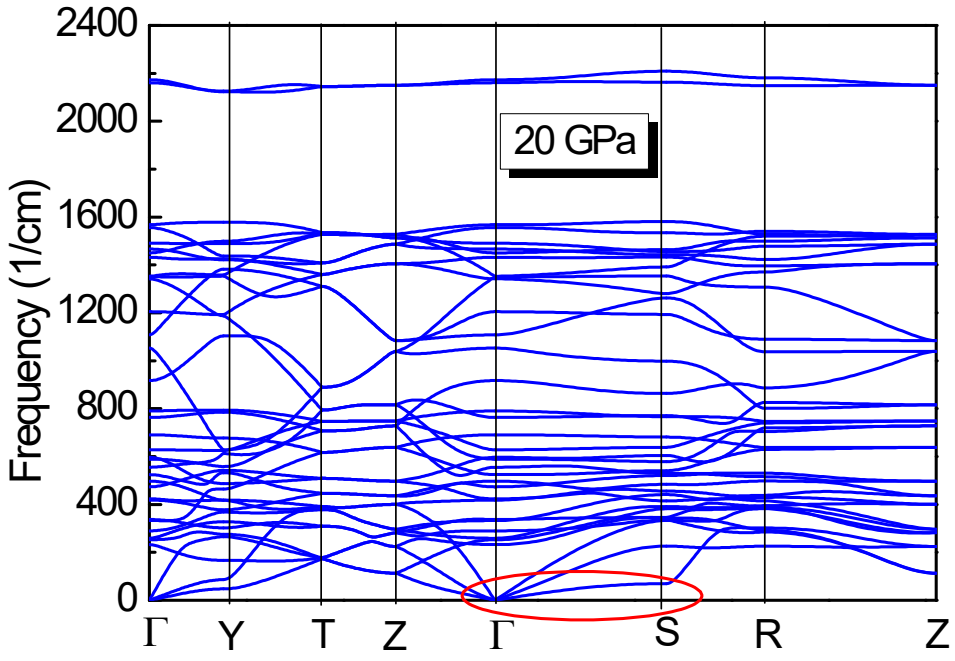


Fig. S5 Calculated phonon spectrum of ort-C24 under the hydrostatic pressure of 20 GPa.

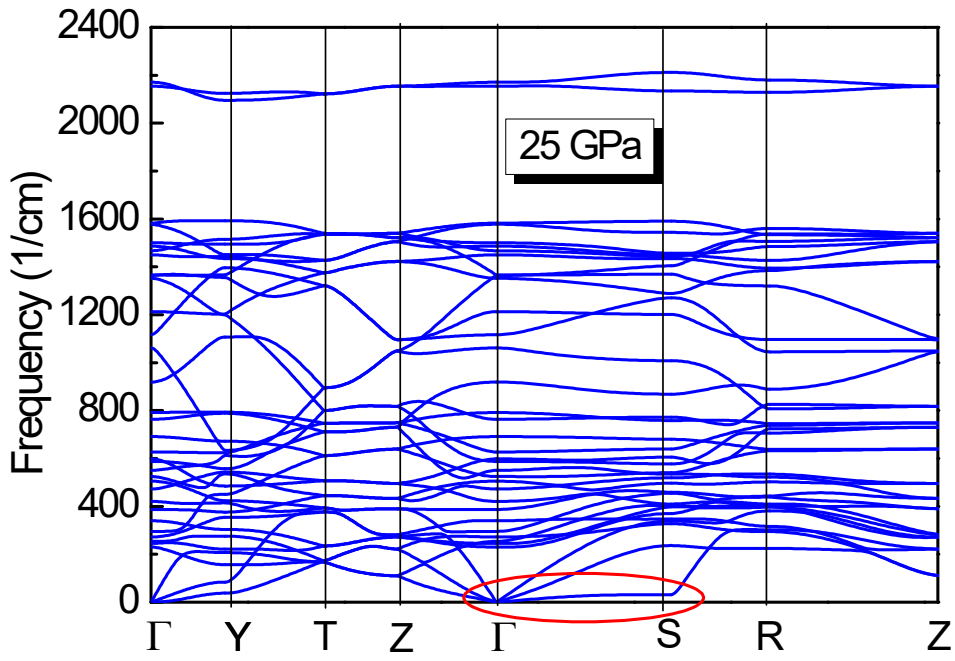


Fig. S6 Calculated phonon spectrum of ort-C24 under the hydrostatic pressure of 25 GPa. Small imaginary frequencies occur at the Γ point and obvious softness of phonon along the Γ-S direction.

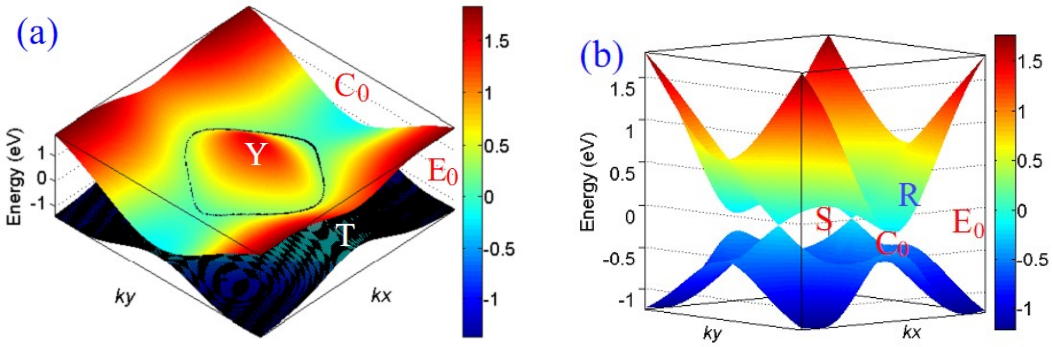


Fig. S7 Calculated energy-momentum relations in the (a) C_0-Y-T-E_0 plane and (b) R-S-C_0-E_0 plane of the Brillouin zone of ort-C24 under 5 GPa.

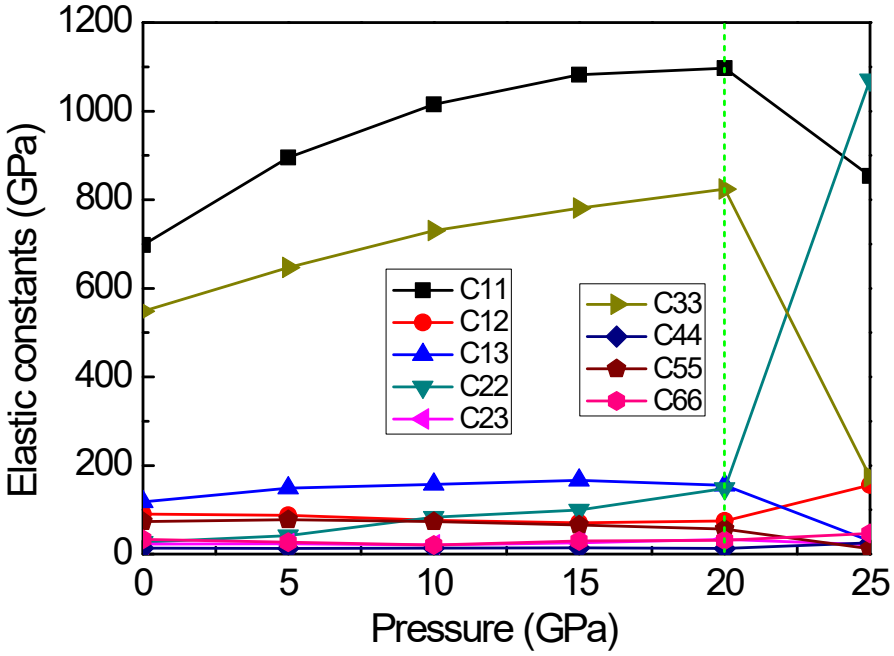
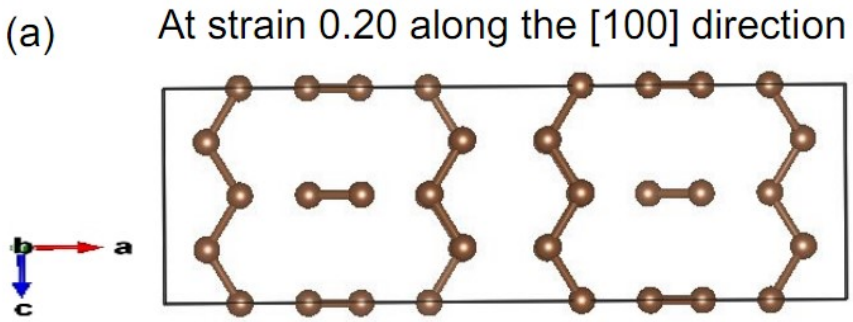


Fig. S8 Calculated elastic constants as a function of hydrostatic pressure up to 25 GPa at 0 K.



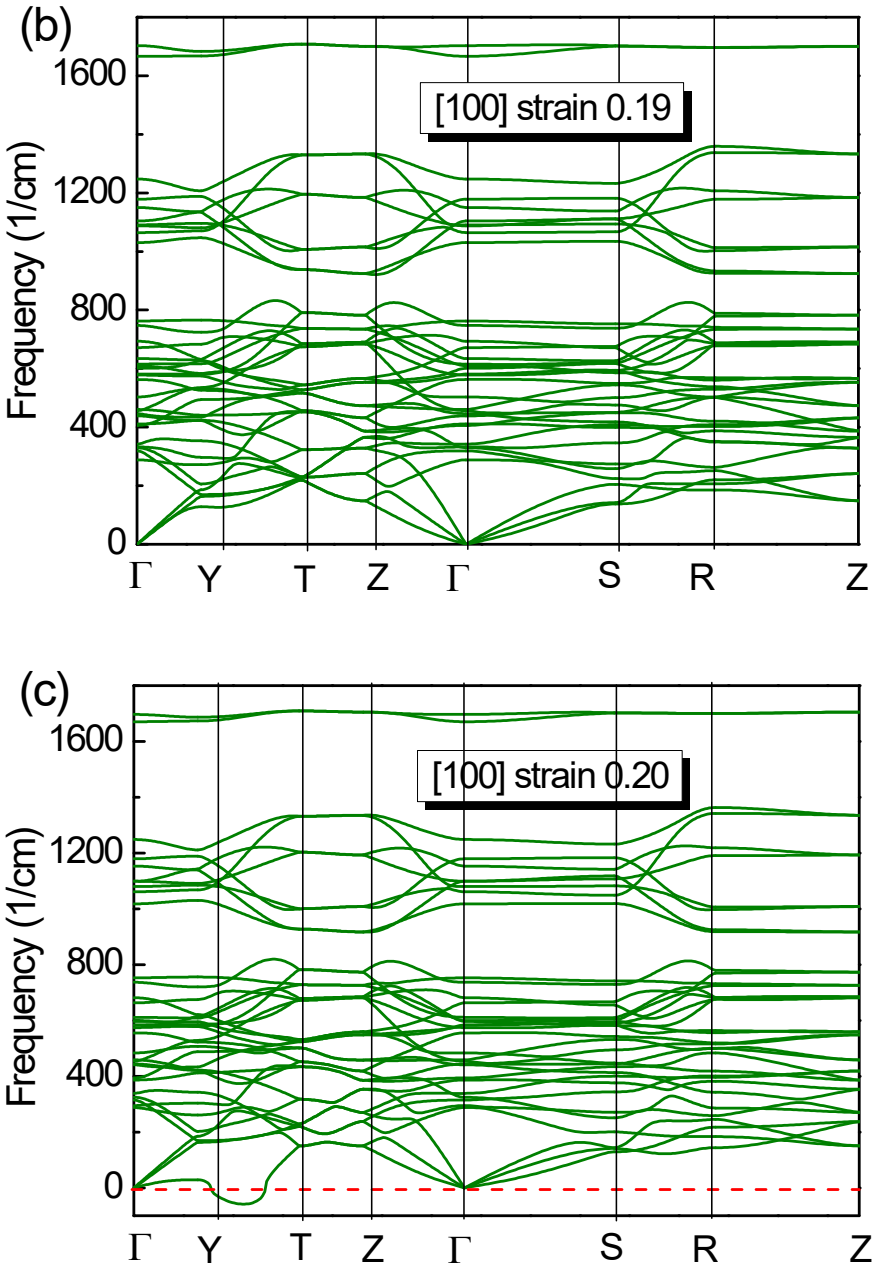


Fig. S9 (a) Crystal structure at the critical strain of 0.20, (b) phonon spectra at strains of 0.19 and (c) 0.20 of ort-C24.

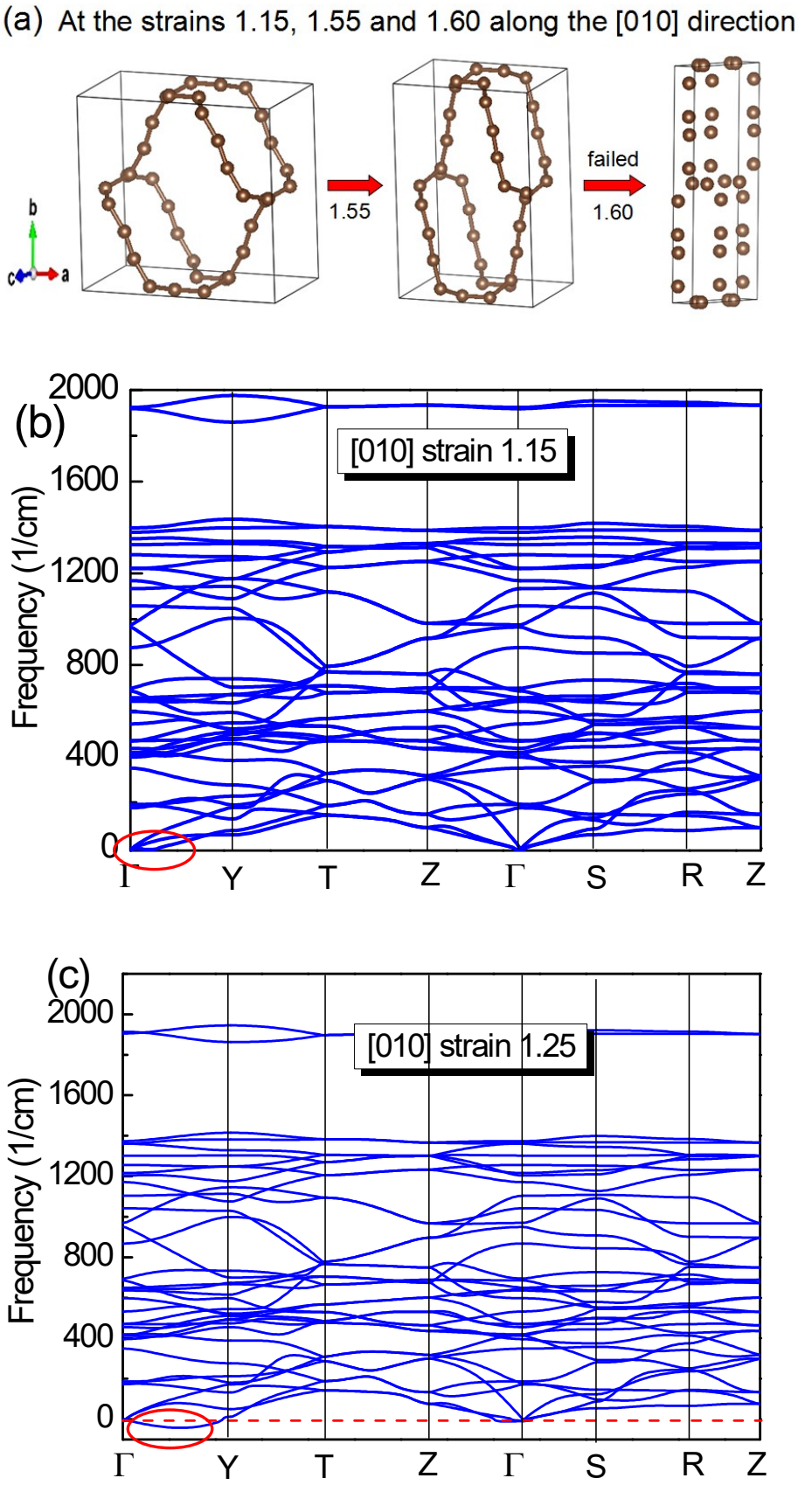


Fig. S10 (a) Crystal structure at the critical strain of 1.55 along the [010] direction, phonon spectra at strains of (b) 1.00 and (c) 1.25 of ort-C24.

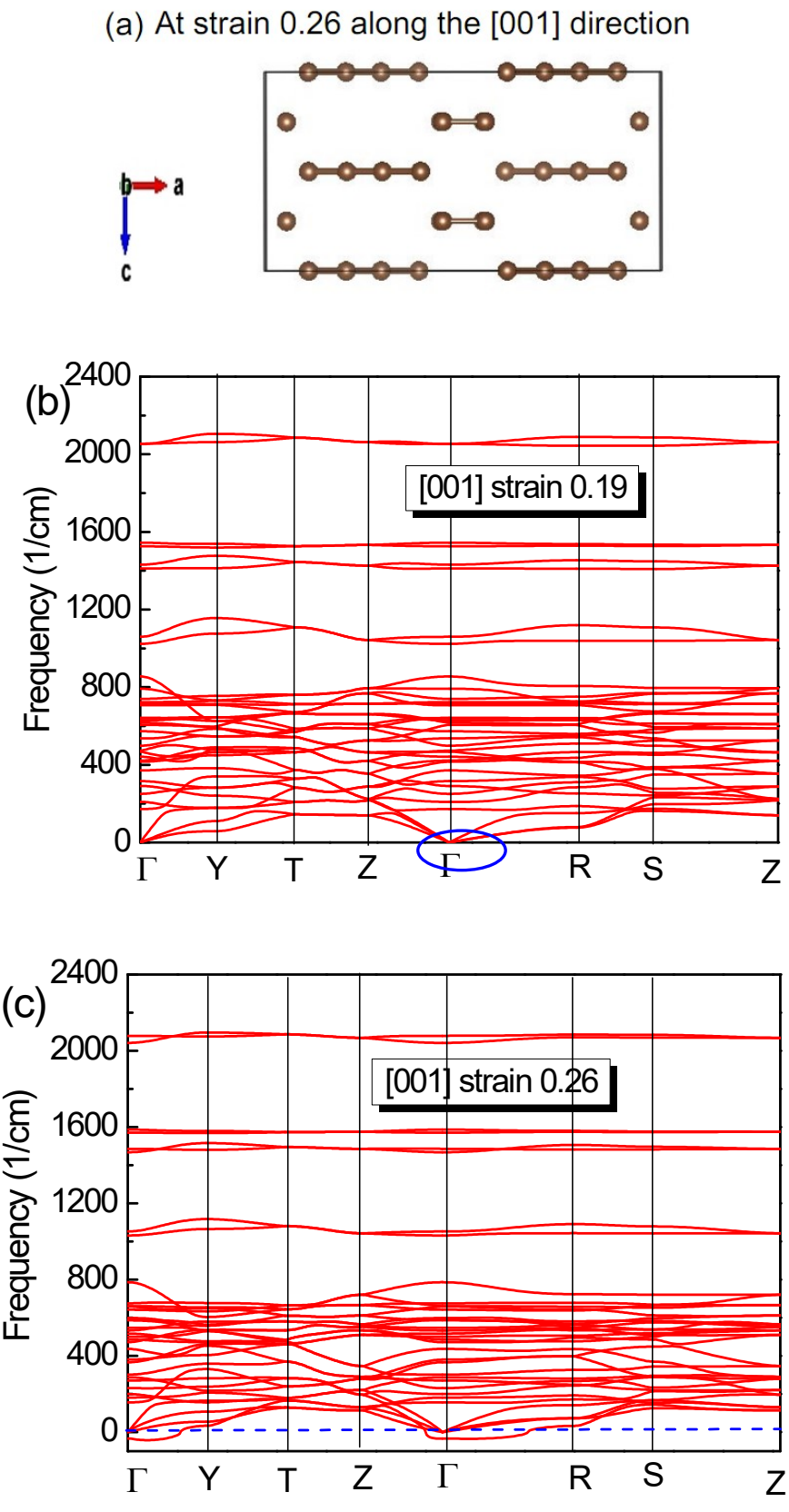


Fig. S11 (a) Crystal structure at the critical strain of 0.26 along the [001] direction, phonon spectra at strains of (b) 0.19 and (c) 0.26 of ort-C24.

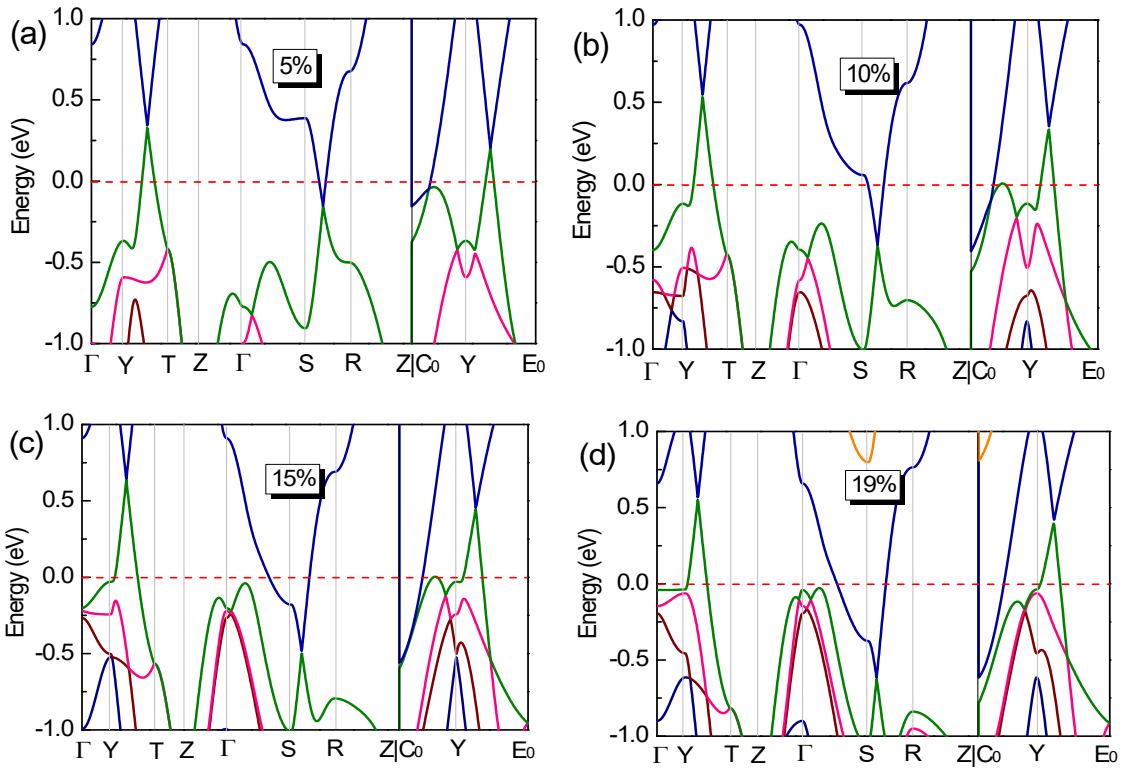


Fig. S12 Band structures of ort-C24 calculated at the strains of (a) 5%, (b) 10%, (c) 15% and (d) 19% along the [100] direction.

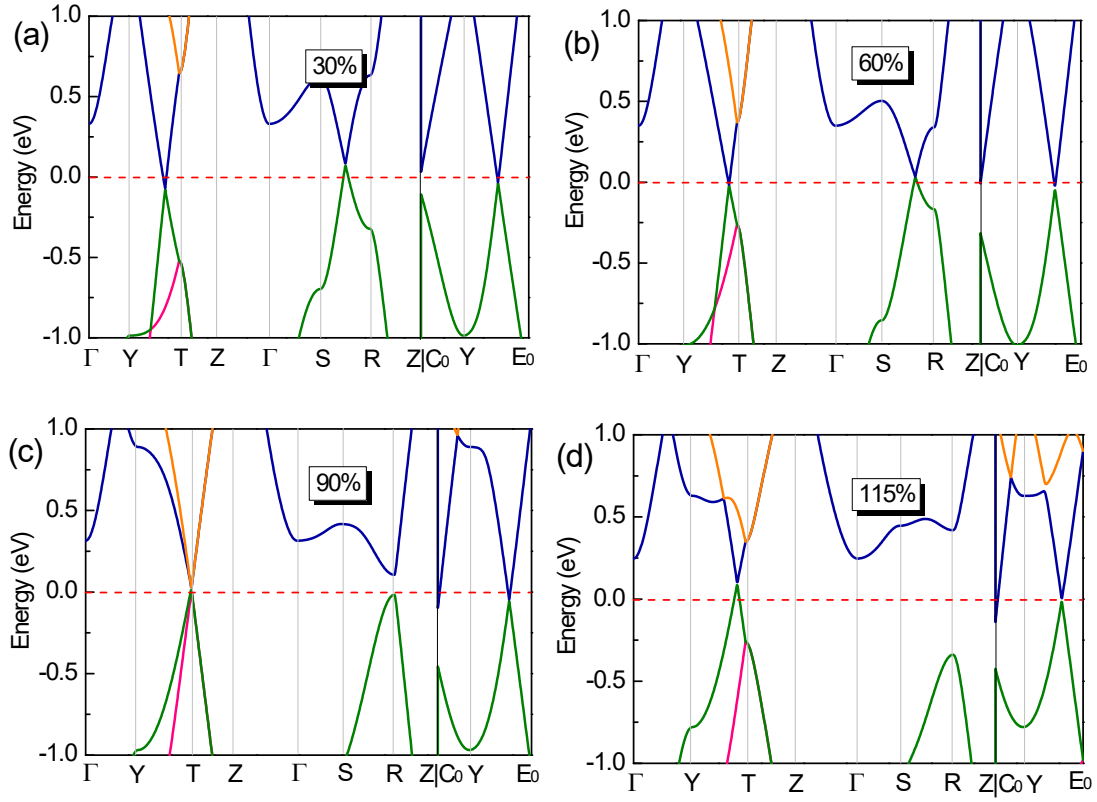


Fig. S13 Band structures of ort-C24 calculated at the strains of (a) 30%, (b) 60%, (c) 90% and (d) 115% along the [010] direction.

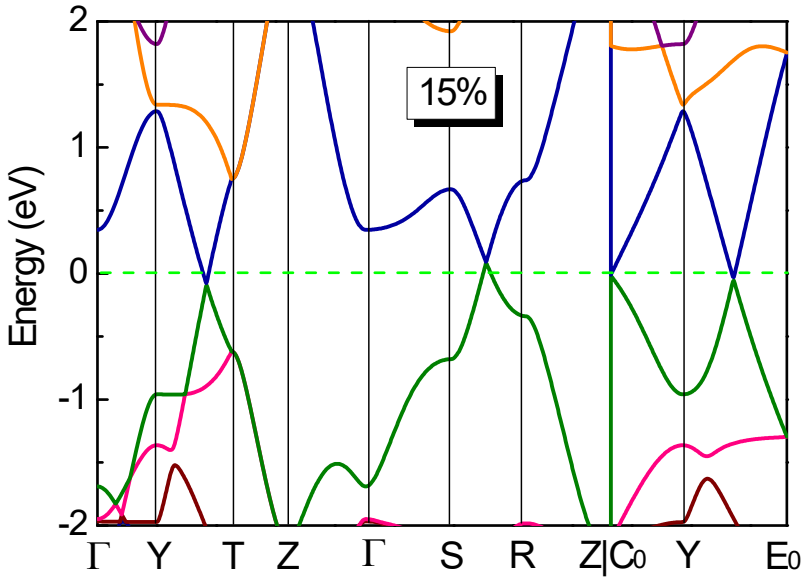


Fig. S14 Calculated band structure of ort-C24 at the strain of 0.15 along the [010] direction.

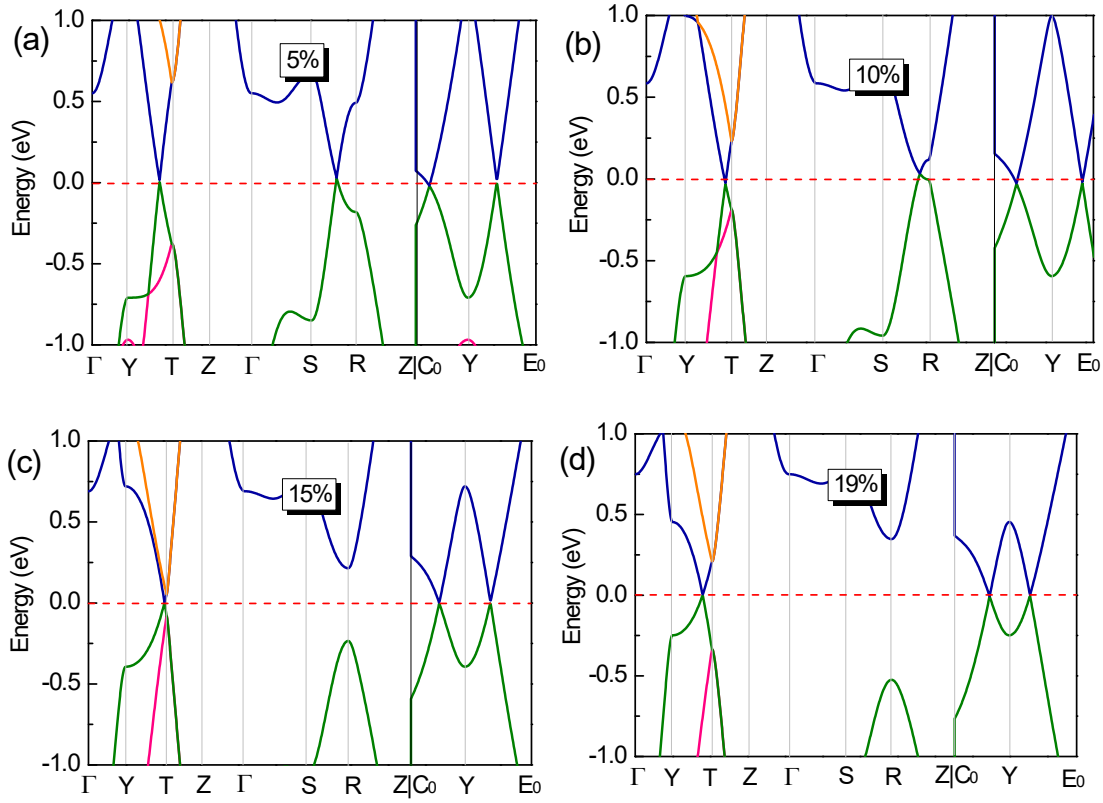


Fig. S15 Band structures of ort-C24 calculated at the strains of (a) 5%, (b) 10%, (c) 15% and (d) 19% along the [001] direction.

Tables:

Table S1. Calculated lattice constants a, b, c (Å), total energy per atom (eV), volume per atom (Å^3), bulk moduli (GPa) and its first-order pressure derivatives of ort-C24 and the selected carbon allotropes.

	a	*b*	*c*	*E*	*V*	*B*	*B'*
graphite	2.459		6.642	-9.211	8.698	274.7	3.63
exp.	2.459 [1]		~[a]				
diamond	3.571			-9.095	5.692	431.7	3.69
exp.	3.567[2]					439.2[3]	3.6[3]
bco-C16	7.807	4.897	3.291	-8.822	7.864	293.1	3.62
bct-C16	6.588		3.377	-8.543	9.160	238.7	3.19
oC24	13.785	8.790	2.478	-9.007	12.511	185.0	3.64
oP-c24	4.920	12.034	3.316	-8.885	8.180	279.5	3.26
ort-C24	12.890	4.004	4.991	-8.682	10.774	179.4	1.94
so-C12	4.332	8.651	2.469	-8.981	7.711	303.0	3.56

~[a] Ref. [1] indicates that temperature has a notable influence on the lattice *c* of graphite, which can vary from 6.672 Å to 6.718 Å when temperature rises from 4.2° to 297°. Although the lattice constant of *c* are reported to be 6.711 Å by P. Truccano and R. Chen [Nature, 258 (1975) 136-137], the temperature is not given, so we omit this value here. In our relaxation and calculation, dispersion correction of the Tkatchenko-Scheffler type was used for graphite (IVDW=20).

Table S2. Lattice constants of ort-C24 at selected temperatures and pressures.

T (K)	*a*	*b*	*c*	*P (GPa)*	*a*	*b*	*c*
0	12.890	4.004	4.991	0	12.890	4.004	4.991
500	12.829	4.109	4.999	5	13.034	3.450	4.973
1000	12.792	4.155	5.001	10	13.079	3.185	4.949
1500	12.764	4.193	5.006	15	13.095	2.989	4.936
2000	12.732	4.180	5.007	20	13.079	2.898	4.916
2500	12.871	3.465	4.907	25	12.717	2.520	4.905

References:

[1] Y. Baskin, L. Meyer, Lattice constants of graphite at low temperature, 100 (1955) 544.

[2] H. Holloway, K.C. Hass, M.A. Tamor, Isotopic dependence of the lattice constant of diamond, Phys. Rev. B, 44 (1991) 7123-7126.

[3] Q. Hu, B. Li, X. Gao, Y. Bi, L. Su, H. Mao, Ultrasound elasticity of diamond at gigapascal pressures, PNAS, 118 (2021) e2118490118.