Supplementary Information for

Bonding Analyses of Unconventional Carbon Allotropes

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Interpenetrating structures

Table S1: Total energies of interpenetrating structures (II) alongside the original versions of the T-allotropes. The energies are given relative to graphite (middle column) and in absolute values (right column).

Structures	**Δ*E* (kJ/mol)**	***E* (eV/atom)**
TY-II-carbon	114.1	–8.036
TY-carbon	114.2	–8.034
T-carbon	125.6	–7.916
T-II-carbon	150.3	–7.661
TY-carbodiimide	–2912.5	–7.881
TY-II-carbodiimide	–2912.7	–7.881

To investigate the reasons for only T-II-carbon being affected, we conducted bond analysis with the same methods as presented for the original T-allotropes. Figure S1 depicts the projected pCOHPs of T-II-carbon, along with the according bond lengths. In comparison with T-carbon, the intra- and inter-tetrahedral bonds become slightly elongated and strengthened. This stabilizing effect is overcompensated by long-range interactions (Fig. S1, bottom half) that are antibonding over a wide energy range from 0 to –16eV and cause an overall rise in total energy of the interpenetrated compound by 25.3 kJ/mol. In the case of TY-II-carbon, there is virtually no change in bond length (Fig. S2 top). The ICOHPs indicate a slight strengthening of all bonds, equivalent to a negligible drop in total energy of 0.1 kJ/mol. The long range contacts approach the order of 5 Å and thus show almost no bonding interaction at all (Fig. S2 bottom).

We also applied the scheme to the proposed TY-carbodiimide structure in order to create an interpenetrated version called TY-II-carbodiimide (Fig. S3). Like in TY-II-carbon, the parent structure of TY-II-carbodiimide is so cavernous that the original and interpenetrating structure basically do not interact with each other. The slight variation in ICOHPs (Fig. S3) cause practically no change in total energy (Δ*E* = 0.2 kJ/mol).

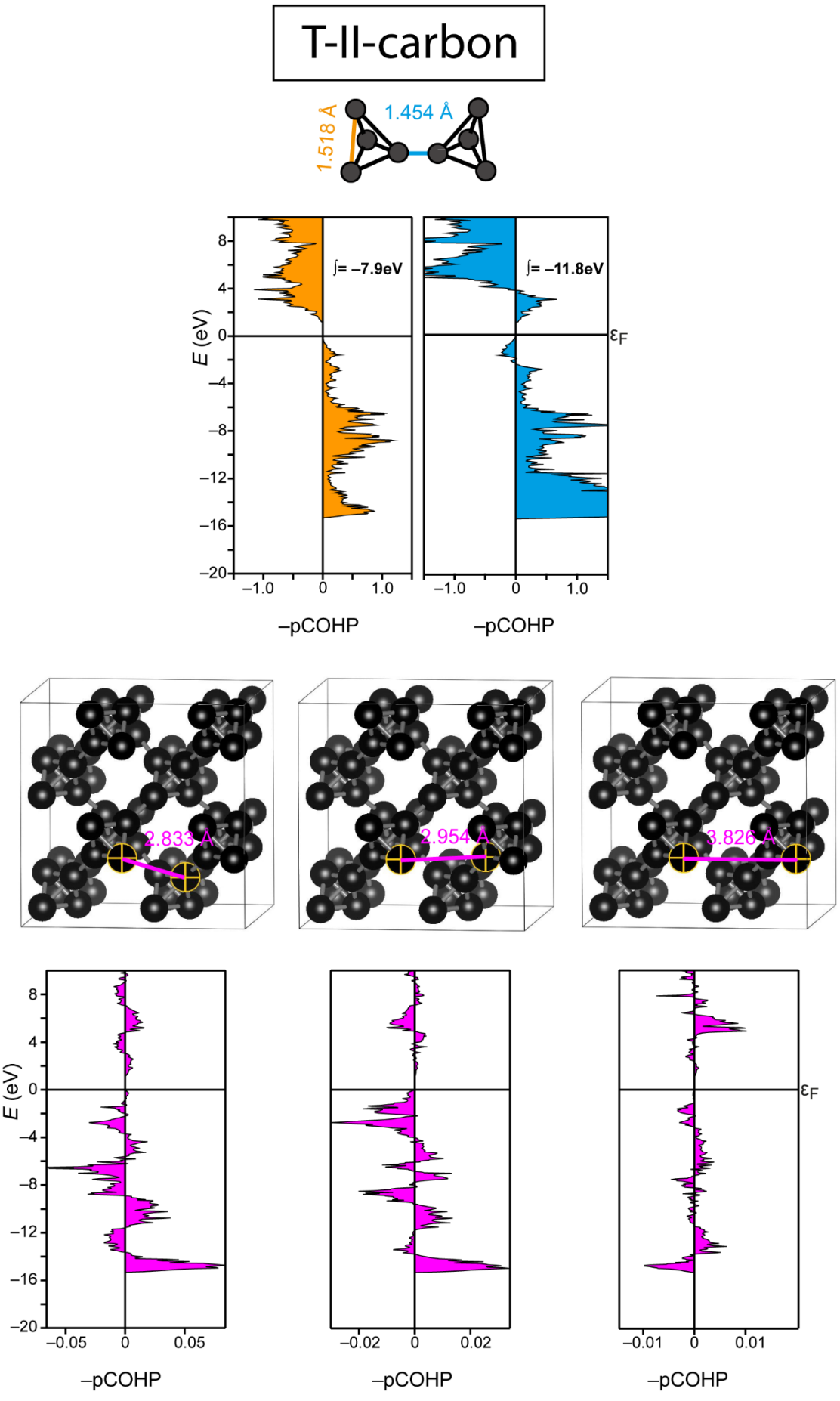

Figure S1: Projected COHPs for the symmetry-inequivalent bonds in T-II-carbon.

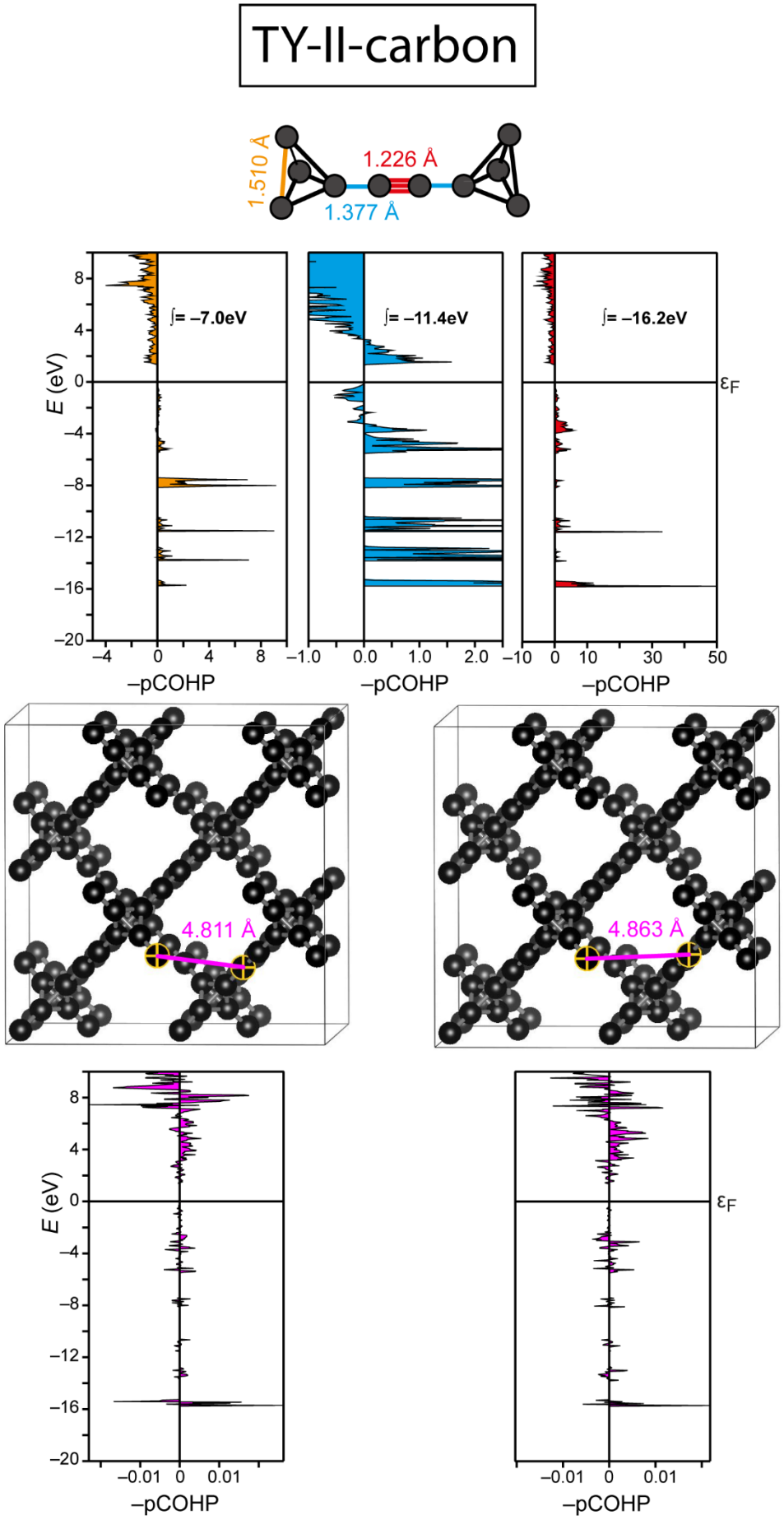

Figure S2: As before but for TY-II-carbon.

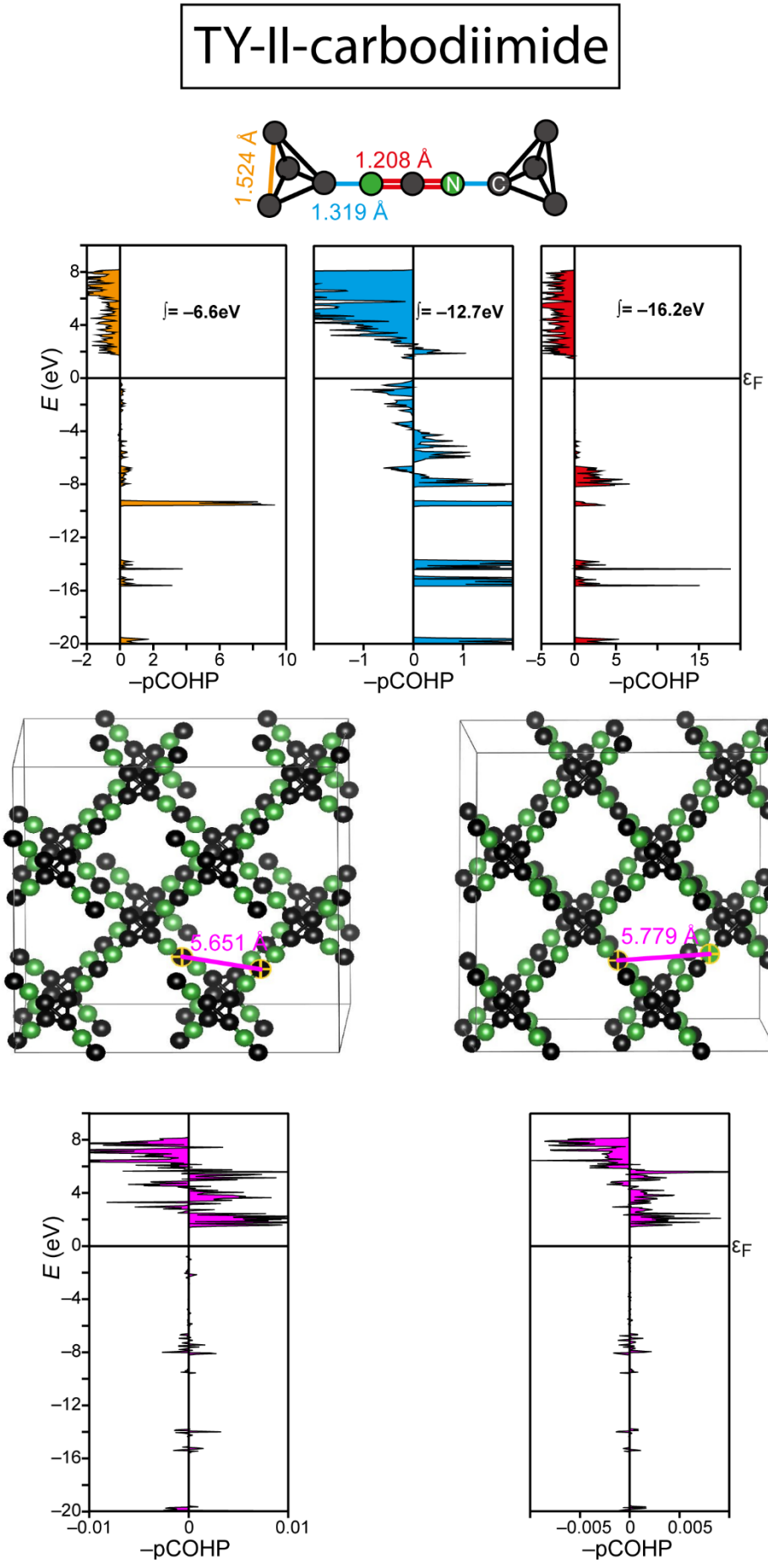

Figure S3: As before but for TY-II-carbodiimide.

Alternative Structures for SiC_2N_4

The proposed structure by Kroll *et al*. (reference [39] in the main text) for the high-temperature phase (Fig. S4, top left) is constructed on the basis of the experimentally available average structure, but allowing the nitrogen atoms to relax out of the connecting vector between the silicon atoms. This leads to a structure which bears similarities with the high-temperature variant (space group *P*–4*n*2) of crystobalite. In addition, a low-temperature phase (space group $P4_322$) was suggested by the authors that is similar to α-crystobalite (Fig. S4, top right). Kroll *et al*. found both suggestions to be very close in energy to the experimental structure, with differences on the order of 1–4 kJ/mol (reference [39] in the main text). In our phonon calculations, both models exhibit the very same kind of imaginary frequencies as the experimental model, caused by vibrations of the NCN-units as calculated for the experimental model and the proposed C_3N_2. Thus, the *P*–4*n*2 and $P4_322$ cells show no advantage over the structure drawn from X-ray diffraction data and are not further considered for the purpose of this work.

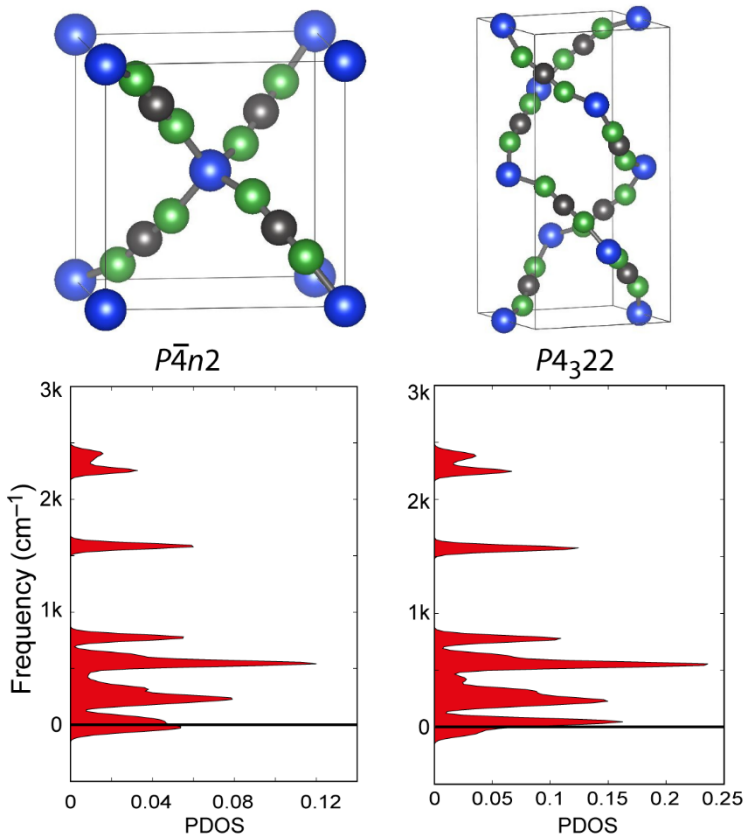

Figure S4: Alternative crystal structures suggested by Kroll *et al.* (top) and their respective phonon-DOS.