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Ab initio electronic structure of the eclipsed and staggered conformations of the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br organic superconductor

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We investigated *ab initio* the electronic structure of both conformers exhibited by the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br organic superconductor at ambient as well as low temperatures. We found that the eclipsed structure is approximatively 0.35 eV/formula more stable than the staggered one. We found that two energy barriers separate both structures: one consistent with the experimental values close to 2000–2600 K. A second energy barrier, for the reversed process and close to 20 K, could explain the ethylene group freezing found at low temperatures.

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Organic superconductors have attracted huge interest during the past 20 years owing to the unusual electric behavior and the occurrence of low critical temperature superconductivity. In spite of an enormous amount of research devoted to this class of compounds, the origin and mechanism of the electric, magnetic, as well as superconducting behavior remain open to investigation. The coexistence of several pressure, temperature, magnetic field, and history-dependent phenomena as structural modifications, magnetic ordering, and metal-superconductor transitions complicates enormously the physical and chemical understanding of these compounds.[1–3] In particular, the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br system (κ-Br) was originally discovered by Kini *et al.*[4] and was characterized as a 11.6 K superconductor. One of the most interesting features of this compound is the existence of several transformations at low temperatures, but above the superconducting transition. At 45 K a phase-transition-like has been identified, while at 77 K a glasslike transformation appears originally attributed to the eclipsed-to-staggered conformations of the terminal ethylene groups of the BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] molecules.[5–8] Recently, Wolter *et al.*[8] determined the degree of ethylene group disorder in κ-Br by means of accurate synchrotron x-ray diffraction experiments. After their work, it has been established that the symmetry of the crystal (*Pnma*) is preserved during cooling of the sample from room temperature to 9 K. They also found the extent of eclipsed to staggered conformers as a function of the sample temperature. It appears now that at room temperature, the eclipsed conformer exists in a 67% proportion which increases to 89% at 100 K and 97% at 9 K. It is claimed that the existence of a significant fraction of the staggered conformer in the sample should modify the electronic properties of the whole crystal. This important finding ruled out a freezing process of the ethylene group at a fixed temperature. A continuous transformation occurs and can be analyzed in terms of equilibrium thermodynamics. In order to characterize this low temperature transformation, we evaluated the energy barrier associated to the free BEDT-TTF molecular interconversion between the eclipsed and staggered conformers. By means of *ab initio* all-electron band-structure methods, the electronic properties of the pure eclipsed and staggered crystals have been investigated.

Solid-state electronic structure calculations of the κ-Br crystal were carried out using a density-functional theory approach to band theory. In a first step, a pseudopotential scheme, the projected-augmented plane-wave method (PAW, VASP code),[9] has been employed to obtain the optimized crystal structures in both the eclipsed and the staggered conformations. The convergence criteria were set to 0.01 meV/Å for the local forces. Then a full potential linear augmented plane-wave (LAPW) method (WIEN2K code[10]) has been employed. For both approaches, the exchange and correlation part of the crystal potential was modeled by means of the generalized gradient approximation.[11] For the LAPW computations, we selected 24 **k** points in the irreducible wedge of the small orthorhombic Brillouin zone. For this set of points, we computed *ab initio* energy eigenvalues. The *muffin-tin* radii were fixed to 1.8, 2.0, 1.1, 1.1, 1.5, and 0.9 a.u. for Cu, Br, C, N, S, and H atoms, respectively. We set $R_{\mathrm{MT}}K_{\mathrm{max}}$ to 2.0, a reasonable value owing to the small radii of some atomic spheres, particularly in the case of hydrogen. The total density of states (DOS) as well as the angular-momentum resolved density of states (PDOS) at each atomic site was computed by the standard tetrahedral integration scheme with a 0.05 eV Gaussian broadening. Additional all-electron *ab initio* density-functional theory (DFT)-based computations of the molecular electronic structure were carried out.[12] The generalized gradient approximation[11] (GGA) density functional was employed and the Gaussian basis set was the 6-31$G\star\star(d,p)$ and improved to aug-cc-PVTZ.[13]

We computed the electronic band structure for the eclipsed conformer of the κ-Br crystal using the lattice parameters reported by Wolter *et al.*[8] at 300 K. The atomic site positions' guess was taken from Geiser *et al.*[14] The hydrogen atom positions were selected by considering a strict sp^3 hybridation for the corresponding C atoms in the ethylene terminal groups. Although the crystal structure of the staggered κ-Br crystal is unknown, we consider an initial guess by imposing a 60° torsion of the terminal ethylene groups. The atomic site positions theoretically determined are in good agreement with those experimentally measured in the case of the eclipsed κ-Br system. For the staggered κ-Br crystal, the equilibrium structure preserves the searched staggered conformation and represents a local minima in the energy potential surface. It is important to note that the eclipsed conformer is more stable than the staggered one by 0.31 (0.39) eV/formula, representing a transformation enthalpy of -30.3 (-37.8) kJ/mol computed with the PAW (LAPW) method. The close values obtained with both methods are indicative of the consistency of our approach. We repeated these computations for the lattice parameters reported by Wolter *et al.*[8] at 100 and 9 K. At 100 K (9 K) we found that the relative stability increases to 0.36 eV/formula (0.37 eV/formula) (PAW computations). Employing the mass-action law and the fractional composition experimentally obtained by Wolter *et al.*,[8] it is possible to estimate the entropy change associated to the eclipsed → staggered transformation. We found that this value is strongly temperature dependent, being -120 J/mol K at 300 K and increasing to -360 J/mol K at 100 K and -4167 J/mol K at 9 K. Assuming that the entropy change at 300 K should be constant, at 9 K the enthalpy change should reduce to -0.06 eV/formula (-1.34 kJ/mol) which is not consistent with our findings at 9 K. This clearly indicates that the processes occurring at temperatures below 100 K are of a different nature.

The energy bands in the orthorhombic Brillouin zone are very similar for both structures. A set of bands crossing the Fermi energy confers a metalliclike behavior to both compounds; the density of states at the Fermi energy is 20.80 (21.10) states/eV-cell for the eclipsed (staggered) system. The form of the Fermi surface (FS) exhibits the particular quasi-two-dimensional behavior and is similar to that previously obtained.[3,15,19,20] The topology of the FS is consistent with previously reported investigations and it is composed by two open sheets of one-dimensional character and a two-dimensional cylinders. This form of the FS is frequent in similar organic conductors based on BEDT-TTF.[3]

The computed total as well as the atomic site projected DOS show strong similarities in both compounds (Fig. 1). However, the structural transformation from the eclipsed to the staggered conformer introduces a number of changes in the interatomic distances. These modifications concern essentially the interaction between the organic electron donor molecule and the inorganic chain. The hydrogen atoms in these structures seem to play the role of bridging both substructures. However, the eight H atoms are tightly bounded with similar *H*-site energies[16,17] (1.8 eV/H). The interlattice interaction energy can be computed as the $\text{BEDT-TTF}_{\text{sublattice}}+\text{inorganic-chain}_{\text{sublattice}} \rightarrow \kappa\text{-Br}$. The total electronic energy of these hypothetical sublattices has been computed and used to evaluate this balance. We found that the eclipsed structure exhibits an interlattice interaction energy of 1.20 eV/formula while the staggered one 1.15 eV/formula at 300 K. This small difference is understandable since the structural modifications introduced by the transformation are small. The H8 atoms, close to the inorganic chain in the eclipsed form, exhibit inorganic chain atoms at 2.843 (N), 3.280(C), and 3.290(Br) Å. This local environment is modified in the staggered structure to 2.623(Br), 4.011(N), 4.273(Cu), and 4.388(C) Å. The longer distances in the staggered structure explain the slight reduction in the inter-

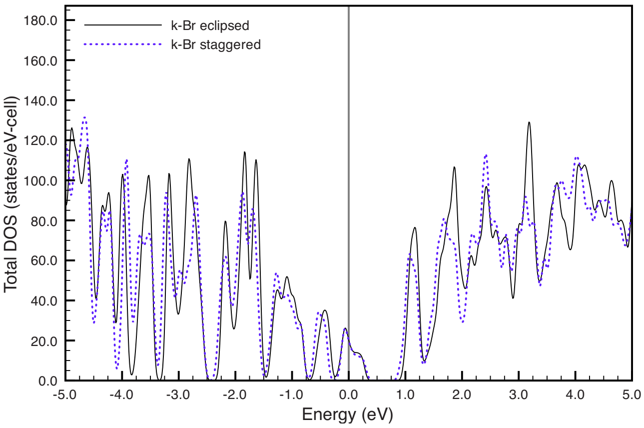

FIG. 1. (Color online) Total density of states (states/eV-cell) for the eclipsed and staggered κ-Br crystals.

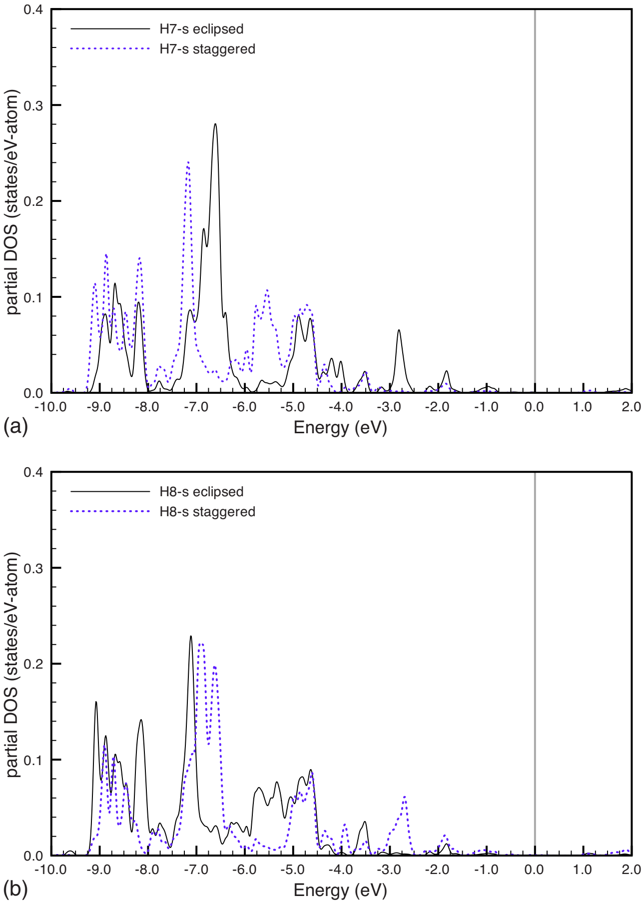

FIG. 2. (Color online) Partial density of states (states/eV-atom) for (a) H7 atom and (b) H8 atom in both conformers. H7 and H8 are the hydrogen atoms closest to the inorganic chain.

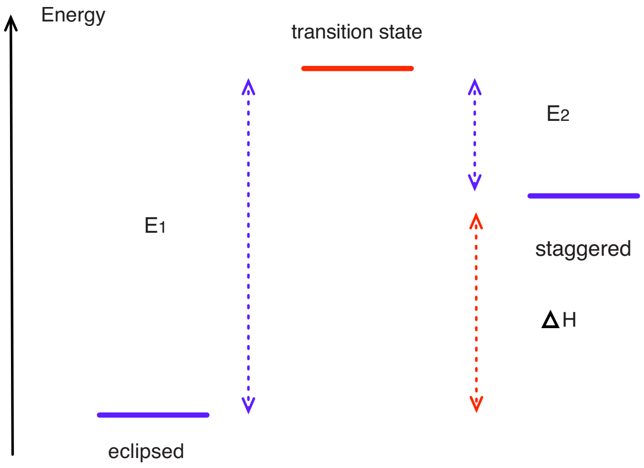

FIG. 3. (Color online) Schematic energy diagram connecting both conformers. E_1 represents the activation energy to the eclipsed→staggered transformation, while E_2 applies for the reversed process. ΔH is the transformation enthalpy.

lattice interaction and the small differences in the electronic structure. However, the nature of the local density of states at the involved H8 atoms (the closest to the inorganic chain) is slightly modified as it can be appreciated in the plot of Fig. 2. We plotted only the PDOS of the two H atoms for which significant changes can be appreciated. At 100 and 9 K, we found that the interlattice interaction energy is essentially temperature independent for both conformations.

In order to complete the energetic description of the eclipsed→staggered transformation, we considered the energy barrier separating both local minima (Fig. 3). The energy barrier of the ethylene groups was then estimated in the free molecule by imposing a particular reaction path. We performed a geometry optimization of the conformers of BEDT-TTF by means of DFT molecular cluster calculations of the total energy. We found that both conformers are energetically equivalent as expected. The staggered conformer is characterized by a dihedral angle formed by the four terminal carbon atoms belonging to the ethylene groups of 49°. The transition states connecting these conformers have been characterized by a geometry scan imposing that the dihedral angle between the ethylene groups remains constant. All the other degrees of freedom were set free during the optimization. In this way we found a transition state at 30°. The small energy barrier attains 0.068 eV (1.57 kcal/mol). Improving the Gaussian basis set to aug-cc-pVTZ, this figure decreases slightly to 0.065 eV (1.50 kcal/mol) without change on the optimized geometries.

The same procedure has been carried out for the molecular cation BEDT-TTF$^+$ showing significant differences mainly associated with the planarity of the molecule which resembles to that observed in the crystal. Our results for the stable conformers are consistent with those previously reported by French and Catlow.[18] The energy barrier is slightly increased to 0.101 eV (2.33 kcal/mol). The energy barrier connecting both conformers is indeed very small and it is thus expected that none of them should be intrinsically favored. However, in the crystal at low temperatures, the molecular interactions between each BEDT-TTF conformer with the anionic chain favor the eclipsed form over the staggered. Using the experimental fraction ratio from Wolter *et al.*,[8] our estimate for the transformation enthalpy, that we assume temperature independent, and a Maxwell-Boltzmann distribution for each conformer, E_2 is 0.0017 eV (0.40 kcal/mol) (see Fig. 3). This value is smaller than our free molecule estimate. The discrepancy probably arises from the overestimation of the free molecule barrier and the fact that, in the solid state, this transformation is a cooperative one. It is well known that cooperative phenomena tend to reduce the observed activation energies.

This small activation energy for the eclipsed-staggered interconversion is consistent with the small interaction energy found between both sublattices. Moreover, the open packing of these structures supports a low interaction between the sublattices. The activation energy has been obtained at temperatures close to 100 K and has been attributed to the conformational motion of the ethylene groups. Surprisingly, this activation energy ranges from 2000 to 2650 K,[5,21–23] which is as high as 0.23 eV, of the order of magnitude of the transformation enthalpy (E_1 in Fig. 3). Our thermodynamical estimate for E_2 (19.7 K) is more consistent with a freezing process of these ethylene groups at low temperatures and continuous eclipsed-staggered transformation equilibria above 20 K.

After precise electronic structure computations of both conformers, we conclude that the interlattice interactions are small and essentially the same for both structures. The evaluation of the activation energy from the eclipsed to the staggered transformation yields an estimate of the order of magnitude expected for conformational transitions: well below the usually attributed value for this process. The continuous equilibria found by Wolter *et al.*[8] seem to correspond to chemical equilibria between two conformers at least above 20 K: our estimate for the energy barrier. Some evidence can be found for this limit from our estimate for the transformation entropy, particularly high at 9 K.

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