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Failure of Conventional Density Functionals for the Prediction of Molecular Crystal Polymorphism: A Quantum Monte Carlo Study

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The Importance of Electron Correlation on the Polymorphism of *para*-diiodobenzene Molecular Crystals: a Benchmark Quantum Monte Carlo Study

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Abstract

We have applied the diffusion Monte Carlo (DMC) method, for the first time, to an organic molecular crystal (*para*-diiodobenzene) in order to determine the relative stability of its two well-known polymorphs. The DMC result predicts that the α phase is more stable than the β phase at zero temperature, in agreement with experiment. In comparison, we evaluated four commonly-used local, semi-local and hybrid density functionals, including an empirical correction to include the effects of dispersion. We conclude that while density-functional theory (DFT) may provide the most practical method for estimating the effects of electron correlation, conventional functionals which do not accurately describe noncovalent interactions may not be considered reliable for determining highly accurate energies in such systems.

KEYWORDS: Quantum Chemistry, Benchmark Study, Diffusion Monte Carlo, Density-functional Theory, Dispersion.

Polymorphism is the ability of a material to exist in more than one crystalline state while retaining the same chemical composition, but potentially very different physical and chemical properties.^{1,2} Recently, much attention has been devoted to the discovery and synthesis of organic molecular crystals for the development of electronic devices.³⁻⁶ It has been demonstrated that the intrinsic crystallographic packing of these materials can strongly affect their overall performance for this task, and a detailed understanding of polymorphism can be of great importance.⁷

Here, we focus on the *para*-diiodobenzene (DIB) molecular crystal. DIB stands out among organic molecular semiconductors because of its remarkable charge-transport properties, having an especially high room-temperature hole mobility (>10 cm²/Vs).⁸ Moreover, it is known to pack into two different crystal lattices, known as the α and β polymorphs.^{9,10} Despite its importance in the field of organic electronics, there are surprisingly few theoretical studies in the literature which rigorously compare the two polymorphs. Brillante *et. al.*¹¹ first investigated the issue in the framework of density-functional theory (DFT).¹² They found that the α phase is less stable than the β phase by about 96 meV per unit cell at zero temperature. This contradicts experiments which demonstrate that the α phase is the most stable up to *ca.* 326 K.^{9,10} However, to the best

of our knowledge, no further theoretical studies have been carried out to accurately investigate the ground-state energies of these polymorphs. Our intention is to study the polymorphism in terms of the relative stability of the α and β phases using benchmark quantum chemical calculations.

The accurate treatment of crystalline materials is a challenging matter for theory in general.^{13,14} Moreover, benchmark studies of polymorphism confront the additional difficulty that the energy differences between polymorphs can be very small (on the order of 1 meV per atom) and at the limit of accuracy for even the most sophisticated methods. Achieving this accuracy for molecular crystals requires a careful treatment of electron correlation to allow the proper description of many interaction types, such as hydrogen-bonding, van der Waals and dispersion, as well as covalent and ionic.

Currently, DFT is the method of choice for incorporating the effects of electron correlation into molecular crystal calculations due to its extremely favorable balance between accuracy and efficiency. As a result, DFT studies have been routinely used by several groups to explore the properties of DIB, such as hole mobility.^{15,16}

Despite its success, however, DFT has some well-known weaknesses. For example, conventional functionals often fail to accurately capture noncovalent interactions, as comprehensively shown in the recent benchmark study of Zhao and Truhlar.¹⁷ In molecular crystal calculations, especially when comparing polymorphs, it is reasonable to expect that an accurate treatment of these interactions is important. Even for some covalent clusters, such as C₂₀ or B₂₀, several commonly-used functionals have been shown to be highly unreliable in predicting geometries and relative ground-state energies.¹⁸ Nevertheless, in most cases, DFT is essentially the most accurate method available due to its favorable computational cost.

Benchmark *ab initio* studies of atoms and molecules have traditionally relied on the well-known hierarchy of wavefunction-based electronic-structure methods,¹⁹ and have been very successful in the treatment of small to medium-sized systems. For solid-state materials, the lowest-order Hartree-Fock (HF) approach may be efficiently implemented in terms of crystalline orbital theory,²⁰ but this is not sufficient for benchmark investigations. Very recently, there has been

progress in extending canonical post-HF methods to the treatment of periodic systems.^{21,22} However, in general, wavefunction methods are overwhelmed by the number of degrees of freedom in these cases, and high-order treatments have been restricted to only 1 or 2-dimensions, or have introduced additional approximations.^{23–26}

An alternative class of methods exist, based on the quantum Monte Carlo (QMC) approach. QMC methods can evaluate the total energy of many-electron systems to high accuracy^{27–29} because they can explicitly take into account many-electron correlation effects at reasonable cost by means of a stochastic approach. Indeed, one of the most accurate QMC methods, diffusion Monte Carlo (DMC), has an accuracy comparable to the high-level wavefunction-based method CCSD(T) (coupled-cluster with single and double substitutions, including non-iterative triples) using a cc-pVQZ basis set.³⁰ While canonical CCSD(T) is generally unfeasible for molecular crystal calculations, DMC can be performed given sufficient computational resources, due to its linear-to-cubic scaling with respect to system size.³¹

In this letter, we benchmark the ability of some well-known DFT functionals to predict the energy ordering of the α and β polymorphs of DIB using the DMC method. This is the first time, to our knowledge, that a DMC calculation has been published for an organic molecular crystal. While DMC can only readily provide the total energy, we believe our DMC results are a valuable cornerstone for the assessment of more approximate methods and to judge their reliability for the prediction of more interesting physical properties.

We now outline the computational details we employed in our DMC and DFT calculations. Further information concerning the standard theory is readily available in the literature.^{12,27–29}

In all our DMC calculations, the core electrons of the carbon and iodine atoms were replaced with a non-local pseudopotential of the Trail-Needs type, taken from the CASINO pseudopotential library.³² To maintain fermion antisymmetry, we assumed the fixed-node approximation²⁷ in which the nodal surface is the same as the correlated trial wavefunction. We employed Slater-Jastrow trial wavefunctions, where the one-electron orbitals constituting the Slater determinant were obtained from DFT calculations using the ABINIT code^{33,34} with a plane wave basis set

(cut-off energy = 40 Hartree) and the Perdew-Wang (1992) local-density exchange-correlation functionals.³⁵ The Jastrow factor³⁶ included one- and two-body Pade-type functions, which have 6 and 4 adjustable parameters, respectively. These parameters were optimized by the variance minimization procedure.³⁷

To attain reasonably converged results, we accumulated the numerical results over 1.2×10^7 steps for both the α and β phases. A target population of 16384 random walkers was used in the DMC simulations and we adopted a time step of 0.001 a.u. All the QMC calculations were performed using the QMCPACK code.³⁸

In the DFT calculations, we considered three approximations to the exchange-correlation functional, i.e., local density approximation (LDA), generalized gradient approximation (GGA), and hybrid functionals. The LDA functional was of Ceperley and Alder type parameterized by Perdew and Zunger.³⁹ We used two commonly-used GGA functionals, namely PW91 (Perdew-Wang 91)³⁵ and PBE (Perdew-Burke-Ernzerhof).⁴⁰ The hybrid functional was B3LYP⁴¹ which is one of the most popular functionals for studying molecular systems. In addition, to explore the effect of dispersion which is not recovered using the above functionals, we also employed a London-type empirical correction as proposed by Grimme.⁴²

The DFT calculations were performed using the the CRYSTAL09 program package⁴³ using an all-electron Gaussian basis set under periodic boundary conditions with a $1 \times 3 \times 4$ Monkhorst-Pack k -point mesh for both crystalline phases. A 6-31G** basis set was used for the hydrogen and carbon atoms and a 3-21G basis for the iodine atoms. The simulation cell was the same as the QMC unit cell. Since the dispersion correction implemented in CRYSTAL09 has been mostly tested and used for molecular crystal calculations in combination with the B3LYP functional, we chose not to add the correction to the other functionals.

Due to the small energy differences, a rigorous study of the polymorph stabilities would ideally include an analysis of both finite-size errors and zero-point energy (ZPE) contributions. Such effects could be significant on an energy scale of 10meV. However, for a relatively weakly bound molecular crystal such as DIB, the majority of the ZPE would come from intramolecular contribu-

tions which should be almost the same for both polymorphs. As a result, it is reasonable to neglect the ZPE correction when predicting the relative stability, as we do here.

In the same way, due to the structural similarity of the two phases, we may also expect the majority of the finite-size errors to cancel out when computing the energy difference. In our DFT calculations we have used k -point meshes which give energies converged to less than 10 meV, but the differences between the Γ -point energies and using more k -points suggested that the finite-size error in our DMC result may be significant. To make a more accurate evaluation, we estimated the error using the *a posteriori* correction scheme of Kwee *et.al.*⁴⁴ We performed this correction using the Quantum Espresso package at the LDA level using Fritz-Haber-Institute (FHI) pseudopotentials with a cutoff energy of 50 Hartree. The result is given below.

We now describe the results of our DMC and DFT calculations of the DIB ground-state energies. The α and β polymorphs are packed into orthorhombic crystal lattices belonging to the $Pbca$ (D_{2h}^{15}) and $Pccn$ (D_{2h}^{10}) space groups, respectively.¹⁰ Both structures have four DIB molecules (48 atoms) per unit cell as shown in Fig. Figure 1, where it is also possible to see the qualitative difference between the α and β packing in terms of the orientation of the individual molecules. In the our calculations, we used both experimental and theoretically-optimized geometries. First we consider the experimental parameters, where the lattice constants and unit cell atomic positions were taken from the Cambridge Structural Database (ZZZPRO03 and ZZZPRO04 for the α and β phases, respectively; <http://www.ccdc.cam.ac.uk/>).

Fig. Figure 2 shows the energy differences between the α and β phases, $\Delta E \equiv E(\alpha) - E(\beta)$, computed with DMC and DFT, including the dispersion correction for B3LYP, labeled B3LYP+D. The DMC finite-size correction was estimated to be +50meV using the scheme of Kwee *et.al.*. Including this correction, the DMC result predicts $\Delta E = -46 \pm 37$ meV per unit cell. i.e. the α phase is more stable, in agreement with experiment. This is a very small energy difference of less than 2 meV per atom. In contrast, all the energy differences per unit cell computed with the conventional GGA and hybrid functionals are positive, ranging from 29 meV using PW91, to 68 meV using B3LYP.

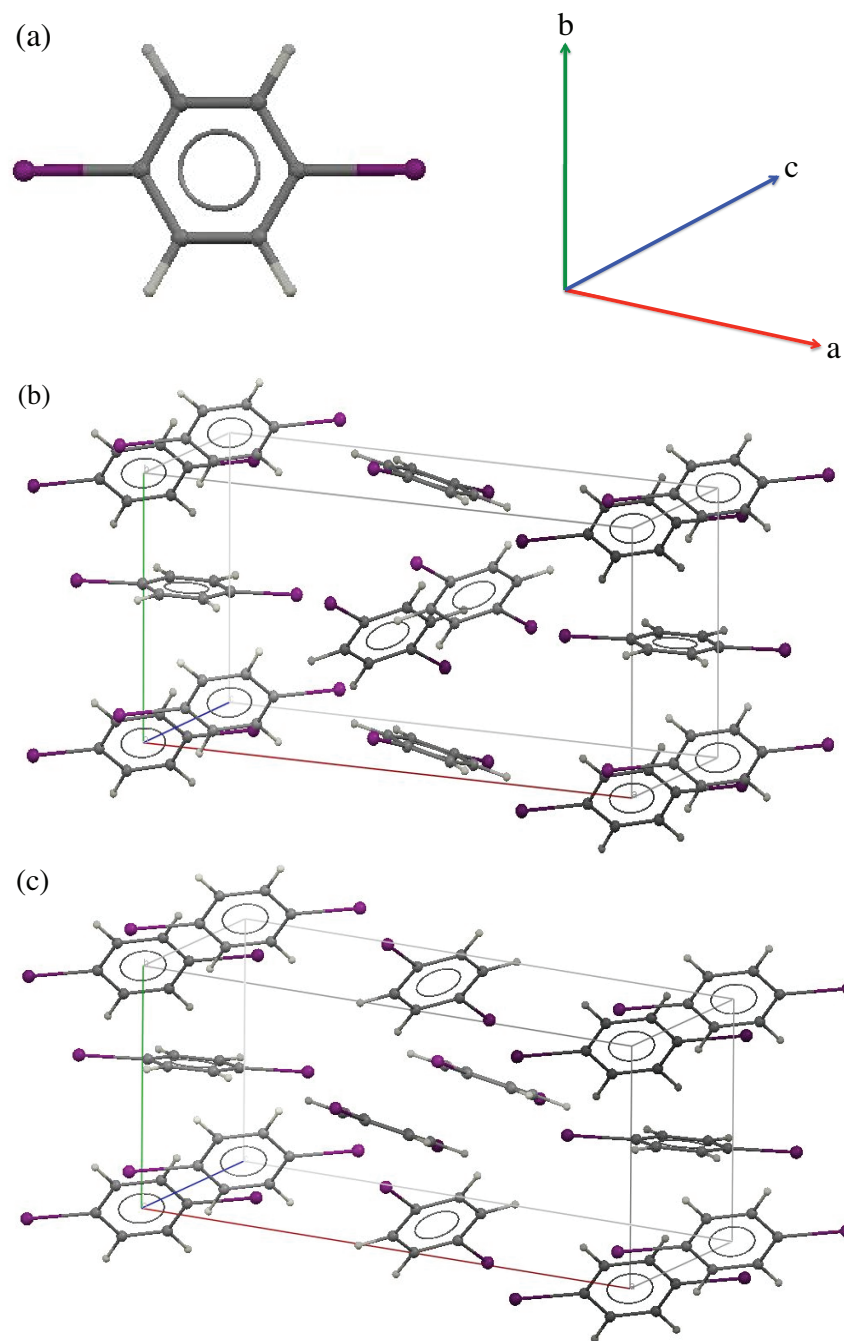


Figure 1: (a) Lattice vectors of the unit cell and the chemical structure of the DIB molecule. (b) α phase crystal structure with lattice constants: $a = 17.000$, $b = 7.323$, and $c = 6.168$ Å. (c) β phase crystal structure with lattice constants: $a = 17.092$, $b = 7.461$, and $c = 6.154$ Å.

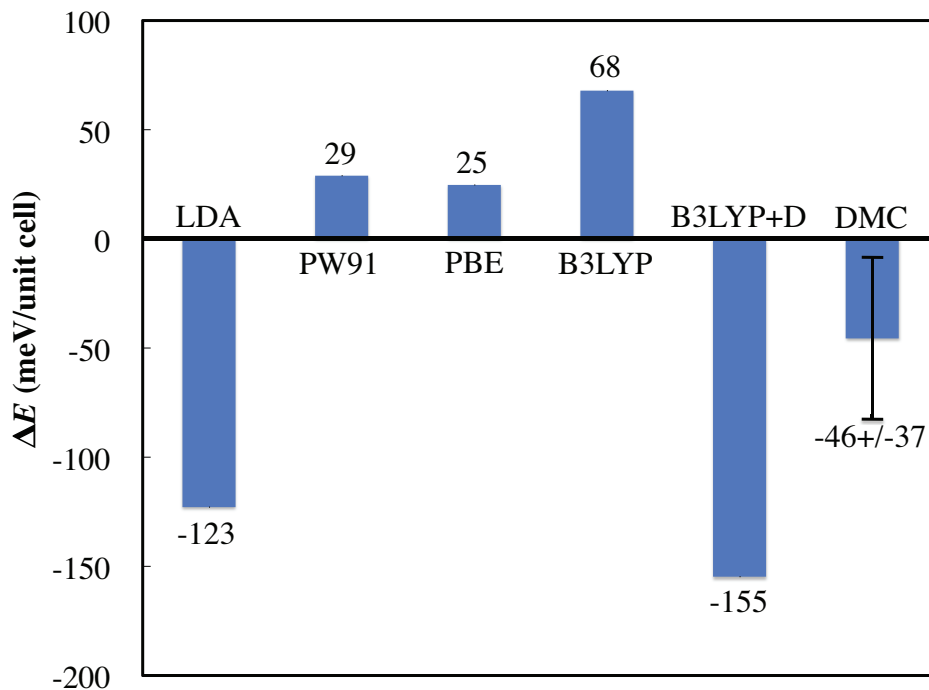


Figure 2: The energy difference between the α and β phases of DIB, $\Delta E \equiv E(\alpha) - E(\beta)$, computed with DMC and four different DFT functionals at the experimental geometry. The DMC result includes a finite-size correction of +50meV / unit cell, and the error bar is shown. In addition, the effect of adding the empirical dispersion correction to the B3LYP result is included, labeled B3LYP+D.

Table 1: DFT energy differences, $\Delta E \equiv E(\alpha) - E(\beta)$, between the α and β phases of *p*-DIB at the experimental (expt) and optimized (opt) geometries using four different functionals. In addition, the effect of adding the empirical dispersion correction to the B3LYP result is included, labeled B3LYP+D. All energies are in units of meV per unit cell.

	LDA	PW91	PBE	B3LYP	B3LYP+D
$\Delta E(\text{expt})$	-123	29	25	68	-155
$\Delta E(\text{opt})$	-129	-165	-12	-16	-163

Table 2: Optimized lattice constants and unit cell volume for the two polymorphs of DIB evaluated using four DFT functionals and compared with experiment. In addition, the effect of adding the empirical dispersion correction to the B3LYP result is included, labeled B3LYP+D. Length and volume are in units of Å and Å³, respectively.

	α phase				β phase			
	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>
LDA	16.300	6.706	5.957	651	16.391	6.788	5.964	664
PW91	18.721	8.993	5.473	921	17.506	8.175	6.091	872
PBE	18.748	8.589	5.555	894	18.498	8.116	5.815	873
B3LYP	18.620	9.733	5.756	1043	18.502	9.948	5.831	1073
B3LYP+D	16.610	6.731	6.046	676	16.966	6.791	5.998	691
Expt	17.000	7.323	6.168	768	17.092	7.461	6.154	785

Next, we investigate the sensitivity of the results to the crystal geometry. To do so, we optimize both the atomic positions and lattice constants to give a fully-relaxed structure. Due to the computational expense, this was only practical for the DFT methods. Table 1 shows the energy differences, ΔE , between the α and β phases using the experimental and optimized geometries. In fact, all five DFT results correctly predict the α phase to be more stable at the optimized geometries. Table 2 reports the optimized lattice cell parameters and unit cell volumes compared to experiment. For both phases, LDA and B3LYP+D give the most compact structures, closest to experiment, while B3LYP strongly overestimates the cell volume.

An analysis of the above results must inevitably focus on the size of the energy difference, ΔE . To accurately and rigorously predict an energy difference of order 50 meV, many factors must be carefully included in the calculation. In this work, we have explored three of the main sources of error: (1) choice of theoretical method, (2) crystal geometry and (3) finite-size effects.

While the DMC result should be of high quality, the estimated error bar in Fig. Figure 2 highlights the computational challenge. We conservatively chose a time step of 0.001 a.u. to minimize the time-step error, but in turn this required significant computational time to reduce the statistical error to within our chosen accuracy of less than 30 meV for each polymorph. A larger time-step would facilitate faster convergence of the statistical error, but could introduce unknown systematic errors. From our final error bars, the probability that the DMC ΔE value has a positive sign is

approximately 21%.

DFT is the most widely-used method for the *ab initio* treatment of molecular crystals, but it is striking that the three commonly-used GGA and hybrid functionals we tested give the wrong qualitative stability for the polymorphs at the experimental geometries. It is not surprising that PW91 and PBE give very similar results since the functionals are very closely related. B3LYP performs the worst and gives a value for ΔE more than 100meV greater than the DMC benchmark. This is significant because B3LYP is the most widely used functional in chemistry.

Perhaps the most striking results in Figure Figure 2 are the LDA and B3LYP+D values, which correctly predict the α phase to be most stable, but strongly overestimate the magnitude of ΔE in comparison to DMC. The B3LYP+D calculation suggests that an accurate treatment of dispersion is important, as we expected, and shifts the predicted stability in favor of the α phase. However, the empirical correction used here is much too large if we take the DMC result as our benchmark. It would therefore be interesting to test more sophisticated dispersion-corrected functionals, or wavefunction-based methods, to explore this issue further, and we are currently doing so.

It is well-known that LDA overbinds. At the experimental geometry, the α unit cell volume is more compact than in the β phase and the α phase is most stable at low temperature. Physically, the stability associated with the more compact unit cell is due to increased van der Waals and other noncovalent interactions. PBE, PW91 and B3LYP cannot recover this energy accurately and fail to predict the relative stability of the α phase, but the tendency for LDA to overbind seems to compensate for the lack of dispersion. Overall, the resulting error cancellation leads to the correct sign for ΔE compared to the GGA and hybrid functionals, but the result is much too negative (-123 meV) and cannot be considered reliable.

These observations are also reflected in the geometry optimizations. In Tables 2 and 3, we may notice that LDA strongly underestimates the optimized unit cell volume, consistent with the overbinding. However, the resulting $\Delta E(\text{opt})$ is very similar to $\Delta E(\text{expt})$ and both are too negative. Somewhat surprisingly, all five DFT methods give the correct sign for $\Delta E(\text{opt})$: the optimized PW91, PBE and B3LYP calculations predict the α phase to be most stable, but they also all give

too large unit cell volumes due to the lack of attractive noncovalent interactions. Moreover, using PW91 and PBE, the α cell volume is greater than the β cell volume, in contradiction with experiment. Thus the more accurate, negative $\Delta E(\text{opt})$, is likely to be fortuitous error cancellation.

More interesting is the B3LYP+D result, which introduces dispersion and dramatically reduces the cell parameters from the B3LYP values towards experiment. Unfortunately, the contraction is too severe along the b -axis and the final structure is somewhat too compact. Nevertheless, the final geometries are the closest to experiment of all five methods. As with LDA, the resulting $\Delta E(\text{opt})$ is very similar to $\Delta E(\text{expt})$, but too negative.

In light of the apparent importance of dispersion effects, it is interesting to compare our DFT results with the benchmark study of Zhao and Truhlar.¹⁷ They tested forty exchange-correlation functionals on 22 noncovalent complexes which have significant hydrogen-bonded or van der Waals interactions, including systems similar to DIB such as the benzene dimer. Overall, their estimated mean errors in the interaction energies were found to increase in the order: PW91 (90 meV), PBE (106 meV), LDA (108 meV) and B3LYP (154 meV). The main point to note is that these errors are of the same order of magnitude as the predicted ΔE energy itself. It could therefore be argued that conventional DFT functionals are not appropriate for the rigorous prediction of quantities such as ΔE in molecular crystals. Certainly, the impact of B3LYP+D in our results seems to support this view.

To conclude, we have studied the relative stabilities of two polymorphs of a molecular crystal using the DMC method. The DMC result correctly predicts that the α phase is more stable than the β phase at zero temperature. In contrast, the DFT results using four common functionals were inconsistent and inconclusive, with variations of the same order of magnitude as the energy difference itself. A proper treatment of electron correlation to include an accurate treatment of noncovalent interactions seems to be important. We hope that our work demonstrates that DMC calculations on molecular crystals which can include these effects are now feasible and can provide crucial benchmarks for testing more approximate methods.

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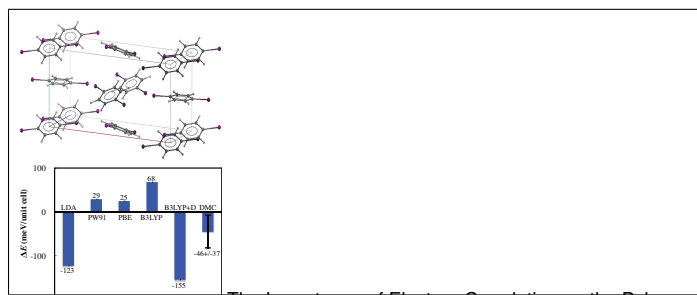
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Graphical TOC Entry



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