Density functional study of molecular crystals: Polyethylene and a crystalline analog of bisphenol-A polycarbonate

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Density functional calculations have been performed on two types of molecular crystal: (a) crystalline (orthorhombic) polyethylene comprising covalently bonded parallel chains with weak interchain interactions, and (b) a crystalline analog of bisphenol-A polycarbonate with a unit cell containing two molecules with 59 atoms each. The local density approximation for the exchange-correlation energy overestimates the strength of the intermolecular bonds in both, and the Becke–Perdew functional (gradient corrected) gives no intermolecular binding in the former and a very weak bond in the latter. The functional of Perdew, Burke, and Ernzerhof leads to binding in both molecules. © *1998 American Institute of Physics.* [S0021-9606(98)52116-2]

I. INTRODUCTION

Density functional (DF) calculations provide an economical method for calculating structural and binding properties of molecules and clusters, as well as for more traditional applications in condensed matter physics. In recent years there has been particular focus on the description of binding provided by the local spin density (LSD) approximation for the exchange-correlation (xc) energy and by its nonlocal modifications. It has been found that modifications involving gradients of the density often lead to better agreement with measured formation energies in small molecules[1] and to an improved description of hydrogen bonds.[2] Approximations involving gradient corrections that have been studied extensively include those for the exchange energy of Becke (B)[3] and for the correlation energy of Perdew (P)[4] and of Lee, Yang, and Parr (LYP).[5] Combinations of these forms for the exchange and correlation energy are often referred to as the ''BP'' and ''BLYP'' approximations.

DF calculations have often been performed for molecules and clusters containing carbon, which readily forms single and multiple bonds and is the basis of countless molecules containing rings and/or chains. Hydrocarbons are prototype organic molecules, and their polymers are among the most important. Work performed in our group and elsewhere has indicated that both LSD and gradient-corrected functionals give a reliable description of structures and rotation barriers in small organic molecules[6] and in chains like polypropylene,[7] although both approximations tend to underestimate reaction barriers.[8] In a recent study of the *interchain* interactions in crystalline polyethylene (PE),[9] we showed that the LD approximation overestimated the strength of the interchain interactions, while the gradient-corrected form BP led to a complete absence of binding between the chains. Similar results were found in other studies of the interactions between rare gas atoms (BP and others)[10] and between two benzene molecules (B, BLYP).[11]

Here we extend our earlier work on PE in two directions. First, we add the approximation developed recently by Perdew, Burke, and Ernzerhof (PBE)[12] to the xc-energy functionals we study. Recent tests of this functional for first- and second-row dimers, rare-gas diatomic molecules, and polyatomic molecules,[13] as well as Si clusters and crystalline C, Al, Si, and GaAs,[14] showed improvements in the calculated formation energies similar to those found previously with other gradient-corrected functionals. Second, we have used all three functionals in calculations of the diphenyl carbonate of 2,2-bis(4-hydroxyphenol)propane. This crystal, which we refer to as C-PC, is a molecular analog of bisphenol-A polycarbonate (BPA-PC). The glassy form of the latter is an important engineering thermoplastic with uses in fields as disparate as compact disks, mobile telephones, and artificial kidneys. Previous calculations on the glass include static molecular modeling[15] and a molecular dynamics (MD) calculation using a parametrized force field.[16] Quantum mechanical calculations have been performed on fragments of the monomer,[17] but we know of no studies of either monomer or glass that are free of adjustable parameters.

The molecular units of C-PC comprise 59 atoms and are shown in Fig. 1. The extended head-to-tail arrangement of the molecules in the crystal is shown in Fig. 2 and has obvious parallels to the periodic propagation of a linear polymer. The crystal has two molecules in a monoclinic unit cell[18] and differs markedly from PE. The structural units are localized to a single unit cell, and the presence of phenylene rings and oxygen atoms (in the carbonyl groups) gives rise to different types of intermolecular bond. The calculations for C-PC then extend significantly both the range of complexity and the type of interaction for which these xc approximations have been investigated.

We provide essential details of the calculations in Sec. II and compare the results with experimental geometries in Sec. III. We summarize and discuss our findings in Sec. IV. A second crystalline analog of BPA-PC—with 236 atoms in the unit cell[19]—is both more mobile and energetically more stable than C-PC. We are studying its structure and bonding

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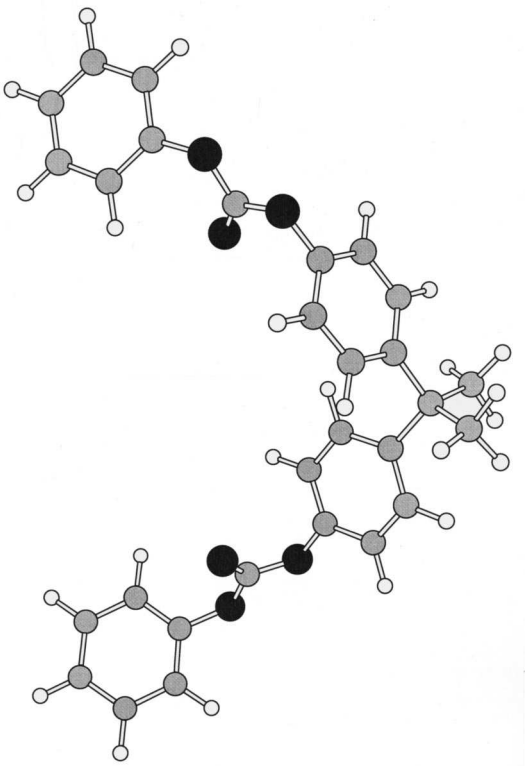

FIG. 1. Structural units in C-PC. Carbon atoms are grey, oxygen atoms black, and hydrogen atoms white.

properties and shall present the results elsewhere.

II. METHOD OF CALCULATION

We optimize the atomic positions at fixed volume and shape of the unit cell by minimizing the forces on all atoms, following the method described in detail previously.[7,9] The electron-ion interaction is represented by ionic pseudopotentials with the (non-local) form suggested by Troullier and Martins.[20] We use s-nonlocality for the O atom. Detailed tests of the convergence of the plane wave basis for small organic molecules[6] and PE[7] showed that reliable energy differences can be obtained using a kinetic energy cutoff of 30 a.u. for systems containing H and C, while 35 a.u. are required for comparable accuracy in computations involving O.

We assume periodic boundary conditions in three dimensions and adopt the smallest unit cell consistent with the experimental structure. In the case of PE, the integration in reciprocal space employed the special points technique.[21] Six **k** points give a well-converged total energy and were used to obtain the results presented here. Atomic positions were optimized by the conjugate gradient method. All lattice constants in PE were varied independently, so that the energy was minimized as a function of *all* atomic positions in this case.

The crystal structure of C-PC has 118 atoms in the unit cell, and we have optimized the structure using a combination of DF calculations with MD[22] and a simulated annealing strategy. The summation in **k** space is performed using a single point ($\mathbf{k}=0$) in the Brillouin zone, although we discuss below the effect of increasing the number of points. The calculations are computationally extremely demanding, and we have limited the optimization of the structure of C-PC to uniform expansions of the unit cell. There are no dominant directions in the inter-molecular interactions in this structure, which is quite different from that of crystalline PE, where the chains cross the unit cell boundaries and the total energy varies very anisotropically with changing unit cell size.

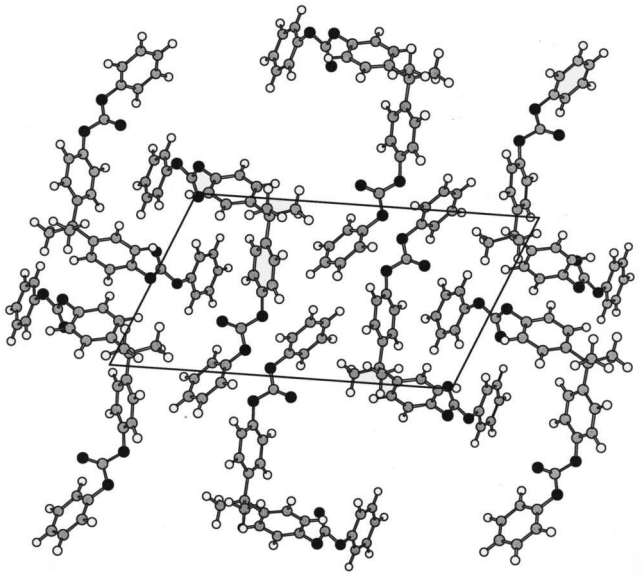

FIG. 2. Projection of the monoclinic structure of C-PC onto the ac plane. Carbon atoms are grey, oxygen atoms black, and hydrogen atoms white.

Additional calculations show that our optimization method leads to structures with energies that are very close to the minimum. First, the structures obtained by minimizing the energy with all the angles defining the unit cell equal to 90° are very close to those found with the (monoclinic) cell, and the energies are only slightly higher. Second, variation of the monoclinic angle around the experimental value (110.63°)[18] causes only a small change in the energy. These and other tests indicate that, for a given unit cell volume, variation of the lattice constants changes the *packing* of the molecules more than their individual structures. The main changes in the latter are in the dihedral angles.

The calculations were started for each functional using the unit cell parameters and atomic coordinates determined from x-ray diffraction data.[18] The simulations were then allowed to proceed without constraint (on symmetry or otherwise) until the magnitude of the *maximum* force on any atom was less than 2.5×10^{-4} a.u. and the *average* force on the atoms was an order of magnitude less. The accuracy of the energy calculation was checked in two ways: The effect of increasing the number of **k** points was emulated by doubling the shortest lattice constant ($b=6.385$ Å, normal to the plane of Fig. 2), and the convergence of the plane-wave expansion was tested by increasing the cut-off energy to 80 Ry. As a result of these tests we estimate the error bar in the energy calculations to be at most 0.1 eV. The energies shown below were calculated with the larger unit cell and the larger (80 Ry) cut-off.

TABLE I. Structural parameters of crystalline PE from x-ray diffraction, and calculated structures for a single chain. Bond lengths are in Å, angles in degrees. Values marked with an asterisk (*) were assumed, and not measured directly.

	r_{CC}	r_{CH}	α_{CCC}	α_{HCH}
X rays[a]	1.534±0.006	1.09*	112.0±0.3	109.5*
X rays[b]	1.533±0.022	1.07±0.022	111.9±1.8	107.0±1.8
X rays[c]	1.527±0.007	1.091*	112±0.8	···
LDA	1.512	1.111	114.3	105.2
BP	1.536	1.111	113.8	105.6
PBE	1.523	1.110	113.0	105.8

[a]Reference 23, monoclinic *n*-hexatriacontane $C_{36}H_{74}$.
[b]Reference 24, orthorhombic *n*-hexatriacontane $C_{36}H_{74}$.
[c]Reference 25.

We have studied three approximations for the xc-energy functional. The ''LSD'' approximation is based on accurate calculations of the xc-energy density in a homogeneous, spin-polarized electron gas (there is no spin contribution in the present case, and we refer to the ''LD'' approximation), the gradient-corrected ''BP'' functional has the exchange and correlation parts due to Becke[3] and Perdew,[4] respectively, and the most recent ''PBE'' form[12] is both relatively simple and free of empirical input. Like the BP functional, this form has a correction to the LSD approximation that depends on the gradient of the local density. However, it incorporates an accurate description of the linear response of the uniform electron gas, and it has a smoother potential and the correct behavior under uniform scaling. The present work appears to be the first application of the PBE approximation to intermolecular forces.

III. RESULTS: GEOMETRICAL STRUCTURES

Polyethylene: The optimized structures calculated for a single chain with LD, BP, and PBE approximations are compared in Table I with experimental values for crystalline PE.[23–25] A comparison with earlier calculations was given in Ref. 9. Although gradient corrections increase the C-C bond length by $\sim 1\%$, the experimental uncertainties mean that all three functionals give reasonable agreement with the measured values. The same is true if we optimize the PE structures in the orthorhombic crystalline form (Table II).

TABLE II. Comparison of measured (x-ray diffraction) and calculated (LDA) lattice constants and interchain distances in PE. The shortest distance between C atoms in different chains is $d_{(C\ldots C)}$, and ϕ is the angle between the ac-plane and the plane of the C atoms in the chain [see Ref. 9]. Distances are in Å, angles in degrees.

Method	a_0	b_0	c_0	ϕ	$d_{(C\ldots C)}$
X rays[a]	7.42±0.01	4.945±0.01	2.546±0.004	41.4	4.14
X rays[b]	7.42±0.01	4.96±0.01	···	47.7	4.15
X rays[c]	7.388±0.008	4.929±0.004	2.539±0.002	45	4.59
LDA	6.73	4.53	2.52	41.3	3.67
PBE	8.28	5.64	2.57	47.4	4.66

[a]Reference 23, monoclinic *n*-hexatriacontane $C_{36}H_{74}$.
[b]Reference 24, orthorhombic *n*-hexatriacontane $C_{36}H_{74}$.
[c]Reference 25.

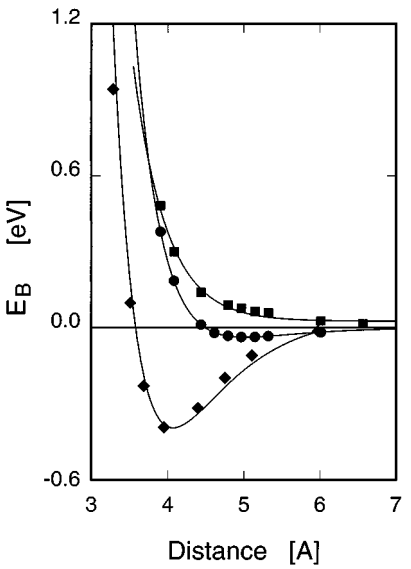

FIG. 3. Binding energy of PE (in eV per unit cell) as a function of interchain separation (in Å) for LD (diamonds), BP (squares), and PBE (circles) approximations.

Structural optimization leads, however, to strikingly different results for the *inter*chain separations. The LD calculations yielded a well-defined minimum in the binding energy curve (Fig. 3), with an interchain separation $\sim 9\%$ (Table II) less than the experimental value. The BP binding energy curve, by contrast, shows no minimum (Fig. 3), and there is a weak minimum in the case of the PBE functional corresponding to an interchain distance 12% larger than the measured value. There are small differences between the density distributions found using the LD and gradient-corrected approximations. Compared with the LD densities for the measured geometry of PE, for example, both BP and PBE functionals lower the electron density slightly between the C atoms and between the chains. There is also a small overall transfer of electrons from the neighborhood of the C nuclei towards the H nuclei.

Polyethylene was the first organic polymer for which band structures were reported, based on angle-resolved photoemission from oriented films of *n*-hexatriacontane $[CH_3(CH_2)_{34}CH_3]$. In Ref. 9, we showed that the energy bands calculated for a single chain using the LD and BP approximations are in good overall agreement with each other and with earlier band structure calculations. The band structure for the PBE functional has been calculated using large lattice parameters in the two directions perpendicular to the chain axis. The minimum distance between neighboring chains was 6.013 Å, so that the calculations are representative of a single PE chain. A comparison of the valence band structures for the different functionals showed that the eigenvalues obtained using BP and PBE functionals coincide to within 0.14 eV throughout the Brillouin zone. Close agreement between the LD and PBE band structures has also been found for bulk Si.[14]

Polycarbonate C-PC: The binding energy of C-PC for the LD, BP and PBE approximations—relative to the energy of two isolated 59-atom units—is shown in Fig. 4. The shape

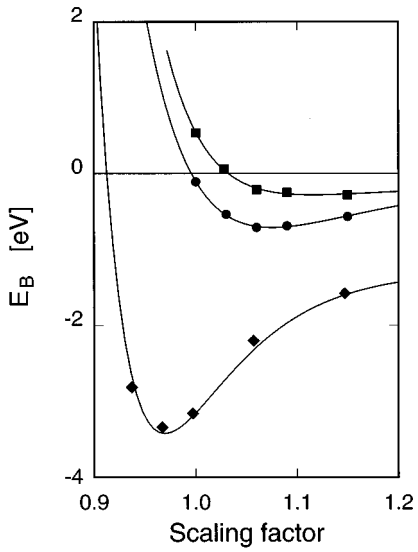

FIG. 4. Variation of binding energy of C-PC (in eV per unit cell) as a function of linear dimension scaling factor for constant unit cell shape for LD (diamonds), BP (squares), and PBE (circles) approximations.

of the unit cell is held constant, and the abscissa is the scaling factor for the linear dimensions, with unity corresponding to the experimental structure. The three curves differ significantly, as in the case of PE, but all lead to a finite equilibrium volume and a positive cohesive energy. The LDA calculation underestimates the equilibrium volume (the scaling factor is 0.97) and predicts a cohesive energy of 3.4 eV per unit cell. The equilibrium volumes for the BP and PBE are larger, with the optimum scaling factors found by fitting the energy curves with a Morse potential (also shown in Fig. 4) are 1.08 and 1.12, respectively. Although the two gradient-corrected functionals have similar forms and lead to similar equilibrium densities, the cohesive energy predicted by the PBE functional (0.78 eV) is almost three times the BP value (0.28 eV). An experimental estimate of the cohesive energy of C-PC would provide a useful criterion for preferring a functional form for describing such molecules. We are not aware of such a measurement, but we note that the PBE functional leads to a unit cell volume in better agreement with experiment than the BP value.

The bonds *between* the molecules are particularly interesting. The BP approximation gives purely repulsive $E(V)$ curves in systems with van der Waals bonds,[10] so that the cohesion predicted in C-PC suggests the presence of weak bonds of another type. The complexity of the structure makes it difficult to identify the nature of these bonds, but we have performed an extensive series of calculations that have provided insight.

We note first that the isolated 59-atom structural unit has a significant dipole moment (6.6 D) that could contribute to the cohesion of the solid. The overall dipole moment of the two molecules in the unit cell is much smaller (2.7 D), so that the long-range dipole-dipole interaction contributes little to cohesion. The contribution from dipole-quadrupole interactions may be more significant. Interesting information can also be found by observing the structural changes that occur during the uniform dilation of the unit cell. The most striking is that some distances between atoms in different molecular units *decrease* with increasing volume, indicating the presence of bonding. The effect is localized to specific pairs of atoms, one of which is hydrogen in each case. These H atoms are bound to a C atom, so that the ''bonds'' to the neighboring molecule are not traditional hydrogen bonds connecting two highly electronegative atoms. Analysis of the structure of the separated 59-atom structural units also revealed short distances between O atoms (in the carbonyl group) and H atoms in the phenylene group. Other short distances occur between H atoms and the aromatic bonds in the phenylene group. The cohesion in both crystalline forms of C-PC arises from a number of weak bonds, rather than from single strong bonds, and we shall provide further details in a subsequent paper.

A comparison of the structures at the experimental unit cell volume showed that the geometries calculated with all three functionals agree well with experiment. For other unit cell volumes there was close agreement between BP and PBE structures, with the LD structures showing familiar differences, including a general shortening of intramolecular bond lengths.

IV. CONCLUDING REMARKS

Previous density functional calculations on single chains of polyethylene (PE) and the orthorhombic crystalline form—using the local density and Becke–Perdew forms of the exchange-correlation energy—have been extended to the approximation proposed recently by Perdew, Burke, and Ernzerhof[12] and to a crystalline analog (C-PC) of bisphenol-A polycarbonate (BPA-PC). The latter has two structural units (59 atoms each) in the unit cell. We find that:

(1) The LD approximation leads to smaller unit cells than those found experimentally, i.e., it overestimates the strength of the intermolecular bonds.
(2) The BP functional leads to *no binding* between the parallel chains in PE and to a very weak bond (<0.3 eV per unit cell) in the polycarbonate.
(3) The PBE form leads in PE to a local minimum in the energy corresponding to an interchain separation 12% greater than the measured values. In C-PC there is an analogous overestimate (22%) of the unit cell volume with minimum energy.

Related results for the LD and gradient-corrected functionals had been found in calculations on other systems, such as rare gas dimers and two benzene molecules, whose binding is viewed to arise from ''van der Waals'' forces. The overestimate of the strengths of such bonds is a well-known deficiency of the LD approximation,[26] and has provided an incentive for developing improved functionals. The BP approximation does not lead to binding in these systems, so it does not fulfill this hope in the context of intermolecular forces. The PBE approximation, on the other hand, led to good results in the same rare gas dimers and to binding in both systems considered here. It is obvious that non-local interactions of van der Waals type are not included in the LD

or gradient-corrected functionals, so that the modest underestimates of bond strengths found in PBE calculations is an encouraging trend.

The focus of the present work has been on the description of intermolecular bonding provided by different xc-energy functionals, and a detailed study of the energy surfaces of both C-PC forms will be given elsewhere. We conclude with two observations: (1) Earlier work has shown that the LD and BP approximations to the xc-energy gave reliable predictions of the structures and rotation barriers in *isolated* organic molecules[6] and chains.[7] We have found here that LD, BP, and PBE approximations reproduce the measured geometries very well if the unit cell is *constrained* to have the experimental dimensions. The same result had also been found in LD calculations on *trans*-polyacetylene[27] and poly(*para*-phenylene).[28] It is often difficult to measure the precise locations of the atoms in the unit cell of complex systems, and DF calculations should play a valuable role in obtaining reliable structural information. (2) Structural optimization for C-PC was carried out for each unit cell size using a simulated annealing strategy with thousands of time steps. An important result of this work is that present-day computers allow such calculations to be performed on complex molecular systems without adjustable parameters. Our ongoing work on the second crystalline form of C-PC shows that such calculations are also practicable for systems with twice as many atoms (236) in the unit cell.

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