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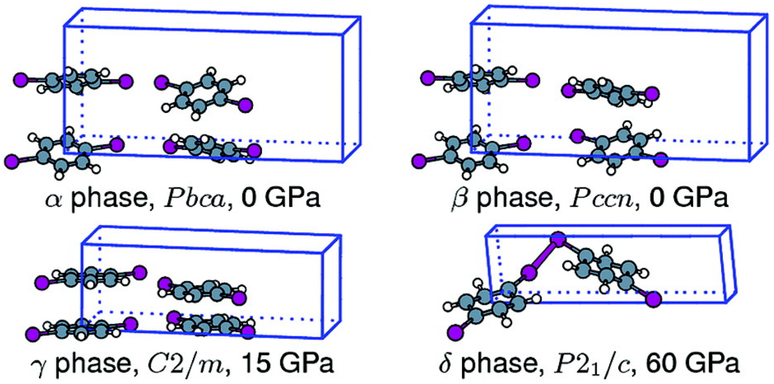

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High-Pressure Dissociation of Crystalline *para*-Diiodobenzene: Optical Experiments and Car−Parrinello Calculations

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Abstract: We have investigated the high-pressure properties of the molecular crystal *para*-diiodobenzene, by combining optical absorption, reflectance, and Raman experiments with Car−Parrinello simulations. The optical absorption edge exhibits a large red shift from 4 eV at ambient conditions to about 2 eV near 30 GPa. Reflectance measurements up to 80 GPa indicate a redistribution of oscillator strength toward the near-infrared. The calculations, which describe correctly the two known molecular crystal phases at ambient pressure, predict a nonmolecular metallic phase, stable at high pressure. This high-density phase is characterized by an extended three-dimensional network, in which chemically bound iodine atoms form layers connected by hydrocarbon bridges. Experimentally, Raman spectra of samples recovered after compression show vibrational modes of elemental solid iodine. This result points to a pressure-induced molecular dissociation process which leads to the formation of domains of iodine and disordered carbon.

I. Introduction

Pressure-induced metallization has been observed in several organic crystals such as Bechgaard salts.[1] Metallization in *monomolecular* organic compounds is still a debated question, due to the competition between chemical effects (high-pressure condensation or dissociation of unsaturated bonds) and physical effects (band gap closure and enhanced density of states at the Fermi level), which is discussed already in early reports.[2] Among monomolecular organic crystals, metallization has been recently reported for iodine-based compounds, such as iodanil[3−5] ($C_6I_4O_2$) at 30 GPa and hexaiodobenzene[6−8] (C_6I_6) at 35 GPa. The presence of iodine atoms bonded to aromatic rings seems to favor metallization, possibly by means of a dissociation process in which metallic domains of solid iodine are eventually formed. However, the mechanism of the insulator−metal transition has not been clarified yet. In fact, while the molecular character of iodanil is claimed to be retained in the metallic state,[3,4] hexaiodobenzene is found to undergo molecular dissociation.[6] The latter observation would be directly related to the interlayer compounds formed by I_2 and aromatic molecules.[9,10] A recent theoretical study[11] suggests that metallization of iodanil occurs via a band edge overlap in the molecular phase, but the same mechanism cannot be invoked for hexaiodobenzene, for which a structural transformation is likely to occur. Loss of molecularity is a likely event at high pressures, due either to breaking of unsaturated chemical bonds (dissociation)[12] or to increased chemical reactivity of nearby molecules with formation of intermolecular networks of molecular units (condensation).[13−17]

The present study is addressed to *para*-diiodobenzene ($C_6H_4I_2$). In light of what has been reported for iodanil and hexaiodobenzene, this system is undoubtedly a promising candidate for

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(1) Vescoli, Y.; Degiorgi, L.; Henderson, W.; Grüner, G.; Starkey, K. P.; Montgomery, L. K. *Science* **1998**, *281*, 1181.

(2) Drickamer, H. G.; Frank, C. W. *Electronic transitions and the high pressure chemisty and physics of solids*; Chapman and Hall: London, 1973; pp 185−209.

(3) Nakayama, A.; Fujihisa, H.; Aoki, K.; Shirotani, I. *Synth. Met.* **1999**, *103*, 1901 and references therein.

(4) Nakayama, A.; Aoki, K.; Matsushita, Y.; Shirotani, I. *Solid State Commun.* **1999**, *110*, 627.

(5) Shirotani, I.; Hayashi, J.; Yakushi, K.; Takeda, K.; Yokota, T.; Shimizu, K.; Amaya, K.; Nakayama, A.; Aoki, K. *Physica B* **2001**, *304*, 6.

(6) Nakayama, A.; Aoki, K.; Carlòn, R. P. *Phys. Rev. B: Condens. Matter* **2001**, *64*, 064104.

(7) Nakayama, A.; Fujihisa, H.; Takemura, K.; Aoki, K.; Carlón, R. P. *Synth. Met.* **2001**, *120*, 767.

(8) Iwasaki, E.; Shimizu, K.; Amaya, K.; Nakayama, A.; Aoki, K.; Carlón, R. P. *Synth. Met.* **2001**, *120*, 1003.

(9) Kuhlman, M. I.; Drickamer, H. G. *J. Am. Chem. Soc.* **1972**, *84*, 8325.

(10) Teitelbaum, R. C.; Ruby, S. L.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 7568.

(11) Tateyama, Y.; Ohno, T. *J. Phys.: Condens. Matter* **2002**, *14*, 10429.

(12) Yakusheva, O. B.; Yakushev, V. V.; Dremin, A. N. *High Temp. High Press.* **1971**, *3*, 261.

(13) Nicol, M.; Yin, G. Z. *J. Phys. (Paris)* **1984**, *C8−45*, 163.

(14) Brillante, A.; Syassen, K.; Hanfland, M.; Hocker, J. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 331.

(15) Ciabini, L.; Santoro, M.; Bini, R.; Schettino, V. *J. Chem. Phys.* **2002**, *116*, 2928.

(16) Pruzan, P.; Chervin, J. C.; Thiéry, M. M.; Itié, J. P.; Besson, J. M.; Forgerit, J. P.; Revault, M. *J. Chem. Phys.* **1990**, *92*, 6910.

(17) Farina, L.; Syassen, K.; Brillante, A.; Della Valle, R. G.; Venuti, E.; Karl, N. *High-Pressure Res.* **2003**, *23*, 349.

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an insulator to metal transition. *para*-Diiodobenzene (pDIB) has been the object of a series of investigations concerning Raman phonon spectra as a function of pressure up to 7.5 GPa[18,19] which hinted at the occurrence of phase transitions even at moderate pressures. Lattice dynamics calculations with empirical atom−atom potentials were employed to model crystallographic structures and phonons as a function of pressure and temperature. We now aim to advance the discussion by linking new experimental observations at high pressures to the results of ab initio Car−Parrinello molecular dynamics (MD) simulations[20] covering pressures up to 100 GPa.

On the experimental side, we show by optical reflectance and absorption spectroscopy that pDIB approaches metallization at around 60 GPa. However, Raman spectra of samples recovered after compression to ≥40 GPa unambiguously show that molecular dissociation takes place in highly compressed pDIB. A possible scenario is the formation of domains of elemental iodine and graphitic carbon (sp^2 hybridization). At lower pressures, at least up to 21 GPa, the molecular identity of pDIB is fully retained, as confirmed by the persistence of intramolecular modes in Raman spectra. The theoretical calculations closely follow the experimental findings, indicating that above 40 GPa a transition occurs to a phase in which the character of molecular crystal of pDIB is lost. The new phase, constituted by an extended three-dimensional network where the iodines form bonded layers perpendicular to the longest cell axis, is characterized by the closure of the electronic gap between the valence and conduction bands at high pressure.

II. Experiments

Single crystals of pDIB were grown from commercial powder (Fluka Chemie, purity >98%) by sublimation in a vacuum or crystallization from CH_2Cl_2. Optical absorption, reflection, and Raman spectra at high pressure were measured in diamond anvil cells using diamonds with different culet sizes, depending on the pressure range. For the Raman and optical absorption experiments, a 4:1 methanol-ethanol mixture provided hydrostatic environment at least up to 10 GPa. Reflectivity experiments up to 80 GPa were performed using diamonds with a culet of 0.2 mm. No pressure medium was used in this case, i.e., deviations from hydrostaticity are largely determined by the shear strength of pDIB. The ruby luminescence method was used to measure the pressure.[21,22] Raman scattering was detected by excitation at the 647.1 nm line of a krypton laser using a Jobin-Yvon T64000 triple spectrometer. Reflection and absorption spectra were collected with a micro-optical bench similar to that described in ref 23.

Optical microscopy observations revealed striking color changes in the pDIB sample: from transparent (ambient *P*), to orange/red (20−30 GPa), to brownish at higher pressures. Above 40 GPa our sample was no longer transparent to the visible light.

Optical absorption spectra of pDIB up to about 30 GPa are shown in Figure 1. The spectra were measured in the range 0.6−4.0 eV using pDIB platelets of about 50 μm size. An absorbance level equal to one is used to determine the shift of the HOMO−LUMO transition energy with pressure, as reported in Figure 2.

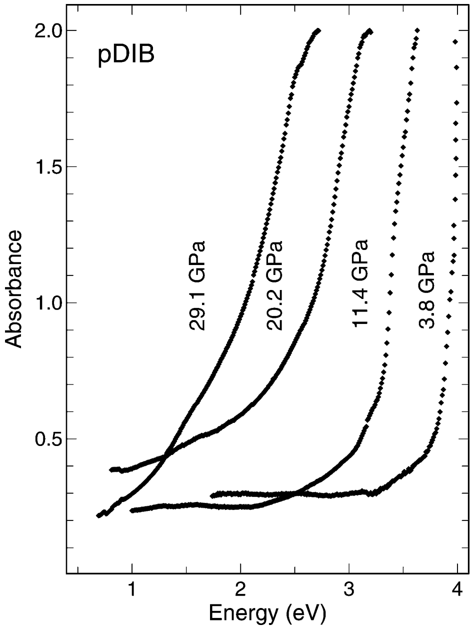

Figure 1. Absorbance spectra of a thin platelet of *para*-diiodobenzene measured at different pressures in a diamond anvil cell. The spectra are not corrected for reflection losses at interfaces.

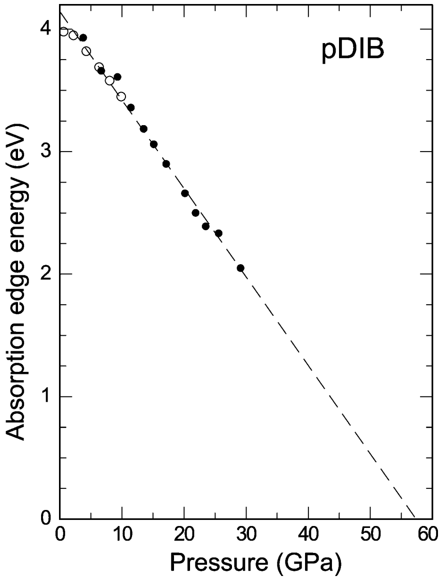

Figure 2. Energy of the optical absorption edge of *para*-diiodobenzene as a function of pressure for two different samples (different symbols). The energy corresponds to a measured absorbance level $A = 1$. The dashed line with slope −0.066 eV/GPa represents a linear extrapolation of the edge shift.

The optical gap decreases nearly linearly with pressure in the whole observed range, a behavior that indicates that the molecular character of pDIB is maintained all the way up to 30 GPa. As shown in Figure 2, linear extrapolation indicates that, in the absence of major phase changes, gap closure would not be expected at a pressure less than 60 GPa.

To investigate the possible metallization accompanying the optical gap reduction with pressure, we have performed reflec-

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(18) Farina, L.; Palazzi, L.; Venuti, E.; Della Valle, R. G.; Brillante, A. *J. Phys. Chem. A* **2000**, *104*, 11070.
(19) Della Valle, R. G.; Brillante, A.; Venuti, E.; Palazzi, L. *Chem. Phys. Lett.* **2000**, *325*, 599.
(20) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.
(21) Piermarini, G. J.; Bloch, S.; Barnett, J. P.; Forman, R. A. *J. Appl. Phys.* **1975**, *46*, 277.
(22) Mao, H. K.; Xu, J.; Bell, P. M. *J. Geophys. Res.* **1986**, *91*, 4673.
(23) Syassen, K.; Sonnenschein, R. *Rev. Sci. Instrum.* **1982**, *53*, 644.

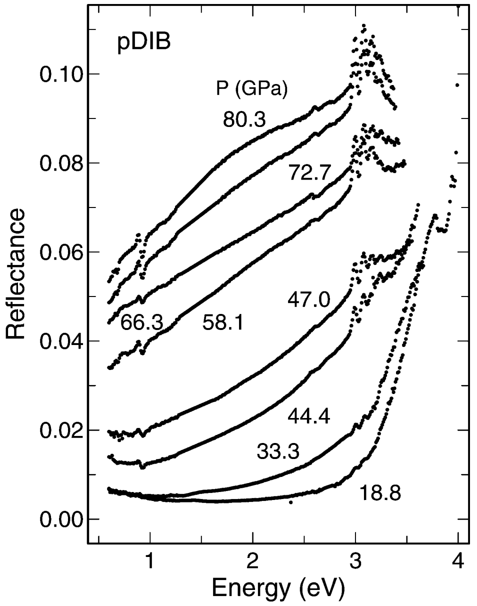

Figure 3. Reflectance spectra of *para*-diiodobenzene at selected pressures (indicated in GPa within the body of the figure). The reflectance refers to the sample−diamond interface. The small peak near 1 eV is the overtone of the O−H stretching from atmospheric moisture. The oscillations near 3 eV are instrumental artifacts.

tivity experiments up to 80 GPa. Like in semiconductors,[24] an enhanced NIR reflectance signal due to a Drude-like contribution might be expected in the low-energy side of the spectrum above a pressure-induced insulator−metal transition. Normalized reflectivity data are reported in Figure 3. Up to 18 GPa all spectra show a low signal as a result of small refractive index differences between sample and diamond. Above 33 GPa the overall reflectance starts to increase on increasing pressure, showing an abrupt jump between 47 and 58 GPa. The increase in the visible and near-infrared reflectivity can be attributed to the shift of optical oscillator strength toward lower energy. At the maximum pressure of 80.3 GPa there is no clear indication of free carriers seen in the near-infrared range. Several hours of laser illumination at 80 GPa produce slightly higher reflectivity. When pressure was reduced from 80 GPa to ambient conditions, the sample remained nontransparent in the visible and showed a grayish luster.

In a recent work[18] we reported detailed lattice phonon Raman spectra of pDIB up to 7.5 GPa and discussed the possibility of pressure-induced phase transitions below 2 GPa. We have now extended the measurements up to 21.2 GPa. Selected Raman spectra are displayed in Figure 4. The important modifications of spectral profiles under pressure are mostly due to the spreading of bands at high pressure[25] and to the increased coupling between inter- and intramolecular Raman-active modes.[19] In the context of the present work, the most significant observation in the spectra reported in Figure 4 is that the molecular identity of pDIB is maintained at least up to 21 GPa, as evidenced by the persistence of the same set of intramolecular modes at all pressures. The complete pressure dependence of vibrational modes will be discussed in more detail elsewhere.

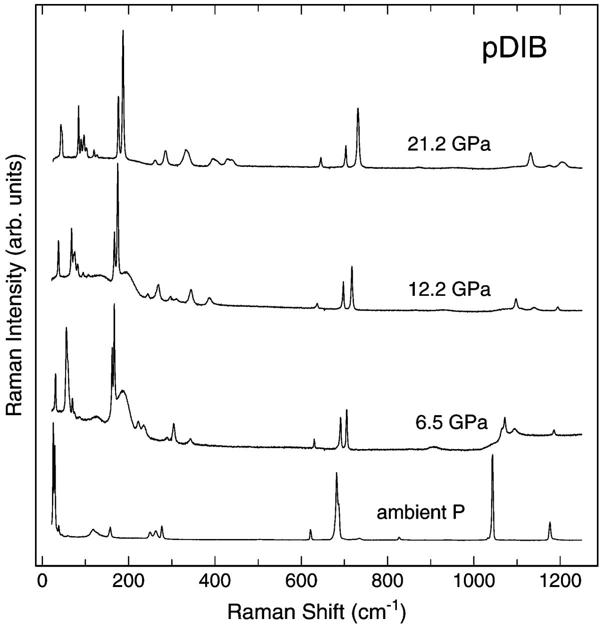

Figure 4. Raman spectra at selected pressures for *para*-diiodobenzene.

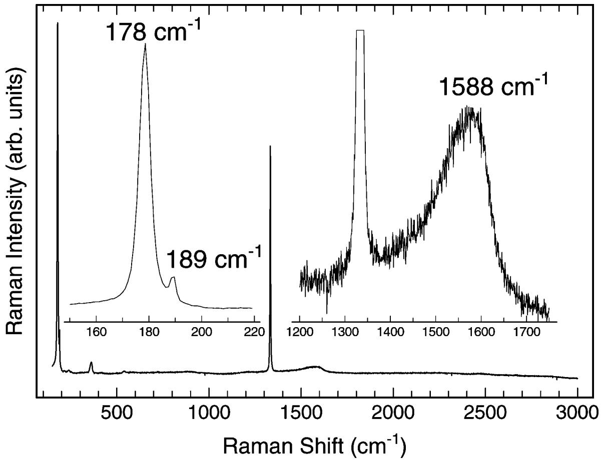

Figure 5. Raman spectrum of *para*-diiodobenzene recovered at 0.3 GPa after compression up to 50 GPa. The two enlargements show features matching the spectra of crystalline I_2 and disordered carbon, as discussed in the text. The peak near 1300 cm^{-1} in the right inset is due to the diamond window.

Samples recovered after pressure cycling beyond 40 GPa were also analyzed by Raman spectroscopy. A typical spectrum, reported in Figure 5, refers to a crystal recovered at 0.3 GPa after a pressure cycle up to 50 GPa. The bands at 178 and 189 are the fingerprints of crystalline I_2, corresponding to in-phase and out-of-phase stretching modes,[26] respectively, whereas the weaker band at about 360 cm^{-1} is assigned to an overtone.[27] These spectral features are reminiscent of the product obtained by unloading hexaiodobenzene after compression up to 47 GPa.[6] Moreover, the enlargement of the same figure shows the additional weaker band at 1588 cm^{-1}, which is attributed[28] to the C−C bond stretchings of a graphitic structure formed after the high-pressure dissociation.

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(24) Goñi, A. R.; Syassen, K. In *Semiconductors and Semimetals*; Suski, T., Paul, W., Eds.; Academic Press: New York, 1998; Vol. 54, pp 247−425.

(25) Weinstein, B. A.; Zallen, R. In *Light scattering in solids*; Cardona, M., Günterodt, G., Eds.; Springer-Verlag: Berlin, 1984; Vol. 4.

(26) Congeduti, A.; Nardone, M.; Postorino, P. *Chem. Phys.* **2000**, *256*, 117.

(27) Congeduti, A.; Postorino, P.; Nardone, M.; Buontempo, U. *Phys. Rev. B* **2001**, *65*, 014302.

(28) Schindler, T. L.; Vohra, Y. K. *J. Phys.: Condens. Matter* **1995**, *7*, L637.

III. Calculations

A. Methods. We have simulated the behavior of pDIB at different pressure regimes using Car−Parrinello MD[20] with variable cell.[29] This technique allows phase transitions, with changes in the symmetry, geometry, and chemical structure of the unit cell, to take place in a simulation run. In fact, the six independent cell parameters, along with the positions of all the atoms, are independent variables that evolve following an equation of motion defined by the Parrinello−Rahman Lagrangian.[30] The simulation cell contains 96 atoms (initially arranged as eight molecules), with periodic boundary conditions. A plane-wave basis set with an energy cutoff of 80 Ry is used for the representation of the electronic wave functions. Only valence electrons are considered in the solution of the electronic problem, while the interactions with the core electrons are taken into account using ab initio norm-conserving atomic pseudo-potentials in the form of Troullier−Martins.[31] Exchange and correlation energy contributions are evaluated using the Becke−Lee−Yang−Parr BLYP functionals.[32]

B. Simulation Procedures in the *PT* Space. As the starting point of our simulations, we have taken the experimental crystallographic structures of pDIB.[33,34] At ambient pressure, pDIB is known to exhibit two crystalline phases, α and β, with space group *Pbca* (D_{2h}^{15}) and *Pccn* (D_{2h}^{10}), respectively.[33,34] Both structures are orthorhombic and contain four molecules per unit cell, located on inversion centers. The α phase is stable up to 326 K, where a transition to the β phase occurs. Both phases are predicted to be *mechanically* stable, as we have theoretically found by fully relaxing the atomic positions and cell parameters in separate simulations at 0 K. The accuracy of the computational methods is assessed by comparing experimental and computed structures of α- and β-pDIB, as discussed below.

Starting from the experimental structure of the α phase, we have first thermalized the system at 200 K for about 1 ps and then simulated a compression process by increasing the pressure with a sequence of steps at 5, 10, 20, 30, 40, 50, and 60 GPa. After each step we have followed the system for 1 ps in a simulation at constant pressure. The density−pressure curve obtained from the simulation is displayed in Figure 6. Two phase transitions have been clearly identified in the simulation, mainly by visually inspecting the configuration of the system at various pressures. In the first transition, which occurs around 10 GPa and appears continuous in the simulation, the angle between the crystallographic axis *b* and the normal to the molecular plane decreases, yielding a layered structure (hereafter labeled phase γ) in which all molecules lie parallel to the crystallographic plane *ac*. The second transition, encountered around 40 GPa, is more abrupt and involves a rearrangement of the atomic bonds, leading to an extended three-dimensional chemically bonded structure, labeled phase δ.

An independent simulation starting from phase β, with a compression process completely identical to that used for phase α, gave an analogous transition to phase γ around 10 GPa, showing that the starting phase is irrelevant. After completing the simulation of the compression processes, separate simulations were then performed for phases γ and δ at 15 and 60 GPa, respectively, to anneal their structures down to 0 K by fully relaxing the cell parameters. Samples of the δ phase were finally decompressed back to ambient conditions to emulate the corresponding experimental process. The computed properties of the various phases are discussed below.

C. Results for Low-Pressure Phases. The computed unit cell structures of α- and β-pDIB annealed at 0 K are displayed in Figure 7, while computed and experimental[33] lattice parameters are compared in Table 1. As in the experiments, the computed structures of α- and β-pDIB are quite similar, with very close cell axis lengths and with centro-symmetric molecules located in identical positions. The molecules on the plane $(x,y,0)$ have the same orientations in α- and β-pDIB, whereas those on the plane $(x,y,{}^{1}/_{2})$ are rotated in opposite directions.[33] Besides this characteristic molecular arrangement, also the experimental lattice parameters are well reproduced by the calculations, except for an overall expansion of the whole unit cell. This expansion is to be attributed to the fact that van der Waals attractive interactions are not taken into account in Car−Parrinello calculations.

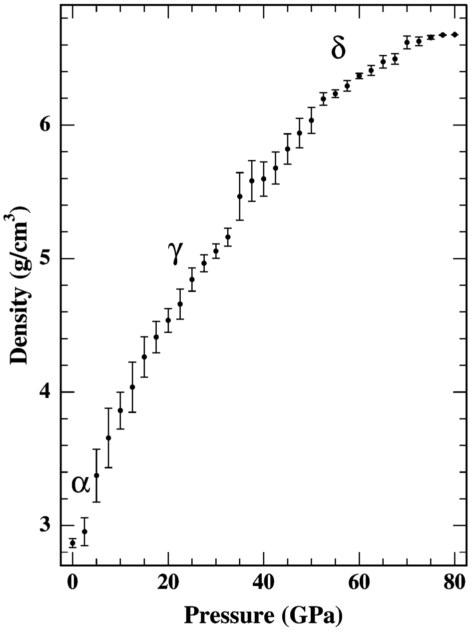

Figure 6. Density as a function of pressure for simulated *para*-diiodobenzene. Points and width of the "error" bars indicate average and standard deviation, respectively, of the density computed over nonoverlapping pressure intervals.

Another minor deficiency of the calculations concerns the ground-state energies. In fact, in the simulations β-pDIB is more stable than α-pDIB, whereas experimentally the most stable phase at low temperatures probably is the α one.[33,34] However, it should be considered that the energy difference has been calculated at 0 K (fully relaxed system) and is very small, ∼0.002 eV/atom (20 K). The long simulations which would be required to check the phase order at nonzero *T* are beyond the scope of this work, which is the behavior of a system under pressure. We must also mention that the lattice dynamics calculations, in which several models from the literature and many alternative charge distributions have been tried,[36] also yield for α- and β-pDIB the same energy order as the simulation.

D. Results for High-Pressure Phases. The computed unit cell structures of the new phases γ and δ are shown in Figure 7, while their crystallographic symmetry and lattice parameters are summarized in Table I. This information was obtained by analyzing[37] the annealed structures at 0 K. The molecular crystal characteristics of α- and β-pDIB are retained in γ-pDIB. This phase, predicted to be stable in the approximate pressure range 10−40 GPa, is monoclinic, with space group *C*2/*m* (C_{2h}^{3}) and four molecules per unit cell. Since it is predicted that compressed α- and β-pDIB and both transform into γ-pDIB, this phase may be interpreted as a transition state between

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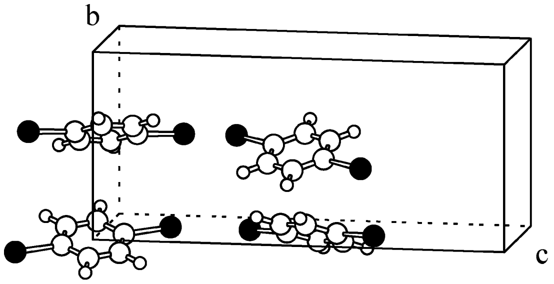
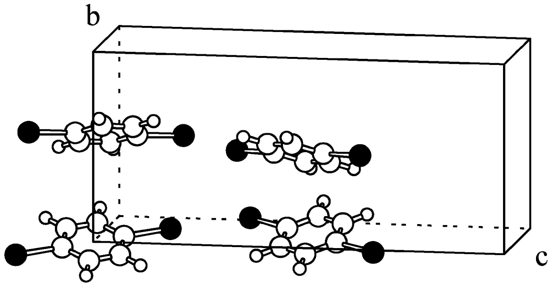
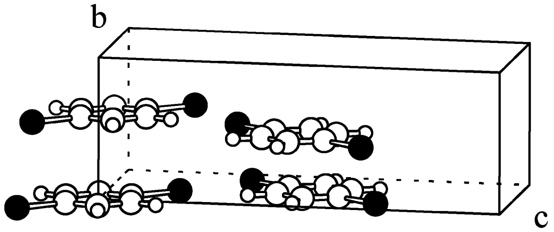
(29) Bernasconi, M.; Chiarotti, G. L.; Focher, P.; Scandolo, S.; Tosatti, E.; Parrinello, M. *J. Phys. Chem. Solids* **1995**, *56*, 501.
(30) Parrinello, M.; Rahman, A. *Phys. Rev. Lett.* **1980**, *45*, 1196.
(31) Troullier, N.; Martins, J. L. *Phys. Rev. B: Condens. Matter* **1991**, *43*, 1993.
(32) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785. Perdew, J. P. *Phys. Rev. B: Condens. Matter* **1986**, *33*, 8822.
(33) Alcobé, X.; Estop, E.; Aliev, A. E.; Harris, K. D. M.; Rodríguez-Carvajal, J.; Rius, J. *J. Solid State Chem.* **1994**, *110*, 20.
(34) Aliev, A. E.; Harris, D. M.; Alcobé, X.; Estop, E. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3797.
(35) Kraulis, P. J. *J. Appl. Crystallogr.* **1991**, *24*, 946; http://www.avatar.se/molscript/.
(36) Palazzi, L. Thesis, Facoltà di Chimica Industriale, Università di Bologna, Bologna, 1998,.
(37) Spek, A. L. *PLATON*; Utrecht University: The Netherlands; http://www.cryst.chem.uu.nl/platon/.



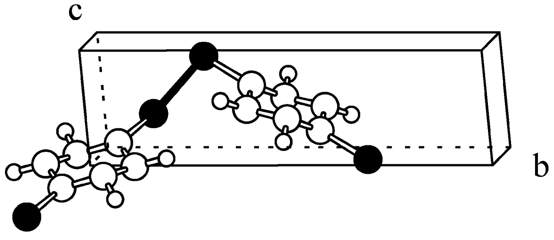
α, $Pbca$, 0 GPa



β, $Pccn$, 0 GPa



γ, $C2/m$, 15 GPa



δ, $P2_1/c$, 60 GPa

Figure 7. Computed unit cells of the phases of *para*-diiodobenzene. The *a* axis is approximately perpendicular to the plane of the page. The molecules lie on the origin (0,0,0) or on the face centers $(0,{}^1/_2,{}^1/_2)$, $({}^1/_2,0,{}^1/_2)$ or $({}^1/_2,{}^1/_2,0)$. The structures are labeled by the phase α, β, γ, or δ, space group, and pressure. Structures drawn with MOLSCRIPT.[35]

Table 1. Computed and Experimental[33] Structures of the Phases of *para*-Diiodobenzene[a]

p	phase		*Z*		*a*	*b*	*c*	*β*	*ρ*
0	α	*Pbca*	4	calcd	6.250	7.836	17.178		2.605
				exptl	6.168	7.323	17.000		2.854
0	*β*	*Pccn*	4	calcd	6.184	7.945	17.161		2.599
				exptl	6.154	7.461	17.092		2.792
15	*γ*	*C*2/*m*	4	calcd	6.296	5.249	15.098	94.473	4.406
60	*δ*	*P*2$_1$/*c*	2	calcd	3.313	12.969	4.164	109.032	6.478

[a] We report pressure (GPa), phase α, β, γ, or δ, plus space group, number *Z* of $C_6H_4I_2$ formula units in the unit cell, cell axes *a,b,c* (Å), monoclinic angle β (degrees), and density ρ (g/cm^3).

the phases α and β. In fact, γ-pDIB can be obtained from either α- or β-pDIB by rotating all molecules onto planes perpendicular to the *b* axis. We thus obtain a *nonprimitive* layered crystal in which a translation by a vector $(a + b)/2$ shifts the molecules on the symmetry plane $(x,0,z)$ into those on the parallel plane $(x,{}^1/_2,z)$.

The nature of a molecular crystal is lost in δ-pDIB. This phase, predicted to be stable at least up to 70 GPa, is monoclinic, with space group $P2_1/c$ (C^5_{2h}) and two $C_6H_4I_2$ formula units per unit cell. Its structure may be derived from that of the phase γ through a cell-halving process in which the new cell axis vectors become $c' \approx (a + b)/2$, $a' \approx (-a + b)/2$, and $b' \approx c$, while the molecules rotate away from their original symmetry planes and establish iodine–iodine bonds. In fact, the δ phase is characterized by an extended three-dimensional network in which the iodine atoms form bonded layers perpendicular to the longest cell axis b', as shown in Figure 8. The length of the I–I contacts is 2.74 Å, which is close to the intramolecular bond length of I_2 at ambient conditions (2.67 Å) and shorter than the interatomic distance in fcc iodine at 60 GPa (3 Å).[38]

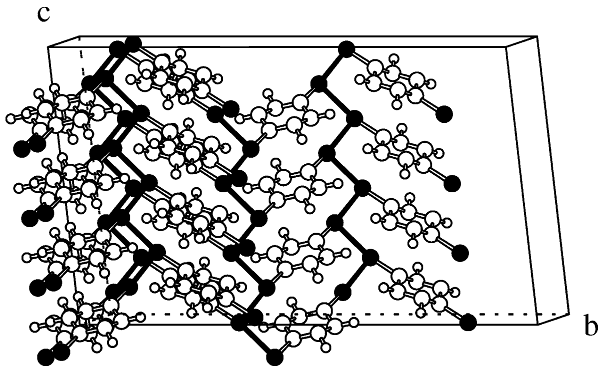


Figure 8. Computed three-dimensional network of phase of δ *para*-diiodobenzene at 60 GPa, shown as a 2 × 2 × 4 replica of the unit cell of Figure 7, with the same orientation. Half of the replicas along the *a* axis have been cut away for clarity.

The density–pressure curve of Figure 6 shows that the transition to the δ phase is associated with a jump in the density, which might be indicative of a first-order transition, and that the density fluctuations at a given pressure decrease considerably after the transition, indicating a higher bulk modulus in phase δ. The most interesting feature of this phase transition is the closure of the electronic gap between the valence and conduction bands. The gap calculated for the annealed structures at 0 K is 2.88 eV at ambient pressure for phases α- and β-pDIB, 1.14 eV at 15 GPa in phase γ, and 0 eV (closed) at 60 GPa in phase δ. The gaps are underestimated in the calculations due to the local density approximation (LDA).[39] Therefore, the calculated critical pressure of 60 GPa should be considered a lower limit for the possible metallization of the δ phase.

To understand better the experimental observations, two simulation runs have been performed to recover the δ phase at ambient temperature and pressure. In the first simulation we bring the system back to zero pressure while maintaining the temperature close to 300 K. The resulting uncompressed system contains no molecular iodine, and presents bonds between carbon atoms of different benzene rings, giving rise to a 1D zigzag chain. In the second simulation, the configuration at 60 GPa was further squeezed to 100 GPa while allowing the temperature to drift up to 1000 K. In the sample recovered at ambient conditions, we notice molecular iodine (one I_2 molecule) and carbon atoms in an almost planar graphitic arrangement. In both cases no return back to the original *para*-diiodobenzene molecular units occurs, and the decompressed systems present disordered structures characterized by extended carbon networks. Most likely the simulation time is too short to allow for reorganization processes, such as, for example, the formation of complete graphitic layers.

IV. Discussion and Conclusions

From our optical experiments, the overall scenario for the properties of pDIB under pressure is that the optical gap

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(38) Fujii, Y.; Hase, K.; Hamaya, N.; Ohishi, Y.; Onodera, A.; Shimomura, O.; Takemura, K. *Phys. Rev. Lett.* **1987**, *58*, 796.

(39) Fiorentini, V.; Baldereschi, A. *Phys. Rev. B: Condens. Matter* **1995**, *51*, 17196.

decreases rapidly for pressures up to 30 GPa, the molecular units remain unbroken at least up to 21 GPa, and the molecules are destabilized by applying pressures above 40 GPa. The latter effect involves nonreversible changes in chemical bonds, such that only a disordered dissociated product can be recovered at ambient conditions. Key ingredients to understanding the effects of pressure are the characterization of structural changes and insight into how the evolution of the structure prepares the system for undergoing pressure-induced chemical modifications. We have addressed these issues by variable-cell Car−Parrinello molecular dynamics simulations of pDIB subject to a compression process.

These simulations predict phases in good agreement with the available experimental evidence. The two known molecular crystal phases α and β are correctly predicted to be stable at ambient pressure. The experimental cell parameters are well reproduced by the simulations, except for a small cell expansion due to the absence of van der Waals interactions in Car−Parrinello calculations. Note that this shortcoming of the method is no longer relevant at high pressure, where the wave function overlap becomes significant and the contribution of the van der Waals interactions is negligible. A transformation to another molecular crystal phase, which represents a transition state between phases α and β, is predicted around 10 GPa. A further transformation to a high density nonmolecular phase, characterized by an extended three-dimensional network, is expected above 40 GPa. This is certainly a condensation process, rather than a dissociation one. The initial condensation occurs by bridging of iodine atoms at the closest intermolecular contacts. The resulting phase, in which chemically bound iodine atoms form layers connected by hydrocarbon bridges, is predicted to exhibit metallic behavior around 60 GPa.

Crucial information on the behavior of pDIB at very high pressures is provided by Raman spectra of samples recovered after compression. The most prominent feature in the spectra is the detection of crystalline iodine, whose irreversible formation occurs at about 50 GPa (section II). However, the sizable peak at 1588 cm^{-1} also indicates the presence of domains of residual aromatic carbons with a layered arrangement, resulting in a graphitic structure. In fact, typical Raman frequencies for C−C stretching modes[40] are around 900, 1650, and 2050 cm^{-1} for single, double, and triple bonds, respectively. Polycrystalline graphite, which is intermediate between single and double bond, exhibits a rather sharp band around 1580 cm^{-1}. The significant inhomogeneous broadening of the corresponding band in our spectra is indicative of a largely disordered and amorphous structure.[40] The negligible asymmetry on the low-energy side of this broad peak indicates the virtual absence of any sp^3 hybridization, giving evidence that the network of the layered carbon atoms is essentially 2D. This agrees very well with the theoretical description of the phase transition from γ to δ. These islands of sp^2 carbon may be random or may be preferentially arranged in sheets separated by iodine layers, as suggested by the theoretical results, where the topochemical arrangement of uncompressed pDIB is maintained also above the transition.

Although an amorphous structure could be conceivable also for the iodines, the presence of sharp bands at frequencies characteristic of crystalline iodine supports the idea of an ordered arrangement. As described in section II, laser annealing above 50 GPa intensifies the reflectivity, possibly indicating an increasing degree of metallization. Indeed, irradiation and heating of iodine under pressure[27] favors the formation of crystalline I_2. In the simulations of the δ phase recovered at ambient conditions, I_2 is obtained only after additional squeezing and heating, suggesting that the δ phase needs to overcome high energy barriers to dissociate into molecular iodine and graphitic carbon.

The experiments show the persistence of the molecular identity of pDIB above 20 GPa, i.e., at pressures well above the limit of the survival of unsaturated bonds commonly found in organic compounds.[12−14,17] It is plausible to think of a special role of iodine atoms acting like spacers and inhibiting ring condensation in the earlier stages of reduced intermolecular contacts under pressure. Related observations on iodanil[3,4] and hexaiodobenzene[6] seem to confirm this stability under pressure.

In conclusion, we obtained a detailed picture of *para*-diiodobenzene under strong compression, most likely involving molecular dissociation followed by condensation into iodine-intercalated amorphous graphite. Besides the interest for the specific case of *para*-diiodobenzene, our work highlights the usefulness of a combined experimental and theoretical approach, which provides important insights into the physical and chemical behavior of compressed hydrocarbons.

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(40) *Handbook of Raman Spectroscopy: from the research laboratory to the process line*; Lewis, I. R., Edwards, H. G. M., Eds.; Marcel Dekker: New York, 2001; p 875.