

# The pressure dependence of the solid state structure of biphenyl from DFT calculations†

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In this work we theoretically investigated the characteristics of the structure of biphenyl at zero temperature. The calculations were carried out with density functional theory using periodic boundary conditions. Semiempirical van der Waals (vdW) corrections were applied. We focused on the phenyl–phenyl dihedral angle and its shift with increasing pressure. We furthermore investigated the bond lengths of different bonds during the compression. The experimental transition pressure of a phase transition could be reproduced with satisfactory accuracy.

## 1 Introduction

The structure of biphenyl widely varies depending on the environment. The most obvious structural difference is the dihedral angle  $\varphi$  of the two phenyl rings. It is well established experimentally<sup>1–3</sup> that in the gas phase the global minimum conformation appears at  $\varphi = 44.4^\circ \pm 1.2^\circ$ . Many attempts have been made to successfully reproduce this value theoretically.<sup>4–17</sup> In solution  $\varphi$  ranges from  $19^\circ$  to  $32^\circ$  depending on the solvent.<sup>18,19</sup> Packing effects such as  $\pi$ – $\pi$  interactions of neighboring rings lead to a further decrease of the torsion angle in the solid state structure.

Many early X-ray studies under ambient conditions reported a rigid planar structure in the solid state ( $\varphi = 0^\circ$ ) whereas in 1977 Charbonneau and Delugeard<sup>20</sup> proposed that the observed pseudo planar structure is in fact the statistical average of two alternately twisted conformations. This indicates that the symmetry point of the molecule equals a crystallographic inversion center in the solid state structure. The high temperature structure (phase I) has been widely examined by X-ray studies<sup>20–27</sup> at 110–298 K and the monoclinic space group  $P2_1/a$  (#14) has been reported. The unit cells of this structure and of all other modifications discussed in this work contain four biphenyl molecules ( $Z = 4$ ). At lower temperatures the thermal energy of the molecules is too low to overcome the barrier of the double well potential of the phenyl–phenyl linkage and the molecules statistically occupy one of the two minima of the torsional potential in an alternating ordered manner. A displacive phase transition between the two phases occurs at 40 K. In phase II, the crystallographic inversion center

observed in phase I has vanished due to the constrained torsional angles in the incommensurate molecules. The loss of the crystallographic inversion center reduces the overall symmetry. Thus the length of the axis of the unit cell in the direction of the long axis of the biphenyl molecule is doubled. The angles observed in the low temperature modification (phase II) are close to  $\pm 10^\circ$ .<sup>28,29</sup>

On further cooling a second phase transition takes place. At 22 K the biphenyl crystal structure belongs to the space group  $Pa$  (#7) (phase III).<sup>30</sup> Other polyphenyls such as *p*-terphenyl and *p*-quaterphenyl show a similar behaviour at low temperatures.<sup>31,32</sup>

In most of the studies published, the properties of biphenyl at various temperatures were investigated, whereas the behavior of biphenyl as a function of pressure was reported less frequently.<sup>33–35</sup>

Zhuravlev and McCluskey<sup>36</sup> applied hydrostatic pressure to biphenyl ( $C_{12}H_{10}$ ) and to perdeuterated biphenyl ( $C_{12}D_{10}$ ) at liquid helium temperatures in order to examine the conformational changes. The disappearance of certain infrared absorption peaks at pressures between 0.07 and 0.45 GPa indicates the transition from phase III to phase IV. Phase IV and phase I belong to the same space group, but the individual molecules in phase IV are actually planar whereas the torsional angle  $\varphi = 0^\circ$  observed in phase I is due to the statistical average. Murugan *et al.*<sup>37</sup> investigated the pressure dependence of biphenyl at room temperature within a Monte Carlo simulation and reported a transition pressure of 0.8 GPa. Lemée-Cailleau *et al.*<sup>35</sup> studied low frequency Raman transitions of biphenyl at hydrostatic pressures up to 200 MPa at low temperatures (6 K). They reported a transition pressure of 0.18 GPa which is consistent with the findings of the infrared study.<sup>36</sup>

In this work, we studied the pressure dependence of the structural properties in the solid phase of biphenyl at 0 K. First principles calculations using DFT were carried out in order to determine the ground state energies of biphenyl at different cell

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† Dedicated to Professor Wolfgang Witschel on the occasion of his 75th birthday.

volumes. We found a decreasing torsion angle with increasing pressure, and we were able to estimate the transition pressure through the decrease of  $\varphi$  to zero.

For comparison, the structure of a single molecule in a very large unit cell was also optimized.

## 2 Details of the calculation

All quantum chemical calculations in this work were carried out with DFT and periodic boundary conditions using the plane wave code VASP.<sup>38</sup> The PBE functional and PAW pseudopotentials were applied. Dispersive forces were considered through the semi-empirical van der Waals corrections implemented in the VASP code by Ortmann.<sup>39</sup> The parameters of hydrogen provided with this patch showed an overestimation of the hydrogen–hydrogen interaction. Thus they had to be reoptimized in advance. They were chosen in such a way that the solid state structure of benzene<sup>40</sup> at a temperature of 218.15 K was reproduced correctly. In order to determine the relevant properties of biphenyl at different pressures we calculated the ground state energies at 26 different volumes of the unit cell from  $0.7V_0$  to  $1.8V_0$ ,  $V_0$  being the volume of the unit cell found experimentally under standard conditions. During each of these calculations the cell volume was kept fixed, whereas all other cell properties such as the cell shape and the positions of the atoms were optimized. All program parameters relevant for reliable results, *i.e.* cutoff energy, *K*-points *etc.*, were set high enough to obtain data converged within 1 meV.

The properties of the free molecule were estimated with a single molecule in a unit cell with a volume of  $3000 \text{ \AA}^3$  using the same parameters given above for the calculation of the solid state structures. The orthorhombic unit cell with the dimensions of  $10 \times 15 \times 20 \text{ \AA}^3$  was chosen to be large enough to avoid intermolecular interferences due to the periodic boundary conditions. The distance to the neighboring molecules exceeded  $10 \text{ \AA}$  in every direction. In order to achieve fast convergence, a correction of electrostatic multipole contributions up to quadrupoles was applied. The output of the VASP calculations was analyzed and imaged using the VMD<sup>41</sup> graphical interface. The structure and the numbering of the atoms are shown in Fig. 1.

## 3 Results

### 3.1 The equations of state

The  $E(V)$ -values of biphenyl obtained for volumes between  $600 \text{ \AA}^3$  and  $1500 \text{ \AA}^3$  are shown in Fig. 2.

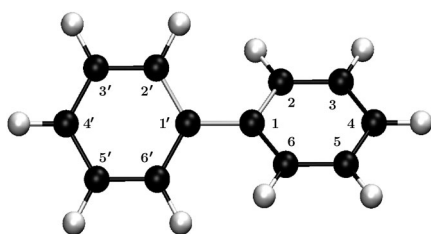


Fig. 1 Shown is the free molecule calculated with periodic boundary conditions in a very large unit cell together with the numbering of the atoms referred to in the text.

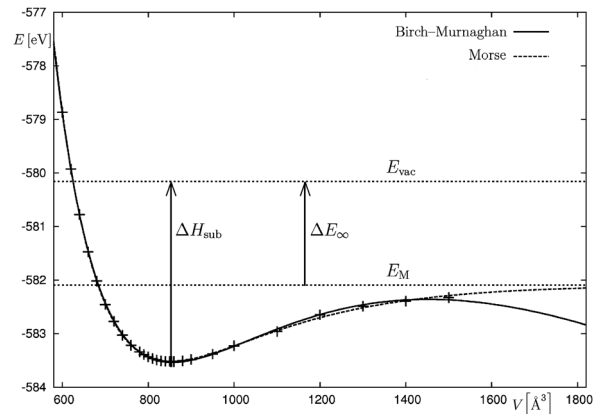


Fig. 2 Shown are the energies  $E(V)$  together with least squares fits to both a Birch–Murnaghan (1) and a Morse eqn (2), respectively. The energies indicated by dotted lines are the energy of a single molecule in vacuum  $E_{\text{vac}} = -580.16 \text{ eV}$  and the limiting value ( $V \rightarrow \infty$ ) of the Morse-like potential  $E_M = -582.09 \text{ eV}$ . The difference between the minimum energy of  $E(V)$  and  $E_{\text{vac}}$  is denoted by  $\Delta H_{\text{sub}}$  and  $\Delta E_{\infty} = E_{\text{vac}} - E_M$ . Details of the calculations are given in the text.

In order to obtain physically relevant parameters such as the minimum energy  $E_0 = E(V_0)$  and the corresponding cell volume  $V_0$  as well as the bulk modulus  $B_0$  and its pressure derivative  $B_1$ , the  $E(V)$ -curve was fitted to the third order Birch–Murnaghan equation of state.<sup>42,43</sup>

$$E_{\text{BM}}(V) = E_0 + \frac{9}{16} V_0 B_0 \left\{ \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^3 B_1 + \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V_0}{V} \right)^{2/3} \right] \right\} \quad (1)$$

All four quantities in eqn (1) refer to vanishing pressure. The nonlinear fit was carried out using gnuplot 4.0.<sup>44</sup> The parameters calculated are:

$$E_0 [\text{eV}] = -583.539 \pm 0.005$$

$$V_0 [\text{\AA}^3] = 857 \pm 1$$

$$B_0 [\text{GPa}] = 6.70 \pm 0.06$$

$$B_1 = 8.50 \pm 0.03$$

The bulk modulus of biphenyl is very small compared to a typical salt such as NaCl ( $B_0 = 31.9 \text{ GPa}$ ), whereas its  $B_1$  value is considerably larger than  $B_1(\text{NaCl}) = 4.7$ . The reference values of rock salt were taken from a theoretical work.<sup>45</sup> In a molecular crystal such as biphenyl, the intermolecular forces are much weaker than the Coulomb forces in an ionic compound. Therefore the bulk modulus of NaCl is much larger than the bulk modulus of biphenyl. With increasing pressure *i.e.* smaller cell volumes the deformation of strong covalent bonds becomes more and more important, which leads to larger  $B_1$  values in molecular crystals.

We were interested in following up the torsion angle  $\varphi$  for larger intermolecular distances, and therefore the calculations

were extended up to volumes much larger than  $V_0$ . The Birch–Murnaghan curve (1) shows an unphysical maximum near a volume of 1450 Å<sup>3</sup>, which is not surprising because the Birch–Murnaghan equation was not dedicated to fit regions of negative pressure.

In order to model the expected asymptotical behaviour at very low densities, we fitted the  $E(V)$ -values to a Morse-like potential  $E_M(V)$ .<sup>46</sup>

$$E_M(V) = D_e(1 - e^{-a(V-V_0)})^2 + E_0 \quad (2)$$

For very large volumes  $E_M(V)$  certainly converges to a physical meaningful limit  $E_\infty$  well above  $E_0$  without attaining a maximum. According to the functional form of eqn (2), the cohesion energy is  $D_e$ . The parameter  $a$  determines the width of the potential, whereas  $E_0$  and  $V_0$  have the same meaning as in eqn (1). The values of the parameters obtained from the fit are given below.

$$D_e [\text{eV}] = 1.42 \pm 0.02$$

$$E_0 [\text{eV}] = -583.524 \pm 0.004$$

$$V_0 [\text{Å}^3] = 852 \pm 1$$

$$a [\text{Å}^{-3}] = 0.00410 \pm 0.00004$$

The cohesive energy of 34 kJ mol<sup>-1</sup> which could be estimated from the actual value of  $D_e$  eqn (2) and a unit cell with  $Z = 4$  molecules is considerably smaller than the enthalpies of sublimation  $\Delta H_{\text{sub}} \approx 80$  kJ mol<sup>-1</sup> reported in the literature from various experiments.<sup>47,48</sup>

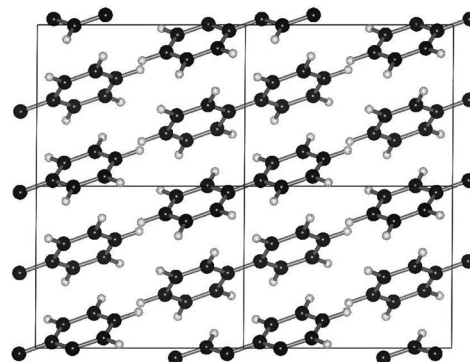
We thus also examined the solid state structures at volumes considerably exceeding  $V_0$ . The energy  $E_{\text{vac}}$  of the single molecule in the vacuum like unit cell was calculated to  $E_{\text{vac}} = -145.04$  eV ( $\hat{=}$   $-580.16$  eV for four molecules). With that we estimated the enthalpy of sublimation  $\Delta H_{\text{sub}} = E_{\text{vac}} - E_0 = 0.835$  eV. This is in remarkably good agreement with  $\Delta H_{\text{sub}} \approx 80$  kJ mol<sup>-1</sup> reported in ref. 47 and 48, although neither vibrational nor thermal corrections were applied in this work.

### 3.2 Layered structures at low density

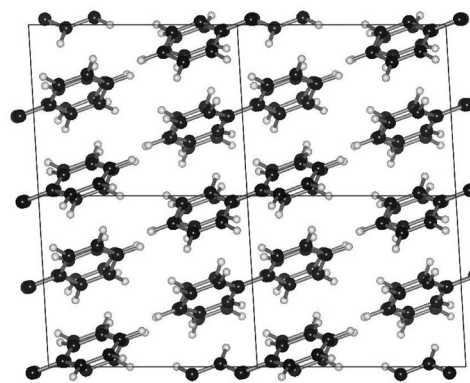
The structures at volumes of the unit cell of 600 Å<sup>3</sup>, 860 Å<sup>3</sup> (*i.e. ca.* the experimental volume at room temperature) and of 1200 Å<sup>3</sup> are shown in Fig. 3–5, respectively.

The packing found experimentally at room temperature is of similar density in all directions. The low density structure displayed in Fig. 5, however, shows an obvious layer structure. We therefore expect that a further increase of the cell volume would primarily lead to larger interlayer distances with only minor changes of the structure within the layers. This behaviour was confirmed with calculations up to a volume of 1500 Å<sup>3</sup>.

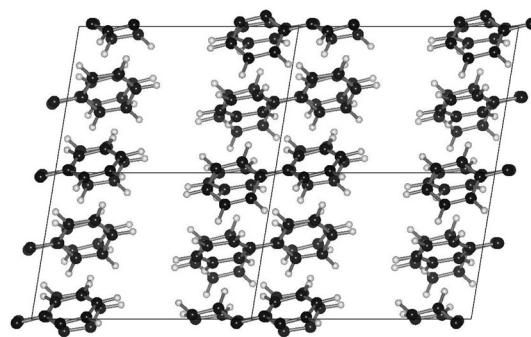
The energy calculated for the large volume of 1200 Å<sup>3</sup> contains a contribution from van der Waals forces of *ca.*  $-2.84$  eV per unit cell, *i.e.*  $-69$  kJ mol<sup>-1</sup>. The intramolecular component of the total energy due to van der Waals forces calculated in the free molecule was *ca.*  $-22$  kJ mol<sup>-1</sup>. Assuming that the intramolecular van der Waals energy does not change very much between the free molecule and the molecules in the layered structure, we obtain an amount of  $\approx -47$  kJ mol<sup>-1</sup> for



**Fig. 3** Shown is the structure of biphenyl in the space group  $P2_1/a$  seen along the  $b$ -direction. The volume of the unit cell is 600 Å<sup>3</sup>. Due to the special alignment of the molecules and the torsion angle of  $\delta = 0^\circ$  the molecules in the front hide the background molecules completely.



**Fig. 4** Shown is the unit cell at a volume of 860 Å<sup>3</sup>. Due to  $\delta \approx 10^\circ$ , the molecules are no longer congruent.



**Fig. 5** Shown is the unit cell at a volume of 1200 Å<sup>3</sup>. At this large volume, the formation of a layered structure is obvious.

the intermolecular van der Waals contribution to the energy in the layered structure. This amount is as large as the energy difference between the layered structure and the free molecule, see Fig. 2. We thus conclude that the binding in the layered structure is (nearly) only due to van der Waals interactions.

### 3.3 The torsion angle

As mentioned in the introduction, the pressure dependent phase transition in the solid state structure of biphenyl is

based on the flattening of the molecule ( $\varphi = 0$ ). We therefore examined the correlation of the torsion angle  $\varphi$  and the volume of the unit cell *i.e.* the applied pressure.

In order to describe the geometric structure of the biphenyl molecules in the solid state more precisely, we now discriminate between two different definitions of the torsion angle. The dihedral angle between  $C_2C_1C_1'C_2'$  is denoted as  $\tau$  and the torsion angle between the averaged planes of the two phenyl rings as  $\delta$ .

Before calculating an average plane through one of the phenyl rings, we oriented them into the  $xy$ -plane. The planes were approximated to least squares in the  $z$ -direction. We started from the equation of a plane

$$b_x x + b_y y + b_z z = c \quad (3)$$

and solved it for  $z$ .

$$z = \frac{c}{b_z} - \frac{b_x}{b_z} x - \frac{b_y}{b_z} y = a_1 + a_2 x + a_3 y \quad (4)$$

Eqn (4) holds approximately for each of the eleven atoms of a phenyl group.

$$a_1 + a_2 x_i + a_3 y_i \approx z_i \quad i = 1, 2, \dots, 11 \quad (5)$$

Using the matrix  $\mathbf{X}$  and the column vectors  $\mathbf{a}$  and  $\mathbf{z}$

$$\mathbf{X} = \begin{pmatrix} 1 & x_1 & y_1 \\ 1 & x_2 & y_2 \\ \vdots & \vdots & \vdots \\ 1 & x_{11} & y_{11} \end{pmatrix}, \mathbf{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}, \mathbf{z} = \begin{pmatrix} z_1 \\ z_2 \\ \vdots \\ z_{11} \end{pmatrix}, \quad (6)$$

eqn (5) can be written as

$$\mathbf{X}\mathbf{a} = \mathbf{z} \quad (7)$$

The optimum solution of the least squares problem (7) can be obtained using the pseudoinverse,<sup>49</sup> p. 299f.

$$\mathbf{a} = (\mathbf{X}^T \mathbf{X})^{-1} \mathbf{X}^T \mathbf{z} \quad (8)$$

and the resulting surface normal  $\vec{n} = (a_2 | a_3 | -1)^T$  with the Cartesian coordinates of the atoms being  $(x|y|z)$ . Table 1 lists the values of  $\delta$  and  $\tau$  for some significant values of the unit cell volume.

It can be seen that the phenyl rings get more and more distorted with decreasing volume. This is most obvious at volumes of  $800 \text{ \AA}^3$  and below. In this range the torsion angle  $\tau$  rises slightly, whereas the  $\delta$  converges to zero. This fact can be easily explained by the increasing steric repulsion of the *ortho* hydrogen atoms which leads to a widening of  $\tau$  vs.  $\delta$ . In unit

**Table 1** Torsion angles

$V [\text{\AA}^3]$	600	700	800	900	1000
$\delta [^\circ]$	0.0	0.0	3.2	18.0	24.3
$\tau [^\circ]$	0.9	0.6	2.9	18.1	24.4

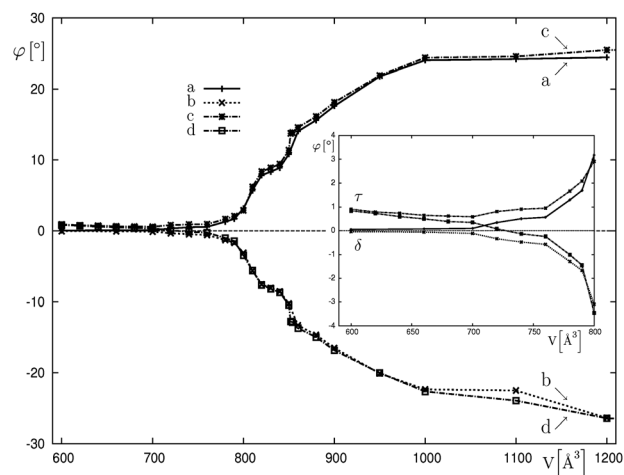
cells with volumes large enough to allow a sufficient distance between the *ortho* hydrogens, the angles  $\delta$  and  $\tau$  concur.

The torsion angle  $\tau$  of the free molecule was estimated to be  $38.4^\circ$ . This is significantly smaller than the experimental value of approximately  $44^\circ$ . In the biphenyl molecule the torsion angle depends on two opposing influences. The overlap of the  $\pi$  system of both rings as well as the steric repulsion of the *ortho* H-atoms increases with decreasing torsion angles. The DFT is known to overestimate  $\pi$ - $\pi$  interactions and therefore leads to the observed smaller value of  $\tau$ .

Fig. 6 shows the torsion angles of the two incommensurate molecules in the unit cell for a wide volume range. The sign of  $\varphi$  was thereby assigned arbitrarily to the molecules. At first it is worth noting that the torsion angle  $\tau$  does not approach the value of the free molecule ( $\tau = 38.4^\circ$ ) with increasing volumes but converges to approximately  $\tau = 26^\circ$  which is in the range of torsion angles of biphenyl in solution. This fact can be explained through the remaining VDW forces within the layered structures at unphysical negative pressures as mentioned above.

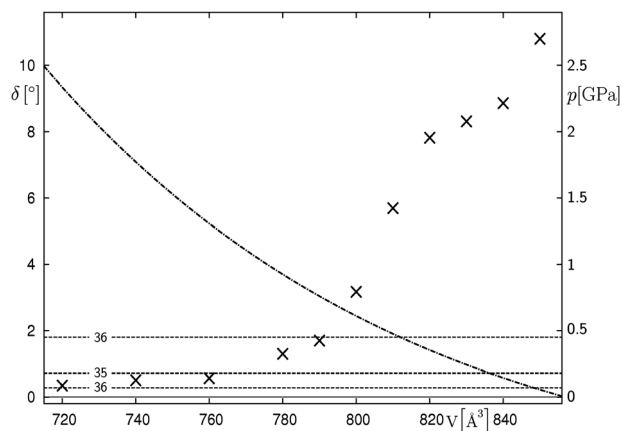
With increasing pressure, the torsion angle decreases rapidly within the range of  $860 \pm 50 \text{ \AA}^3$ , *i.e.* at volumes close to the volume of the unit cell under ambient conditions (pressure  $p = 0$ ). In order to evaluate the pressure  $p(V)$ , we calculated the derivative  $-dE/dV = p$  of the Birch-Murnaghan equation of state. Fig. 7 shows the dependence of  $\delta$  on the volume  $V$  of the unit cell together with the calculated pressure  $p(V)$ . In the upper part of the range reported for the transition pressure in the experimental studies,<sup>35,36</sup> the torsion angle decreases very steeply with increasing pressure.

High pressure experiments are usually carried out using a diamond anvil cell (DAC)<sup>50</sup> which limits the diameter of the observation window to the size of the diamond. As a result the



**Fig. 6** Shown are the angles  $\varphi$  between the two phenyl-rings of the two incommensurate molecules in the unit cell. The region  $600\text{--}800 \text{ \AA}^3$  is magnified in the inset. The curves c and d show the dihedral angle  $\tau$  between  $C_2\text{--}C_1\text{--}C_1'\text{--}C_2'$  (see Fig. 1), whereas the curves a and b represent the torsion angle  $\delta$  between the phenyl planes fitted through the carbon atoms of the rings. The angle between the planes vanishes for small cell volumes while the torsion angle remains finite. This indicates the distortion of the molecule due to the steric interaction of the  $\alpha$ -hydrogen atoms.





**Fig. 7** Shown are the angles  $\delta$  (crosses) between the averaged planes of the phenyl rings together with the pressure  $p$  (dotted) as a function of the volume  $V$  of the unit cell. The values of the angles are shown at the left hand side, whereas the pressure scale is drawn at the right hand side. Experimental values of the transition pressure are shown as horizontal dotted lines. They refer to the references indicated at  $730 \text{ \AA}^3$ . The steepest decrease of the torsion angle with pressure (at  $V = 810 \text{ \AA}^3$ ) is observed slightly above the interval of experimental transition pressures. The calculations thus reproduce these transition pressures with fair accuracy.

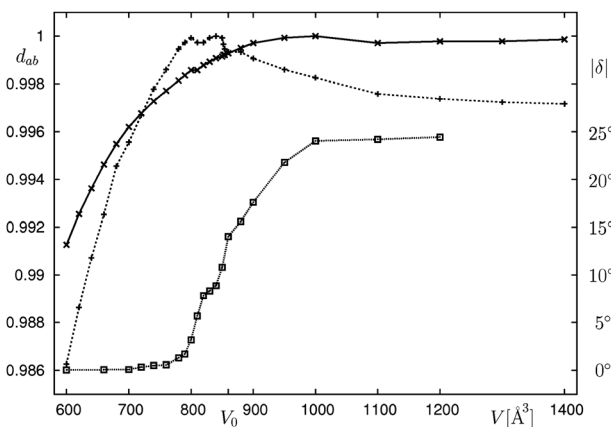
spectra that arise from X-ray or Raman spectroscopy provide less information than those recorded under ambient conditions. It is therefore questionable if structures with torsion angles close to zero can be clearly associated with either space group  $P2_1/a$  (planar) or space group  $Pa$  (twisted). The point of inflection of the  $\vartheta(V)$  curve (at  $810 \text{ \AA}^3$ ) shown in Fig. 7 corresponds to a pressure of *ca.* 0.5 GPa. This indicates that our calculations slightly overestimate the transition pressure. We identified the point of inflection at  $V = V_1$  by fitting the  $E(V)$  values between 760 and  $840 \text{ \AA}^3$  to a phenomenological equation  $f(V) = a \tanh(V - V_1) + b(V - V_1) + c$ .

In order to reproduce the phase transition more clearly we considered the bond lengths of several C–C bonds under varying pressure conditions. The distance between the two bridging carbon atoms is directly influenced by two opposing factors. A smaller value of the torsion angle leads to a greater overlap of the  $\pi$  system and hence to a shortening of the bond length. On the other hand a smaller torsion angle results in a strong repulsion between the  $\alpha$ -hydrogen atoms and therefore a longer bond length. The distance between the carbon atoms in *ortho* and *para* positions to C–C' in contrast is expected to be influenced by the  $\pi$  system only.

We consider the relative distances  $d_{ab}(V)$  between two atoms  $a$  and  $b$  as a function of volume  $V$ .

$$d_{ab}(V) = \frac{D_{ab}(V)}{D_{ab}^{\max}}$$

The distance  $D_{ab}(V)$  between  $a$  and  $b$  depends on  $V$ , too. The maximum value of  $D_{ab}(V)$  is denoted as  $D_{ab}^{\max}$ . Fig. 8 shows the relative distances of C<sub>1</sub>–C<sub>1'</sub> and C<sub>2</sub>–C<sub>3</sub> as well as the torsion angle  $\delta$  at different volumes. It can be seen that the C<sub>2</sub>–C<sub>3</sub> distance monotonically rises with increasing volume to the asymptotical value of the molecule in the layered structure. The distance between the carbon atoms C<sub>1</sub> and C<sub>1'</sub> reaches a maximum at volumes shortly below  $V_0$  and afterwards shrinks to the asymptotical value. In this



**Fig. 8** Shown are the relative lengths  $d_{ab}$  of the (C<sub>1</sub>–C<sub>1'</sub>) bond between the two phenyl rings (dotted) and of the C<sub>2</sub>–C<sub>3</sub> bond within the ring (solid) together with the absolute value  $|\delta|$  (squares) of the angle between the planes of the phenyl rings as a function of the cell volume  $V$ . The special structure of C<sub>1</sub>–C<sub>1'</sub> just below  $V_0$  is explained in the text. The numbering of the carbon atoms refers to Fig. 1.

volume range the torsion angle changes rapidly from  $\delta \approx 0$  to  $\delta \approx 15$ . This change allows the alpha hydrogen atoms to situate in positions with much less mutual repulsive forces.

## 4 Conclusions

The solid state structure of biphenyl under various pressure conditions was calculated by first principles methods including dispersive forces. We therefore focused on the torsion angle between the two phenyl rings. It was shown that with increasing pressure the torsion angle rapidly decreases within a small pressure range. Pressures above 0.5 GPa lead to torsion angles below  $6^\circ$  and indicate an ongoing phase transition from space group  $Pa$  to space group  $P2_1/a$ . The pressure range estimated for the phase transition is in fair coincidence with the experimental values. The augmentation of the unit cell to volumes larger than  $V_0$  does not result in a sublimation of solid biphenyl to single molecules but yields layered structures due to intermolecular van der Waals interactions. A calculation of the cohesion energy reproduced the experimental enthalpy of sublimation with an unexpected accuracy. We showed that the distance of the phenyl rings passes a maximum with increasing cell volumes due to the repulsive forces of the  $\alpha$ -hydrogen atoms at small torsion angles.

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