Unequal torsional rotations driven by normal to modulated phase transition in 4-biphenylcarboxy coupled L-phenylalaninate governed by non-covalent constraints

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(Dated: July 15, 2022)

Abstract

Amongst the derivatives of 4-biphenylcarboxylic acid and amino acid esters, the crystal structure of 4-biphenylcarboxy-(L)-phenylalaninate is unusual owing to its monoclinic symmetry within a pseudo-orthorhombic lattice. The distortion is described by disparate rotational property around the chiral centers (ϕ_{chiral} ≃ -129 degrees and 58 degrees) of the two molecules in the asymmetric unit. Each of these molecules comprise of planar biphenyl moieties (ϕ_{biphenyl} = 0 degrees). Using temperature dependent single crystal X-ray diffraction experiments we show that the compound undergoes a phase transition below T ∼ 124 K that is characterized by a commensurate modulation wave vector, q = δ(101), δ = 1/2. The (3+1) dimensional modulated structure at T = 100 K suggests that the phase transition drives the biphenyl moieties towards non coplanar conformations with significant variation of internal torsion (ϕ_{max}^{biphenyl} ≤ 20 degrees). These intramolecular rotations lead to dimerization of the molecular stacks that are described predominantly by intermolecular tilts and small variations in intermolecular distances. Atypical of modulated structures and super-structures of biphenyl and other polyphenyls, ϕ_{biphenyl} of one independent molecule is two to four times larger than the other. We suggest that while the rotations arise from intramolecular steric factors, competing intermolecular H–C⋯C–H contacts and weak C–H⋯O hydrogen bonds govern the distinctively unequal torsional property of the molecules.

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I. INTRODUCTION

Molecular biphenyl has been investigated extensively for its stability and conformation in different thermodynamic states. At ambient conditions, the differences in the conjugation states of the $\pi$-electrons are governed primarily by the twist about the central C–C single bond in the order: 40 deg - 45 deg in gas phase, 20 deg - 25 deg in solution and 0 deg (mutually coplanar) in the solid state in centrosymmetric monoclinic space group $P2_1/a$ [1–4]. The planar conformation due to constraints from intermolecular interactions is energetically unfavourable and steric hindrance between the ortho hydrogen atoms is compensated for by out of plane dynamic disorder and in plane displacements of those hydrogens away from each other [4–9]. A recent study has also suggested the role of intramolecular exchange energy between single bonded carbon atoms in stabilizing the planar conformation [10]. Absorption and fluorescence studies showed additional bands in their spectra at low temperatures ($T$) [11, 12]. $T$-dependent Raman spectroscopy and Brillouin scattering experiments have suggested two phase transitions at $T_{c1} = 42$ K and $T_{c2} = 17$ K respectively [13–16]. The phase transition at $T_{c1}$ is continuous and governed by a soft mode associated with the torsion about the central C–C single bond followed by discontinuous changes at $T_{c2}$. Inelastic neutron scattering experiments on its deuterated form confirmed the phase transitions with appearance of additional satellite reflections [17]. The modulation wave vector ($q$) was determined to be $q_I = \delta_a a^* + \frac{1}{2}(1 - \delta_b)b^*$ and $q_{II} = \frac{1}{2}(1 - \delta_b)b^*$ at the intermediate and low temperature phases respectively and were found to vary with temperature, suggesting an incommensurate nature of the modulation [17]. The modulated structure of the low temperature phase II was described within an acentric superspace group symmetry $P\alpha(0\sigma_2 0)$ [18–20] and found to be essentially associated with small modulation of translation and rotation ($\omega$) normal to the mean molecular plane, and a significant torsion ($\varphi$) between the phenyl rings [21–24]. Theoretical studies have suggested that competition between intramolecular and intermolecular forces drives the phase transition towards the incommensurately modulated states [25–28].

The fundamental property of flexibility in conformations have made biphenyl an excellent candidate to tune in multifaceted properties in materials. Torsion between the rings has been demonstrated to regulate conductivity of single molecule biphenyl-dithiol junctions [29–32], tune in thermopower as function of twist angle [31], degeneracy of energy states on substrates [33] and theoretically suggest wide band gap semiconducting properties of its derivatives [34].
On the other hand, biphenyl derivatives have also been reported to influence and increase the efficiency of photophysical properties [35, 36]. Planar biphenyl molecule in solid state favours maximum intramolecular conjugation of \( \pi \) electrons as well as increases the probability of interactions between delocalized electrons that could aid in optimal stacking of molecules. Coupling reaction mechanism [37] was successfully employed to synthesize 4-biphenylcarboxy protected amino acid esters of L-serine, L-tyrosine, L-alanine, L-leucine and L-phenylalanine [38, 39]. In solid state, the compounds crystallize either in acentric orthorhombic space group symmetry \( P2_12_12_1 \) or the monoclinic subgroup \( P2_1 \) [38, 39]. Crystal packing in these systems is determined by \( \pi \cdots \pi \) stacking between the biphenyl fragments and linear strong hydrogen bonds between the amino acid ester moieties.

We presumed that the biphenyl moieties in these chemically coupled systems could influence the bioactive amino acid esters and vice-versa with respect to evolution or suppression of translational and rotational degrees of freedom in their crystal structures at some thermodynamic condition. Reanalyzing all their crystal structures, the system of 4-biphenylcarboxy-(L)-phenylalaninate attracted our attention because the structure appeared to be similar to the L-tyrosine analogue albeit the monoclinic distortion (Table I,[39]) and two crystallographically independent formula units \( Z' = 2 \) [40], Fig. 1(a)] in the crystal structure of the former. The torsion about the chiral center is significantly different for the independent molecules while the rest of the rotations are similar [Fig. 1(a), [39]]. Each of these molecules consist of coplanar biphenyl moieties which are stacked along \( \mathbf{a} \) and \( \mathbf{b} \) respectively while the amide groups are connected by intermolecular N–H⋯O hydrogen bonds [Fig. 1(b),[39]].

In the present study, \( T \)-dependent phase transition of 4-biphenylcarboxy-(L)-phenylalaninate has been investigated using single crystal X-ray diffraction experiments. The low temperature phase II is found to be a \( 2a \times b \times 2c \) superstructure of the high temperature (phase I) structure. The superstructure is described within the \( (3 + 1)D \) superspace approach as a commensurately modulated structure [18, 41–44]. Structural properties of the phase I and the modulated structure have been tabulated and compiled within \( t \)-plots (\( t = \text{phase of the modulation} \)). The origin and stability of phase II is discussed in terms of intra- and intermolecular HC⋯CH contacts and intermolecular hydrogen bonds and plausible mechanism of the phase transition is suggested.
II. EXPERIMENTAL

A. Temperature dependent single crystal X-ray diffraction

Single crystals of the compound used in this study were obtained from those reported by Sasmal et al. [39]. The crystals were protected in oil under mild refrigeration. Single crystal X-ray diffraction (SCXRD) experiments were performed on a Agilent SuperNova, Eos diffractometer employing CuKα radiation. Temperature of the crystal was maintained by a open flow nitrogen cryostat from Oxford Cryosystems. During cooling, visual inspection of diffraction images revealed weaker reflections in addition to strong reflections at low temperatures. Diffraction images collected at $T = 150$ K, 140 K and 130 K to 114 K in steps of $\Delta T = 2$ K showed that the weaker diffuse features appear at $T = 124$ K that condense into satellite reflections at $T = 122$ K (Table I, Fig. S1 in [45]). The transition temperature is significantly higher than that of molecular biphenyl ($T_{c,biphenyl} = 42$ K). On the other hand, related polyphenyls $p$-terphenyl and $p$-quarterphenyl undergo phase transition towards superstructure phases at much higher critical temperatures ($T_{c,terphenyl} \approx 190$ K [46], $T_{c,quarterphenyl} \approx 233$ K [47]). Complete diffraction data were collected at $T = 160$ K and $T = 100$ K respectively.

Determination of lattice parameters and data reductions were performed using the software suite CrysAlisPro [48] (Table I, Table S1 in [45]). Satellite reflections of first order ($m = 1$) observed below $T_c$ could be indexed with modulation wave-vector $\mathbf{q} = (\sigma_1,0,\sigma_3)$, $\sigma_1 = \sigma_3 \simeq \frac{1}{2}$ with respect to the basic monoclinic lattice. Here, the $\mathbf{q} = \frac{1}{2}(101)$ is perpendicular to the $b$ axis consistent with monoclinic symmetry while in molecular biphenyl $\mathbf{q}_I$ violates monoclinic symmetry and $\mathbf{q}_{II}$ is parallel to $b$ [17]. Using the plugin program NADA [49] in CrysAlisPro, deviation of the $\sigma$'s as function of $T$ from a rational value of 0.5 were found to be within their e.s.d.s (Table I), indicating a commensurate nature of the modulation. Reflections at $T = 100$ K were indexed by four integers ($hklm$) using a basic monoclinic $b$-unique lattice (Table I, Table S1 in [45]) and modulation wave vector, $\mathbf{q} = (\frac{1}{2},0,\frac{1}{2})$ and data integration was performed. Empirical absorption correction was performed using AbsPack program embedded in CrysAlisPro. The monoclinic lattice as well as the reflection conditions suggest the superspace group $P2_1(\sigma_10\sigma_3)0$ with $\sigma_1 = \sigma_3 = \frac{1}{2}$ [19, 20].
TABLE I. Temperature dependence of lattice parameters and the components of the modulation wave vector, $\sigma_1$ and $\sigma_3$. See Table S1 in [45] for reflections used.

| $T$ (K) | $a$ (Å)  | $b$ (Å)  | $c$ (Å)  | $\beta$ (°) | $\sigma_1$ | $\sigma_3$ | $V$ (Å$^3$) |
|---------|----------|----------|----------|-------------|------------|------------|-------------|
| 200[39] | 5.0560(3)| 8.6622(4)| 42.242(3)| 90.349(4)   | 1850.00(18)|            |             |
| 160     | 5.0479(2)| 8.6330(4)| 42.1525(15)| 90.513(3)   | 1836.87(13)|            |             |
| 150     | 5.0498(7)| 8.6161(8)| 42.136(11)| 90.607(11)  | 1833.2(5)  |            |             |
| 140     | 5.0484(6)| 8.6093(7)| 42.145(10)| 90.661(10)  | 1831.6(5)  |            |             |
| 130     | 5.0451(7)| 8.6014(8)| 42.120(11)| 90.713(11)  | 1827.6(6)  |            |             |
| 128     | 5.0446(7)| 8.6002(8)| 42.113(11)| 90.723(11)  | 1826.9(6)  |            |             |
| 126     | 5.0440(6)| 8.5992(7)| 42.114(10)| 90.720(9)   | 1826.5(5)  |            |             |
| 124     | 5.0443(6)| 8.5978(7)| 42.100(10)| 90.733(9)   | 0.499(9)   | 0.51(7)   | 1825.7(5)  |
| 122     | 5.0440(7)| 8.5970(7)| 42.100(10)| 90.745(10)  | 0.498(6)   | 0.49(4)   | 1825.5(5)  |
| 120     | 5.0433(7)| 8.5984(7)| 42.100(10)| 90.746(10)  | 0.497(5)   | 0.52(3)   | 1825.5(5)  |
| 118     | 5.0441(7)| 8.5958(8)| 42.092(11)| 90.764(10)  | 0.500(4)   | 0.50(3)   | 1824.8(5)  |
| 116     | 5.0432(6)| 8.5926(7)| 42.087(9) | 90.775(9)   | 0.500(4)   | 0.51(3)   | 1823.6(5)  |
| 114     | 5.0422(6)| 8.5923(7)| 42.090(10)| 90.787(10)  | 0.500(4)   | 0.53(3)   | 1823.3(5)  |
| 100     | 5.0377(2)| 8.5898(3)| 42.0432(14)| 90.884(3)  | 0.5         | 0.5       | 1819.11(11)|

B. Structure refinement of the modulated structure

The crystal structure of the room temperature phase (phase I hereon) was redetermined at $T = 160$ K using SUPERFLIP [50] and refined using JANA2006 [51] and JANA2020 [52]. Atoms were renamed with suffixes ‘a’ and ‘b’ for the two independent molecules ‘A’ and ‘B’ [Fig. 1(a)]. Anisotropic atomic displacement parameters (ADPs) of all non-hydrogens atoms were refined. Hydrogen atoms (H) were added to carbon and nitrogen atoms using riding model in ideal chemical geometry with constraints for isotropic ADPs [$U_{iso}(H) = 1.2U_{eq}(N)$, $U_{iso}(H) = 1.2U_{eq}(C_{aromatic})$ and $U_{iso}(H) = 1.5U_{eq}(C_{sp3})$]. Since $\beta$ is close to 90°, the integrated data was tested for twinning employing twofold rotation parallel a as twin law. This twin law is a true symmetry element in case of a hypothetical orthorhombic lattice with point group symmetry 222 [53, 54]. The fit of the structure model improved (compare $R_F^{obs} = 0.0463$ to 0.0408) and volume of the second component refined to $\sim 2\%$ (Table
S2 in [45]). Finally, positions of the H atoms of NH groups and parameter corresponding to isotropic extinction correction was refined that further improved $R_{\text{ref}}$ values ($= 0.0393$, Table S2 in [45]). The crystal structure reproduced the values for intramolecular rotations reported those for the structure at $T = 200$ K [$\varphi_{\text{chiral}} = \varphi_1$ (hereon) and $\psi$ in Fig. 1(a)]. In addition, we also observe that the coplanar biphenyl rings are significantly rotated with respect to the amide groups [at $T = 200$ K: $\varphi_2 = 32.8$ deg and 31.2 deg [39], at $T = 160$ K in Fig. 1(a)] which also remains invariant as function of temperature.

![Figure 1](image1.jpg)

**FIG. 1.** (a) Two independent formula units of 4-biphenylcarboxy-(L)-phenylalaninate (C$_{23}$H$_{21}$NO$_3$) with atomic labels of non-hydrogen atoms (‘a’ and ‘b’ for molecule ‘A’ and ‘B’ respectively) in phase I at $T = 160$ K. $\varphi_1^A = -130.1$ deg, $\varphi_1^B = 56.1$ deg; $|\varphi_2^A| = 32.8$ deg, $|\varphi_2^B| = 30.8$ deg; $\varphi_3^A = \varphi_3^B = 0$ deg; $\psi_A = 36.4$ deg, $\psi_B = 36.2$ deg. Viewing direction along [001]. (b) View of corresponding layered structure along [111] emphasizing biphenyl stacks (AA)$_n$ and (BB)$_n$ along a, (ABAB)$_n$ along b and N–H···O bonds (dashed orange) along $[\mp100]$ directions. Phenyl rings of the ester groups (transparent) stack only along a.

The modulated structure of phase II at $T = 100$ K was refined using JANA2006 and JANA2020. Fractional co-ordinates of all non-hydrogen atoms from the crystal structure at $T = 160$ K were used as starting model and the average structure was refined against main reflections. In successive steps, an incommensurate (IC) model described by one harmonic wave for displacive modulation describing the atomic modulation functions (AMFs) and basic parameters for anisotropic ADPs for all atoms was refined against main and satellite
reflections that resulted in good fit to the diffraction pattern ($R_{\text{obs}} = 0.0425$). However, ADPs of four non-hydrogen atoms were found to be non-positive definite. Since the components of $q$, $\sigma_1$ and $\sigma_3$ are rational, three commensurately modulated structures were pursued by fixing the initial phase of the modulation to values, $t_0 = 0$, $\frac{1}{4}$ and $\frac{1}{8}$ respectively. While the former two $t_0$ values describe monoclinic $B2_1$ space group symmetry for the equivalent 3D $2a \times b \times 2c$ superstructure, the third corresponds to triclinic $B1$ symmetry. The commensurately modulated structure (C) model corresponding to $t_0 = \frac{1}{4}$ resulted in the best fit to the diffraction data ($R_{\text{obs}} = 0.0426$) including ADPs of all atoms positive definite. As the atomic modulation functions (AMFs) have sinusoidal character, the residual values are similar to the IC model (Fig. 2, Fig. S2-S4 and Table S2 in [45]) However, the C model at $t_0 = \frac{1}{4}$ is described with either cosine or sine waves for the AMFs (equal to number of refinable fractional coordinates in the equivalent superstructure) reducing significantly the number of refinable parameters as compared to the IC model (compare $N_C = 649$ to $N_{IC} = 811$, further tests in [45]). The final C model was further improved by refining the parameter corresponding to isotropic extinction correction and AMFs and positions of hydrogen atoms of NH groups ($R_{\text{obs}} = 0.0419$, Table S2 in [45]).

III. RESULTS AND DISCUSSION

A. Structural phase transition and unequal distortion of molecules

In the present case, the monoclinic symmetry is retained below $T_c$ unlike monoclinic to triclinic distortion at disorder–order phase transition of $p$-terphenyl [55] and $p$-quarterphenyl [56]. In the final commensurately modulated structure model with $t_0 = \frac{1}{4}$, sections corresponding to $t = \frac{1}{4}$ and $\frac{3}{4}$ (Fig. 3, Fig. S5 in [45]) are physically relevant that corresponds to atomic positions in the equivalent twofold superstructure in 3D (Fig. 4, Fig. S6 in [45]). Crystal structures of phase I and phase II have group-subgroup relations and the doubling of the $a$ and $c$ axes describes the additional $B$-centering of the superstructure in II. The superstructure derived using JANA2006 comprises of four molecules in the asymmetric unit ($Z' = 4$); two each corresponding to molecule ‘A’ and ‘B’ of phase I (Fig. 4). The covalent bond distances are similar for the independent set of molecules and are practically unaffected by modulation (Table S6 in [45]). In the present study, discussion is based on the modu-
FIG. 2. \((x_{si}, x_{s4})\)-sections of Fourier map centered on carbon atoms (black) (a) C23a of molecule ‘A’ and (b) C23b of molecule ‘B’ respectively. The contour line and the width of the maps are 0.5 e\(\text{Å}^{-3}\) and 2.5 Å respectively.

lated structure in order to establish unique relations between phase I and II respectively [24, 57–61].

The modulated structure suggests that the phase transition is dominated by evolution of internal torsional degrees of freedom \((\varphi^3 > 0^\circ)\) within the biphenyl moieties [Fig. 3(a)]. The twists about the central C–C bond are significantly different for the two molecules where the torsional modulation of ‘A’ are 2-4 times larger than those of ‘B’ (dihedral angle: \(| \varphi^3_A | = 15.6 \text{ deg}, 20.5 \text{ deg}; | \varphi^3_B | = 4.1 \text{ deg}, 9.3 \text{ deg})}. These torsions are described by highly anisotropic AMFs \(u\) along the three basis vectors where the maximum amplitude are along \(b\) for the carbon atoms of biphenyl (Fig. 2 and Table S4 in [45]). Notably, the rotations in the present structure are significantly larger than those reported for molecular biphenyl \((\varphi \simeq \pm 5.5 \text{ deg in ref.}[21, 22])\) but smaller than those in the low temperature superstructure of \(p\)-terphenyl and \(p\)-quarterphenyl (Maximum \(\varphi_{terphenyl, quarterphenyl} \simeq 23 \text{ deg in ref.}[55, 56, 62])\).
Another distinctive property of the modulated structure is the unequal modulation for the two different moieties where $u_{\text{biphenyl}} > u_{\text{phenylalaninate}}$ (Table S4 in [45]). Therefore, the variation in torsions $\varphi^1$ and $\psi$ are smaller [Fig. 3(c),(d)]. A possible reason for the weaker modulations of the atoms around the chiral centers is the directional strong intermolecular N–H···O bonds makes large intramolecular rotations unfavorable. Note that the observed changes in the rotations $\varphi^2$ [Fig. 3(b)] of molecule ‘A’ are predominantly described by strong modulations of the molecule’s biphenyl moiety. Nevertheless, the unequal values at the relevant $t$-sections of $\varphi^3$ are correlated to those of $\varphi^2$ [compare Fig. 3(a) and Fig. 3(b)] suggesting the chemical influence of the amide groups on the phenyl rings and vice-versa.

In the modulated structure, the biphenyl moieties in (AA)$_n$ and (BB)$_n$ stacks are tilted with respect to each other [Fig. 3(e)] which are parallel in phase I. These tilts ($\theta_{AA/BB}$) are of the order of the internal twists, $\varphi^3$ of the independent biphenyl moieties [compare Fig. 3(e) to Fig. 3(a)] The orientation between the biphenyl moieties within the (ABAB)$_n$ stacks also vary with $\Delta\theta_{AA/BB} \simeq 12$ deg where the value is intermediate to $\varphi^3_A$ and $\varphi^3_B$ [compare Fig. 3(e) to Fig. 3(a)]. In addition, intermolecular distances between the biphenyl moieties within the stacks at the two $t$-sections are different and vary up to $\Delta d_{AA/BB} \simeq 0.05$ Å and $\Delta d_{ABAB} \simeq 0.02$ Å[Fig. 3(f)]. However, these variations in $d$ are small compared to the molecular tilts, $\theta$. It could therefore be argued that the dimerization of biphenyl molecular stacks below $T_c$ are predominantly governed by distortion described by molecular rotations rather than intermolecular distances. On the other hand, intermolecular distances between aromatic rings of L-phenylalaninate vary similarly to the biphenyls albeit significantly smaller interstack rotations, $\theta < 3$ deg (Fig. S5 in [63]).

The increased distortions are also accompanied by suppression of dynamic disorder below $T_c$. For example, the carbon atoms at ortho (C14, C16, C19, C23) and meta (C13, C17, C20, C22) positions are strongly displaced (Fig. 5, Table S4 and S5 in [45]). Subsequently, the ADPs are significantly reduced as compared to phase I (Fig. 5, Table S5 in [45]). Notably, decrease of the ADPs ($U_{eq}$) from $T = 160$ K to $T = 100$ K is larger for those of molecule ‘A’ than those for ‘B’, while the square of the amplitude of modulations ($u^2$) are greater for ‘A’ than those for ‘B’ [compare Fig. 5(b) to Fig. 5(a)].
FIG. 3. $t$-plots of intramolecular rotations of molecule ‘A’ (blue) and ‘B’ (red) as well as intermolecular tilts and distances between stacks of 4-biphenylcarxy-(L)-phenylalaninate. (a) Dihedral angle, $|\varphi^3|$ represents internal torsion within biphenyl; (b) Dihedral angle, $|\varphi^2|$ represents torsion between the inner ring of biphenyl and the amide groups; (c) $\varphi^1$ represents torsion of the amide groups with respect to the -COOCH$_3$ groups; (d) $\psi$ represent torsion of -COOCH$_3$ groups with respect to amide groups. (e) $|\theta_{AA/BB}|$ represent tilt between biphenyl rings of ‘A’ and ‘A’$^{ii}$ (blue); and of ‘B’ and ‘B’$^{ii}$ (red) and $|\theta_{AB/BA}|$ (dashed-dotted black curve) represent tilt between inner aromatic rings of biphenyl (bonded to amide groups) of ‘A’ and outer ring of ‘B’ and vice-versa. (f) Intermolecular distances ($d$) between biphenyl rings of ‘A’ and ‘A’$^{ii}$ (blue), between those of ‘B’ and ‘B’$^{ii}$ (red) and between those of ‘A’ and ‘B’ (black). Horizontal dashed lines represent those angles and distances in phase I ($|\varphi^3| = |\theta_{AA/BB}| = 0$ deg). Vertical dashed lines indicate $t$ values corresponding to angles and distances in the 3D superstructure.

B. Competitive forces governing modulations

Structural studies in the 3D phase of molecular biphenyl have suggested that the ortho-hydrogen atoms are displaced away in the plane of the rings to minimize steric hindrance [3, 4, 6]. On the other hand, dynamic disorder predominantly governed by torsional vibrations around the long molecular axis [22] is predicted to balance the planar conformation of
FIG. 4. Comparison of structures in phase I and phase II across the phase transition highlighting the effect of internal torsion (ϕ3) within biphenyl on the stacking arrangements along a. The tilt between the biphenyl stacks, θAA/BB are different for the inner rings (bonded to amide rings) and the outer rings [corresponding values in t-plot in Fig. 3(e)]. See full unit cells in Fig. S6 in [45]. View along [100].

biphenyl favourable for crystal packing [9]. As short as 1.98 Å in phase I (Table II), these contacts are shorter than the predicted values for twice van der Waals radius for hydrogen (r = 1.1–1.2 Å [64, 65]). In the modulated structure, we observe that the distances between the ortho-hydrogen atoms are marginally but consistently larger than those in phase I (Table II) that could suggest that the torsional modulations aid in minimization of the presumed steric hindrance below Tc [63, 66].

A peculiar property of the modulated structure under discussion is the significant difference in the torsional amplitude ϕ3 of the independent molecules. This aspect cannot be explained solely based on the intramolecular steric factors. Analysis of the crystal packing shows that each of these independent biphenyl moieties maintains close intermolecular CH···HC contacts with the phenyl rings of L-phenylalaninate in AB and BA fashion (Fig. 4). These distances are significantly longer (intermolecular dH···H ≥ 2.4 Å, Table II) compared to the intramolecular H···H distances. On the other hand, the aromatic rings of
FIG. 5. Scatter plots of equivalent value of anisotropic ADPs ($U_{eq}$) and square of the amplitude of modulations ($u^2$) of the carbon atoms of biphenyl moieties (C12 through to C23, see Fig. 1.) of molecule ‘A’ (blue) and ‘B’ (red). (a) $U_{eq}$ of the carbon atoms at $T = 160$ K (open circles) and at $T = 100$ K (full circles). (b) $u^2$ (diamonds) of the corresponding carbon atoms of molecule ‘A’ and ‘B’. See Table S5 in [45].

L-phenylalaninate interact with adjacent oxygen atoms of –COOCH$_3$ via C–H···O hydrogen bonds (Fig. 4 and Table II). These hydrogen bonds are weaker [67] but highly directional ($\angle$(C–H···O) = 159–164 deg) with very little variation in the distances. Interestingly, those H···H distances involving biphenyl moieties of ‘B’ are consistently smaller than those of ‘A’ in both phases (Table II). We argue that in the presence of both the van der Waals interactions and weak C–H···O bonds, the larger distortions of ‘A’ is favored by weaker CH···HC interactions while that is suppressed in ‘B’. The four different values of intramolecular torsion $\phi^3$ within the biphenyl moieties is distinctively governed by intra- and intermolecular non-bonded H···H contacts as well as weak hydrogen bonds.
TABLE II. Comparison of non-bonded hydrogen···acceptor and hydrogen···hydrogen distances (Å) involved in hydrogen bonds and steric factors in phase I ($T_1$) and phase II ($T_2$; $t = \frac{1}{4}; \frac{3}{4}$) respectively. Symmetry codes: Phase I– (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $-x+1, y+\frac{1}{2}, -z+1$; (iv) $-x+2, y-\frac{1}{2}, -z$.
Phase II– (i) $x-1, y, z, t$; (ii) $x+1, y, z, t$; (iii) $-x+1, y+\frac{1}{2}, -z+1, -t$; (iv) $-x+2, y-\frac{1}{2}, -z, -t$.

| Interaction class | Atom group labels | Phase | distances (Å) |
|-------------------|-------------------|-------|---------------|
| N–H···O           | H1n1a···O3a<sup>i</sup> | I     | 2.00          |
|                   |                   | II    | 1.97; 1.95    |
|                   | H1n1b···O3b<sup>ii</sup> | I     | 2.00          |
|                   |                   | II    | 1.98, 2.00    |
| C–H···O           | H1c10a···O2a<sup>iii</sup> | I     | 2.72          |
|                   |                   | II    | 2.72; 2.68    |
|                   | H1c10b···O2b<sup>iv</sup> | I     | 2.78          |
|                   |                   | II    | 2.74; 2.73    |
| Intra H···H       | H1c14a···H1c19a   | I     | 1.98          |
|                   |                   | II    | 2; 2          |
|                   | H1c14b···H1c19b   | I     | 1.98          |
|                   |                   | II    | 2; 2          |
|                   | H1c16a···H1c23a   | I     | 2.03          |
|                   |                   | II    | 2.1; 2.2      |
|                   | H1c16b···H1c23b   | I     | 2.02          |
|                   |                   | II    | 2.03; 2.06    |
| Inter H···H       | H1c21a···H1c7b    | I     | 2.59          |
|                   |                   | II    | 2.6; 2.6      |
|                   | H1c21b···H1c7a<sup>ii</sup> | I | 2.45 |
|                   |                   | II    | 2.4; 2.5      |

IV. CONCLUSIONS

The single crystal to single crystal phase transition of 4-biphenylcarboxy-(L)-phenylalaninate below $T = 124$ K drives the 3D structure directly to a locked-in twofold superstructure. The
commensurately modulated structure at $T = 100$ K is accompanied by pronounced amplitudes of torsion within biphenyl that are characteristic of modulated and superstructures of other polyphenyls. The phase transition temperature is significantly higher than that in biphenyl yet significantly smaller than for p-terphenyl and p-quarterphenyl. Consistent with the $T_c$, the maximum amplitude of torsion is also intermediate and in the order $\varphi_{\text{quarterphenyl}} \geq \varphi_{\text{terphenyl}} > \varphi_{\text{4-biphenylcarboxy-L-phenylalaninate}} > \varphi_{\text{biphenyl}}$.

Topologically separated, conformations of both the weaker C–H⋯O bonds and stronger N–H⋯O bonds are rigid and that underlines their role in stabilizing the crystal packing in both phases. A unique property of the present polyphenyl coupled amino acid ester is the distinctively unequal torsional amplitude ($\varphi_A > \varphi_B$) within the independent molecules which is governed by multiple level of competitions involving unequal van der Waals constraints in presence of weak hydrogen bonds between the biphenyl and L-phenylalaninate moieties. The unusual nature of the phase transition is described by the fact that unequal displacive modulations of the two molecules are complimented by unequal suppression of the dynamic disorder of their atoms below $T_c$. This difference in the torsion as well as the phase transition conditions highlights how conjugation of polyphenyls can possibly be influenced by amino acid esters which in turn influences supramolecular assemblies.

**ACKNOWLEDGMENTS**

We thank Prof. Sreenivasan Ramakrishnan, Dr. Vaclav Petricek, Dr. Sitaram Ramakrishnan, Prof. Venkataramanan Mahalingam and Dr. Saumya Mukherjee for helpful comments and fruitful discussions. Financial support from SERB-DST (DST-SERB:PDF/2018/002502) and Alexander von Humboldt foundation is gratefully acknowledged.

[1] O. Bastiansen, The molecular structure of biphenyl and some of its derivatives, Acta Chem. Scand. 3, 408 (1949).

[2] H. Suzuki, Relations between electronic absorption spectra and spatial configurations of conjugated systems. I. Biphenyl, Bull. Chem. Soc. Jpn 32, 1340 (1959).

[3] J. Trotter, The crystal and molecular structure of biphenyl, Acta Crystallogr. 14, 1135 (1961).
A. Hargreaves and S. H. Rizvi, The crystal and molecular structure of biphenyl, Acta Crystallogr. 15, 365 (1962).

G. Casalone, C. Mariani, A. Mugnoli, and M. Simonetta, The molecular structure of biphenyl in the gas and solid phases, Mol. Phys. 15, 339 (1968).

G. P. Charbonneau and Y. Delugeard, Structural transition in polyphenyls. III. Crystal structure of biphenyl at 110 K, Acta Crystallogr. B 32, 1420 (1976).

G. P. Charbonneau and Y. Delugeard, Biphenyl: Three-dimensional data and new refinement at 293 K, Acta Crystallogr. B 33, 1586 (1977).

W. R. Busing, Modeling the phase change in crystalline biphenyl by using a temperature-dependent potential, Acta Crystallogr. A 39, 340 (1983).

A. T. H. Lenstra, C. van Alsenoy, K. Verhulst, and H. J. Geise, Solids modelled by crystal field ab initio methods. 5. The phase transitions in biphenyl from a molecular point of view, Acta Crystallogr. B 50, 96 (1994).

P. L. A. Popelier, P. I. Maxwell, J. C. R. Thacker, and I. Alkorta, A relative energy gradient (REG) study of the planar and perpendicular torsional energy barriers in biphenyl, Theor. Chem. Acc. 138, 12 (2019).

R. M. Hochstrasser, R. D. McAlpine, and J. D. Whiteman, Low energy magnetic and electric dipole transitions of the biphenyl crystal, J. Chem. Phys. 58, 5078 (1973).

N. I. Wakayama, Low-energy electronic transitions and phase transition of the biphenyl crystal, Chem. Phys. Lett. 83, 413 (1981).

P. S. Friedman, R. Kopelman, and P. N. Prasad, Spectroscopic evidence for a continuous change in molecular and crystal structure: Deformation of biphenyl in the low temperature solid, Chem. Phys. Lett. 24, 15 (1974).

A. Bree and M. Edelson, A study of the second order phase transition in biphenyl at 40 K through Raman spectroscopy, Chem. Phys. Lett. 46, 500 (1977).

A. Bree and M. Edelson, Further evidence for phase transitions in biphenyl near 40 K and 16 K, Chem. Phys. Lett. 55, 319 (1978).

C. Ecolivet and M. Sanquer, Brillouin scattering in polyphenyls. II. Through the incommensurate phases of biphenyl, J. Chem. Phys. 78, 6317 (1983).

H. Cailleau, F. Moussa, and J. Mons, Incommensurate phases in biphenyl, Solid State Commun. 31, 521 (1978).
[18] P. M. de Wolff, The pseudo-symmetry of modulated crystal structures, Acta Crystallogr. A 30, 777 (1974).

[19] H. T. Stokes, B. J. Campbell, and S. van Smaalen, Generation of (3 + d)-dimensional superspace groups for describing the symmetry of modulated crystalline structures, Acta Crystallogr. A 67, 45 (2011).

[20] S. van Smaalen, B. J. Campbell, and H. T. Stokes, Equivalence of superspace groups, Acta Crystallogr. A 69, 75 (2013).

[21] J. L. Baudour and M. Sanquer, Structural phase transition in polyphenyls. VIII. The modulated structure of phase III of biphenyl (\(T \simeq 20\) K) from neutron diffraction data, Acta Crystallogr. B 39, 75 (1983).

[22] V. Petricek, P. Coppens, and P. Becker, Structure analysis of displacively modulated molecular crystals, Acta Crystallogr. A 41, 478 (1985).

[23] C. B. Pinheiro and A. M. Abakumov, Superspace crystallography: a key to the chemistry and properties, IUCrJ 2, 137 (2015).

[24] A. Schoenleber, Organic molecular compounds with modulated crystal structures, Z. Kristallogr. 226, 499 (2011).

[25] Y. Ishibashi, A tentative phenomenological theory of incommensurate phase transitions in biphenyl, J. Phys. Soc. Jpn. 50, 1255 (1981).

[26] C. Benkert, V. Heine, and E. H. Simmons, The incommensurate phase transition of biphenyl, J. Phys. C: Solid State Phys. 20, 3337 (1987).

[27] C. Benkert and V. Heine, Excitations in biphenyl’s incommensurate phase III, Phys. Rev. Lett. 58, 2232 (1987).

[28] K. Parlinski, W. Schranz, and H. Kabelka, Phenomenological theory of incommensurate phases in biphenyl, Phys. Rev. B 39, 488 (1989).

[29] D. Vonlanthen, A. Mishchenko, M. Elbing, M. Neuburger, T. Wandlowski, and M. Mayor, Chemically controlled conductivity: Torsion-angle dependence in a single-molecule biphenyldithiol junction, Angew. Chem. Int. Ed. 48, 8886 (2009).

[30] A. Mishchenko, D. Vonlanthen, V. Meded, M. Buerkle, C. Li, I. V. Pobelov, A. Bagrets, J. K. Viljas, F. Pauly, F. Evers, M. Mayor, and T. Wandlowski, Influence of conformation on conductance of biphenyl-dithiol single-molecule contacts, Nano Lett. 10, 156 (2010).

[31] M. Buerkle, J. K. Viljas, D. Vonlanthen, A. Mishchenko, G. Schoen, M. Mayor, T. Wandlowski,
and F. Pauly, Conduction mechanisms in biphenyl dithiol single-molecule junctions, Phys. Rev. B 85, 075417 (2012).

[32] H. Jeong, H. B. Li, L. Domulevicz, and J. Hihath, An on-chip break junction system for combined single-molecule conductance and Raman spectroscopies, Adv. Funct. Mater. 30, 2000615 (2020).

[33] M. Cranney, G. Comtet, G. Dujardin, J. W. Kim, T. U. Kampen, K. Horn, M. Mamatkulov, L. Stauffer, and P. Sonnet, Electronic structure of biphenyl on Si(100), Phys. Rev. B 76, 075324 (2007).

[34] R. Khatua, S. R. Sahoo, S. Sharma, and S. Sahu, Anisotropic charge transport and optoelectronic properties of wide band gap organic semiconductors based on biphenyl derivatives: A computational study, Synth. Met. 267, 116474 (2020).

[35] K. Oniwa, T. Kanagasekaran, T. Jin, M. Akhtaruzzaman, Y. Yamamoto, H. Tamura, I. Hamada, H. Shimotani, N. Asao, S. Ikeda, and K. Tanigaki, Single crystal biphenyl end-capped furan-incorporated oligomers: Influence of unusual packing structure on carrier mobility and luminescence, J. Mater. Chem. C 1, 4163 (2013).

[36] J. Wei, B. Liang, R. Duan, Z. Cheng, C. Li, T. Zhou, Y. Yi, and Y. Wang, Induction of strong long-lived room-temperature phosphorescence of N-phenyl-2-naphthylamine molecules by confinement in a crystalline dibromobiphenyl matrix, Angew. Chem. Int. Ed. 55, 15589–(2016).

[37] C. C. C. J. Seechurn, M. O. Kitching, T. J. Colacot, and V. Snieckus, Palladium-catalyzed cross-coupling: A historical contextual perspective to the 2010 Nobel Prize, Angew. Chem. Int. Ed. 51, 5062 (2012).

[38] S. Sasmal, D. Podder, M. Debnath, S. K. Nandi, and D. Haldar, Assembly-induced diverse optical property of 4-biphenylcarboxy-protected serine and tyrosine, ChemistrySelect 4, 10302–(2019).

[39] S. Sasmal, S. K. Nandi, S. Kumar, and D. Haldar, Atomic-level insight of self-assembled nanorods from 4-biphenylcarboxy protected L-phenylalanine, ChemistrySelect 4, 11172 (2019).

[40] K. M. Steed and J. W. Steed, Packing problems: High Z’ crystal structures and their relationship to cocrystals, inclusion compounds, and polymorphism, Chem. Rev. 115, 2895 (2015).

[41] A. Janner and T. Janssen, Symmetry of periodically distorted crystals, Phys. Rev B 15, 643
(1977).

[42] T. Wagner and A. Schoenleber, A non-mathematical introduction to the superspace description of modulated structures, Acta Crystallogr. B 65, 249 (2009).

[43] S. van Smaalen, Incommensurate Crystallography, 1st ed. (Oxford University Press, 2012).

[44] T. Janssen, G. Chapuis, and M. de Boissieu, Aperiodic Crystals: From Modulated Phases to Quasicrystals: Structure and Properties, 2nd ed. (Oxford University Press, 2018).

[45] See Supplemental Material for details on structure refinements, powder X-ray diffraction experiments, diffraction images, t-plots, Fourier maps, crystal packing diagrams and tables of crystallographic data, bond distances, modulation amplitudes and atomic displacement parameters, which includes Ref. [51, 52].

[46] Y. Yamamura, K. Saito, I. Ikemoto, and M. Sorai, Entropic evidence of the order-disorder nature of the phase transition in p-terphenyl crystal, J. Phys.: Condens. Matter 10, 3359 (1998).

[47] K. Saito, T. Atake, and H. Chihara, Molar heat capacity and thermodynamic properties of p-quaterphenyl, J. Chem. Thermodynamics 17, 539 (1985).

[48] CrysAlisPro Software system, Rigaku Oxford Diffraction, Rigaku Corporation, Oxford, UK (2019).

[49] A. Schoenleber, M. Meyer, and G. Chapuis, NADA - a computer program for the simultaneous refinement of orientation matrix and modulation vector(s), J. Appl. Crystallogr. 34, 777 (2001).

[50] L. Palatinus and G. Chapuis, SUPERFLIP - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions, J. Appl. Crystallogr. 40, 786 (2007).

[51] V. Petricek, M. Dusek, and L. Palatinus, Crystallographic computing system JANA2006: General features, Z. Kristallogr. 229, 345 (2014).

[52] V. Petricek et al, JANA2020, Institute of Physics, Prague, Czech Republic (2022).

[53] V. Petricek, M. Dusek, and J. Plasil, Crystallographic computing system JANA2006: solution and refinement of twinned structures, Z. Kristallogr. 231, 583 (2016).

[54] M. Nespolo, The chromatic symmetry of twins and allotwins, Acta Crystallogr. A 75, 551 (2019).

[55] A. P. Rice, F. S. Tham, and E. L. Chronister, A temperature dependent X-ray study of the order-disorder enantiotropic phase transition of p-terphenyl, J. Chem. Crystallogr. 43, 14
J. L. Baudour, Y. Delugeard, and P. Rivet, Structural phase transition in polyphenyls. VI. Crystal structure of the low-temperature ordered phase of \( p \)-quaterphenyl at 110 K, Acta Crystallogr. B 34, 625 (1978).

T. Rekis, A. Schoenleber, L. Noohinejad, M. Tolkiehn, C. Paulmann, and S. van Smaalen, Toward understanding high-\( Z' \) organic molecular crystals through the superspace method: The example of glycyl-L-valine, Cryst. Growth Des. 21, 2324 (2021).

S. Ramakrishnan, A. Schoenleber, C. B. Huebschle, C. Eisele, A. M. Schaller, T. Rekis, N. H. A. Bui, F. Feulner, S. van Smaalen, B. Bag, S. Ramakrishnan, M. Tolkiehn, and C. Paulmann, Charge density wave and lock-in transitions of \( \text{CuV}_2\text{S}_4 \), Phys. Rev. B 99, 195140 (2019).

S. Dey, A. Schoenleber, S. Mondal, S. J. Prathapa, S. van Smaalen, and F. K. Larsen, The \( Z' = 12 \) superstructure of \( \text{A-cobalt(III)} \) sepulchrate trinitrate governed by C–H⋯O hydrogen bonds, Acta Crystallogr. B 72, 372 (2016).

L. Noohinejad, S. Mondal, S. I. Ali, S. Dey, S. van Smaalen, and A. Schoenleber, Resonance-stabilized partial proton transfer in hydrogen bonds of incommensurate phenazine-chloranilic acid, Acta Crystallogr. 71, 228 (2015).

A. Schoenleber, P. Pattison, and G. Chapuis, The (3 + 1)-dimensional superspace description of the commensurately modulated structure of \( p \)-chlorobenzamide (\( \alpha \)-form) and its relation to the \( \gamma \)-form, Z. Kristallogr. 218, 507 (2003).

J. L. Baudour, Y. Delugeard, and H. Cailleau, Transition structurale dans les polyphenyles. I. Structure cristalline de la phase basse temperature du-\( p \)-terphenyle a 113 K, Acta Crystallogr. B 32, 150 (1976).

S. Dey, A. Schoenleber, S. van Smaalen, W. Morgenroth, and F. K. Larsen, Incommensurate phase in \( \text{A-cobalt (III)} \) sepulchrate trinitrate governed by highly competitive N—H⋯O and C—H⋯O hydrogen bond networks, Chem. Eur. J. 28, e202104151 (2022).

R. S. Rowland and R. Taylor, Intermolecular nonbonded contact distances in organic crystal structures: Comparison with distances expected from van der waals radii, J. Phys. Chem. 100, 7384 (1996).

S. Alvarez, A cartography of the van der waals territories, Dalton Trans. 42, 8617 (2013).

S. Dey, A. Schoenleber, S. Mondal, S. I. Ali, and S. van Smaalen, Role of steric hindrance in
the crystal packing of \( Z' = 4 \) superstructure of trimethyltin hydroxide, Cryst. Growth Des. \textbf{18}, 1394 (2018).

[67] G. R. Desiraju and T. Steiner, \textit{The Weak Hydrogen Bond: In Structural Chemistry and Biology}, 1st ed. (Oxford University Press, 2001).
Supplemental material

Unequal torsional rotations driven by normal to modulated phase transition in 4-biphenylcarboxy coupled L-phenylalaninate governed by non-covalent constraints

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Details of structure refinements of different modulated structure models

Structure refinements have been performed using JANA2006\textsuperscript{1} and JANA2020\textsuperscript{2}. Structural model at $T = 160$ K has been used as an initial model for the basic structure of the modulated structure at $T = 100$ K. All atoms were set to isotropic for displacement parameters and the model was refined against main reflections [$R^\text{obs}(m=0) = 0.0723$]. In the next step, first order harmonic for displacive modulation was described for all atoms and an incommensurate (IC) model was refined against main and satellite reflections. Refinement led to improved fit to the main reflections [$R^\text{obs}(m=0) = 0.0586$, $R^\text{obs}(m=1) = 0.1215$]. Refinement of the anisotropic atomic displacement parameters (ADPs) of all non-hydrogen atoms resulted in significant improvement to the residual values [IC model A: $R^\text{obs}(m=0) = 0.0374$, $R^\text{obs}(m=1) = 0.0771$] and residual features ($\Delta \rho_{\text{min}}/\Delta \rho_{\text{max}}$) decreased from -0.68/1.23 eÅ$^{-3}$ to -0.33/0.31 eÅ$^{-3}$. However, ADPs of four non-hydrogen atoms were found to be non-positive definite.

In the next step, IC model A was used as a starting model to describe three commensurate (C) models by fixing the initial phase of the modulation, $t_0 = 0$, $\frac{1}{4}$ and $\frac{1}{8}$ respectively. The former two $t_0$ values correspond to $2a \times b \times 2c$ superstructure in 3D with monoclinic symmetry $B2_1$ while the later correspond to a superstructure with triclinic $B1$ symmetry. Restrictions on $t_0$ values also impose constraints on the refinable variables corresponding to atomic modulation functions (AMFs). These restrictions follow the argument that the total number of refinable parameters in the equivalent 3D superstructure and their (3+1)D commensurately modulated structural models must be equal. In the present case, either sin or cos waves can be refined for structural models with $t_0 = 0$ and $\frac{1}{4}$ because the point group symmetry is same in their corresponding 3D superstructure models. On the other hand, assumed monoclinic to triclinic distortion in the 3D superstructure (space group $B1$)corresponding to (3+1)D C model with $t_0 = \frac{1}{8}$ can be derived by using both components of the Fourier series. It must be noted that such restrictions on sin and cos waves cannot be formally imposed on the AMFs of hydrogen atoms in JANA2006 and JANA2020 as their modulations are fully determined by geometrical conditions of the riding model. $t_0 = \frac{1}{4}$ yielded the best fit to the diffraction data (Table S3) with reduced number of parameters as compared to the IC model A (compare $N_{C,t_0=0.25} = 649$ to $N_{IC,\text{model} A} = 811$). Most importantly, ADPs of all non-hydrogen atoms are positive definite.

Notably, the residual values of the IC model as well as the C model at $t_0 = \frac{1}{8}$ is marginally
smaller than for the C model at \( t_0 = \frac{1}{4} \). Assuming all the three models should fit similarly to the diffraction data for equivalent descriptions of structural models further tests included attempts to refine the IC model and C model at \( t_0 = \frac{1}{8} \) with reduced number of parameters (= 649) similar to \( t_0 = \frac{1}{4} \). Refinements led to worse fit with large \( R \)-values (Table S3).

In the final step, all reflections were averaged in monoclinic symmetry corresponding to \( t_0 = 0 \). One parameter corresponding to isotropic extinction correction was refined. Finally, fractional co-ordinates and AMFs for hydrogen atoms belonging to N–H groups involved in strong hydrogen bonds improved the fit to the diffraction data marginally (\( R_{\text{obs}}^2 = 0.0419 \) in Table S2).

Additional refinement was performed including first order harmonic for anisotropic ADPs of all non-hydrogen atoms. Refinement of this model with additional 324 parameters converged with marginal improvement of \( R_{\text{obs}}^2 \) (= 0.0406) values. However, the residual density \( \Delta \rho_{\text{min}}/\Delta \rho_{\text{max}} \) remained unchanged [compare -0.26/0.28 e/Å\(^3\) to -0.25/0.29 e/Å\(^3\)] and 306 parameters refined to values within three times their standard uncertainties. The model was therefore discarded. Thus the superspace approach reduced the total numbers of refinable parameters by \( \sim 33 \% \).

**Additional X-ray diffraction experiments**

Powder X-ray diffraction experiments were performed on thoroughly ground powder of the compound at ambient conditions using a Rigaku SmartLab with a CuK\( \alpha \) radiation. JANA2006 was used to index the diffraction patterns. For reference, lattice parameters at ambient conditions were obtained from single crystal X-ray diffraction (SCXRD) experiment at ambient conditions (Table S7). The PXRD pattern could not be indexed using the lattice parameters as obtained from the SCXRD data [Fig. S7(a)] that suggest that the compound undergoes phase transition upon grinding. Lattice parameters were calculated employing the singular value decomposition (SVD)-Index algorithm in TOPAS\(^3\).\(^4\). The PXRD pattern could be indexed using a primitive triclinic cell (Cell 1) with unit cell volume comparable to that of single crystal [Table S7, Fig. S7(b)]. Another triclinic cell (Cell 2) could also describe the pattern [Fig. S7(c)]. Le Baile refinements of the patterns against both the cells resulted in similar residual values (Table S7). However, Cell 1 fits better to the PXRD than Cell 2 [compare inset plots of Fig S7(b) and Fig S7(c)]. In addition, the unit cell volume of Cell 2 is larger than 7.5 % to that of the single crystal that implies different density of the ground material.

Based on this difference of phases between single crystals (monoclinic structure) and pulverised material (triclinic structure), \( T \)-dependent PXRD experiments to complement the single crystal to single crystal phase transition in this material was not pursued.
Figure S1: Diffraction images across the normal (phase I) to commensurately modulated (phase II) phase transition. Red arrows depict Bragg peaks in phase I and main Bragg peaks in phase II. The satellites are diffuse at $T = 124$ K (green arrow) that becomes stronger at lower temperatures. Reflections at $T = 126$ K are indexed using three integers ($hkl$) and at $T_c = 124$ K and lower temperatures by four integers ($hklm$), where $m = 0$ and $m = 1$ for main and satellite reflections respectively. Image resolution range in $d \sim 2.2$ to 1.1 Å.
Figure S2: \((x_{si}, x_{sd})\)-sections of Fourier map centered on nitrogen atoms (light blue) of amide groups (a) atom N1a of molecule ‘A’ and (b) atom N1b of molecule ‘B’. The contour line and the width of the maps are 0.5 eÅ\(^{-3}\) and 2.5 Å respectively.
Figure S3: \((x_{s1},x_{s4})\)-sections of Fourier map centered on carbon atoms (black) (a) C8a of molecule ‘A’ and (b) C8b of molecule ‘B’ respectively belonging to the phenyl ring of L-phenylalaninate moieties. The contour line and the width of the maps are 0.5 e\(\text{Å}^{-3}\) and 2.5 \(\text{Å}\) respectively.
Figure S4: (a) and (b) $(x_{si},x_{s4})$-sections of Fourier map centered on oxygen atoms (orange) O2a of molecule ‘A’ and O2b of molecule ‘B’ respectively belonging to carboxylate groups of L-phenylalaninate moieties. The contour line and the width of the maps are $0.5 \text{ eÅ}^{-3}$ and $2.5 \text{ Å}$ respectively.
Figure S5: $t$-plots of (a) angle ($\theta$) and (b) distances ($d$) describing the tilt and intermolecular distances between phenyl rings of L-phenylalaninate moieties within stacks along $\mathbf{a}$. 
Figure S6: Crystal packing of 4-biphenylcarboxy-(L)-phenylalaninate at (a) $T = 160$ K (phase I) and (b) $2a \times b \times 2c$ superstructure at $T = 100$ K (phase II). Dashed orange lines depict linear N–H···O hydrogen bonds along [±100] directions, while green dashed lines represent C–H···O hydrogen bond dimers. Displacement ellipsoids are cut at 50% probability level. Viewing direction along [010].
Figure S7: Comparison of fit of the experimental powder X-ray diffraction pattern to (a) as obtained unit cell from SCXRD, (b) Calculated unit cell 1 with volume 1901 Å³ and (c) calculated unit cell with volume 2029 Å³. Experimental pattern, calculated profile and difference are given in black cross points, red curve and black curve respectively. The insets in 2θ = 7-20 deg are given in the right column corresponding to the area (dashed rectangle) in left.
Table S1: Technical details of SCXRD measurements and number of reflections used for calculation of lattice parameters and components of modulation wave vector, $q$.

| $T$ (K) | Number of runs | Number of images | $d_{\text{max}}$ (Å) | Number of reflections |
|---------|----------------|------------------|----------------------|----------------------|
| 160     | 27             | 1345             | 0.84                 | 3437                 |
| 150     | 9              | 45               | 0.84                 | 130                  |
| 140     | 9              | 45               | 0.84                 | 140                  |
| 130     | 9              | 45               | 0.84                 | 136                  |
| 128     | 9              | 45               | 0.84                 | 134                  |
| 126     | 9              | 45               | 0.84                 | 139                  |
| 124     | 9              | 45               | 0.84                 | 135                  |
| 122     | 9              | 45               | 0.84                 | 147                  |
| 120     | 9              | 45               | 0.84                 | 152                  |
| 118     | 9              | 45               | 0.84                 | 149                  |
| 116     | 9              | 45               | 0.84                 | 159                  |
| 114     | 9              | 45               | 0.84                 | 161                  |
| 100     | 26             | 1486             | 0.84                 | 3948                 |
Table S2: Experimental and crystallographic data

| Crystal data |       |
|--------------|-------|
| Chemical formula | C$_{23}$H$_{21}$NO$_3$ |
| $M_r$     | 359.42 |
| Temperature (K) | 160 100 |
| Crystal system | Monoclinic $b$-unique |
| $a$, $b$, $c$ (Å) | 5.0479(2), 8.6330(4), 42.1525(15) 5.0377(2), 8.5898(3), 42.0432(14) |
| $\beta$ (deg) | 90.513(3) 90.884(3) |
| $V$ (Å$^3$) | 1836.87(13) 1819.11(11) |
| Wave vector $(\mathbf{q})$ | $\frac{1}{2}\mathbf{a}^* + \frac{1}{2}\mathbf{c}^*$ |
| Space group | $P2_1$ |
| Superspace group | $P2_1(\sigma_10\sigma_3)0$ |
| Commensurate section | $t_0 = \frac{1}{4}$ |
| Supercell | $2a \times b \times 2c$ |
| Supercell space group | $B2_1$ |

| Diffraction data |       |
|------------------|-------|
| Wavelength CuK$\alpha$ |
| $d$ (Å) | 0.84 0.84 |
| $\Delta\omega$ (deg) | 1 1 |
| Absorption correction | multiscan |
| Criterion of observability | $I > 3\sigma(I)$ |

| Unique reflections |       |
|-------------------|-------|
| all (obs/all) | 4219/4555 5940/8898 |
| $m = 0$ (obs/all) | – 4150/4390 |
| $m = 1$ (obs/all) | – 1790/4508 |
| $R_{int}$ (obs/all) | 0.0200/0.0202 0.0248/0.0274 |
| $GoF$ (obs/all) | 1.57/1.54 1.60/1.40 |
| $R_F^{obs}/wR_F^{all}$ |       |
| all (obs/all) | 0.0393/0.0492 0.0419/0.0526 |
| $m = 0$ (obs/all) | – 0.0368/0.0460 |
| $m = 1$ (obs/all) | – 0.0791/0.1191 |
| $\Delta\rho_{min}/\Delta\rho_{max}$ (e/Å$^3$) | $-0.26/0.28$ |
| No. of parameters | 494 662 |
| H-atom treatment | mixed mixed |
| Twin law | $2 \parallel \mathbf{a}$ $2 \parallel \mathbf{a}$ |
| Twin volumes | 0.9760(8)/0.0240(8) 0.9758(7)/0.0242(7) |
Table S3: Statistical parameters ($R^{\text{obs}}_F$, $wR^{\text{all}}_F$) of the (3+1)D incommensurately modulated (IC) and commensurately modulated (C) refinements of models with different values of the phase $t_0$. Number of reflections (obs/all) used in the refinements are averaged for the lowest triclinic point group symmetry: ($m=0$) = 4911/5241, ($m=11$) = 2031/5537. Space group (SG) symmetries of the equivalent 3D superstructures corresponding to different C structures are given which for the IC structure is meaningless.

| SG             | IC       | $t_0 = 0$ | $t_0 = \frac{1}{8}$ | $t_0 = \frac{1}{4}$ |
|----------------|----------|-----------|---------------------|---------------------|
| No. of parameters | 811      | 649       | 649                 | 811                 |
| $GoF^{(\text{obs/all})}$ | 1.55/1.35 | 2.93/2.56 | 2.68/2.38           | 1.56/1.33            |
| ($R^{\text{obs}}_F$ (all)) | 0.0428   | 0.0745    | 0.0691              | 0.0428              |
| $wR^{\text{all}}_F$ (all) | 0.0539   | 0.1035    | 0.0961              | 0.0533              |
| $R^{\text{obs}}_F (m = 0)$ | 0.0381   | 0.0424    | 0.0401              | 0.0384              |
| $wR^{\text{all}}_F (m = 0)$ | 0.0473   | 0.0515    | 0.0492              | 0.0475              |
| $R^{\text{obs}}_F (m = 1)$ | 0.0777   | 0.3119    | 0.2838              | 0.0758              |
| $wR^{\text{all}}_F (m = 1)$ | 0.1232   | 0.3174    | 0.3653              | 0.1166              |
| $\Delta \rho^{\text{min}}/\Delta \rho^{\text{max}}$ (e/Å$^3$) | -0.33/0.31 | -1.28/1.30 | -1.04/1.09          | -0.31/0.30          |
| -ve ADPs | 4        | 4         | 1                   | none                |
| correlations > 0.6 | 1        | 20        | 1                   | 98                  |

S13
Table S4: Components of the amplitude of atomic modulation functions ($|u_x|$, $|u_y|$ and $|u_z|$) along the three basis vectors $a$, $b$ and $c$ respectively for molecules A and B.

| Atom | $|u_x|$ (Å) | $|u_y|$ (Å) | $|u_z|$ (Å) |
|------|------------|------------|------------|
|      | A          | B          | A          | B          | A          | B          |
| C1   | 0.0015     | 0.0086     | 0.0996     | 0.0198     | 0.0340     | 0.0092     |
| O1   | 0.0070     | 0.0050     | 0.0670     | 0.0120     | 0.0294     | 0.0071     |
| C2   | 0.0156     | 0.0166     | 0.0739     | 0.0129     | 0.0319     | 0.0198     |
| O2   | 0.0181     | 0.0433     | 0.0721     | 0.0283     | 0.0311     | 0.0483     |
| C3   | 0.0121     | 0.0081     | 0.0498     | 0.0077     | 0.0336     | 0.0134     |
| C4   | 0.0408     | 0.0045     | 0.0730     | 0.0112     | 0.0340     | 0.0172     |
| C5   | 0.0348     | 0.0070     | 0.0610     | 0.0077     | 0.0265     | 0.0244     |
| C6   | 0.0242     | 0.0010     | 0.0876     | 0.0009     | 0.0290     | 0.0311     |
| C7   | 0.0045     | 0.0066     | 0.0945     | 0.0002     | 0.0219     | 0.0286     |
| C8   | 0.0040     | 0.0196     | 0.0936     | 0.0112     | 0.0172     | 0.0378     |
| C9   | 0.0217     | 0.0388     | 0.0910     | 0.0361     | 0.0328     | 0.0563     |
| C10  | 0.0337     | 0.0136     | 0.0515     | 0.0198     | 0.0328     | 0.0357     |
| N1   | 0.0030     | 0.0247     | 0.0610     | 0.0180     | 0.0399     | 0.0387     |
| O3   | 0.0055     | 0.0045     | 0.0936     | 0.0249     | 0.0294     | 0.0345     |
| C11  | 0.0025     | 0.0035     | 0.0129     | 0.0155     | 0.0282     | 0.0189     |
| C12  | 0.0171     | 0.0141     | 0.0137     | 0.0120     | 0.0256     | 0.0210     |
| C13  | 0.1083     | 0.0171     | 0.1898     | 0.0636     | 0.0029     | 0.0433     |
| C14  | 0.1098     | 0.0146     | 0.1898     | 0.0584     | 0.0027     | 0.0391     |
| C15  | 0.0191     | 0.0257     | 0.0266     | 0.0180     | 0.0277     | 0.0202     |
| C16  | 0.1501     | 0.0821     | 0.1623     | 0.0352     | 0.0597     | 0.0130     |
| C17  | 0.1657     | 0.0539     | 0.1787     | 0.0283     | 0.0631     | 0.0029     |
| C18  | 0.0237     | 0.0247     | 0.0275     | 0.0103     | 0.0467     | 0.0219     |
| C19  | 0.1264     | 0.0640     | 0.1366     | 0.0455     | 0.0446     | 0.0042     |
| C20  | 0.1446     | 0.0423     | 0.1580     | 0.0507     | 0.0500     | 0.0105     |
| C21  | 0.0081     | 0.0332     | 0.0060     | 0.0258     | 0.0332     | 0.0399     |
| C22  | 0.0972     | 0.0463     | 0.1349     | 0.0567     | 0.0244     | 0.0483     |
| C23  | 0.0922     | 0.0348     | 0.1572     | 0.0618     | 0.0160     | 0.0416     |
Table S5: Equivalent value of the ADP tensors, \((U_{eq})\) of atoms of the biphenyl moieties at \(T = 160\) K (phase I) and \(T = 100\) K (phase II); and the sum of the square of the amplitudes of their atomic modulation functions along three basis vectors \(u^2\) for molecules A and B. \(u^2 = (u_x)^2 + (u_y)^2 + (u_z)^2\).

| Atom label | Molecule | \(U_{eq,\text{PhaseI}} (\text{Å}^2)\) | \(U_{eq,\text{PhaseII}} (\text{Å}^2)\) | \(u^2 (\text{Å}^2)\) |
|------------|----------|-----------------------------------|-----------------------------------|-----------------|
| C12        | A        | 0.0271                            | 0.0193                            | 0.0011          |
|            | B        | 0.0235                            | 0.0182                            | 0.0008          |
| C13        | A        | 0.0489                            | 0.0250                            | 0.0478          |
|            | B        | 0.0430                            | 0.0369                            | 0.0062          |
| C14        | A        | 0.0505                            | 0.0267                            | 0.0481          |
|            | B        | 0.0439                            | 0.0371                            | 0.0051          |
| C15        | A        | 0.0274                            | 0.0203                            | 0.0018          |
|            | B        | 0.0248                            | 0.0185                            | 0.0014          |
| C16        | A        | 0.0439                            | 0.0256                            | 0.0525          |
|            | B        | 0.0414                            | 0.0334                            | 0.0081          |
| C17        | A        | 0.0430                            | 0.0233                            | 0.0634          |
|            | B        | 0.0393                            | 0.0310                            | 0.0037          |
| C18        | A        | 0.0275                            | 0.0193                            | 0.0035          |
|            | B        | 0.0279                            | 0.0202                            | 0.0012          |
| C19        | A        | 0.0482                            | 0.0286                            | 0.0366          |
|            | B        | 0.0419                            | 0.0304                            | 0.0062          |
| C20        | A        | 0.0535                            | 0.0314                            | 0.0484          |
|            | B        | 0.0442                            | 0.0311                            | 0.0045          |
| C21        | A        | 0.0363                            | 0.0270                            | 0.0012          |
|            | B        | 0.0354                            | 0.0232                            | 0.0034          |
| C22        | A        | 0.0497                            | 0.0311                            | 0.0282          |
|            | B        | 0.0418                            | 0.0293                            | 0.0077          |
| C23        | A        | 0.0488                            | 0.0272                            | 0.0335          |
|            | B        | 0.0356                            | 0.0262                            | 0.0068          |
Table S6: Comparison of interatomic bond distances (Å) of molecules A and B in phase I ($T = 160$ K) and phase II ($T = 100$ K).

| Atom groups | phase I | phase II |
|-------------|---------|----------|
|             | A       | B        | $t = \frac{1}{4}$ | $t = \frac{3}{4}$ | $t = \frac{1}{4}$ | $t = \frac{3}{4}$ |
| C1–O1       | 1.45    | 1.45     | 1.44           | 1.45         | 1.45           | 1.45         |
| O1–C2       | 1.31    | 1.33     | 1.32           | 1.32         | 1.33           | 1.33         |
| C2–O2       | 1.18    | 1.20     | 1.20           | 1.19         | 1.20           | 1.21         |
| C2–C3       | 1.52    | 1.53     | 1.52           | 1.52         | 1.52           | 1.52         |
| C3–C4       | 1.53    | 1.55     | 1.54           | 1.54         | 1.55           | 1.56         |
| C4–C5       | 1.51    | 1.51     | 1.50           | 1.51         | 1.51           | 1.51         |
| C5–C6       | 1.39    | 1.40     | 1.38           | 1.39         | 1.39           | 1.40         |
| C6–C7       | 1.39    | 1.38     | 1.38           | 1.38         | 1.38           | 1.38         |
| C7–C8       | 1.37    | 1.38     | 1.39           | 1.40         | 1.38           | 1.38         |
| C8–C9       | 1.38    | 1.39     | 1.38           | 1.38         | 1.40           | 1.39         |
| C9–C10      | 1.39    | 1.40     | 1.39           | 1.39         | 1.38           | 1.38         |
| C10–C5      | 1.39    | 1.38     | 1.40           | 1.39         | 1.39           | 1.39         |
| C3–N1       | 1.45    | 1.45     | 1.45           | 1.46         | 1.45           | 1.45         |
| N1–C11      | 1.34    | 1.33     | 1.33           | 1.33         | 1.32           | 1.33         |
| C11–O3      | 1.23    | 1.23     | 1.24           | 1.24         | 1.24           | 1.23         |
| C11–C12     | 1.50    | 1.50     | 1.50           | 1.50         | 1.50           | 1.51         |
| C12–C13     | 1.37    | 1.37     | 1.39           | 1.38         | 1.37           | 1.37         |
| C13–C14     | 1.39    | 1.39     | 1.39           | 1.38         | 1.39           | 1.39         |
| C14–C15     | 1.38    | 1.38     | 1.40           | 1.39         | 1.39           | 1.39         |
| C15–C16     | 1.38    | 1.37     | 1.40           | 1.38         | 1.38           | 1.38         |
| C16–C17     | 1.39    | 1.39     | 1.39           | 1.39         | 1.38           | 1.39         |
| C17–C12     | 1.37    | 1.38     | 1.39           | 1.38         | 1.39           | 1.38         |
| C15–C18     | 1.49    | 1.50     | 1.48           | 1.49         | 1.50           | 1.50         |
| C18–C19     | 1.39    | 1.40     | 1.39           | 1.40         | 1.39           | 1.39         |
| C19–C20     | 1.39    | 1.38     | 1.38           | 1.38         | 1.39           | 1.38         |
| C20–C21     | 1.36    | 1.38     | 1.39           | 1.39         | 1.37           | 1.38         |
| C21–C22     | 1.36    | 1.37     | 1.38           | 1.37         | 1.37           | 1.37         |
| C22–C23     | 1.39    | 1.38     | 1.39           | 1.39         | 1.37           | 1.39         |
| C23–C18     | 1.38    | 1.39     | 1.39           | 1.40         | 1.40           | 1.39         |
Table S7: Comparison of lattice parameters and residual values from Le baile fit of the PXRD pattern based on two unit cells. Lattice parameters obtained from SCXRD data has been given as reference.

|       | SCXRD         | PXRD          |
|-------|---------------|---------------|
|       | Cell 1  | Cell 2   |
| \(a\) (Å) | 5.0646(2) | 14.5357(12) | 13.7041(10) |
| \(b\) (Å) | 8.7483(3) | 8.6153(6)  | 13.0856(9)  |
| \(c\) (Å) | 42.4157(15)| 16.5541(12)| 11.4692(8)  |
| \(\alpha\) (deg) | 90    | 108.248(5) | 89.337(7)   |
| \(\beta\) (deg)  | 90    | 103.902(4) | 99.307(5)   |
| \(\gamma\) (deg) | 90    | 80.233(5)  | 89.436(7)   |
| \(V\) (Å³)       | 1879.27(12)| 1901.1(3)  | 2029.4(3)   |
| GoF           | –     | 3.51       | 3.53        |
| \(R_p/wR_p\)   | –     | 0.0422/0.0642 | 0.0416/0.0646 |
References

[1] V. Petricek, M. Dusek, and L. Palatinus, Z. Kristallogr. 229, 345 (2014).

[2] V. Petricek et al, JANA2020, Institute of Physics, Prague, Czech Republic (2022).

[3] A. A. Coelho, J. Appl Crystallogr. 51, 210 (2018).

[4] A. A. Coelho, J. Appl Crystallogr. 36, 86 (2003).