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ARTICLE

Concomitant Conformational Dimorphism in 1,2-Bis(9-anthryl)acetylene

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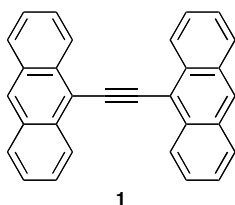
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Previous literature reports have shown that single crystals of 1,2-bis(9-anthryl)acetylene (**1**), in which the molecule is essentially planar, can be fabricated as organic field effect transistors. We have identified a new conformational polymorph of **1** in which the two anthracene moieties are twisted out of plane by more than 60°. Occasionally, both the planar (**1α**) and twisted (**1β**) polymorphic forms crystallize out together representing a rare example of concomitant conformational polymorphism in a pure hydrocarbon. The two polymorphic forms also show distinctly different colours and morphologies - the planar form (**1α**) grows as long orange-red needles whereas the twisted form (**1β**) appears as yellow blocks. Furthermore, a variety of electronic structure-based calculations show that the planar molecule forms the more stable polymorph (**1α**), despite the conformation being close to the maximum in conformational energy. This may be attributed to **1α** being stabilized by greater intermolecular dispersion forces as the planar conformation allows a denser packing. The new polymorph (**1β**) is a long-lived metastable structure, because of the marked difference in crystal packing. Since the conformation in **1β** is more stable in isolation, and probably in solution state, this discovery raises questions about the control of crystallization of anthracene-based functional materials and the assumptions about conformational polymorphism commonly made in crystal structure prediction studies.

Introduction

Small molecules with extended π -conjugation have attracted much attention in recent years for the fabrication of organic electronic devices.¹ In this regard, anthracene-based compounds have been especially promising as their stability toward oxidative and photochemical degradation, solubility, processability, and molecular packing lead to desirable optoelectronic properties.^{1a, 1c, 2} It was recently demonstrated by Li, Hu, and coworkers that single-crystalline ribbons of the H-type molecule, 1,2-bis(9-anthryl)acetylene (**1**), could be fabricated into high performance, short-channel, organic field-



effect transistors (OFET) with their organic ribbon mask technique.³ Compound **1** has been also used as a reference for comparison to other anthracene-based functional materials.⁴ The crystal structure of **1** was first reported by Becker *et al.* nearly 30 years ago.⁵ That structure, identified as DITBEN in the Cambridge Structural Database⁶ revealed an essentially planar, centrosymmetric molecule. [The structure was redetermined more recently in connection with the OFET work noted above and the nearly planar geometry was confirmed.³] In a subsequent paper published in 1987,⁷ however, Becker and Andersson noted that the X-ray structure initially reported⁵ was from orange-red needle shaped crystals obtained by slow crystallization from dichloromethane at room temperature. Importantly, they also made the curious observation that recrystallization of **1** “from a stirred hot methylene chloride solution gives a “cubic” modification of lemon-yellow crystals.”⁵ The X-ray structure of these cube shaped crystals, however, was not determined. In the course of carrying out an unrelated project, we synthesized **1** and obtained the orange-red crystals from dichloromethane, referred to as **1α** in this study, previously described by Becker *et al.*^{5,7} On other occasions, however, notably from toluene, yellow block-like crystals were formed exclusively and are likely those observed by Becker and Andersson.⁷ We determined the molecular structure of these yellow crystals by single-crystal X-ray crystallography and report herein that they are composed of a new, nonplanar,

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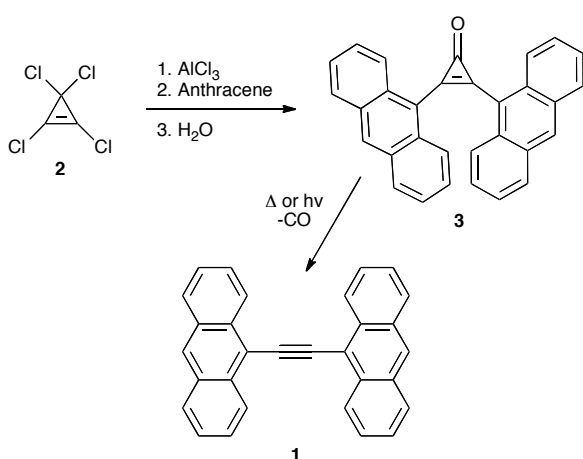
Electronic Supplementary Information (ESI) available: The CIF files CCDC 1059941 and 1036772 have been deposited with the Cambridge Crystallographic Data Centre. A supporting information file has also been supplied with further experimental and computational details]. See DOI:

conformational polymorph of **1** that we denote as the **1 β** form. Remarkably, every once in a while, under conditions that are rather capricious, both the **1 α** and **1 β** grow concomitantly from solvents such as dichloromethane and 1,4-dioxan, and column fractions of hexanes/ethyl acetate. Although conformational polymorphism⁸ and concomitant polymorphism⁹ are individually well known, but usually separate, phenomena, *concomitant, conformational polymorphism* is less common, and especially rare in a pure hydrocarbon.¹⁰ Thus energy calculations were undertaken on these two polymorphs of **1**.

Experimental

Synthetic Procedure

For this work we synthesized **1** by the method of Wadsworth and Donatelli as shown in Scheme 1.¹¹ Thus, the AlCl₃-promoted Friedel-Crafts reaction of tetrachlorocyclopropene (**2**) with anthracene and subsequent hydrolysis afforded the cyclopropanone **3**. Decarbonylation of **3** to produce **1** was carried out either thermally, as in the original procedure,¹¹ or photochemically following the modification of Becker *et. al.*⁵



Scheme 1. Synthesis of **1** via cyclopropanone **3**.

X-Ray Crystallography

X-ray data were collected at 173 K for both polymorphs, **1 α** and **1 β** , on a Bruker Smart Apex CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data were processed with the Bruker Apex2 suite of programs.¹² Full details are provided in the Supporting Information.

Computational Methods

Relaxed conformational scans of isolated molecule **1** were performed using Gaussian03 (G03),¹³ starting from the fully optimised geometries. The lattice energies of the two polymorphs were fully optimised using the PBE exchange-correlation functional and two different dispersion correction

schemes, Tkatchenko-Scheffler's scheme (TS)¹⁴ and Grimme's scheme (G06),¹⁵ as the dispersion correction can make a significant difference to the relative lattice energies.¹⁶ CASTEP7.0.2¹⁷ was used with on-the-fly ultrasoft pseudopotentials, a cutoff energy of 700 eV and k-point spacing of 0.04 Å⁻¹. An alternative estimate of the lattice energy, $E_{latt} = U_{inter} + \Delta E_{intra}$, was made by using PBE0/6-31G(d,p) isolated molecule calculations to give the conformational energy penalty, ΔE_{intra} and provide a distributed multipole model¹⁸ of the charge density for the electrostatic contribution to the intermolecular lattice energy, U_{inter} . The repulsion-dispersion contribution to U_{inter} was estimated from the FIT empirical potential, and U_{inter} was minimised using DMACRYS,¹⁹ keeping the molecule rigid at the experimental conformation with C-H bond lengths standardised to 1.08 Å.

The morphologies of the crystal were estimated using the BFDH model as implemented in Mercury²⁰ to use just the crystal structure data.²¹ The morphologies were also predicted using the attachment energy model, modelling the intermolecular forces from the FIT potential and PBE0 atomic charges.²² Further computational details are in the ESI.

Results and Discussion

Polymorph 1 α : This form is typically obtained from slow evaporation of dilute solutions of dichloromethane. A photograph of the long, needle-like, orange-red crystals of this polymorph is shown in Figure 1a, and its crystal structure can be seen in Figure 1b. This nearly planar conformer is consistent with the DITBEN structure.^{3, 5} In the **1 α** polymorph, the molecule adopts a centrosymmetric conformation, with the two anthryl rings parallel to each other. When viewed side-on the two rings are not quite co-planar, but have a small step between the two ring planes, with torsion τ (C₂-C₁-C_{1a}-C_{2a}) of 1.02°. The almost planar, centrosymmetric molecules pack in a herring-bone motif on the *bc* plane with close contacts between ring hydrogen atoms and the face of the anthryl ring of a neighbouring molecule.

Polymorph 1 β : This form can be obtained by slow evaporation of dilute toluene solutions. Its yellow, block-like appearance is shown in Figure 2a. The crystal structure of this new conformational polymorph in which the two anthryl rings are substantially twisted away from each other (τ (C₂-C₁-C_{1a}-C_{2a}) = 63.31° and C₁₄-C₁-C_{1a}-C_{14a} = 68.89° in the C₂ symmetry molecule) is depicted in Figure 2b. The molecules first form a one-dimensional chain with the two anthryl rings of **1** stacked face-on with the molecules before and after it. Stacking between two of these one-dimensional chains is achieved by the alternating edge-on interactions between the ring hydrogens of one chain with the anthryl rings of the other. The closest distances between the ring hydrogens and the aromatic ring in **1 β** are slightly longer than the equivalent interactions in the herring-bone motif of **1 α** , and the density is 2% lower.

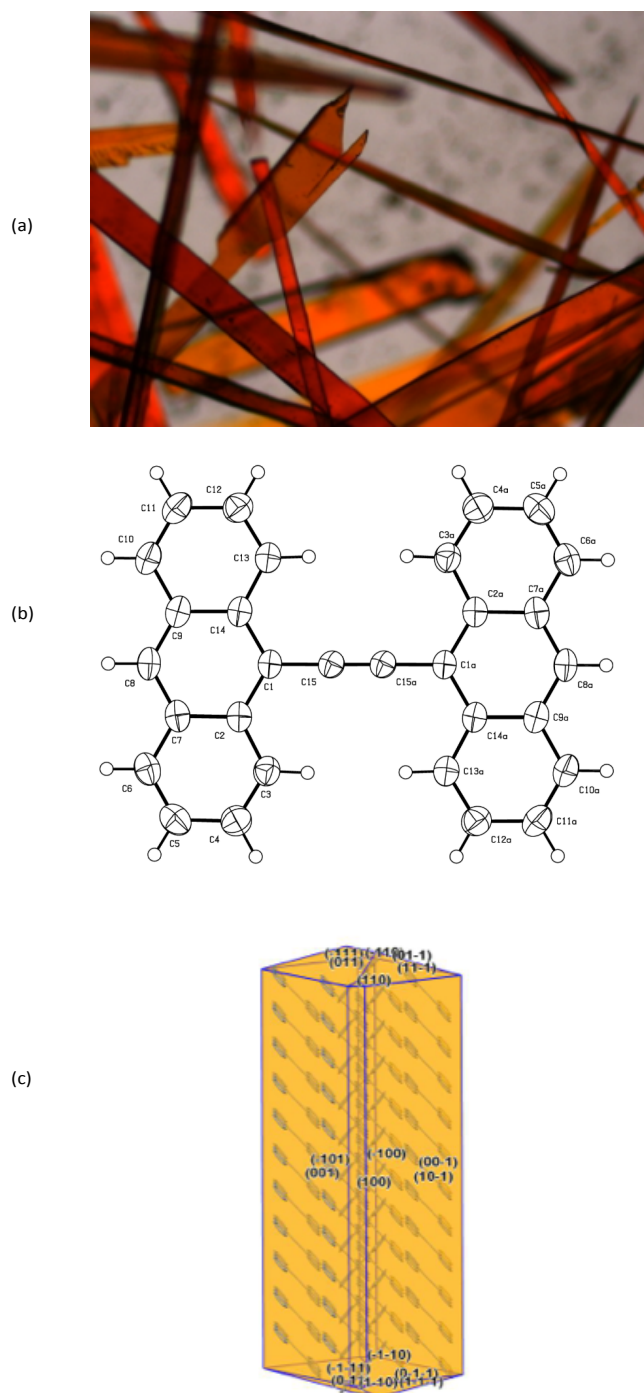


Figure 1 (a) A photograph showing the orange-red needles of polymorph **1α**. (b) The ORTEP diagram of **1α** showing its nearly planar conformation. (c) The crystal packing of **1α** superimposed on the BFDH generated morphology.

Concomitant conformational polymorphism: As noted earlier, both forms **1α** and **1β** sometimes crystallize together from the same solution, but the precise conditions that lead to this phenomenon continue to elude us. The top and middle photographs in Figure 3 shows test tubes used to collect column fractions that contain both polymorphs after slow

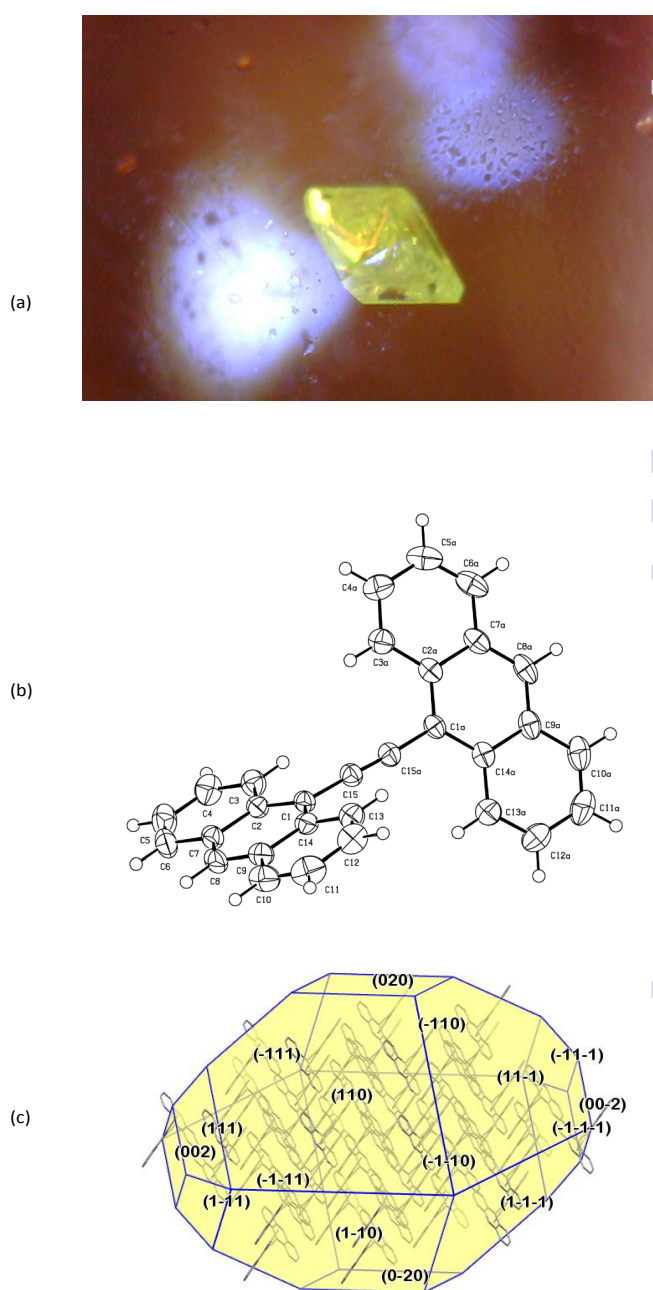


Figure 2 (a) A photograph showing the yellow, block-like crystal of polymorph **1β**. (b) The ORTEP diagram of **1β** shows a conformer in which the two anthryl planes are twisted away from each other. (c) The crystal packing of **1β** superimposed on the BFDH generated morphology.

evaporation of the solvents (hexanes/ethyl acetate) at ambient temperature. The bottom photograph shows a vial in which the two polymorphs grow in different regions of a vial. The near-planar conformation in **1α** is very close to a maximum in the isolated molecule's conformational energy (Figure 4). This is remarkable, given that conformational polymorphism is defined by being associated with different conformational minima.^{8b} In contrast, the conformation in **1β** lies between the twisted minimum energy structure ($\tau =$

35.60°) and the other local maximum in conformational energy at 90°.

functional gives a slightly larger energy barrier than previously reported B3LYP/6-311+G(d,p) results.²³ This dependence on

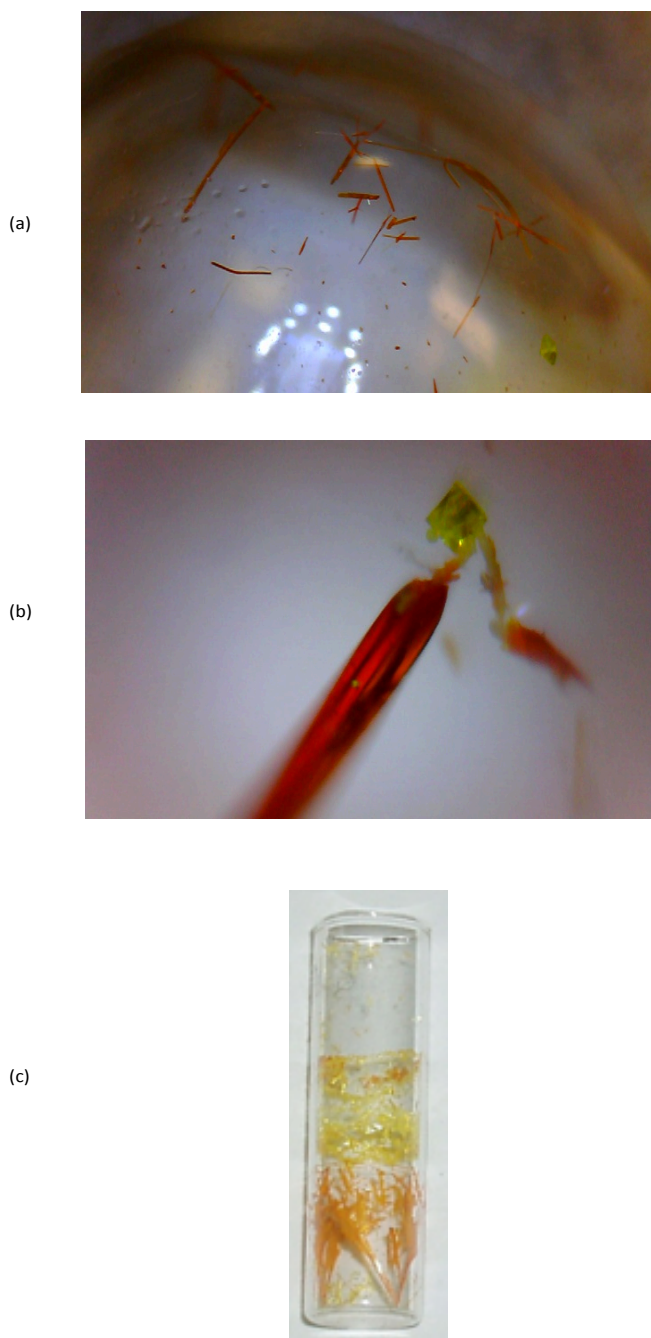


Figure 3 (a) A test tube used to collect a column fraction shows both polymorphs **1 α** and **1 β** after the solvents (hexanes/ethyl acetate) had evaporated slowly at ambient temperature over several days. The yellow crystal of **1 β** , which is a little harder to see in the photograph, is near the lower right corner. (b) Another test tube, also used to collect a column fraction with the same solvent system, shows the yellow **1 β** polymorph growing at the tip of an orange-red needle of the **1 α** . (c) A photograph showing the two polymorphs growing in different regions of a vial.

Thus, the new polymorph **1 β** contains the molecule in the more stable conformation. The energy difference is very dependent on the theoretical method used: PBE0/6-31G(d,p)

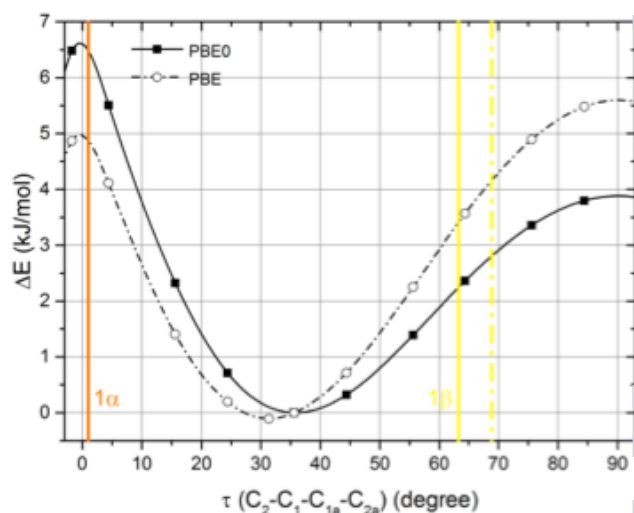


Figure 4 Relaxed conformational energy scan of **1** at the PBE0/6-31G(d,p) and PBE/6-31G(d,p) level. The conformations in the observed polymorphs are given in orange (**1 α**) and yellow (**1 β**), with the near equivalent angle $\tau(C_{14}-C_1-C_{1a}-C_{14a})$ given as a dashed line.

method arises because of the important role of intramolecular dispersion, as well as electronic conjugation and steric effects in giving conformational maxima for both planar and perpendicular aromatic rings.²⁴

Although the new polymorph **1 β** has the molecule in the more stable conformation, it is calculated to be metastable. The periodic electronic structure calculations reproduce the experimental 173 K structures well, even reproducing the slight deviation from linearity at the triple bond ($C_1-C_{15}-C_{15a}$ = 179° for **1 α** , 175° for **1 β**). The lattice energy differences ($E_{1\beta} - E_{1\alpha}$) are 6.84 and 5.13 kJ mol⁻¹ for the PBE functional with the TS and G06 dispersion corrections respectively. The estimate of the intermolecular contribution to the lattice energy difference is 10.9 kJ mol⁻¹, with the repulsion-dispersion energy dominating both the lattice energy and the difference. (Table 19 in ESI). If this estimate of U_{inter} is combined with $\Delta E_{intra} = 4.0$ kJ mol⁻¹ from Figure 4, then **1 α** is more stable than **1 β** by 6.9 kJ mol⁻¹. The rather good agreement between the estimates of the relative stability of the two forms is partly due to the fact that aromatic hydrocarbons have been widely studied for parameterising empirical *exp-6* potentials and partly fortuitous, as even the lattice energy of benzene has only recently²⁵ be determined to an accuracy of 1 kJ mol⁻¹ through an elaborate set of hierarchically more complicated quantum mechanical methods. Nevertheless, the estimate of 5 - 7 kJ/mol corresponds to an unusually large polymorphic energy difference, even allowing for the neglect of the difference in vibrational contributions to the free energy.

The effect of different solvents on the polymorphic outcome shows that the solvent is important in determining the relative rates of crystallisation of the two forms. Given that a twisted conformation is more stable than the planar conformation in isolation (gas phase), it is probably more stable in many

solvents, as indicated in polarizable continuum model (PCM) calculations in reference.²³ It seems plausible that toluene, a solvent that primarily gives **1 β** , might interact sufficiently strongly with the aromatic rings of **1** to retard the conformational change needed to lay down and stack the planar molecules in the elongated needles of **1 α** . Both the BFDH (Figure 1(c) and 2(c)) and attachment energy (ESI) predicted morphologies, which take no account of solvent effects, are only qualitatively correct and also suggest that the solvents are playing a significant role in the growth process.

The lessons from the computational work on these two polymorphs are important lessons for developing our ability to computationally predict polymorphs. Crystal structure prediction methods that have proved successful for smaller molecules²⁶ would not have included conformations that were far from a conformational energy minimum in the search, let alone at a conformational maximum. The new form **1 β** is much more metastable than would normally be considered as a plausible potential polymorph worth searching for.²⁷ Solvent effects are clearly important in the formation of the metastable polymorph and its concomitant growth: but their role in nucleation and growth is an area of very active research for much smaller molecules.²⁸

The detection of the novel polymorph can be attributed to its difference in colour and morphology. These and various other properties that are important in organic electronic devices, require advances in computational methods before crystal structure prediction methods can fulfil their potential for the design of new materials. The conformational flexibility about the acetylenic bond²⁹ is clearly a feature that may allow the design of a molecule whose crystal structure has a desirable combination of properties for optoelectronic devices. In the case of **1**, the tendency to concomitant crystallisation, and long life-time of the metastable form means that the commercial production of **1** for organic electronic devices would need a process designed to avoid **1 β** structural impurities.³⁰

Conclusions

A polymorph of 1,2-bis(9-anthryl)acetylene was first detected in 1987 alongside the orange-red and needle-like crystals of the stable form. We have characterised this yellow block-like, long-lived metastable polymorph (**1 β**) by X-ray crystallography. As in the heavily studied ROY polymorphs,³¹ the change in colour does correspond to a significant change in molecular conformation. The crystal structure of the yellow block polymorph (**1 β**) is highly metastable, despite containing a lower energy conformation because it has a less dense and less favourable crystal packing than the previously known polymorph. The more stable form **1 α** is unusual in that the molecule is approximately at a conformational energy transition state, meaning that it might not have been considered in a crystal structure prediction study. The observation of concomitant polymorphism in certain solvents suggests that there is a balance between desolvation, conformational change and crystal growth which would repay

further investigation. Such investigations could also include the study of solid-state UV-visible spectral data to discern the connections between color and structure. These polymorphs reveal the challenges and yet potential for the computational design of organic electronic materials.

Acknowledgements

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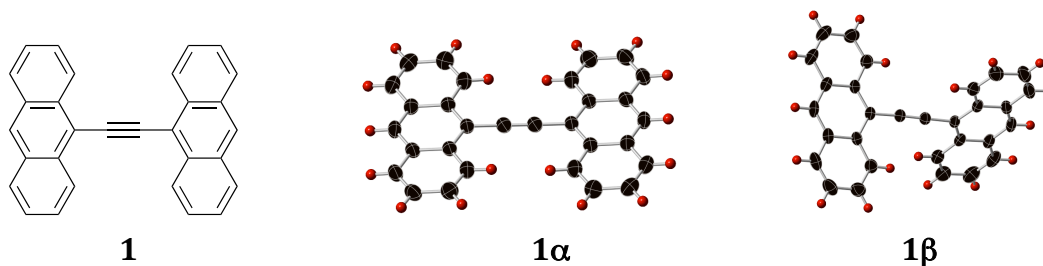
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Graphical Abstract



A new polymorph (**1β**) of 1,2-bis(9-anthryl)acetylene (**1**) has been discovered and its crystal structure determined. In this polymorph the two anthracene planes are twisted away from each other by about 60°. Occasionally the **1β** polymorph crystallizes jointly with the previously known (quasi-planar) **1α** form, representing a rare case of *concomitant conformational polymorphism* in a pure hydrocarbon. Detailed computational studies on the structures, energies, and morphologies of both polymorphs offer key insights into the experimental observations.