

Supramolecular synthons mediated by weak hydrogen bonding: forming linear molecular arrays *via* $\text{C}\equiv\text{C}-\text{H}\cdots\text{N}\equiv\text{C}$ and $\text{C}\equiv\text{C}-\text{H}\cdots\text{O}_2\text{N}$ recognition

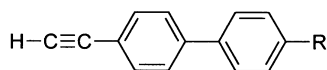
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In crystalline 4-cyano-4'-ethynylbiphenyl and 4-ethynyl-4'-nitrobiphenyl, molecules are connected with the hitherto unreported $\text{C}\equiv\text{C}-\text{H}\cdots\text{N}\equiv\text{C}$ and $\text{C}\equiv\text{C}-\text{H}\cdots\text{O}_2\text{N}$ supramolecular synthons to form linear arrays.

The identification of useful supramolecular synthons is an important aspect of current crystal engineering strategies and is helpful in the design of materials with predetermined properties.¹ This study is concerned with the crystallisation of linear molecules containing polarisable donor (D) and acceptor (A) groups. Typical acceptors are the nitro and cyano moieties. Both form synthons with suitable donor groups (D: I, Br, NMe₂, NH₂), leading in appropriate cases to chains of molecules linked *via* $\text{C}\equiv\text{N}\cdots\text{D}$ or $\text{NO}_2\cdots\text{D}$ synthons.^{2–4} With the aim of setting-up and studying new intermolecular interactions of the type described above, we decided to explore the utility of the ethynyl group $\text{C}\equiv\text{C}-\text{H}$ as a suitable acidic hydrogen bond donor to the cyano and nitro groups. Accordingly, 4-cyano-4'-ethynylbiphenyl (**1**) and 4-ethynyl-4'-nitrobiphenyl (**2**) were prepared.⁵ Molecules **1** and **2** were selected for several reasons: (i) the acidic nature of the ethynyl group that tends to lead to the formation of $\text{C}-\text{H}\cdots\text{O}/\text{N}$ hydrogen bonds;⁶ (ii) enhancement of this acidity when the ethynyl group is conjugated with electron-withdrawing groups; (iii) the very small number of reported structures containing both the ethynyl and either cyano or nitro groups.[†] In



1 R = CN
2 R = NO₂



effect, we hoped to assess the viability of synthons **I** and **II**.

Compounds **1** and **2** were obtained by the palladium-catalysed cross-coupling of trimethylsilylacetylene with 4-cyano-4'-iodobiphenyl and 4-iodo-4'-nitrobiphenyl respectively, followed by hydrolysis of the TMS group in aqueous, methanolic (or dioxane) KOH medium.⁵ Purification was by standard chromatographic techniques, followed by recrystallisation from hot EtOH.‡ X-Ray quality crystals of **1** and **2** were obtained by slow evaporation from EtOAc.§ The crystal structure of **1** is dominated by the anticipated linear $\text{C}\equiv\text{C}-\text{H}\cdots\text{N}\equiv\text{C}$ synthon, **I**, which strings together translation-related molecules to form infinite chains parallel to [010] (Fig. 1). There are four symmetry-independent molecules. Two of these are oriented in the same sense along [010] and the third one in the opposite sense. Curiously, the fourth one is disordered with respect to interchange of the ethynyl and cyano groups and based on the refinements we estimate that 60% of the chains formed by this disordered

‡ Data for **1**: mp 206.0–207.0 °C; ¹H NMR (CDCl₃) δ_H 7.74 (d, 2H, *J* 8.8), 7.68 (d, 2H, *J* 8.8), 7.61 (d, 2H, *J* 8.6), 7.56 (d, 2H, *J* 8.6 Hz), 3.19 (s, 1H, C≡CH); ¹³C NMR (CDCl₃) δ_C 141.46, 137.19, 130.64, 130.49, 125.46, 124.93, 120.39, 116.56, 109.20, 80.84, 76.53; *m/z* (%) 203 ([M]⁺, 100), 175 ([M – CN]⁺, 14). Data for **2**: mp 206.5–207.5 °C (decomp.); ¹H NMR (CDCl₃) δ_H 8.32 (d, 2H, *J* 9.2), 7.74 (d, 2H, *J* 9.2), 7.62 (d, 2H, *J* 8.8), 7.60 (d, 2H, *J* 8.8 Hz), 3.20 (s, 1H, C≡CH); ¹³C NMR (CDCl₃) δ_C 144.39, 136.80 (2 peaks?), 130.67, 125.57, 125.09, 122.01, 120.67, 80.77, 76.69; *m/z* (%) 223 ([M]⁺, 100), 193 ([M – NO]⁺, 14), 176 ([M – HNO₂]⁺, 65). Both **1** and **2** gave good elemental analyses for C, H and N.

§ Crystal data. **1**: 4-Cyano-4'-ethynylbiphenyl (C₁₅H₉N, *M* = 203.23). Triclinic, space group *P* $\bar{1}$; *a* = 9.2577(5), *b* = 15.5808(9), *c* = 16.2243(9) Å, α = 73.787(1), β = 76.459(1), γ = 88.203(1)°, *V* = 2183.2(2) Å³, *Z* = 8, *D*_c = 1.237 g cm^{–3}, μ = 0.072 mm^{–1}, Siemens P4, charge-coupled detector, *T* = 163 K, Mo-Kα, ω scans, 8000 unique reflections, 7500 with *I* > 2σ(*I*), no absorption correction. Structure solution and refinement with standard methods (SHELXS86 and SHELXL93); H atoms were fixed and allowed to refine as riding atoms except for ethynyl H atoms which were located from Fourier map and refined isotropically. Final *R* = 0.0569 (observed), 0.0602 (all), *wR*(*F*²) = 0.1425 (observed), 0.1459 (all). **2**: 4-Ethynyl-4'-nitrobiphenyl (C₁₄H₉NO₂, *M* = 223.22). Triclinic, space group *P* $\bar{1}$; *a* = 8.5221(6), *b* = 9.7649(7), *c* = 14.9832(10) Å, α = 80.873(1), β = 76.547(1), γ = 64.854(1)°, *V* = 1095.19(13) Å³, *Z* = 4, *D*_c = 1.354 g cm^{–3}, μ = 0.092 mm^{–1}, Siemens P4, charge-coupled detector, *T* = 163 K, Mo-Kα, ω scans, 4003 unique reflections, 2850 with *I* > 2σ(*I*), Siemens area detector absorption corrections. Structure solution and refinement with SHELXS86 and SHELXL93; H atoms were fixed and allowed to refine as riding atoms. Final *R* = 0.0562 (observed), 0.0808 (all), *wR*(*F*²) = 0.1509 (observed), 0.1639 (all). CCDC reference number 440/090.

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† CSD (version 5.14, 175093 entries). Only two structures in the CSD contained the $\text{C}\equiv\text{CH}\cdots\text{N}(\text{C})$ synthon when the search constrained the (C≡)C(H)⋯N(C) distance to lie in the range 2.0–3.9 Å and the C–H⋯N angle to be 120–180°. These compounds are cyanoacetylene and (S)-4-[(R)-3-cyano-1-ethynyl-1-methylpropyl]-2-pyrrolidone (refcodes CAACTY and DOJHAL respectively). Only two structures contained the $\text{C}\equiv\text{CH}\cdots\text{O}_2\text{N}$ synthon when the search constrained the (C≡)C(H)⋯O₂(N) distance to lie in the range 2.0–3.9 Å (with the hydrogen bond from the ethynyl H atom bifurcated to both nitro O atoms), and the C–H⋯N angle to be 100–180°. The two hits were 5-(*p*-nitrophenyl)-2-(pent-4-yn-1-yl)pyrimidine and (E)-4-ethynyl-4'-nitrostilbene (refcodes KIRHIC and TICYEJ respectively). Both structures have unsymmetrical (C≡)CH⋯O contacts.

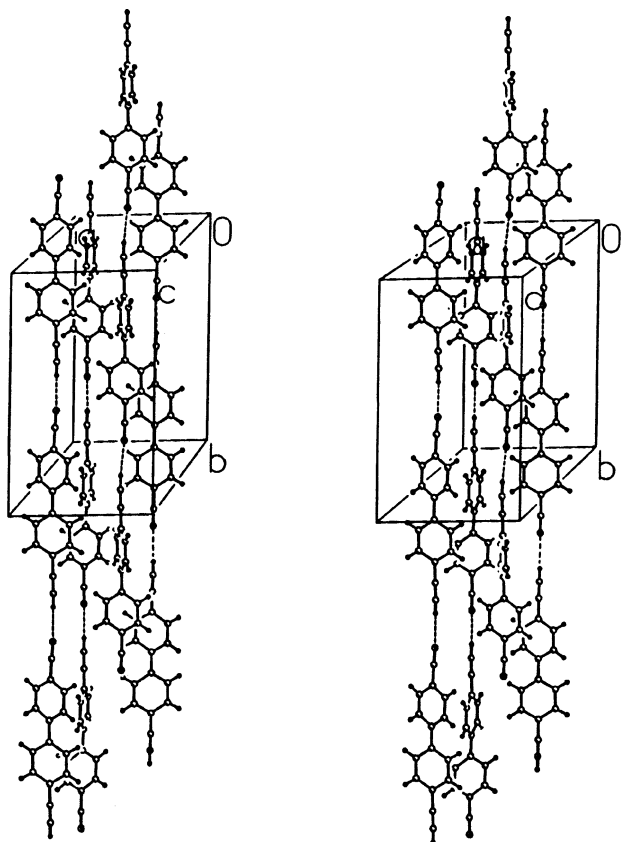


Fig. 1 Stereoview of biphenyl **1**. The four symmetry-independent molecules form linear chains along [010]. Each chain consists of translation-related molecules linked with synthon **I**. The molecules in the chain on the extreme right are disordered. All hydrogen bonds are shown as dashed lines

molecule are aligned parallel to the first two chains while 40% are parallel to the third chain. The C—H \cdots N interaction lengths vary between 2.20 and 2.30 Å for H \cdots N and between 3.282(3) and 3.364(3) Å for C \cdots N.⁷ The C \equiv N bond length varies between 1.149(3) and 1.167(3) Å. The C—H \cdots N angles lie between 165 and 176°.¶ The IR (C \equiv)C—H stretching frequency of **1** increases from 3265 cm⁻¹ to 3302 cm⁻¹ on going from solid-state (KBr disc) to solution (CDCl₃) measurement, respectively. On this basis, we assess these hydrogen-bonding interactions to be of significance. A similar interaction is found in the classical structure of cyanoacetylene (CAACTY) and in (*S*)-4-[(*R*)-3-cyano-1-ethynyl-1-methylpropyl]-2-pyrrolidone (DOJHAL), and indeed the ribbon structure in **1** may be considered to be the biphenylogous extension of that of cyanoacetylene. The linear chains are laterally held together by weak C—H \cdots N, C—H \cdots (C \equiv C) and C—H \cdots phenyl interactions.

In the crystal structure of **2** (Fig. 2), there are two symmetry-independent molecules in the asymmetric unit, A and B. These are oriented in the same direction and form linear ribbons parallel to [001], consisting of molecules of A (or B) connected with synthon **II**. In both ribbons, the ethynyl H atom forms a bifurcated hydrogen bond with the two O atoms of the NO₂ group. The ribbons are further connected in alternate [400] planes by weak phenyl C—H \cdots O, C—H \cdots (C \equiv C) and C—H \cdots phenyl interactions (dotted lines in Fig. 2). Other weak C—H \cdots O and C—H \cdots (C \equiv C) hydrogen bonds complete the structure and are also shown in Fig. 2. The C \equiv C—H \cdots O₂N synthon may be regarded as newly

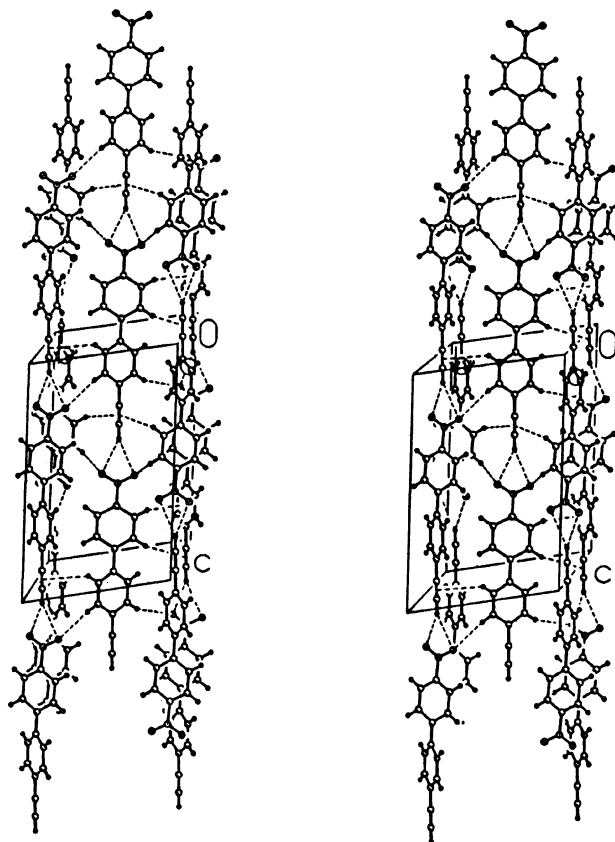


Fig. 2 Stereoview of biphenyl **2** showing the linear-chain arrangement of molecules connected with synthon **II** and parallel to [001]. Notice the C—H \cdots O and C—H \cdots π(C \equiv C) cross-links between chains

identified, though not without precedent—both 5-(*p*-nitrophenyl)-2-(pent-4-yn-1-yl)pyrimidine (KIRHIC) and (*E*)-4-ethynyl-4'-nitrostilbene (TICYEJ) contain an infinite linear arrangement of molecules connected by unsymmetrically bifurcated C \equiv C—H \cdots O₂N contacts. In **2**, the relevant geometrical parameters for synthon **II** are: (D, θ) 3.508(3), 3.473(3) Å, 154.7, 152.1° for A and 3.485(3), 3.418(4) Å, 155.0, 152.7° for B. These are in accord with the mean C \cdots O distance for C—H \cdots O hydrogen bonds formed by alkynes (3.46 Å)⁶ and are considerably more symmetrical than those found for either of the above literature cases. Again, the IR (C \equiv)C—H stretching frequency of **2** increases on going from the solid-state (KBr disc) to solution (CDCl₃) measurement (3252 cm⁻¹ to 3303 cm⁻¹), indicative of a significant (C \equiv)C—H \cdots O₂N interaction.

Both **1** and **2** form centrosymmetric structures. However, second-harmonic generation (SHG) experiments on bulk samples revealed both to be weakly SHG-active, resulting from some form of non-centrosymmetric packing. Whilst polymorphism is always a possibility, this appears to be ruled out in this case following further SHG experiments on single crystals of **1** and **2** (six of each) grown from EtOAc: each and every crystal clearly generated a green SHG response to 1064 nm laser irradiation. It is clear from the crystal structure of **1** at least that orientational disorder is responsible for the phenomenon in this case. It is conceivable that a similar disorder exists in the structure of **2**, but at a level too low (a few percent or less) to be detected by diffraction experiments; the stronger polar character of **2** (compared with **1**) would, in contrast, render such disorders discernible to the highly sensitive SHG technique. Impurities (specifically 4,4'-dinitrobiphenyl) have been held accountable⁸ for such irregularities in the crystal structure of the recently reported 4-iodo-4'-nitro-

¶ In this and other related calculations of crystal geometry, the H atom positions are normalised.

biphenyl,² via $I \cdots O_2N(C_6H_4)_2NO_2 \cdots I$ interactions. However, GCMS analyses of polycrystalline samples of **1** and **2** have indicated both samples to be greater than 99.8% pure. An alternative possibility can be found in a recently developed thermodynamic model to account for orientational defects arising purely due to the intrinsic nature of the molecule under consideration.⁹ This model has revealed that such disorder is a feasible property of certain elongated, rigid-rod type A,D-disubstituted molecules. Similar disorder has also been observed for several 1-cyano-4-halogenobenzenes^{3d} and related biphenyls,^{3c} though again sample purity might be questioned.

The usefulness of these two relatively new $C \equiv C-H \cdots O/N$ synthons cannot yet be fully gauged because of the paucity of structural information. For example, it would be of interest to ascertain if the packing of 1-cyano-4-ethynylbenzene would resemble **1** or the recently reported 1,4-diethynylbenzene,¹⁰ wherein molecules are connected by orthogonal (T-shaped) $C \equiv C-H \cdots \pi(C \equiv C)$ (triple-bond centroid) interactions, leading to zigzag chains. Nevertheless, as crystal engineering proceeds through the stages of identification and then increasingly frequent occurrences of particular supramolecular synthons, the present study is of interest in that it was possible to predict successfully the packing motifs in both **1** and **2**. The question as to why such parallel-aligned chains of **1** and **2** and other dipolar biphenyls (e.g. 4-cyano-4'-iodobiphenyl^{3c}) crystallise around centres of symmetry, while closely related analogues (e.g. 4-iodo-4'-nitrobiphenyl) pack in polar space groups, is an important one to both structural and materials scientists and remains open to debate, depending as it does on tertiary control of crystal structure.

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References

- (a) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; (b) G. R. Desiraju, *Chem. Commun.*, 1997, 1475.
- (a) F. H. Allen, J. P. M. Lommerse, V. J. Hoy, J. A. K. Howard and G. R. Desiraju, *Acta Crystallogr., Sect. B*, 1997, **53**, 1006; (b) J. A. R. P. Sarma, F. H. Allen, V. J. Hoy, J. A. K. Howard, R. Thaimattam, K. Biradha and G. R. Desiraju, *Chem. Commun.*, 1997, 101; (c) V. R. Thalladi, B. S. Goud, V. J. Hoy, F. H. Allen, J. A. K. Howard and G. R. Desiraju, *Chem. Commun.*, 1996, 401; (d) F. H. Allen, B. S. Goud, V. J. Hoy, J. A. K. Howard and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1994, 2729.
- (a) C. V. K. Sharma and G. R. Desiraju, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2345; (b) D. S. Reddy, B. S. Goud, K. Panneerselvam and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1993, 663; (c) D. Britton and W. B. Gleason, *Acta Crystallogr., Sect. C*, 1991, **47**, 2127; (d) G. R. Desiraju and R. L. Harlow, *J. Am. Chem. Soc.*, 1989, **111**, 6757.
- T. W. Panunto, Z. Urbánczyk-Lipkowska, R. Johnson and M. C. Etter, *J. Am. Chem. Soc.*, 1987, **109**, 7786.
- (a) P. J. Langley, D. Abeln, O. König, H.-B. Bürgi and J. Hulliger, in preparation; (b) S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627.
- (a) G. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441; (b) T. Steiner, *Chem. Commun.*, 1997, 727.
- M. Mascal, *Chem. Commun.*, 1998, 303.
- N. Masciocchi, M. Bergamo and A. Sironi, *Chem. Commun.*, 1998, 1347.
- J. Hulliger, *Z. Krist.*, 1998, **213**, 441.
- H.-C. Weiss, D. Bläser, R. Boese, B. M. Doughan and M. M. Haley, *Chem. Commun.*, 1997, 1703.

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