

## 4,4'-Dicyanobiphenyl

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## Key indicators

Single-crystal X-ray study

T = 173 K

Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$ 

R factor = 0.052

wR factor = 0.116

Data-to-parameter ratio = 8.6

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

4,4'-Dicyanobiphenyl,  $\text{C}_{14}\text{H}_8\text{N}_2$ , has a normal structure with a twist angle of  $31.8(2)^\circ$ . The molecules stack with overlapping  $\pi$  systems and form chains held together by antiparallel  $\text{C}-\text{N}\cdots\text{C}-\text{N}$  interactions. In addition, there are a number of  $\text{C}-\text{H}\cdots\text{N}$  interactions.

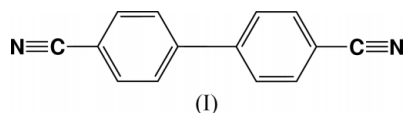
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## Comment

A number of *para*-disubstituted biphenyls crystallize in isomorphous structures with  $Z = 8$  in space group No. 14. These include dimethyl (Casalone *et al.*, 1969), dichloro (Brock *et al.*, 1978), dibromo (Kronebusch *et al.*, 1976*b*), bromofluoro (Gleason *et al.* (1991), bromocyano (Kronebusch *et al.*, 1976*a*), and iodocyano (Britton & Gleason, 1991) derivatives. In the bromocyano compound, the cyano group replaces a bromine without destroying the isomorphism. It seems of interest to see whether the dicyano compound packs in the same manner, with approximately end-to-end  $\text{C}-\text{N}\cdots\text{N}-\text{C}$  contacts, or whether some other form, with better  $\text{C}-\text{N}\cdots\text{N}-\text{C}$  contacts, occurs. The structure of the dicyano compound, 4,4'-dicyanobiphenyl, (I), is reported here.



There is one molecule in the asymmetric unit. The anisotropic displacement ellipsoids and atom labeling are shown in Fig. 1. Chemically equivalent bond lengths and angles agree within experimental error. The dihedral angle between the two rings is  $31.8(2)^\circ$ . The entire molecule is bent about  $10^\circ$  away from the mean plane of the two rings; bending of this sort is quite common in biphenyls.

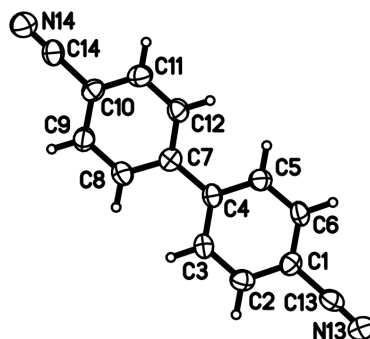
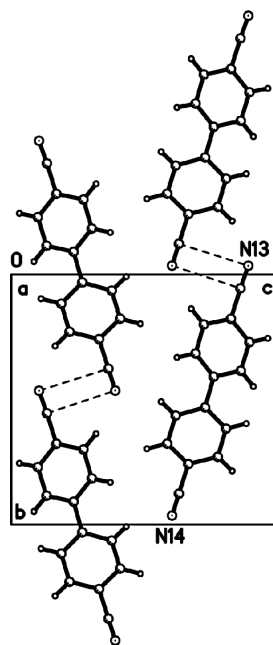


Figure 1

View of the title molecule, with displacement ellipsoids shown at the 50% probability level. H atoms are shown with arbitrary radii.



**Figure 2**

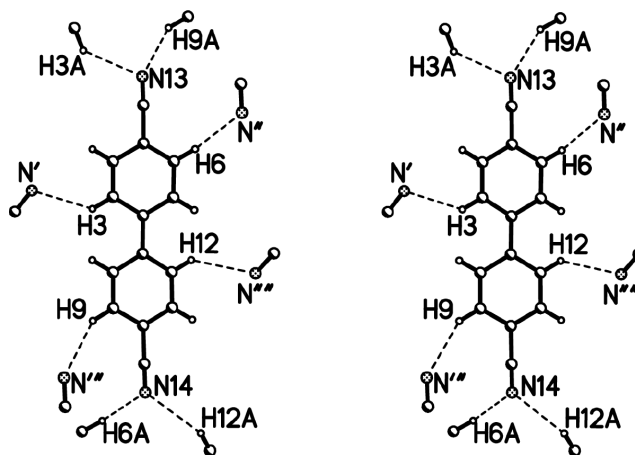
View along *a*. The antiparallel C—N...C—N contacts are shown as dashed lines. The chains are not parallel but lie alternately along the [10 $\bar{1}$ ] and [101] directions

The molecules stack in columns parallel to the *a* axis. Fig. 2 shows a view along the stacks. The ring-to-ring distances are 3.415 (2) Å for the C1–C6 rings and 3.615 (2) Å for the C7–C12 rings. The difference arises from the different tilt of the two rings with respect to the *a* axis.

The molecules form chains, as can also be seen in Fig. 2. These chains lie alternately along the [10 $\bar{1}$ ] and [101] directions. They are held together by antiparallel C—N...C—N interactions; the distances are C13...N14(1 + *x*, 1 – *y*, *z*) = 3.514 Å and N14...C13 = 3.610 Å. These are comparable to the distances in the corresponding interactions in both polymorphs of *p*-dicyanobenzene, *viz.* of 3.56 Å in polymorph 1 (Colapietro *et al.*, 1984) and 3.66 Å in polymorph 2 (Kubiak & Janczak, 1996).

There are four H...N—C contacts where the H...N distance is shorter than 2.8 Å. The metric details are in Table 1. These can all be viewed as weak C—H...N hydrogen bonds. For an extended discussion of C—H...N interactions, see Desiraju & Steiner (1999).

Masunov *et al.* (1992) have discussed packing in various 4,4'-disubstituted biphenyls and showed that they could generally be fitted into two classes. In the first class, the substituents do not interact strongly, and the packing is determined by C—H...C—H contacts. In the second class, interactions between substituents on adjacent molecules are the primary intermolecular interactions and lead to chains of molecules held together by these end-to-end contacts. In dicyanobiphenyl, the interactions between the substituents again appear to be primary, but, because the C—N...C—N interactions involve antiparallel CN groups, the molecules in the chains are tilted with respect to each other. Hence, the dicyanobiphenyl does not fit into either of the classes mentioned above.



**Figure 3**

Stereoview showing the H...C—N interactions as dashed lines. The metric details are in Table 1.

## Experimental

The sample used was provided by Professor Paul G. Gassman.

### Crystal data

C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>  
*M<sub>r</sub>* = 204.22  
 Monoclinic, *P*2<sub>1</sub>  
*a* = 3.7798 (10) Å  
*b* = 11.368 (4) Å  
*c* = 12.089 (4) Å  
 $\beta$  = 94.54 (3)°  
*V* = 517.8 (3) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.310 Mg m<sup>−3</sup>  
 Mo *K*α radiation  
 Cell parameters from 2992 reflections  
 $\theta$  = 2.5–27.3°  
 $\mu$  = 0.08 mm<sup>−1</sup>  
*T* = 173 (2) K  
 Needle, colorless  
 0.30 × 0.10 × 0.05 mm

### Data collection

Bruker SMART area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002; Blessing, 1995)  
*T<sub>min</sub>* = 0.970, *T<sub>max</sub>* = 0.996  
 5937 measured reflections

1249 independent reflections  
 1099 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.068  
 $\theta_{\text{max}}$  = 27.5°  
*h* = −4 → 4  
*k* = −14 → 14  
*l* = −15 → 15

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.052  
*wR* (*F*<sup>2</sup>) = 0.116  
*S* = 1.15  
 1249 reflections  
 146 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.111P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.16 \text{ e } \text{Å}^{-3}$

**Table 1**

Distances and angles (Å, °) in the C—H...N≡C contacts.

H	X	C—H	C—H...N	H...N	H...N≡C	C...N
H3	N13 <sup>i</sup>	0.95	151	2.63	115	3.366 (2)
H6	N14 <sup>ii</sup>	0.95	157	2.59	115	3.481 (6)
H9	N13 <sup>iii</sup>	0.95	148	2.71	135	3.550 (6)
H12	N14 <sup>iiii</sup>	0.95	119	2.77	125	3.325 (6)

Symmetry codes: (i) 2 – *x*, ½ + *y*, 2 – *z*; (ii) *x*, *y* – 1, *z*; (iii) *x* – 1, 1 + *y*, *z*; (iiii) –*x*, *y* – ½, 1 – *z*

A number of crystals were examined and all were twinned. The crystal used was indexed using *GEMINI* (Sparks, 2000). The twin law was [100/010/0.5,0,1]. The fraction of the major component was

0.633 (3). The HKLF 5 file was made using *ROTWIN* (Young & Pink, 2003) using 608 reflections from the major component and 648 overlapped reflections from both components. With no atom heavier than N present, refinement including the Friedel pairs gave a meaningless Flack (1983) parameter, 0.3 (80). Accordingly, the Friedel pairs were averaged before the final refinement.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank the late Professor Paul. G Gassman for the compound sample.

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