packing forces tend to incline both molecules about 5° away from parallel to the b axis, but in the two cases where we propose a linear interaction the angles are less than 5°. Furthermore in the iodo compound (Fig. 4) where we would expect a stronger interaction, iodine being a stronger Lewis acid than bromine, the effect is greater. When the iodine is replaced with fluorine, which does not show Lewis acidic behavior at all, the crystals are not isomorphous and there is no short F···N contact (Gleason, Brostrom, Etter & Johnson, 1991).

The small amount of disorder, described earlier, does not affect the preceding argument. Since we regard the CN···I interaction as a specific one, we feel that the disorder probably occurs for entire chains rather than for isolated molecules, but the crystallographic data can be interpreted equally well with either model. In further support of the suggested disorder, in their recent reexamination of the structures of the 4-halobenzonitriles, Desiraju & Harlow (1989) suggest that disorder occurs in 4-bromobenzonitrile and in one of the forms of 4-chlorobenzonitrile although they do not report any measure of the amount of disorder.

All of the compounds in Table 5 have two molecules in the asymmetric unit related by pseudosymmetry. This has been described in detail by Brock, Kuo & Levy (1978) in their determination of the isomorphous 4,4′-dichlorobiphenyl.

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Acta Cryst. (1991). **C47**, 2131–2134

Structure of 4-Cyano-4′-fluorobiphenyl

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Abstract. 4′-Fluorobiphenyl-4-carbonitrile, $C_{13}H_8FN$, $M_r = 197{\cdot}2$, orthorhombic, $Pbca$, $a = 22{\cdot}525\ (2)$, $b = 11{\cdot}730\ (2)$, $c = 7{\cdot}568\ (2)$ Å, $V = 1999{\cdot}7$ Å^3, $Z = 8$, $D_x = 1{\cdot}31$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}8$ cm^{-1}, $F(000) = 816$, $T = 298\ (1)$ K, $R = 0{\cdot}033$ for 840 observed reflections. A number of isomorphous 4,4′-disubstituted biphenyl derivatives have been reported with the prototype being 4,4′-dimethyl-

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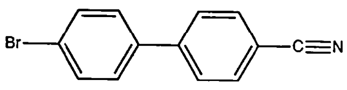
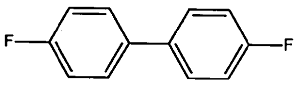
biphenyl which contains two molecules in the asymmetric unit. In contrast this derivative has one molecule in the asymmetric unit. The dihedral angle between the two ring planes is 30·28 (9)° in contrast to the planar biphenyl and 4,4′-difluorobiphenyl molecules. There is no evidence of close halogen–cyanide contacts.

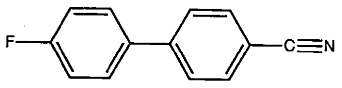
Introduction. The biphenyl system is an attractive one for studying the influence of crystal packing on molecular conformation because it has only one conformational variable, the inter-ring twist angle. The title compound could be considered to be derived from 4-bromo-4′-cyanobiphenyl (I) by replacement of the bromine with fluorine or from 4,4′-difluorobiphenyl (II) by replacement of one of the fluorines by cyanide. In the solid the related compound (I), 4-bromo-4′-cyanobiphenyl (Kronebusch, Gleason & Britton, 1976*a*) is non-planar and exhibits weak intermolecular halogen–cyanide interactions. The structure of the planar molecule 4,4′-difluorobiphenyl (II) has been determined at 100 K (Bielushkin, Natkaniec, Wasicki, Khomenko, Teleshenko & Wasiutynski, 1986) and a crystal structure and thermal-motion analysis have been reported (Lemee, Toupet, Delugeard, Messager & Cailleau, 1987). Here we report the crystal structure of 4-cyano-4′-fluorobiphenyl (III).



(I)



(II)



(III)

Experimental. The title compound was synthesized from 4-bromo-4′-fluorobiphenyl using a procedure described previously (McNamara & Gleason, 1976). The material was purified by preparative thin-layer chromatography and suitable single crystals obtained by slow evaporation of an ethanol solution. A crystal of approximate dimensions 0·20 × 0·20 × 0·30 mm was mounted on a glass fiber with epoxy adhesive. Intensities were measured with an Enraf–Nonius CAD-4 diffractometer using variable speed (1–7° min^{-1}) ω scans and a θ-dependent scan width of $(1·1 + 0·350\tan\theta)°$. Unit-cell constants were determined from a least-squares fit to angular data for 25 reflections in the angular range $10 < \theta < 15°$. Data were collected to $(\sin\theta)/\lambda = 0·57$ Å^{-1}, $0 \le h \le 25$, $0 \le k \le 13$, $-8 \le l \le 8$. Three standard reflections (12,0,2, 060, $\bar{2}0\bar{4}$) were monitored hourly during data collection; no intensity decay was observed. 3392 reflections were measured and averaged ($R_{\rm int}$ = 1·3%) to 1561 unique data, 840 reflections with $I > 2\sigma(I)$ were considered observed. The structure was solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). All parameters were refined by full-matrix least-squares refinement of the function $\sum[w(|F_o| - |F_c|)^2]$, where $w = 1/[\sigma(F_o)]^2$. No absorption correction was applied. H atoms at calculated positions ($r_{\rm C—H}$ = 0·95 Å, $B_{\rm iso}$ = 5·0 Å^2) were included in the structure-factor calculations but were not refined, all other atoms refined anisotropically for 136 variables. Final R = 0·034, wR = 0·042, S = 1·41. Final $(\Delta/\sigma)_{\rm max}$ = 0·01; $\Delta\rho_{\rm max}$ = 0·15 (2), $\Delta\rho_{\rm min}$ = −0·12 (2) e Å^{-3} on final difference map. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computer programs used were those of Enraf–Nonius (1982) *SDP*.

Discussion. Atomic parameters are given in Table 1,* bond lengths and bond angles in Table 2. The atomic numbering scheme is shown in Fig. 1 and an illustration of the contents of the unit cell is given in Fig. 2.

We have previously reported the crystal structure of 4-bromo-4′-cyanobiphenyl (Kronebusch, Gleason & Britton, 1976*a*) where the inter-ring twist angle was found to be 42° in both of the crystallographically non-equivalent molecules. There also appeared to be a weak intermolecular CN···Br interaction (distances = 3·24 and 3·18 Å; sum of van der Waals radii = 3·45 Å). The crystal structure of 4-cyano-4′-iodobiphenyl (Britton & Gleason, 1991) is isomorphous with the bromo compound and has a twist angle of approximately 42° in the two molecules in the asymmetric unit. In the iodo compound short CN···I contacts (distances = 3·24 and 3·18 Å; sum of van der Waals radii = 3·65 Å) are also observed. Although we have synthesized 4-chloro-4′-cyanobiphenyl, attempts to obtain suitable crystals have been unsuccessful. The strength of the CN···X (X = halogen) interaction is expected to decrease as the series is changed from iodine to fluorine as a result of the decreased polarizability of fluorine com-

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes, torsion angles and calculated H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54098 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
F	0·35357 (6)	0·4383 (1)	0·9118 (2)	7·59 (4)
N	−0·08874 (9)	0·1531 (2)	0·5207 (4)	8·55 (8)
C1	0·12393 (9)	0·3035 (2)	0·7222 (3)	4·10 (5)
C2	0·11024 (10)	0·1878 (2)	0·7120 (3)	4·92 (6)
C3	0·05552 (10)	0·1502 (2)	0·6621 (4)	5·35 (6)
C4	0·01139 (9)	0·2280 (2)	0·6212 (3)	4·98 (6)
C5	0·02313 (10)	0·3432 (2)	0·6333 (3)	5·23 (6)
C6	0·07856 (10)	0·3797 (2)	0·6831 (3)	4·87 (6)
C7	0·18414 (9)	0·3410 (2)	0·7715 (3)	4·08 (5)
C8	0·23329 (9)	0·2741 (2)	0·7296 (3)	4·59 (6)
C9	0·28991 (10)	0·3066 (2)	0·7751 (4)	5·22 (6)
C10	0·29683 (10)	0·4064 (2)	0·8636 (3)	5·13 (6)
C11	0·25075 (12)	0·4758 (2)	0·9064 (3)	5·22 (6)
C12	0·19429 (10)	0·4430 (2)	0·8596 (3)	4·72 (5)
C13	−0·04546 (11)	0·1882 (2)	0·5649 (4)	6·09 (7)

Table 2. *Interatomic distances* (Å) *and angles* (°)

F—C10	1·381 (2)	C4—C13	1·428 (3)
N—C13	1·110 (3)	C5—C6	1·372 (3)
C1—C2	1·394 (3)	C7—C8	1·393 (3)
C1—C6	1·389 (3)	C7—C12	1·389 (3)
C1—C7	1·474 (3)	C8—C9	1·375 (3)
C2—C3	1·363 (3)	C9—C10	1·357 (3)
C3—C4	1·385 (3)	C10—C11	1·360 (4)
C4—C5	1·381 (3)	C11—C12	1·375 (3)
C2—C1—C6	116·9 (3)	C1—C7—C12	122·0 (2)
C2—C1—C7	120·5 (2)	C8—C7—C12	117·7 (2)
C6—C1—C7	122·7 (2)	C7—C8—C9	121·6 (2)
C1—C2—C3	122·0 (3)	C8—C9—C10	118·0 (2)
C2—C3—C4	119·9 (2)	F—C10—C9	118·1 (2)
C3—C4—C5	119·5 (3)	F—C10—C11	118·8 (2)
C3—C4—C13	119·7 (2)	C9—C10—C11	123·2 (2)
C5—C4—C13	120·8 (2)	C10—C11—C12	118·5 (3)
C4—C5—C6	119·8 (2)	C7—C12—C11	121·2 (3)
C1—C6—C5	121·8 (3)	N—C13—C4	177·2 (3)
C1—C7—C8	120·4 (2)		

pared to iodine. Thus one expects the fluorine/cyanide interaction ordinarily to be weak, but an 'accident of packing' might cause a close contact. The F···N distance was found to be 3·68 (1) Å which is larger than the sum of van der Waals radii for fluorine and nitrogen (2·85 Å), so clearly there is no weak intermolecular interaction.

The structure of a number of isomorphous 4,4′-*XY* disubstituted biphenyls have been reported which contain two molecules in the asymmetric unit related by pseudosymmetry. These include 4,4′-dimethylbiphenyl (bitolyl) (Casalone, Mariani, Mugnoli & Simonetta, 1969), 4,4′-dibromobiphenyl (Kronebusch, Gleason & Britton, 1976*b*), 4-bromo-4′-cyanobiphenyl (Kronebusch, Gleason & Britton, 1976*a*), 4,4′-dichlorobiphenyl (Brock, Kuo & Levy, 1978) and 4-cyano-4′-iodobiphenyl (Britton & Gleason, 1991). A comparison of the packing of these related compounds is given by Britton & Gleason (1991). It is interesting that the compound reported herein is not isomorphous with those mentioned above. Although one might argue that halogen/cyanide or halogen/halogen interactions are somehow necessary for packing in a prototypical (two molecules in the asymmetric unit) structure, the fact that the methyl-substituted compound, bitolyl, can achieve this structure indicates that no special interactions are required.

The twist angle observed in 4-cyano-4′-fluorobiphenyl [30·28 (9)°] is also significantly smaller than that found in the iodo and bromo derivatives. The structure of another related material, 4,4′-difluorobiphenyl, has recently been determined (Bielushkin *et al.*, 1986; Lemee *et al.*, 1987) and it is planar. It thus appears that there is a shallow torsional potential for inter-ring twist and that the final twist angle in the solid state is strongly influenced by packing forces. This subject has recently been reviewed by Brock & Minton (1989) who examined 101 biphenyl fragments without *ortho*

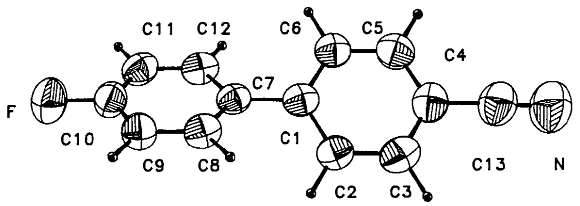

Fig. 1. *ORTEP*II (Johnson, 1976) diagram showing the atom-numbering scheme. Non-H-atom ellipsoids at 50% probability level, H atoms given arbitrary radius.

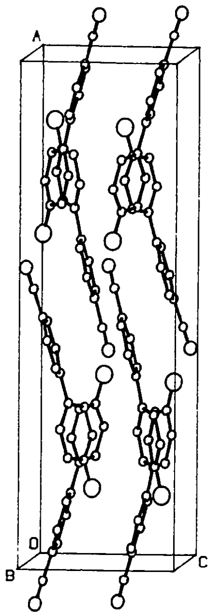

Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) packing diagram of 4-cyano-4′-fluorobiphenyl.

substituents, including the compound reported herein.

We thank M. J. Dylla, College of St. Catherine, for the synthesis of the title compound.

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Structure of 4-Dibenzofurancarboxaldehyde, $C_{13}H_8O_2$

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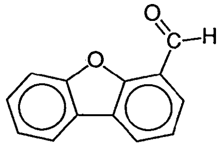
(*Received* 7 *December* 1990; *accepted* 13 *March* 1991)

Abstract. $M_r = 196{\cdot}21$, monoclinic, $P2_1/n$, $a = 6{\cdot}589\,(1)$, $b = 9{\cdot}784\,(2)$, $c = 14{\cdot}394\,(2)$ Å, $\beta = 95{\cdot}69\,(1)^\circ$, $V = 923{\cdot}4\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}41$ g cm^{-3}, $\lambda(\text{Mo }K\overline{\alpha}) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}89$ cm^{-1}, $F(000) = 408$, $T = 296$ K, $R = 0{\cdot}048$ for 964 unique reflections having $I > 3\sigma_I$. The average C—C bond length within the benzenoid rings in 4-dibenzofurancarboxaldehyde is 1·388 (9) Å; the average interior angle is 120·0 (2·6)°. While two of the three rings of 4-dibenzofurancarboxaldehyde are planar, the benzenoid ring to which the carbonyl group is attached is slightly non-planar. The dihedral angle between the two benzenoid rings measures 1·4(1)°. The structure is composed of pairs of 4-dibenzofurancarboxaldehyde molecules related by inversion centers. This structure is further characterized by approaches of both the carbonyl and the furan O atoms to ring H atoms with separations which are slightly less than the sum of the relevant van der Waals radii.

Introduction. In conjunction with continuing studies of positional disorder of the type displayed by dibenzofuran (Reppart, Gallucci, Lundstedt & Gerkin, 1984) interest has arisen in the structure of substituted dibenzofurans. This report presents an investigation of crystalline 4-dibenzofurancarboxaldehyde (I), whose structure had not previously been described.



(I)

Experimental. 4-Dibenzofurancarboxaldehyde (Gilman, Tolman, Yeoman, Woods, Shirley & Avakian, 1946) (I) was prepared by lithiation of dibenzofuran (Aldrich Chemical Company) with *sec*-butyllithium in tetrahydrofuran at 195 K followed by quenching with dimethylformamide. The crude product was purified by flash chromatography (Still, Kahn & Mitra, 1978), which produced an off-white powder. The 4-dibenzofurancarboxaldehyde was then sublimed under vacuum for 2 h at 353 K followed by continued sublimation for 2 days at

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