

## Crystal Structure and Thermal-Motion Analysis of 4,4'-Difluorobiphenyl

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### Abstract

The crystal structure of 4,4'-difluorobiphenyl has been determined at different temperatures between 155 and 293 K. This compound is isostructural with biphenyl ( $P2_1/a$ ,  $Z = 2$ ). We have carefully analysed the evolution of thermal motion by refining the translational and librational tensors. At any temperature, the molecules appear planar with a large librational amplitude around the long molecular axis and this amplitude remains slightly smaller than that observed in biphenyl. Crystal data at 293 K:  $C_{12}H_8F_2$ ,  $M_r = 190.2$ ,  $a = 7.78$  (1),  $b = 5.847$  (9),  $c = 9.99$  (1) Å,  $\beta = 92.85$  (9)°,  $V = 227$  (2) Å<sup>3</sup>,  $D_x = 1.386$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $R = 0.057$  for 417 reflections.

### Introduction

It is well known that the molecular conformation of biphenyl in the crystalline state results from a delicate balance between antagonistic intramolecular and intermolecular forces (Cailleau, Baudour, Meinel, Dworkin, Moussa & Zeyen, 1980). The isolated molecule, consisting of two aromatic rings connected by an aliphatic bond, is non-planar, as a torsional angle exists between the planes of the phenyl rings. In the crystalline state at 293 K, molecules are planar with a large librational amplitude around the long molecular axis (torsional motion). At low temperature, biphenyl undergoes incommensurate structural phase transitions associated with a stabilization of the molecules in non-planar conformation. The molecular nature of this structural instability mechanism has been extensively discussed by different authors (Cailleau *et al.*, 1980; Cailleau, 1986; Natkaniec, Bielushkin & Wasiutynski, 1981; Takeuchi, Suzuki, Dianoux & Allen, 1981; Wasiutynski, Natkaniec & Bielushkin, 1981; Plakida, Bielushkin, Natkaniec & Wasiutynski, 1983; Raich & Bernstein, 1984; Heine & Price, 1985). An illustration of the molecular mechanism described above can be given by a study of the influence of hydrostatic pressure. The increase in the relative strength of crystal-packing forces results in the structural instability vanishing around 2 kbar (Cailleau, Messenger, Moussa, Bugaut, Zeyen & Vettier, 1986).

Another way to change the balance between intramolecular and intermolecular forces is to substitute some hydrogen atoms by halogens. Substitution in the *ortho* position leads to a large static torsional angle in the crystalline state (Romming, Seip & Aanesen Oymo, 1974). This is due to the strong increase of steric hindrance between *ortho* atoms, and one can expect less drastic effects for substitution in the *para* position. In fact the molecules of 4,4'-dichlorobiphenyl (Brock, Kuo & Levy, 1978) and 4,4'-dibromobiphenyl (Kronebusch, Gleason & Britton, 1976) exhibit non-zero dihedral angles again in the crystalline state, at room temperature. On the other hand the behaviour of 4,4'-difluorobiphenyl in the solid state is quite different. In combination with a high-resolution NMR study (Halstead, Spiess & Haeberlen, 1976; Halstead, Tagenfeldt & Haeberlen, 1981), a preliminary determination of the room-temperature space group indicated that the structure of this compound is certainly close to that of biphenyl.

We have undertaken a complete determination of the crystalline structure of 4,4'-difluorobiphenyl at five temperatures between 155 and 293 K. In particular, we have studied the behaviour of the thermal motion in order to compare it with that of biphenyl. Simultaneously with our study, another group has determined the crystal structure of this compound at 100 K (Bielushkin, Natkaniec, Wasicki, Khomenko, Telezhenko & Wasiutynski, 1986).

### Experimental

The title compound (Fig. 1) was crystallized from ethanol solution. The sample used had the form of a plate of dimensions  $0.3 \times 0.3 \times 0.1$  mm.

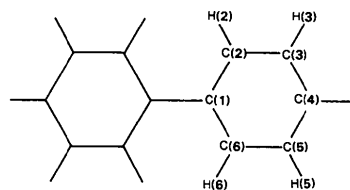


Fig. 1. Schematic drawing of the 4,4'-difluorobiphenyl molecule showing the atom numbering.

Table 1. *Data collection parameters*

Temperature (K)	155	180	241	262	293
Total number of reflections	899	905	923	934	783
Number of observed reflections [ $F > \sigma(F)$ ]	568	540	522	513	417
Decrease in standard reflections	1.7%	2.3%	8.8%	21.2%	1.5%
$R$	0.063	0.069	0.079	0.066	0.057
$wR$	0.053	0.058	0.068	0.059	0.057
$\Delta/\sigma_{\max}$	0.04	0.03	0.23	0.14	0.03
$\Delta\rho_{\max}(\text{e } \text{\AA}^{-3})$	—	—	—	—	0.424
$\Delta\rho_{\min}(\text{e } \text{\AA}^{-3})$	—	—	—	—	0.397

Table 2. *Structure of 4,4'-difluorobiphenyl at 293 K*

Unit-cell parameters:

$$a = 7.78 (1) \text{ \AA} \quad V = 227 (2) \text{ \AA}^3$$

$$b = 5.847 (9) \text{ \AA} \quad D_x = 1.386 \text{ g cm}^{-3}$$

$$c = 9.99 (1) \text{ \AA}$$

$$\beta = 92.85 (9)^\circ$$

Fractional coordinates and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses:

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
F	0.2183 (3)	-0.0039 (4)	0.4653 (2)	0.081 (2)
C(1)	0.0334 (3)	0.0003 (5)	0.0714 (2)	0.040 (2)
C(2)	-0.0047 (4)	0.1742 (6)	0.1596 (3)	0.056 (2)
C(3)	0.0572 (5)	0.1727 (6)	0.2906 (3)	0.063 (2)
C(4)	0.1572 (4)	-0.0024 (6)	0.3359 (3)	0.053 (2)
C(5)	0.1990 (4)	-0.1771 (6)	0.2546 (3)	0.063 (2)
C(6)	0.1369 (4)	-0.1759 (6)	0.1228 (3)	0.056 (2)
H(2)	-0.071 (3)	0.285 (5)	0.129 (2)	0.05*
H(3)	0.027 (3)	0.277 (5)	0.351 (2)	0.05*
H(5)	0.277 (3)	-0.282 (5)	0.285 (2)	0.05*
H(6)	0.166 (3)	-0.296 (5)	0.068 (2)	0.05*

\* Isotropic thermal parameter fixed.

Table 3. *Bond lengths (\text{\AA}) and angles ( $^\circ$ ) of 4,4'-difluorobiphenyl at 293 K with e.s.d.'s in parentheses*

F-C(4)	1.355 (2)	C(3)-C(4)	1.350 (3)
C(1)-C(1)	1.494 (3)	C(3)-H(3)	0.89 (2)
C(1)-C(2)	1.388 (3)	C(4)-C(5)	1.355 (3)
C(1)-C(6)	1.390 (3)	C(5)-C(6)	1.380 (3)
C(2)-C(3)	1.373 (3)	C(5)-H(5)	0.91 (2)
C(2)-H(2)	0.87 (2)	C(6)-H(6)	0.93 (2)
C'(1)-C(1)-C(2)	122.2 (2)	F-C(4)-C(3)	119.5 (2)
C'(1)-C(1)-C(6)	121.3 (2)	F-C(4)-C(5)	119.0 (2)
C(2)-C(1)-C(6)	116.5 (2)	C(3)-C(4)-C(5)	121.5 (2)
C(1)-C(2)-C(3)	121.7 (2)	C(4)-C(5)-C(6)	119.1 (2)
C(1)-C(2)-H(2)	118. (1)	C(4)-C(5)-H(5)	119. (1)
C(3)-C(2)-H(2)	121. (1)	C(6)-C(5)-H(5)	122. (1)
C(2)-C(3)-C(4)	119.6 (2)	C(1)-C(6)-C(5)	121.7 (2)
C(2)-C(3)-H(3)	123. (1)	C(1)-C(6)-H(6)	120. (1)
C(4)-C(3)-H(3)	117. (1)	C(5)-C(6)-H(6)	118. (1)

Measurements were made on an Enraf-Nonius CAD-4 diffractometer, with Zr-filtered Mo  $K\alpha$  radiation. For the low-temperature experiments, the crystal was cooled in a stream of cold nitrogen gas (van Bolhuis, 1971). Five data collections, summarized in Table 1, were thus obtained at 155 (2), 180 (2), 241 (2), 262 (2) and 293 (2) K. Unit-cell parameters were refined from 25 independent reflections. Intensities were collected to  $2\theta_{\max} = 50^\circ$  (scan  $\omega/2\theta = 1$ ,  $t_{\max} = 60$  s). No absorption correction was made.

Structures were solved by direct methods and refined on  $|F|$  by full-matrix least-squares techniques. The following weighting scheme was introduced and used throughout the refinement:

$$w = 4|F|^2[\sigma^2(|F|^2) + (0.04|F|^2)^2]^{-1}.$$

At any temperature, thermal parameters of hydrogen atoms were fixed at  $0.05 \text{ \AA}^2$ . Because the accurate determination of these temperature factors at each temperature was too difficult, this value of  $0.05 \text{ \AA}^2$  corresponds to a mean in the studied temperature range. For example, unit-cell parameters, atomic coordinates, bond lengths and angles at 293 K are presented in Tables 2 and 3.\*

We performed additional refinements on  $|F|$  by using the WAGG program (Baudour, 1972). Assuming that the half-molecule is a rigid body, this program allows global librational and translational tensors of the molecule to be calculated. During all these refinements, mean amplitudes of hydrogen-atom vibrations were fixed at  $0.077 \text{ \AA}$  along the C-H bond,  $0.116$  and  $0.150 \text{ \AA}$  in the perpendicular directions (Johnson, 1980). The usual weighting scheme ( $w = 1$  for all the reflections) was applied. After a series of converging fits under these conditions, we tried to improve our results by adding an independent thermal motion for the fluorine atoms. Note that this motion must be weak with respect to the rigid-block one. The tensor values related to these fluorine atoms presented standard deviations too large to have any physical meaning. Consequently, they have not been taken into account in the final results.

## Results and discussion

The temperature dependence of the unit-cell parameters (Fig. 2) presents a normal behaviour. As previously reported (Halstead, Spiess & Haerberlen, 1976; Halstead, Tagenfeldt & Haerberlen, 1981), the space group is monoclinic,  $P2_1/a$ , and the dimensions of the unit cell are very close to those of biphenyl. This already indicates quite a similar structure for these two compounds, very different from that of other 4,4'-dihalogenobiphenyls (Brock, Kuo & Levy, 1978; Kronebusch, Gleason & Britton, 1976). Indeed, at the different temperatures studied, 4,4'-difluorobiphenyl (Fig. 3) is isostructural to the room-temperature structure of biphenyl (Charbonneau & Délugeard, 1977). Note that our results are in good agreement with the crystal structure determined at 100 K by Bielushkin *et al.* (1986). The unit cell

\* Corresponding results at other temperatures, lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP44076 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

contains two molecules each placed on a centre of symmetry and related to one another by a twofold screw axis or the perpendicular glide plane. As in the high-temperature phase of biphenyl (Charbonneau & Délugeard, 1977), the centre of symmetry imposes on the molecule of 4,4'-difluorobiphenyl a zero mean torsional angle around the long molecular axis, which is in complete agreement with vibrational spectroscopy (Toupet & Girard, 1980; Barrett & Steele, 1972) or NMR studies (Halstead, Spiess & Haebleren, 1976; Halstead, Tagenfeldt & Haebleren, 1981).

From a comparison of the 293 K structures of the title compound and biphenyl it is possible to understand the resulting change of the unit-cell parameters. The increase of the  $c$  parameter in 4,4'-difluorobiphenyl is due to the larger size of the fluorine compared with the hydrogen atoms. Indeed, these atoms are located on the long molecular axis, which

is quite close to the crystallographic  $c$  direction. The increase in  $b$  and the decrease in  $a$  are the result of a rotation around the long molecular axis of 4,4'-difluorobiphenyl with respect to biphenyl, which brings the molecule into the plane defined by  $b$  and  $c$ . Indeed, with regard to the geometric considerations on the origin of incommensurability in biphenyl (Heine & Price, 1985), the angle between  $b$  and the projection of the aromatic ring at height  $\frac{1}{4}c$  is  $35^\circ$  in biphenyl and  $31^\circ$  in 4,4'-difluorobiphenyl. Moreover, the angle  $\beta$  in the fluorinated crystal ( $92.85^\circ$ ) is smaller than in the biphenyl crystal ( $95.1^\circ$ ), and the angle between  $c$  and the long molecular axis is  $20^\circ$  in 4,4'-difluorobiphenyl and  $23^\circ$  in biphenyl. Consequently, the molecular direction with respect to  $[001]$  is quite similar in the two compounds.

The endocyclic angle  $C(2)C(1)C(6)$  is less than the ideal angle of  $120^\circ$  and the bond lengths  $C(1)-C(2)$  and  $C(1)-C(6)$  are slightly longer than the expected value. This geometry, quite similar to that observed in the gaseous state (Almenningen, Bastiansen, Gundersen, Samdal & Skancke, 1985) allows the steric repulsion of the *ortho* hydrogen atoms to be reduced as in biphenyl (Charbonneau & Délugeard, 1976). The carbon-fluorine bond distance does not depend on temperature and is the same in the gaseous state (Almenningen *et al.*, 1985).

The use of the WAGG program (Baudour, 1972) allows the thermal motion to be analysed in terms of librational and translational tensors. The results of these refinements are given in Table 4. The temperature dependence of the molecular tensors appears linear and this behaviour is consistent with the classic treatment of thermal motion. Translational tensors in 4,4'-difluorobiphenyl are slightly smaller than in biphenyl (Baudour, Toupet, Délugeard & Ghemid,

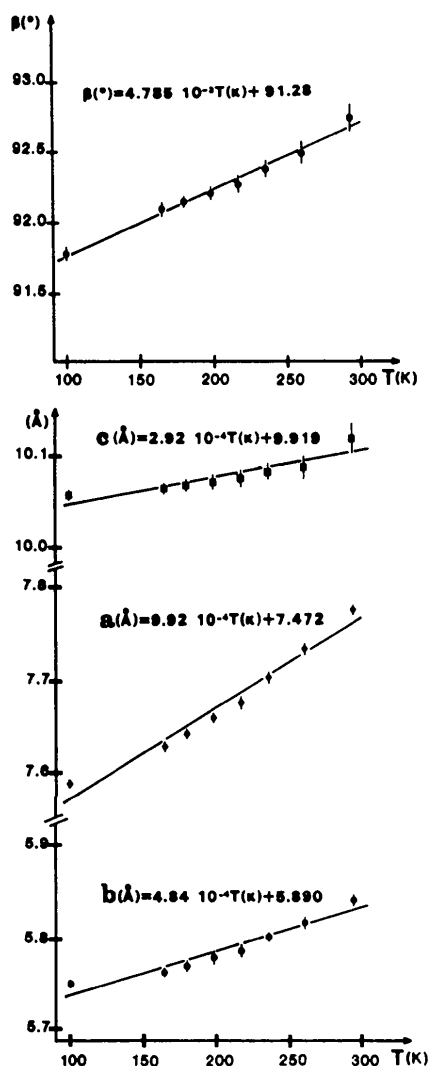


Fig. 2. Unit-cell parameters of 4,4'-difluorobiphenyl versus temperature.

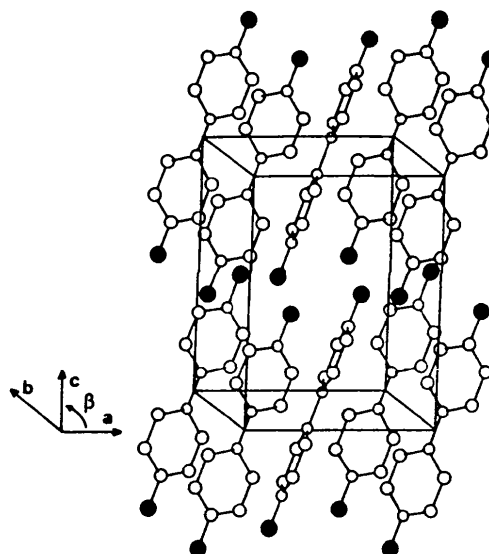


Fig. 3. Crystal structure of 4,4'-difluorobiphenyl (● fluorine atom).

Table 4. *Translational and librational tensors of 4,4'-difluorobiphenyl at different temperatures and comparison with biphenyl (Baudour, Toupet, Délugeard & Ghemid, 1986)*

	4,4'-Difluorobiphenyl					Biphenyl
	155	180	241	262	293	293
Temperature (K)	155	180	241	262	293	293
Number of reflections	516	487	476	432	404	414
Final residuals	0.060	0.066	0.076	0.066	0.067	0.064
Translational tensor ( $\times 10^4 \text{ \AA}^2$ )						
$T_{11}$	154 (17)	185 (13)	285 (14)	291 (12)	384 (17)	403 (12)
$T_{22}$	297 (7)	266 (11)	328 (11)	332 (10)	427 (11)	593 (6)
$T_{33}$	114 (12)	148 (11)	263 (12)	289 (10)	359 (12)	453 (9)
$T_{12}$	17 (5)	10 (7)	4 (8)	17 (6)	33 (9)	18 (5)
$T_{13}$	86 (5)	122 (7)	118 (8)	88 (7)	112 (9)	0 (4)
$T_{23}$	6 (5)	-2 (7)	-8 (8)	4 (6)	7 (8)	-12 (5)
Librational tensor ( $\text{deg}^2$ )						
$L_{11}$	3.1 (3)	3.1 (4)	4.0 (5)	5.6 (4)	6.3 (6)	11.5 (5)
$L_{22}$	43.0 (3)	55.0 (4)	63.0 (4)	74.0 (4)	94.0 (5)	109.2 (3)
$L_{33}$	2.3 (4)	3.9 (6)	5.0 (6)	6.5 (7)	8.1 (9)	8.4 (5)

1986). This disparity is due to the size of fluorine atoms which hinder translational motion. As in biphenyl, 4,4'-difluorobiphenyl presents an unusually large librational motion around the long molecular axis. However, at any temperature, the mean-square amplitude, given by  $L_{22}$  (Fig. 4), is always lower than that observed in biphenyl in its high-temperature phase (Baudour, Toupet, Délugeard & Ghemid, 1986). The torsional motion gives the principal contribution to this mean-square amplitude. As the moments of inertia about the long molecular axes are the same in the two compounds, the frequencies of torsional modes in 4,4'-difluorobiphenyl are higher than those of biphenyl. The enhancement by the mesomeric effect of  $\pi$ -conjugation of the aliphatic central bond, a consequence of the substitution of fluorine atoms at the 4 and 4' positions, although weak, may explain this stronger tendency to coplanarity of the aromatic rings. These results may be compared with those of accurate calorimetry measurements (Saito, 1986; Saito, Atake & Chihara, 1986; Saito, Chihara, Atake & Saito, 1985). In contrast to biphenyl, no thermal anomaly was apparent between 4 and 300 K, in the limit of the experimental precision

( $0.005 \text{ J K}^{-1} \text{ mol}^{-1}$ ). Moreover, these thermodynamic studies revealed an interesting behaviour of the specific heat at low temperature. Above  $\sim 12 \text{ K}$  the specific heat of 4,4'-difluorobiphenyl is higher than that of biphenyl, but below  $\sim 12 \text{ K}$  it becomes lower. This behaviour may be explained as follows. Owing to the mass difference and to the hindering of translational motions (see above), the frequencies of the acoustic modes are expected to be lower in 4,4'-difluorobiphenyl than in biphenyl. This explains the heat-capacity behaviour above  $\sim 12 \text{ K}$ . In order to explain the behaviour below  $\sim 12 \text{ K}$ , it is necessary to consider that the torsional motions contribute differently in the two compounds. In biphenyl, the contribution to the specific heat of characteristic low-frequency torsional incommensurate excitations (phasons) remains important at very low temperature. By contrast, in 4,4'-difluorobiphenyl, if the high-symmetry phase subsists at absolute zero the frequencies of the torsional modes are finite. Consequently, they contribute to a lower extent to the specific heat at very low temperature. This is another indication of the incomplete softening of the torsional modes in 4,4'-difluorobiphenyl which is consistent with their higher frequencies at high temperature, with regard to biphenyl (see above).

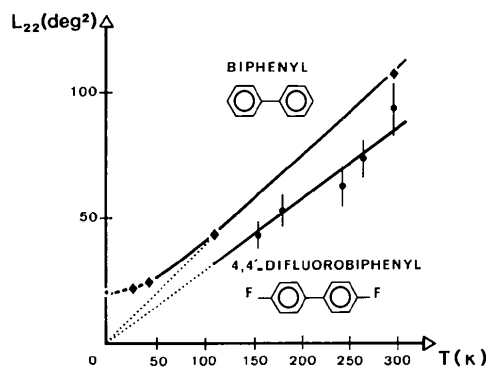


Fig. 4. Variation with temperature of  $L_{22}$ , reflecting libration around the long molecular axis in 4,4'-difluorobiphenyl (●). Comparison with biphenyl (◆).

### Concluding remarks

The 4,4'-difluorobiphenyl crystal is isostructural to the high-symmetry phase of biphenyl. By accurately analysing thermal motions, we have shown that the torsional frequencies in 4,4'-difluorobiphenyl are higher than those in biphenyl. This is an indication that the substitution of *para* hydrogen atoms by fluorine atoms has a sufficient effect on the delicate balance between the intramolecular and crystal packing forces to allow the mean planar molecular geometry to subsist, even at absolute zero. However, only dynamic calculations would be able to explain whether the surprising stability of the planar confor-

mation of 4,4'-difluorobiphenyl is mainly due to the modification of intramolecular potential by inductive and mesomeric effects or to the perturbation of packing forces, as is observed in biphenyl under pressure. This absence of any structural transition at low temperature shows 4,4'-difluorobiphenyl to be a very good candidate for studies of lattice dynamics for non-rigid molecules.

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*Note added in proof:* Recent calculations on the stability of the molecular geometry in 4,4'-difluorobiphenyl (Saito, Atake & Chihara, 1987) let us expect that the planar conformation is the most stable one at 0 K.

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*Acta Cryst.* (1987). **B43**, 470-479

## Comparison Between Structural Analyses of Plastic and Brittle Crystals

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#### Abstract

The structures of adamantane (C<sub>10</sub>H<sub>16</sub>) and fluoroadamantane (C<sub>10</sub>H<sub>15</sub>F), in their plastic phases, are refined according to a Frenkel model or to the determination of the molecular orientational probability. A comparison is proposed between the  $A_{mm}^l$  coefficients refined in the second method and the librational amplitudes deduced from the Frenkel model. The experimental technique employed to obtain a good crystal in the low-temperature phase is described and the order-disorder transition process is discussed from the point of view of these structural studies. Crystal data for adamantane at 188 K:  $M_r =$

136.3, tetragonal,  $P\bar{4}_2c$ ,  $a = 6.639(7)$ ,  $c = 8.918(9)$  Å,  $V = 393.1(12)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.15$  Mg m<sup>-3</sup>, Mo K $\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.064$  mm<sup>-1</sup>,  $F(000) = 152$ ,  $R = 3.6\%$  for 211 independent reflections.

#### I. Introduction

Structural studies of disordered crystalline phases are commonly performed according to two different methods. In the first, the 'Frenkel model' describes the molecular disorder by discrete equilibrium positions and the thermal vibrations are split into librations and translations. In the second method, the