

Structure and Barrier to Internal Rotation of Biphenyl Derivatives in the Gaseous State. Part 5. A Reinvestigation of the Molecular Structure and Internal Rotation of Perfluorobiphenyl

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The gas-phase electron-diffraction structure of the title compound has been determined. One static and three dynamic models have been applied to simulate the large amplitude motion about the inter-ring C–C bond. The structure parameters (r_a , \angle_a) for the dynamic models were found to be: $r(\text{C–F}) = 1.3275(9)$, $r(\text{C1–C2}) = 1.404(4)$, $r(\text{C2–C3}) = 1.391(7)$, $r(\text{C3–C4}) = 1.384(10)$, $r(\text{C1–C1}') = 1.492(5)$ Å, and $\angle\text{C1C2F} = 119.6(3)$, $\angle\text{C2C3F} = 120.1(6)$, $\angle\text{C2C1C6} = 117.9(4)$, and $\angle\text{C1C2C3} = 120.9(8)^\circ$. The numbers in parentheses are one standard deviation as given by least-squares refinement using a diagonal weight matrix. Perfluorobiphenyl is non-planar with a dihedral angle of $64.4(7)^\circ$.

We have previously determined the molecular structure and barrier to internal rotation for nine non-*ortho*-substituted biphenyl derivatives.^{1–4} The deformation of the phenyl group for these molecules and the potential energy function for internal rotation are in good agreement with the results obtained by other methods and theoretical calculations. We wish to extend our previous work to investigate *ortho*-substituted biphenyl derivatives such as 2,6-dihalo- and 2,2'-dihalobiphenyls, and also biheterocyclic rings with N atoms, in order to obtain information about the potential energy distribution for internal rotation and deformation of the ring systems.

Perfluorobiphenyl has previously been investigated by the Oslo group.⁵ However, no account was taken of deformation of the phenyl group, shrinkage corrections or the variation of the root-mean-square amplitudes of vibration with the torsional angle. Different potential energy functions were tested. In the light of the good results obtained for the non-*ortho*-substituted biphenyl derivatives, a reinvestigation should be justified.

Experimental

The photographic plates and the experimental conditions used were as described previously.⁵ The same four photographic plates as used for the two nozzle-to-plate distances in the previous investigation were retraced using a modified Joyce-Loeble microdensitometer at the Department of Astrophysics. The data were then processed in the usual way.⁶ Ordinarily, a modified molecular intensity function^{6,7} is used in the structural refinements; however, due to some uncertainty in the blackness correction for the

older data the $sM(s)$ method⁸ was selected for the structural refinements. The modification function is the inverse of the theoretical background. Review articles^{7,8} provide further details concerning the two different methods. The background was determined by fitting polynomials to the intensities from each plate using theoretical molecular $sM(s)$ intensities. A 9th and 11th degree polynomial was used for the 48 cm and 20 cm nozzle-to-plate distances, respectively. The background subtraction program is based on the same principles as described by L. Hedberg.⁹

The $sM(s)$ intensity curves for the two camera distances are shown in Fig. 1, and the corresponding radial distribution curves are shown in Fig. 2.

Structural analysis

The numbering of the atoms in perfluorobiphenyl is shown in Fig. 2. An overall D_2 symmetry has been assumed, and the following ten independent structural parameters were selected to describe the molecular geometry: $r(\text{C1–C1}')$, $r(\text{C1–C2})$, $r(\text{C2–C3})$, $r(\text{C3–C4})$, $r(\text{C–F})$, $\angle\text{C2C1C6}$, $\angle\text{C1C2C3}$, $\angle\text{C1C2F}$, $\angle\text{C2C3F}$ and the dihedral angle, φ , defined as 0° for the planar form. All C–F bond distances have been assumed equal in accordance with the results obtained for perfluorobiphenyl in the solid state.¹⁰ The C_6F_5 fragments are assumed planar.

An approximate valence force field based on the force constants for benzene derivatives,^{11,12} biphenyl^{13,14} and halogenated biphenyl derivatives¹⁵ was used to calculate the root-mean-square amplitudes of vibration (u) and the perpendicular correction coefficients (K). A program written by Hilderbrandt¹⁶ was used for these calculations. For

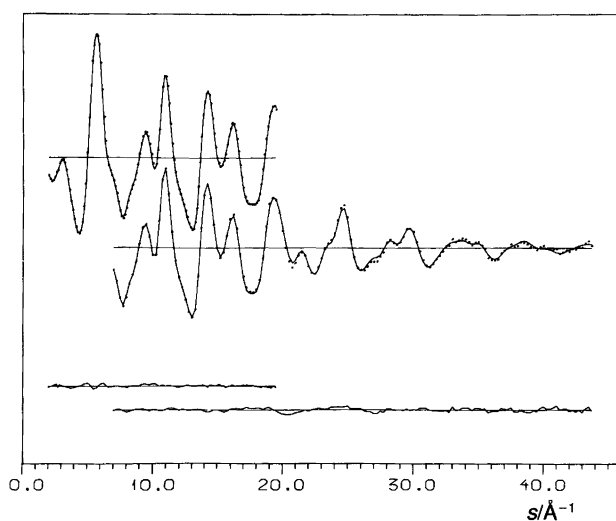


Fig. 1. Experimental (dots) and theoretical (full line) intensity curves, and difference curves for perfluorobiphenyl.

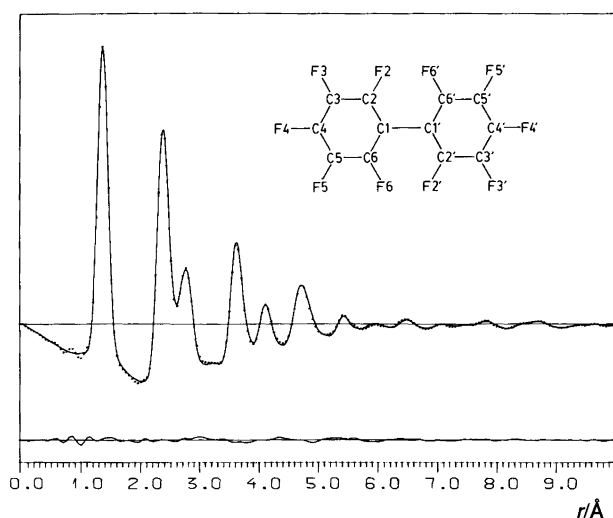


Fig. 2. Experimental (dots) and theoretical (full line) radial distribution curves for perfluorobiphenyl with an artificial damping constant $B = 0.0020\text{\AA}^2$. Theoretical intensities have been used below $s = 2.0\text{\AA}^{-1}$. The numbering of the atoms is also given. The well resolved peaks are assigned to the distances specified in Tables 1 and 3.

framework u and K values the contribution from the torsion about $C1-C1'$ is ignored, and a geometrically consistent r_a -structure is refined in order to account for the shrinkage effect.

During the initial part of the analysis, all intra-ring C-C bond distances were assumed equal and all angles were fixed at 120° . These constraints were gradually removed during the analysis.

Three different potential energy functions were tested for simulation of the large amplitude motion about the inter ring C-C bond. The same procedure as for the other biphenyl derivatives has been used.¹⁻⁴ The three different potential energy functions are:

Model I:

$$V(\varphi) = P_1 \sin^3 \varphi + P_2 \cos^3 \varphi \quad 0^\circ \leq \varphi \leq 90^\circ,$$

which is one of the functions used in the previous investigation;⁵

Model II:

$$V(\varphi) = 0.5V_2(1 - \cos 2\varphi) + 0.5V_4(1 - \cos 4\varphi),$$

which is used for the other biphenyl derivatives⁴ and for 2,2'-bipyrimidine;¹⁷

Model III:

$$V(\varphi) = \sum a_n \varphi^n,$$

which is a 5th degree polynomial in which the coefficients a_n are expressed as functions of V_0 , V_{90} and φ_{\min} by solving the set of six linear equations:

$$\left[\frac{dV}{d\varphi} \right]_{\varphi=0} = \left[\frac{dV}{d\varphi} \right]_{\varphi=90} = \left[\frac{dV}{d\varphi} \right]_{\varphi=\varphi_{\min}} = 0$$

$$V(0) = V_0; V(90) = V_{90}; V(\varphi_{\min}) = 0$$

The parameters V_0 , V_{90} and φ_{\min} were determined by the least-squares method. This approach has been used successfully for methyl vinyl sulfide.¹⁸

The first two models, I and II, are two-parameter models and V_0 , φ_{\min} and V_{90} are not independent. Model III is a three-parameter model where V_0 , φ_{\min} and V_{90} may be determined independently, and is therefore more flexible than the first two models. It should be remembered that the electron-diffraction method can only give information in cases where the population is large, i.e. at potential minima, and where the barrier is low. The determination of the rotational barriers is discussed elsewhere.⁴

Results and discussion

The final geometrical parameters are shown in Table 1. The potential energy functions for the three different models are shown in Fig. 3, and the corresponding parameters are given in Table 2. Calculated and observed amplitudes of vibration for torsional independent distances are given in Table 3.

The skeletal parameters for the three different large-amplitude models are identical, as can be seen from Table 1. The correlation between the geometrical parameters and parameters determining the potential energy functions is low, not exceeding 0.26, which is the highest value found for the three models. This indicates that the geometrical parameters are very little influenced by the different models, as can be seen from Table 1.

In Table 4, the skeletal parameters are compared with the corresponding solid-state parameters,¹⁰ and with the estimated deformation^{19,20} of the benzene ring assuming the

Table 1. Final geometrical parameters^a for perfluorobiphenyl.

	Static	Model I	Model II	Model III
$r(\text{C}-\text{F})$	1.3279(9)	1.3275(9)	1.3275(9)	1.3275(9)
$r(\text{C}1-\text{C}2)$	1.403(3)	1.404(4)	1.404(4)	1.404(4)
$r(\text{C}2-\text{C}3)$	1.394(8)	1.391(7)	1.391(7)	1.391(7)
$r(\text{C}3-\text{C}4)$	1.385(11)	1.384(11)	1.384(11)	1.384(10)
$r(\text{C}1-\text{C}1')$	1.495(6)	1.492(5)	1.492(5)	1.492(5)
$\angle\text{C}1\text{C}2\text{F}$	119.2(4)	119.6(5)	119.6(3)	119.6(3)
$\angle\text{C}2\text{C}3\text{F}$	119.8(6)	120.0(6)	120.1(6)	120.1(6)
$\angle\text{C}2\text{C}1\text{C}6$	117.6(6)	117.9(5)	117.9(5)	117.9(4)
$\angle\text{C}1\text{C}2\text{C}3$	120.9(9)	120.9(8)	120.9(8)	120.9(8)
φ	64.3(1.0)	63.6	62.8	64.4(7)
$R2^b$	4.40	4.16	4.16	4.15

^aDistances are r_a and angles \angle_α . Uncertainties are one standard deviation from least-squares refinement. Uncertainties due to the electron wavelength and correlation among data are not incorporated. ^b $R2$ -factor is defined as: $R2 = (\sum w_i^2 \Delta_i^2 / \sum w_i^2 (\text{obs})^2)^{1/2}$, where $\Delta_i = |(\text{obs}) - |(\text{calc})|$.

substitution effects in benzene derivatives to be additive.^{19,21} This additivity hypothesis has been strongly supported by *ab initio* calculations.^{22,23} The agreement between the solid- and gaseous-state geometry, and the estimated deformation of the benzene ring are consistent but by no means perfect. The angle $\angle\text{C}2\text{C}1\text{C}6$ is significantly less than 120° , but it is 1.5° larger in the gaseous state than in the solid state. The estimated $\angle\text{C}2\text{C}1\text{C}6$ angles are 3.5° and 2.2° , respectively, smaller than found in the gaseous state. However, in the estimation of the deformation a phenyl group was used instead of a pentafluorophenyl group, for which no parameters are available. The pentafluorophenyl group is more electronegative²⁴ than a phenyl group, and this should increase the angle $\angle\text{C}2\text{C}1\text{C}6$.²⁵ Our results can

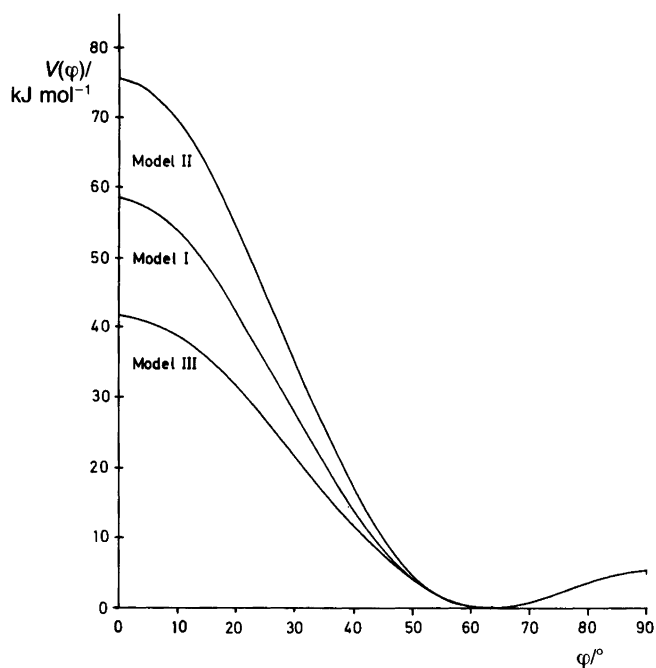


Fig. 3. Potential energy functions for internal rotation about the inter-ring bond of perfluorobiphenyl for three different models.

Table 2. Parameters determining the potential energy function for rotation about the inter-ring C–C bond for perfluorobiphenyl.

	Model I ^a	Model II ^b	Model III	Ref. 30
$V_0(\text{kJ/mol})$	58.5	75.6	41.8	121
$\varphi_{\min}(\text{°})$	63.6	62.9	64.4(7)	70
$V_{90}(\text{kJ/mol})$	5.4	5.2	5.7(10)	1.3

^a P_1 and P_2 are 52.3(9.6) and 105(20) kJ mol^{-1} respectively; $\varphi_{\min} = \arctan(P_2/P_1)$. ^b V_2 and V_4 are 70(16) and $-30.1(6.3)$ kJ mol^{-1} respectively; $\varphi_{\min} = \arccos(-V_2/4V_4)$.

be used indirectly to estimate the deformation parameters¹⁹ for a pentafluorophenyl group. Values of $\Delta\alpha = 1.3^\circ$ and $\Delta\beta = -0.5\Delta\alpha$ will give $\angle\text{C}2\text{C}1\text{C}6 = 117.9^\circ$ and $\angle\text{C}1\text{C}2\text{C}3 = 121.3^\circ$, which is a much better prediction of the molecular deformation. A positive value of $\Delta\alpha$ is what should be expected for an electronegative group.²⁴

The estimated intra-ring bond distances are such that $r(\text{C}1-\text{C}2) > r(\text{C}2-\text{C}3) > r(\text{C}3-\text{C}4)$, which is indeed found both in the solid and the gaseous state. It is encouraging to observe the internal consistency even if the experimental differences are not significant by statistical criteria. As shown in Table 4, the intra-ring bond distances determined by X-ray diffraction are shorter than the corresponding distances determined by electron diffraction, which can be explained by the displacement of the electron density towards the centre of the benzene ring compared to the nuclear skeleton. As a consequence of this displacement of the electron density a longer C–F bond in X-ray diffraction compared to electron diffraction would be expected, and this is also found experimentally.

The average r_a intra ring-bond distance in perfluorobiphenyl is 1.393 Å, which is shorter than the values of 1.396 Å and 1.398 Å for 4-fluoro- and 4,4'-difluorobiphenyl, respectively.³ This is also in agreement with the general trend found from *ab initio*²⁶ calculations for increasing fluorine substitution in benzene. The average intra-ring bond distance in the previous analysis⁵ of perfluorobi-

Table 3. Observed and calculated root-mean-square amplitudes of vibration for some of the torsional independent distances in perfluorobiphenyl.^a

r	u_{obs}	u_{calc}	r	u_{obs}	u_{calc}
C–F	0.0407	0.0447	C2...F3	0.0610	0.0620
C1–C2	0.0433	0.0473	C4...F3	0.0610	0.0620
C2–C3	0.0442	0.0482	C1...C3	0.0551	0.0561
C3–C4	0.0449	0.0489	C2...C4	0.0550	0.0560
C1–C1'	0.0449	0.0489	C2...C6	0.0536	0.0546
F3...F5	0.0807	0.0778	C2...C1'	0.0673	0.0683
F3...C1'	0.0862	0.0832	C3...C5	0.0548	0.0558
C4...F2	0.1991	0.1961	C1...F2	0.0605	0.0615
F2...F4	0.0807	0.0777	C3...F2	0.0609	0.0619
F2...F6	0.0804	0.0774	C3...F4	0.0610	0.0620
C1...F3	0.0643	0.0637	C6...F3	0.0669	0.0653
C5...F3	0.0644	0.0638	C4...C1'	0.0718	0.0702
C3...C1'	0.0694	0.0688	C1...F4	0.0674	0.0658
C2...F4	0.0645	0.0639	C3...F6	0.0670	0.0654
C2...F6	0.0636	0.0630	C1...C4	0.0625	0.0617
C4...F2	0.0645	0.0639	C2...C5	0.0620	0.0612
			F2...F3	0.1041	0.1033
			F3...F4	0.1044	0.1036
			C1...F2'	0.1075	0.1067

^aNumbering of the atoms is shown in Fig. 2. u -values were refined in one group and uncertainties are one standard deviation obtained using a diagonal weight matrix.

Table 4. Comparison of the structure parameters for perfluorobiphenyl in the gaseous and solid state, and with their estimated values.

	ED ^a Model III	X-ray Ref. 10	Estimates ^b		$(r-r_{\text{av}})_{\text{ED}}$	$(r-r_{\text{av}})_{\text{XR}}$
			Ref. 21	Ref. 20		
$r(\text{C–F})$	1.3290(9)	1.344				
$r(\text{C1–C2})$	1.405(4)	1.385[2] ^d		0.008	0.011	0.012
$r(\text{C2–C3})$	1.393(7)	1.368[17]		–0.007	–0.002	–0.005
$r(\text{C3–C4})$	1.386(10)	1.365[0]		–0.009	–0.009	–0.008
$r(\text{C–C})^c$	1.395	1.373				
$r(\text{C1–C1}')$	1.494(5)	1.486[5]				
$\angle \text{C1C2F}$	119.6(3)	119.4[5]				
$\angle \text{C2C3F}$	120.1(6)	120.0[8]				
$\angle \text{C2C1C6}$	117.8(4)	116.3[2]	114.3	115.6		
$\angle \text{C1C2C3}$	120.9(8)	121.7[3]	123.0	122.6		
φ	64.4(7)	59.6				

^a r_g in Å and \angle_a in degree. ^bEstimated effects on the parameters due to substitution. Parameters for a phenyl group are used since no parameters are available for the pentafluorophenyl group. ^cAverage C–C intra-ring distances. ^dAverage of two distances and [] is the difference.

phenyl was found to be 1.395(4)Å, in good agreement with our reinvestigation.

The inter-ring r_a bond distance is 1.492(5)Å, which is intermediate between the corresponding values of 1.497(3)Å and 1.483(4)Å found for 4-fluoro- and 4,4'-difluorobiphenyl, respectively. The range of the inter-ring C–C bond distance for all biphenyl derivatives^{1–3} examined lately in our group is between 1.480Å and 1.513Å. The corresponding distance in the previous investigation⁵ was found to be 1.51(1)Å.

As seen in Table 4, the average C–F bond distance in the gaseous state [$r_a(\text{C–F}) = 1.3275(9)\text{Å}$] is much shorter than in the solid state [$r(\text{C–F}) = 1.344\text{Å}$] but in good agreement with the previous result,⁵ i.e. $r(\text{C–F}) = 1.325(4)\text{Å}$. Compared to the value of $r(\text{C–F}) = 1.355(4)\text{Å}$ in monofluorobenzene,²⁷ the C–F distance in perfluorobiphenyl is shorter by almost 0.03Å, but compared to the C–F distances in perfluorobenzene²⁸ [1.327(7)Å] and pentafluorobenzene sulfonyl chloride²⁹ [1.324(1)Å], the agreement is very good. This is also in accordance with the general trend

found by *ab initio* calculation,²⁶ that C–F bond distances in benzene derivatives decrease with increasing fluorine substitution.

Perfluorobiphenyl is non-planar both in the gaseous and the solid state. The dihedral angle in the gaseous state is 64.3(1.0)° for the static model, which should be considered as an average over the rotational vibrational states, and 64.4(7)° for the dynamic model III, which corresponds to the minimum in the potential energy function. The dihedral angle was found to be 70.0(2.0)° in the previous investigation,⁵ while it is 59.6° in the solid state.¹⁰

The dihedral angles corresponding to the minimum for the three different potential energy functions and their barriers at 0° and 90° are given in Table 2.

The dihedral angles determined using three different potential energy functions are very consistent, and slightly smaller than found previously. As mentioned earlier, V_0 , φ_{\min} and V_{90} are not independent for models I and II, but independent for model III. Therefore, we believe the best estimates are the results for model III with a dihedral angle of 64.4(7)°. The barriers at 90° are also very consistent for the three models, with values of 5.4, 5.2 and 5.7 kJ mol⁻¹, respectively. The estimate of this barrier height in the previous investigation was 1.7–8.4 kJ mol⁻¹, and molecular mechanics calculations³⁰ give a barrier height of 1.3 kJ mol⁻¹. The barrier at 0° is large compared to the barrier at 90° due to the steric repulsion of the fluorine atoms. A high barrier means low population and therefore very little information from the electron diffraction data. Refinements on V_{90} for model III gave values of about 40 kJ mol⁻¹ with a standard deviation of the same magnitude, as also should be expected. The value of V_{90} has been varied substantially with practically no influence on the other parameters.

Compared to the barrier heights for non-*ortho*-substituted biphenyl derivatives,⁴ the torsional angle has increased by about 20° and the barrier at 0° is much higher, while the barrier at 90° is of the same order of magnitude.

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