ACTA CHEMICA SCANDINAVICA 22 (1968) 1013–1024

An Electron Diffraction Investigation of the Molecular Structure and the Torsional Oscillations in Decafluorobiphenyl

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Gaseous decafluorobiphenyl has been studied by electron diffraction. All the valence angles seem to be close to 120°, all the CF bond lengths and all the CC bonds in the rings must be nearly equal. The results with estimated standard deviations are

CC (ring): 1.395 (0.004) Å, CC (bridge): 1.51 (0.01) Å
CF: 1.325 (0.004) Å.

The angle between the ring planes is 70.0° (2.0°). This value is compared to the corresponding angles observed in similar compounds and to calculated values. The change in the potential energy with the angle between the ring planes was investigated. The difference in the potential energy for $\alpha = 90°$ and $\alpha = 70°$ seems to be in the range 0.4–2.0 kcal/mole.

While biphenyl is planar in the crystalline state,[1] the angle between the ring planes (α) was found to be about 42° in the gaseous phase.[2] A number of biphenyl derivatives have also been investigated by electron diffraction.[3–5] An attempt to estimate the amplitudes for the oscillations around the CC single bond has been made.[5] In 3,3′-dibromobiphenyl and 3,5,3′,5′-tetrabromobiphenyl the root-mean-square amplitude of the torsional oscillations was found to be in the range 15–22°. In the present investigation we have tried to estimate the potential energy as a function of the angle α.

EXPERIMENTAL AND THEORY

The sample of decafluorobiphenyl was obtained from Dr. D. R. MacKenzie, Brookhaven National Laboratory. The electron diffraction photographs were taken in the usual way with the Oslo apparatus.[6] The nozzle temperature was about 100°C and the electron wave length 0.06443 Å. Two nozzle to plate distances, *i.e.* 47.91 cm and 19.29 cm, giving intensity data in the s ranges 2–19 Å^{-1} and 7–44 Å^{-1}, were applied. Four plates were used for each nozzle to plate distance. The data were corrected and

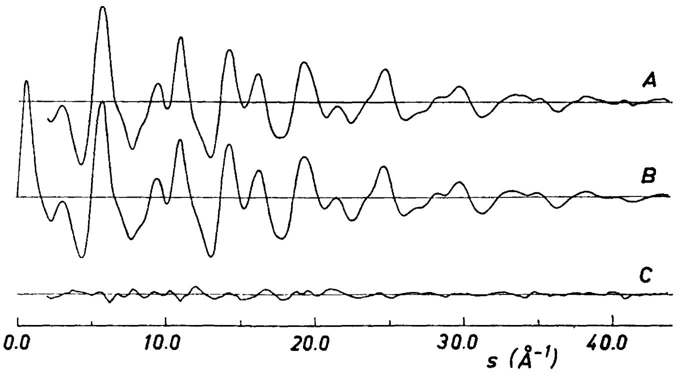

Fig. 1. Experimental (A) and theoretical (B) intensity curves. Curve B was calculated using the probability function $P_1(\alpha)$ [eqn. (5)] with p_1 and p_2 from Table 2 *a*. The curve C shows the difference between the curves A and B.

treated in the usual way.[7,8] Four intensity curves were obtained; each of these contained intensity data from two plates, one from each nozzle to plate distance. The mean of these curves is shown in Fig. 1 (curve A).

The modified molecular intensity may be expressed by [8]

$$I(s) = \text{const.} \sum_{i<j}^{M} \sum^{M} g_{ij/kl}(s) \exp(-\tfrac{1}{2}u_{ij}^2 s^2) \frac{\sin(R_{ij}s)}{R_{ij}} \tag{1}$$

M is the number of atoms in the molecule. R_{ij} is the distance between the atoms i and j and u_{ij} the corresponding root-mean-square amplitude of vibration.

$$g_{ij/kl}(s) = \frac{|f_i(s)||f_j(s)|}{|f_k(s)||f_l(s)|} \cos(\eta_i(s) - \eta_j(s)) \tag{2}$$

where $f_i = |f_i| \cos(i\eta_i)$ is the scattering amplitude of atom i. In this case we have chosen $f_k = f_C$ and $f_l = f_F$. We have then three different g functions:

$$g_{CC/CF} = |f_C|/|f_F|$$
$$g_{CF/CF} = \cos(\eta_C - \eta_F)$$
$$g_{FF/CF} = |f_F|/|f_C|$$

The scattering amplitudes were calculated on a CDC 3600 computer using a program written by J. Peacher.[9]

The expression (1) is based on the assumption that each pair of atoms (i,j) may be treated as a harmonic oscillator. This approximation is usually quite good for the bond distances, but may be rather rough for the non-bonded distances, especially if internal rotation is involved.

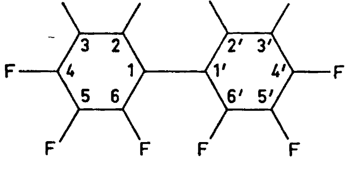

Fig. 2. The numbering of the atoms in decafluorobiphenyl.

STRUCTURAL ANALYSIS

The numbering of the atoms in decafluorobiphenyl is shown in Fig. 2. Approximate structure parameters were obtained from a radial distribution curve[7] (see Fig. 3, curve A) calculated by a Fourier inversion of the experimental intensity curve, *i.e.*

$$\sigma(r) = r\int I(s)\exp(-ks^2)\sin(rs)\,ds \tag{3}$$

k is an artificial damping constant. The structure was refined by the least-squares method applying eqn. (1). In the first refinement the perfluorobiphenyl groups were assumed to be planar with all the CC bonds in the rings equal, all CF bonds equal and all bond angles equal to 120°. The three bond distances and the angle α between the ring planes were treated as independent structure parameters. The u values were estimated and not refined. The results were:

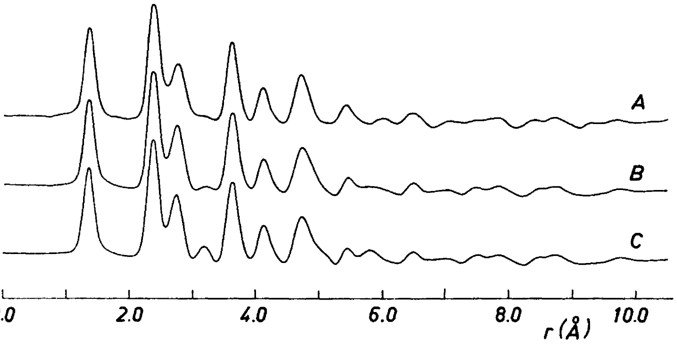

Fig. 3. Experimental (A) and theoretical (B,C) radial distribution curves [$\sigma(r)$]. (k = 0.0016 Å^2). The curves A and B were calculated by Fourier inversion of the intensity curves in Fig. 1. Curve C was obtained with the angle between the ring planes equal to 70.3°

CC (ring): 1.3911 (0.0010) Å
CC (bridge): 1.5325 (0.0089) Å
CF: 1.3251 (0.0011) Å
α: 70.3° (0.52°)

The standard deviations given in parentheses are as obtained in the least-squares calculation without corrections.

To test the assumptions about the molecular geometry six distances (all independent of α) and the corresponding u values were refined as independent parameters. The other distance- and u values were as in the previous calculation. Table 1, column a shows the results obtained by applying the mean intensity curve. The results in column b were calculated from the values obtained using the four observed intensity curves separately. The mean value and the standard deviation for this value were obtained giving the four results

Table 1. Least-squares results for some of the distances in $C_{12}F_{10}$ that do not depend on the angle between the ring planes. The standard deviations given in parentheses are in 10^{-4} Å.

	a		*b*		*c*		*d*	*e*
	R	*u*	*R*	*u*	*R*	*u*	*u*	*R*
C—C(ring)	1.3942 (22)	0.0409 (30)	1.3960 (10)	0.0378 (25)	1.3939 (7)	0.030 (22)	0.047	
C—F	1.3256 (17)	0.0375 (22)	1.3246 (15)	0.0350 (18)	1.327 (8)	0.031 (13)	0.048	
$C_1 \cdots C_3$	2.4239 (89)	0.0630 (84)	2.4267 (52)	0.0577 (48)		0.046 (26)	0.055	2.4149
$C_1 \cdots F_2$	2.3510 (36)	0.0574 (27)	2.3490 (21)	0.0553 (6)		0.050 (9)	0.065	2.3557
$C_1 \cdots F_3$	3.6130 (19)	0.0677 (16)	3.6133 (22)	0.0672 (8)		0.055 (13)	0.064	3.6240
$C_1 \cdots F_4$	4.1036 (46)	0.0711 (38)	4.1033 (27)	0.0704 (4)		0.060 (31)	0.063	4.1140

a. Results obtained by least-squares refinement on the mean intensity curve.
b. The mean values and the standard deviation for these values calculated from the results obtained using the four observed intensity curves.
c. Distances and *u* values for hexafluorobenzene obtained by electron diffraction (temperature *ca.* 285°K).
d. *u* values for hexafluorobenzene at 373°K calculated from spectroscopic data.
e. Distances calculated from the bond distances in column *a*.

equal weights. The standard deviations in *b* are smaller than the corresponding values in *a* except for $R(C_1F_3)$.

The columns *c* and *d* give some results for hexafluorobenzene. The values in *c* were obtained by electron diffraction,[10] and the *u* values in *d* have been calculated from spectroscopic data.[11] The bond distances in the two compounds are very nearly equal. The *u* values in decafluorobiphenyl are somewhat larger than the electron diffraction results for hexafluorobenzene; the general agreement with the values in column *d* is rather better.

Column *e* (Table 1) gives the values for the non-bonded distances calculated from the bond distances in column *a*. The CF distances in *e* are slightly greater than the corresponding distances in *a*. This is to be expected if the phenyl groups have the assumed symmetry, since the molecule is not rigid. A certain "shrinkage effect" caused by the molecular vibrations, is observed for non-bonded distances.[11,12] The C_1C_3 distance is on the other hand slightly smaller in *e* than in *a*. The difference is close to the standard deviation for this distance.

The results in Table 1 indicate that the perfluorobiphenyl groups do not deviate much from the assumed symmetry, though it is, of course, not possible to exclude small deviations. Theoretical radial distribution and intensity curves calculated with $\angle C_1CF_{ortho} = \angle C_{1'}CF_{ortho} = 125°$ gave furthermore definitely less good agreement with the experimental curves than obtained with all the CCF angles equal to 120°.

ANALYSIS OF THE TORSIONAL MOTION

Twenty non-bonded distances depend on the angle between the ring planes (α). For the distances we replace

$$\exp(-\tfrac{1}{2}u^2s^2)\ \frac{\sin[R(\alpha)s]}{R(\alpha)}$$

in eqn. (1) by

$$\int \exp[-\tfrac{1}{2}u_{fr}^2(\alpha)s^2]\ \frac{\sin[R(\alpha)s]}{R(\alpha)}\ P(\alpha)d\alpha \qquad (4)$$

$P(\alpha)d\alpha$ is the probability that the angle between the ring planes is between α and $\alpha + d\alpha$. $u_{fr}(\alpha)$ (fr. for framework) is the root-mean-square amplitude for a hypothetical molecule with the angle between the ring-planes equal to α and no oscillations around the central CC bond. In some molecules (for example ethane) u_{fr} may be obtained unambigously from spectroscopic data.[13] For molecules with lower symmetry the torsion belongs to the same symmetry species as one or more of the other vibrations and the separation is not fully justified. We have further assumed that $u_{fr}(\alpha)$ is independent of α. This approximation is surely not justified in the whole range $0° \leq \alpha \leq 90°$. However, it seems probable that the variation in u_{fr} with α is not very large in the interval around the mean value of α ($\bar{\alpha}$) where $P(\alpha)$ is great.

Three analytical forms of $P(\alpha)$ were investigated, *i.e.*

$$P_I(\alpha) = N(p_1,p_2)\exp[-p_1(R_\alpha - p_2)^2] \qquad (5)$$

$$P_{II}(\alpha) = N(p_1,p_2)\{\exp[-p_1(\alpha - p_2)^2] + \exp[-p_1(\pi - \alpha - p_2)^2]\} \qquad (6)$$

$$P_{III}(\alpha) = N(p_1,p_2)\exp[-p_1(\sin^3\alpha + p_2\cos^3\alpha)] \qquad (7)$$

Table 2. Some results obtained in the refinements of the probability distribution $P(\alpha)$ (*cf.* eqns. (5–7)). $\bar{\alpha}$ is the mean value of α and α_{max} is the α value giving the maximum value of $P(\alpha)$. ΔV is the difference in the potential energy for $\alpha = 90°$ and $\alpha = \alpha_{\text{max}}$. $W\Delta^2$ = weight × $(I^{\text{obs}} - I^{\text{calc}})^2$. The sum in column *a* was arbitrary given the value 1.000.

	a	*b*	*c*	*d*	*e*	*f*	*g*
P function applied	P_{I}	P_{II}	P_{III}	P_{I}	P_{I}	P_{I}	P_{I}
p_1	5.7 (2.2)	16.5 (5.4)	35 (16)	6.5 (2.5)	6.7 (2.3)	4.5 (1.9)	3.8 (1.5)
p_2	3.138 (0.036)	1.22 (0.020)	0.407 (0.024)	3.128 (0.028)	3.122 (0.033)	2.969 (0.050)	2.939 (0.054)
$\bar{\alpha}$	69.8°	69.8°	70.2	70.2°	69.2°	65.4°	64.2
α_{max}	70.2°	70.0°	67.9	70.5°	69.3°	65.7°	64.7
ΔV(kcal/mole)	1.28 (0.51)	0.98 (0.68)	0.78 (0.38)	1.41 (0.57)	1.65 (0.60)	1.59 (0.70)	1.44 (0.69)
$\sum W\Delta^2$	1.000	1.000	1.000	0.495	1.047	1.651	1.659

a, b, c: Estimated *u* values were kept constant, the bond distances were refined.
d: The *u* values were refined in groups (see text); the bond distances were refined.
e: The *u* values applied in *a* were used and kept constant. Estimated shrinkage values were applied. $R(C_1-C_1')$ was refined.
f: $\angle C_1CF_{ortho} = \angle C_1'CF_{ortho} = 125°$. Otherwise as in *e*.
g: The angles between the CF_{ortho} bonds and the ring planes were 2.5°. Otherwise as in *f*.

N is the normalisation constant. p_1 and p_2 are parameters to be refined. R_α in eqn. (5) is the shortest distance between F atoms in *ortho* positions on different rings, *i.e.* $R(F_2 - F_{2'})$.

The parameters p_1 and p_2 were refined by the least-squares method. The integration in eqn. (4) was carried out numerically using Gauss' integration formula.[14]

Table 2 gives some results obtained in these refinements. The values in the three first columns were obtained with the $P(\alpha)$ functions given in eqns. (5—7). The values for u_{fr} were estimated and kept constant. The bond distances were refined. The agreement between the experimental and theoretical intensity values was very similar for the three functions. This fact is reflected in the values for $\sum W\Delta^2$. Curve B in Fig. 1 shows the theoretical intensity curve calculated with $P_{\mathrm{I}}(\alpha)$ and the parameters in Table 2 *a*. The difference between the experimental and theoretical curves is given by curve C. Fig. 3 shows the experimental and two theoretical curves for $\sigma(r)$ (*cf.* eqn. (3)). Curve B was obtained from the theoretical intensity curve in Fig. 1, and curve C was obtained with α fixed at 70.3°. The theoretical curves are very similar, the greatest difference being at $r \approx 3.1$ Å.

The functions $P(\alpha)$ calculated with the parameters in Table 2 (*a*, *b*, and *c*) are shown in Fig. 4. ΔV was calculated assuming that the classical expression could be applied, *i.e.**

$$\Delta V = RT \ln (P(\alpha_{\max})/P(90°)) \qquad (8)$$

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* If the energy levels of an harmonic oscillator are occupied according to the Maxwell-Boltzmann distribution law, the probability of finding the particle between x and $x + dx$ is given by the Gaussian function [15]

$$\frac{1}{\sqrt{2\pi}\, u} \exp\left(-\chi^2/2u^2\right) dx$$

where

$$u^2 = \frac{h\nu}{2f} \operatorname{cotgh}\left(\frac{h\nu}{2kT}\right)$$

ν is the frequency of the oscillator, f is the force constant, k is Boltzmann's constant, and T is the temperature.

The classical distribution is proportional to

$$\exp(-V/kT) = \exp\left(-\frac{f}{2kT}\, x^2\right)$$

Since

$$2u^2 = \frac{h\nu}{f} \operatorname{cotgh}\left(\frac{h\nu}{2kT}\right) = \frac{2kT}{f}\left(1 + \frac{1}{3}\left(\frac{h\nu}{2kT}\right)^2 - \frac{1}{45}\left(\frac{h\nu}{2kT}\right)^4 \cdots\right)$$

the classical expression may be applied if $h\nu/2kT < 1$. If we put $\nu = 100$ cm^{-1} and $T = 100$°C we find

$$\left(\frac{h\nu}{2kT}\right)^2 = 0.037$$

A similar agreement between the exact and the classical distribution with a potential of the form $V = V_0\ (1 - \cos n\varphi)/2$ as shown by Almenningen *et al.*[16]

ΔV was calculated by using the nozzle temperature for T. The population of the vibration levels does not necessarily correspond to this temperature.[17-19] This is now being investigated by measuring the shrinkage in C_3O_2.[20]

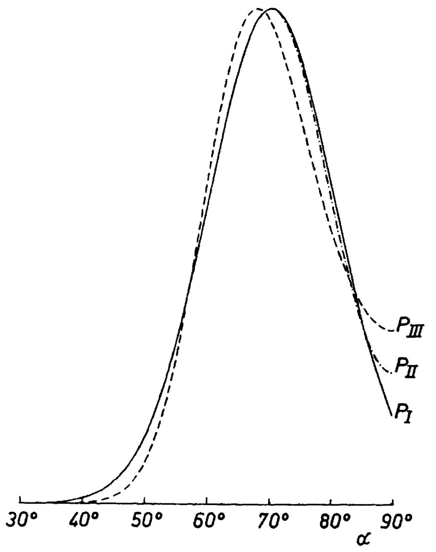

Fig. 4. Probability distribution functions $P(\alpha)$ [*cf.* eqns. (5−7)].

$P_{\rm I}(\alpha)$ gives probably a too large value for ΔV. The function has not a proper behaviour near $\alpha = 90°$; since $\partial P_{\rm I}(\alpha)/\partial\alpha \neq 0$ for $\alpha = 90°$. It is seen that $\bar{\alpha}$ and $\alpha_{\max}$ do not deviate much from the α value obtained when this parameter was refined as an independent variable (*cf.* p. 1015).

Calculations applying the four observed intensity curves separately was also carried out. The results are given in Table 3. The variation in $\bar{\alpha}$ and $\alpha_{\max}$ is rather small.

Table 3. Some results obtained in the refinements of the probability function $P(\alpha)$ applying four observed intensity curves.

Intensity curve No.	Function applied	α	$\alpha_{\max}$	ΔV (kcal/mole)
1	$P_{\rm I}$	69.9	70.1	1.48 (0.76)
2	$P_{\rm I}$	68.5	69.7	0.92 (0.73)
3	$P_{\rm I}$	70.3	71.1	1.03 (0.65)
4	$P_{\rm I}$ $P_{\rm III}$	70.3 71.2	70.6 68.9	1.37 (0.77) 0.94 (0.53)

The results obtained in the refinements described so far are based on a number of approximations. A series of calculations applying $P_I(\alpha)$ was carried out to find if the results for $\bar{\alpha}$, α_{max}, and ΔV were very sensitive to any of these approximations.

The previous results were obtained with estimated values for u_{fr}. It was impossible to refine all the u values. To get an idea of the variation in $P(\alpha)$ with changes in u_{fr} a calculation was carried out refining the u values in the following way: The distances that depend on α were divided in two groups; the longer of these distances in one group, the shorter in the other group. The u values for the distances given in Table 1 and $u(F_4—F_{4'})$ were refined independently, $u(C_1—C_{1'})$ was kept constant. The other distances that do not depend on α, were divided in three groups. The u values in each group were now given the same shifts in the least-squares refinements. Some results of this calculation are given in Table 2 *d*. The values should be compared to the results in column *a*. The agreement between the experimental and theoretical intensity curves has been considerably improved as is seen by comparing the values for $\sum W\Delta^2$. Thus our first estimate of the u values was not very accurate. However, the changes in the given results are much smaller than the corresponding standard deviations. This does not imply that the results are not sensitive to changes in the u values. The correlation coefficients between the parameter p_1 (this parameter determines the amplitude of the torsional oscillations) and the u values for the distances that depend on α, are appreciable, (0.26 and 0.64 for the two u parameters described above). A much better estimate of the barrier could be obtained if reliable values for u_{fr} could be calculated from spectroscopic data. This problem is now investigated.[21]

Only the three bond distances and α are necessary to calculate all the nonbonded distances for a rigid molecule with the assumed symmetry. The distances observed by electron diffraction will deviate somewhat from the values calculated for a rigid molecule as mentioned on p. 1015.

The shrinkage has been calculated from spectroscopic data for some molecules, among them hexafluorobenzene.[11] However, the shrinkage values are not known in decafluorobiphenyl. The values were therefore estimated, the largest being 0.055 Å. Since a distribution function $P(\alpha)$ was applied the shrinkage should correspond to a hypothetic molecule not oscillating around the central CC bond. When the estimated shrinkage was applied we obtained the results in Table 2 *e*. $\bar{\alpha}$ and α_{max} are close to the results in column *a*, while the increase in ΔV is somewhat smaller than the corresponding standard deviation. There is a slight increase in $\sum W\Delta^2$.

The results in Table 3 *f* and *g* were obtained if the molecule deviated from the symmetry assumed in the previous calculations. $\sum W\Delta^2$ is considerably larger in these columns than in *a*, but the change in the parameters is not too large.

Our final results are given below.* σ_α is the root-mean-square amplitude of the torsional motion calculated assuming the peaks in Fig. 4 to be Gaussian.

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* It has been discovered that the value applied for the electron wavelength may be about 0.2 % too large. The values given have not been corrected for this error.

CC (ring) : 1.395 (0.004) Å
CC (bridge): 1.51 (0.01) Å
CF : 1.325 (0.004) Å
$\bar{\alpha}$: 70° (2.0°)
ΔV : 0.4—2.0 kcal/mole
σ_α : 8—13°

The value for CC (ring) is the same as in benzene[22] and hexafluorobenzene.[10] $\bar{\alpha}$ did not change much in the various least-squares calculations and is probably well determined. The value is, as expected, larger than in biphenyl.

THEORETICAL CALCULATION OF THE POTENTIAL ENERGY

I. Fischer-Hjalmars[23] has calculated the variation in the potential energy for biphenyl as a function of the angle between the ring planes. The conjugation, and the van der Waals' energy, were included, *viz.*

$$V = E_{\text{conj}} + E_{\text{V}}$$

She found that the conjugation energy could be expressed by

$$E_{\text{conj}}(\alpha) \approx E_{\text{conj}}(0)\cos^2(\alpha) \tag{9}$$

with $E_{\text{conj}}(0) \approx -6.2$ kcal/mole. Various expressions were applied for the H···H interaction energy. α_{max} was found to be 30—40°.

We have made similar calculations for biphenyl and some of its halogenoderivatives. It was assumed that eqn. (9) with the value of $E_{\text{conj}}(0)$ given above could be applied also for the derivatives. This seems rather probable, since the bond lengths in benzene and in the halogenoderivatives of benzene are very similar,[10,22,24–26] though the assumption should perhaps be investigated further.

The van der Waals' energy was expressed by[27]

$$E_{\text{V}} = \varepsilon\,[-2.25\,a^{-6} + 8.28 \times 10^5 \exp(-a/0.0736)] \tag{10}$$

$a = r/(r_1^* + r_2^*)$ where r^* denotes the van der Waals' radius. The values for ε and r^* were taken from Ref. 27.

The potential energy difference $\Delta V = V(90) - V(\alpha_{\text{max}})$ was found to be 2.5 kcal/mole for decafluorobiphenyl. This is somewhat more than the observed value. Further results are given in Table 4. The energy contributions have been given for the α values corresponding to the minima of the potential energy functions. The functions for difluoro-, dichloro-, and dibromobiphenyl show two minima. The *trans* conformation gives the lowest value for the potential, mainly because the conjugation energy is larger in absolute value for the *trans* form than for the *cis* form. The electron diffraction investigations[3,4] indicated that the molecules exist in the *cis* form. However, a critical reexamination of the published radial distribution curves suggests that a small amount of the *trans* form may be present. Reinvestigations of these compounds are planned.

Table 4. van der Waals' and conjugation energy in biphenyl and some derivatives.

The calculations have been carried out for the angles between the ring planes corresponding to minima in the potential functions [α(calc)].

α(obs) is the observed value between the ring planes. α = 0 for the planar *cis* conformation. X = halogen. The error limits for the observed values may be ±(5−10°).

	van der Waals' energy											
	CC	CX	XX	CH	HH	HX	E_V	E_{conj}	V	α(calc)	α(obs)	Ref.
Biphenyl	+0.05	—	—	−0.14	+0.25	—	+0.15	−5.24	−5.09	23	42	2
3,3′-Dibromobiphenyl											45	5
3,5,3′,5′-Tetrabromobiphenyl										22	45	5
4,4′-Difluorobiphenyl											44	4
2-Fluorobiphenyl	−0.08	+0.01	—	−0.22	−0.02	+0.22	−0.09	−4.38	−4.47	33	49	4
2,2′-Difluorobiphenyl	−0.20	−0.20	0.18	−0.19	−0.05	−0.01	−0.47	−3.41	−3.88	42	60	4
»	−0.13	−0.09	−0.01	−0.17	−0.00	+0.12	−0.29	−3.97	−4.25	143		
Decafluorobiphenyl	−0.25	−0.53	−0.06	—	—	—	−0.85	−2.95	−3.80	46	70	This work
2,2′-Dichlorobiphenyl	−0.47	−0.71	−0.30	−0.21	−0.02	−0.07	−1.78	−0.57	−2.35	72	74	3
»	−0.39	−0.21	−0.12	−0.22	−0.00	−0.25	−1.19	−1.57	−2.76	120		
2,2′-Dibromobiphenyl	−0.50	−0.98	−0.52	−0.21	−0.01	−0.13	−2.36	−0.12	−2.48	82	75	3
»	−0.45	−0.49	−0.25	−0.21	−0.00	−0.33	−1.74	−0.90	−2.63	112		
2,2′-Diiodobiphenyl	−0.51	−1.17	−0.73	−0.20	−0.01	−0.27	−2.90	−0.02	−2.92	93	79	3

The difference between the angle found by I. Fischer-Hjalmars and the value given in Table 4 originates mostly from the difference in the CH potentials.

If only the *cis* forms are considered, the calculated values predict an increase in α from top to bottom of Table 4 in agreement with the observations. Note for example that the change in the van der Waals' energy makes the angle somewhat larger in decafluorobiphenyl than in 2,2'-difluorobiphenyl in agreement with the observations. However, most of the calculated values are rather different from the observed angle. The shortest distances observed between *ortho* atoms on different rings are usually much closer to the sum of the van der Waals' radii than predicted by the calculations. It seems possible that the halogen...halogen interaction energy is more important and conjugation energy perhaps less important for the determination of the angles between the ring planes, than the present calculations indicate.

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Received October 25, 1967.