

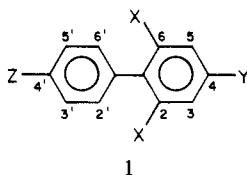
# The Conformation of Biphenyls in Nematic Liquid Crystalline Solution. The Relationship between the Torsional Angles and the Size of the Halogens in 2,6-Dihalogenated Derivatives

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**Abstract:** Analysis of the NMR spectrum of 4'-bromo-4-chloro-2,6-difluorobiphenyl in a nematic liquid crystalline solvent, together with the previously reported<sup>1</sup> work of Field, Sternhell, and Tracey shows that the ground-state torsional angles in this series are a smooth monotonic function of the size of the halogens at C-2 and C-6. There are indications that through-conjugation plays a very minor role in determining the torsional angles and that results of this type could be used as an independent method of determining some van der Waals radii.

In a previous communication<sup>1</sup> we have reported the results of the analyses of NMR spectra in liquid crystalline solvents for a number of 2,6-dihalogenated biphenyls (1) and compared them with previously published<sup>2-4</sup> results for biphenyls lacking substituents at C-2 and C-6.



We have now completed this series by the analysis of the eight-spin system of 4'-bromo-4-chloro-2,6-difluorobiphenyl (1, X = F, Y = Cl, Z = Br) in liquid crystalline phase<sup>5</sup> (Table I) and are in position to consider the effect of substituents at C-2 and C-6 in this series on the magnitude of the ground-state torsional angles ( $\theta$ ) (Table II). It can be seen (Figure 1) that a smooth monotonic relationship is observed, indicating that in biphenyls not bearing substituents at C-2' and C-6', the torsional angle is controlled by the size<sup>6</sup> of the substituents at C-2 and C-6. For symmetrical cases examined here we have considered a simple model (Figure 2), which implies that the ground-state torsional angle is determined solely by the van der Waals radii<sup>6</sup> of the substituents at C-2 and C-6 and the van der Waals radius of hydrogen. Simple projections *assuming* standard bond lengths<sup>6</sup> and angle ( $120^\circ$ ) lead to internuclear distances ( $d$  in Table III) which may be compared with the sum of the van der Waals radii. Clearly, while the agreement is not perfect, we believe that the simple model (Figure 2) accounts for the magnitudes of torsional angles remarkably well considering the number of assumptions made in the analysis of data<sup>1</sup> and the further assumptions inherent in obtaining the internuclear distances.

If the model is valid, it follows that it offers in principle an independent method of determining van der Waals radii of spherically symmetrical atoms. Thus halving the internuclear distance (2.16 Å) for unsubstituted cases (entry 1, Table III) leads to an apparent van der Waals radius of  $1.08 \pm 0.03$  Å for hy-

drogen, which may be compared with the standard value<sup>6</sup> of 1.2 Å. Similarly for the fluorine case (entry 2, Table III) the subtraction of that value from the internuclear distance of 2.50 Å leads to an apparent van der Waals radius for fluorine of  $1.42 \pm 0.07$  Å, which may be compared with the standard value<sup>6</sup> of 1.47 Å. It can be seen, however (Table III), that while the values of thus calculated apparent van der Waals radii for chlorine, bromine, and iodine are of the right order, the discrepancies with standard values increase as one moves down the periodic table. This may be due to the accumulated errors associated with the assumptions we have made but it could also be related to a fundamental physical effect formulated as follows. The restoring torque leading *toward* coplanarity in biphenyls is due only to rather weak through conjugation and therefore the more diffuse electron clouds of the larger halogens may offer more "resistance" in our systems than even in the weak intermolecular situations<sup>6</sup> from which the standard van der Waals radii are derived. In other words, chlorine, bromine, and iodine may indeed act as "larger" here than is usually assumed, while the "hard-edged" hydrogen and fluorine appear to be their usually assumed size.

While the above must be considered highly speculative, it is of interest that intramolecular distances in flexible molecules could offer a method of estimating van der Waals radii which is completely independent of *intermolecular* measurements on which these parameters are normally based.<sup>6</sup> Clearly the obvious extension of this work should involve systems where internal restoring forces are more substantial and need not rely on NMR spectroscopy in oriented systems for structural data. Further work is actively pursued in these laboratories.

We have also attempted to test the hypothesis that altering the restoring force may affect the magnitude of the ground-state torsional angle in biphenyls by extending the conjugation path. For that purpose we synthesized compounds 1 (X = Cl, Y = NO<sub>2</sub>, Z = Br and X = Cl, Y = NO<sub>2</sub>, Z = F) and analyzed their NMR spectra in EBBA. The results summarized in Table IV show a gratifyingly narrow range for the torsional angles, which are identical within the accuracy of the experiment with those previously<sup>1</sup> determined for 2,6-dibromo derivatives lacking through-conjugation (see Table II). This is not surprising in view of the fact that the restoring force due to the extended conjugation path would be at its maximum for the planar conformation and possibly negligible for the interring angles observed in this series.

We have also attempted to probe the assumptions<sup>1</sup> which lead to the derivation of a single value for the torsional angle from NMR data in oriented media. As the potential energy function for our series cannot be perfectly symmetrical, one could argue that the population of higher energy states (if significant) should alter the value of the apparently unique torsional angle. It follows that, if the assumptions made<sup>1</sup> are in serious error, the torsional angles derived from spectra taken at different temperatures should exhibit a range of values. It is experimentally difficult to obtain NMR spectra in liquid crystalline solvents over very wide tem-

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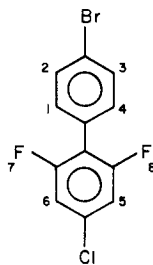
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Table I. Proton NMR data for 4'-Bromo-4-chloro-2,6-difluorobiphenyl<sup>g</sup>

chemical shifts and isotropic coupling constants ( $J$ ) in acetone- $d_6$ (ca. 5% w/v) at 304 K		parameters describing the 270-MHz NMR spectrum in anisotropic medium (Hz) at 295 K		internuclear distances (Å), dihedral angles (deg), and order parameters	
$\nu_1 = \nu_4^a$	$7.4413 \pm 0.0001$	$D_{12} = D_{34}$	$-7541.9 \pm 0.1$	$r_{12} = r_{34}^d$	$2.469 \pm 0.003$
$\nu_2 = \nu_3^a$	$7.7005 \pm 0.0001$	$D_{13} = D_{24}$	$122.4 \pm 0.1$	$r_{23}$	$4.299 \pm 0.004$
$\nu_5 = \nu_6^a$	$7.2733 \pm 0.0002$	$D_{14}$	$721.0 \pm 1.6$	$z_5 = z_6^e$	$-4.351 \pm 0.003$
$J_{12} = J_{34}$	$8.35 \pm 0.01$	$D_{15} = D_{16} = D_{45} = D_{46}$	$-529.4 \pm 0.3$	$r_{56}$	$4.324 \pm 0.002$
$J_{13} = J_{24}$	$0.42 \pm 0.01$	$D_{17} = D_{47} = D_{18} = D_{48}$	$-531.3 \pm 1.0$	$r_{57} = r_{68}$	$5.195 \pm 0.005$
$J_{14}$	$2.25 \pm 0.01$	$D_{23}$	$721.1 \pm 1.6$	$r_{67} = r_{58}$	$2.560 \pm 0.005$
$J_{17} = J_{18} = J_{47} = J_{48}$	$1.32 \pm 0.01$	$D_{25} = D_{26} = D_{35} = D_{36}$	$-226.7 \pm 0.3$	$\theta$	$47.8 \pm 0.05$
$J_{23}$	$2.26 \pm 0.01$	$D_{27} = D_{37} = D_{28} = D_{38}$	$-481.6 \pm 1.0$	$S_{XX}$	$-0.2343$
$J_{36}$	$2.14 \pm 0.05$	$D_{56}$	$568.6 \pm 0.2$	$S_{ZZ}$	$0.4730$
$J_{57} = J_{68}$	$-1.78 \pm 0.05$	$D_{57} = D_{68}$	$50.3 \pm 0.2$	$S_{XY}$	$0.0450$
$J_{58} = J_{67}$	$9.54 \pm 0.05$	$D_{58}$	$-6315.8 \pm 0.2$		
$J_{78}$	$6.40 \pm 0.05^b$	$D_{78}$	$395.5 \pm 0.5$		
rms error <sup>f</sup> (no. of assigned transitions)	0.065 (100)	$\nu_1 = \nu_4^c$	$106.9 \pm 1.5$		
		$\nu_5 = \nu_6^c$	$141.4 \pm 0.9$		
		rms error <sup>f</sup> (no. of assigned transitions)	0.75 (167)		

<sup>a</sup>  $\delta$  values (ppm) referenced to Me<sub>4</sub>Si. <sup>b</sup> Sign taken as positive by analogy with 1,3-difluorobenzene (See J. A. Ferretti, R. K. Harris, and R. B. Johannesen, *J. Magn. Reson.*, 3, 84 (1970)). <sup>c</sup> Referenced to  $\nu_2 = \nu_3 = 0$ . <sup>d</sup>  $r_{14}$  is assumed to be 4.300 Å. <sup>e</sup> Referenced to  $z_1 = z_4 = 0.0$ . <sup>f</sup> Taken directly from computer output. <sup>g</sup> For numbering convention and definition of the system of coordinates see ref 1.

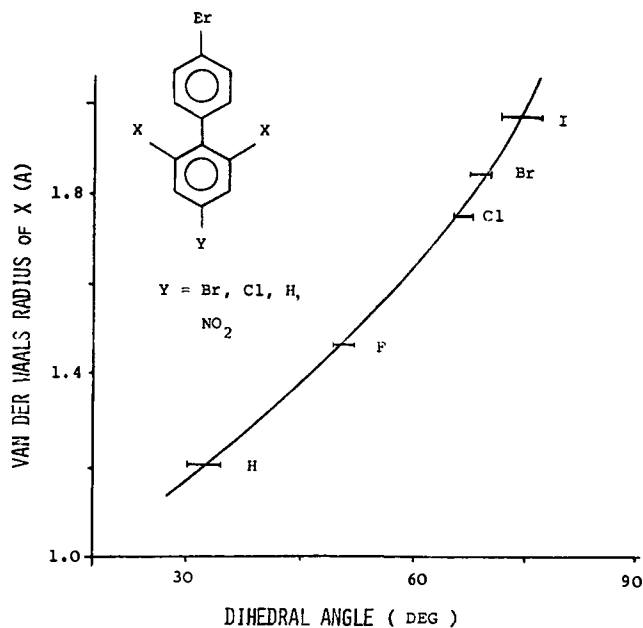


Figure 1. The correlation between the ground-state torsional angle ( $\theta$ ) in 1 and the van der Waals radius<sup>6</sup> of the ortho substituents (X).

perature ranges, but we have succeeded in obtaining the spectra of 2,6-dichloro-4'-fluoro-4-nitrobiphenyl (1, X = Cl, Y = NO<sub>2</sub>, Z = F) at two temperatures 20 °C apart. As can be seen from the results summarized in Table IV, the values of torsional angles are the same within experimental limits, although as expected, the order parameters are greatly changed (the spectrum taken at 295 K was approximately 11.5 KHz wide and that taken at 315 K approximately 7.3 KHz wide). Due to our ignorance of the shape and asymmetry of the potential energy function, it is difficult to attach quantitative significance to this negative result, but we offer it as giving some support to the treatment of data employed here and previously.<sup>1</sup>

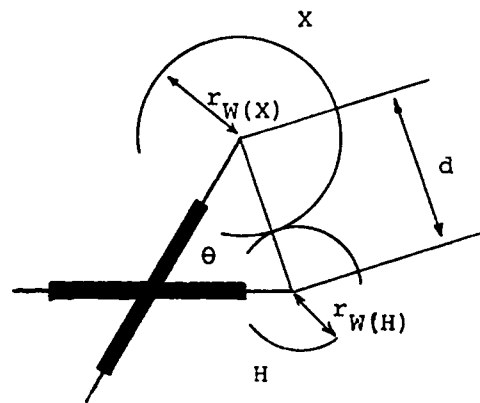


Figure 2. Projection along the aryl-aryl bond in a biphenyl showing the relationship between  $\theta$  and the sum of the van der Waals radii of the ortho substituents (X and H).

### Experimental Section

**NMR Spectra.** Nematic-phase NMR spectra were obtained at 270 MHz. Approximately 1200 FID's of 8K data points were accumulated at the temperatures indicated. Generally spectral widths of 10 kHz, pulse widths of 4–6  $\mu$ s, and pulse delays (time between successive pulses) of 500 ms were used. The FID's were resolution enhanced by deconvolution<sup>7</sup> and transformed over 32K data points. Compounds were dissolved in mixtures of 2 parts of *N*-(*p*-ethoxybenzylidene)-*p*-butylaniline (EBBA) and 3 parts of Nematic Mixture X11643 (Eastman) (solute/solvent  $\approx$  10% w/w).

Isotropic spectra were recorded on a Varian XL100 spectrometer operating in the FT mode.

**4'-Bromo-4-chloro-2,6-difluorobiphenyl (1, X = F, Y = Cl, Z = Br).** 4-Chloro-2,6-dinitroaniline<sup>8</sup> (25 g) was dissolved in hot acetic acid (300 mL, 17 M) and added to a stirred solution of sodium nitrite (11 g) in sulfuric acid (100 mL, 18 M) at a rate such that the temperature remained below 40 °C. The mixture was stirred for 1 h at 40 °C and added cautiously to a chilled solution of copper(I) bromide in hydro-

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Table II. Ground-state Torsional Angles ( $\theta$ ) in Biphenyl Derivatives (1) from NMR Data in Liquid Crystalline Solvents

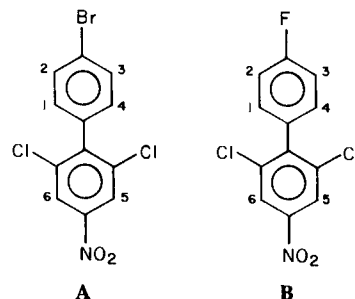
X	$\theta$ , <sup>a</sup> deg	ref
H	31.8 ± 0.03–35.3 ± 0.7	2–4
F	51.2 ± 0.3	this work
Cl	68.1 ± 0.4–68.3 ± 0.5	1
Br	69.6 ± 0.6–71.7 ± 0.7	1
I	77.6 ± 2.2	1

<sup>a</sup> Range of values reflects experimental error and also encompasses data for substances with various groups Z and Y.

Table III. The Relationship between the Internuclear Distance ( $d$ ) between Substituents X at Positions 2 and 6 and the Protons at 2' and 6' and the Sum of Their Van der Waals Radii<sup>d</sup>

X	$\theta$ , deg	$r_{W(X)}$ , <sup>a</sup> Å	internuclear distance <sup>b</sup> ( $d$ )	$r_{W(H)} + r_{W(X)}$ , Å	apparent van der Waals radius, <sup>c</sup> Å
H	33 ± 3	1.2	2.16 ± 0.06	2.4	1.08 ± 0.03
F	49 ± 1.5	1.47	2.50 ± 0.04	2.67	1.42 ± 0.07
Cl	69 ± 2	1.75	3.12 ± 0.06	2.95	2.04 ± 0.09
Br	71 ± 2	1.85	3.23 ± 0.06	3.05	2.15 ± 0.09
I	78 ± 2.5	1.98	3.46 ± 0.07	3.18	2.38 ± 0.1

<sup>a</sup> The van der Waals radius<sup>6</sup> of X. <sup>b</sup> Calculated from  $\theta$ , assuming normal bond angles and bond lengths. The error quoted is due to the error in  $\theta$  only. <sup>c</sup> See text. <sup>d</sup> See Table II and Figure 2 for definitions of terms.

Table IV. Proton NMR Data for 4'-Bromo-2,6-dichloro-4-nitrophenyl (1A) and 2,6-Dichloro-4'-fluoro-4-nitrophenyl (1B)<sup>h</sup>

	chemical shifts and isotropic coupling constants ( $J$ ) in acetone- $d_6$ (ca. 5% w/v) at 304 K		parameters describing the 270-MHz NMR spectra in anisotropic media (Hz) at 295 K		internuclear distances (Å), dihedral angles (deg), and order parameters				
	A	B	A	B	A	B, 295 K	B, 315 K		
$\nu_1 = \nu_4^a$	7.3168 ± 0.0005	7.4250 ± 0.0002	$D_{12} = D_{34}$	-65.26.2 ± 0.2	-65.70.7 ± 0.3	$r_{12} = r_{34}^d$	2.481 ± 0.003	2.499 ± 0.003	2.500 ± 0.001
$\nu_2 = \nu_3^a$	7.7510 ± 0.0002	7.3459 ± 0.0002	$D_{13} = D_{24}$	191.5 ± 0.2	203.1 ± 0.2	$r_{17} = r_{47}$		4.492 ± 0.009	4.493 ± 0.006
$\nu_5 = \nu_6^a$	8.3560 ± 0.0001	8.3630 ± 0.0002	$D_{14} (D_{23})^b$	805.9 ± 0.2	856.4 ± 0.1	$r_{23}$	4.312 ± 0.003	4.300 <sup>e</sup>	4.300 <sup>b</sup>
			$D_{15} = D_{16} = D_{45} = D_{46}$	-382.7 ± 0.5	-394.2 ± 0.3	$r_{56}$	4.300 <sup>e</sup>	4.300 <sup>e</sup>	4.300 <sup>b</sup>
$J_{12} = J_{34}$	8.24 ± 0.04	8.59 ± 0.01	$D_{17} = D_{47}$		-629.3 ± 2.0	$z_5 = z_6^f$	-4.270 ± 0.07	-4.259 ± 0.02	-4.271 ± 0.009
$J_{13} = J_{24}$	0.48 ± 0.04	0.42 ± 0.01	$D_{25} = D_{26} = D_{35} = D_{36}$	-188.3 ± 0.4	-193.9 ± 0.2	$\theta$	69.1 ± 2.0	68.2 ± 0.4	68.0 ± 0.3
$J_{14}$	2.26 ± 0.05 <sup>b</sup>	2.79 ± 0.02	$D_{27} = D_{37}$		809.2 ± 2.0	$S_{XX}$	-0.1469	-0.1434	-0.086 76
$J_{17} = J_{47}$		5.31 ± 0.03	$D_{56}$	364.2 ± 0.3	347.0 ± 0.2	$S_{ZZ}$	0.4149	0.4269	0.2690
$J_{23}$	2.26 ± 0.05 <sup>b</sup>	2.37 ± 0.02	$D_{57} = D_{67}$		-145.0 ± 0.2	$S_{XY}$	0.0623	0.0693	0.0520
$J_{27} = J_{37}$		8.91 ± 0.03	$\nu_1 = \nu_4^c$	71.5 ± 4.0	16.1 ± 1.0				
rms error <sup>g</sup> (no. of assigned transitions)	0.05 (22)	0.06 (33)	$\nu_5 = \nu_6^c$	78.6 ± 2.0	76.1 ± 0.6				
			rms error <sup>g</sup> (no. of assigned transitions)	0.61 (49)	0.65 (82)				

<sup>a</sup>  $\delta$  values (ppm) referenced to Me<sub>4</sub>Si. <sup>b</sup>  $J_{14}$  and  $J_{23}$  could not be determined independently.  $D_{14}$  and  $D_{23}$  could not be determined independently. <sup>c</sup> Referenced to  $\nu_2 = \nu_3 = 0$ . <sup>d</sup>  $r_{14}$  is assumed to be 4.300 Å. <sup>e</sup> Assumed distance. <sup>f</sup> Referenced to  $z_1 = z_4 = 0.0$ . <sup>g</sup> Taken directly from computer output. <sup>h</sup> For numbering convention and definition of the system of coordinates see ref 1.

bromic acid (450 mL, 48%). The mixture was heated for 1 h at 80 °C, diluted with water (2.5 L), and stirred at room temperature for 16 h to allow complete precipitation of the product. The precipitate was removed by filtration, washed with water, and recrystallized from aqueous ethanol to give 4-chloro-2,6-dinitrobromobenzene as a yellow crystalline solid (25.5 g): mp 98-99 °C; NMR (acetone- $d_6$ )  $\delta$  8.38 (s Ar-H).

A mixture of 4-bromiodobenzene (10.5 g), 4-chloro-2,6-dinitrobromobenzene (5 g), and copper powder (20 g) was heated in a sealed reaction bomb for 3 h at 170 °C. At higher temperatures or with a higher proportion of 4-chloro-2,6-dinitrobromobenzene in the reaction mixture, the mixture decomposed explosively. The mixture was extracted exhaustively with chloroform and removal of the solvent afforded a crude product (9.7 g) which was purified by column chromatography on alumina (600 g). Elution with light petroleum afforded unreacted 4-bromiodobenzene (6 g). Elution with light petroleum/ether (75:25) and crystallization from methanol afforded 4'-bromo-4-chloro-2,6-dinitrobiphenyl (8.1 g, 65%): mp 102-103 °C; UV (methanol) 228 (4.45) nm; IR (chloroform solution) 3080 (m b), 1540 (s b), 1490 (m s), 1450 (m s), 1420 (m b), 1370 (s b), 1280 (m b), 1180 (m s), 1105 (w s), 1080 (m s), 1025 (m s), 1010 (s s), 925 (m s), 890 (s s), 830 (s s), 710 (m b)  $\text{cm}^{-1}$ ; NMR (acetone- $d_6$ )  $\delta$  8.418 (2 H, s, H-3,5), 7.3-7.8 (4 H, AA'BB',  $\delta_2$ , =  $\delta_6$ , = 7.357,  $\delta_3$  =  $\delta_5$  = 7.689,  $J_{2,3}$  =  $J_{5,6}$  = 8.37 Hz,  $J_{2,5}$  =  $J_{3,6}$  = 0.56 Hz,  $J_{2,6}$  = 2.21 Hz,  $J_{3,5}$  = 2.19 Hz); mass spectrum,  $m/e$  (relative intensity) 360 (17), 359 (10), 358 (76), 357 (11), 356 (55), 277 (14), 185 (24), 174 (30), 150 (100), 75 (52).

Anal. Calcd for  $\text{C}_{12}\text{H}_6\text{BrClN}_2\text{O}_4$ : C, 40.3; H, 1.7; Br, 22.4; Cl, 9.9; N, 7.8; O, 17.9. Found: C, 40.3; H, 1.8; Br, 22.3; Cl, 9.9; N, 7.8; O, 0.0.

4'-Bromo-4-chloro-2,6-dinitrobiphenyl (8.1 g) was dissolved in a mixture of ethanol (50 mL) and hydrochloric acid (30 mL, 10 M) and heated under reflux with granulated tin (30 g) for 1 h. The solution was diluted with water (100 mL), and most of the ethanol was removed under vacuum. The mixture was basified with sodium hydroxide, filtered, and extracted with ether (4  $\times$  50 mL). The combined organic phases were extracted with hydrochloric acid (2  $\times$  50 mL, 3 M). The aqueous phase was basified and extracted with ether (3  $\times$  50 mL). Workup in the usual manner afforded crude 2,6-diamino-4'-bromo-4-chlorobiphenyl as a light brown crystalline solid (4.1 g, 65%) which was used without further purification.

The diamine (4.1 g) was dissolved in tetrafluoroboric acid (15 mL, 40%), heated to 80 °C, and cooled to -5 °C. A solution of sodium nitrite (0.8 g) in water (3 mL) was cooled to 0 °C. The two solutions were added simultaneously to tetrafluoroboric acid (15 mL), keeping the sodium nitrite always slightly in excess and the temperature below 0 °C. The yellow precipitate was collected and dried at the pump, washed with 0.5 mL of chilled water, and dried overnight under vacuum. The dry tetrazonium bis(tetrafluoroborate) salt (1.2 g) was mixed with an equal volume of dry sand, placed in a long (20 cm) Pyrex test tube fitted with a water condenser, and heated with a flame until the evolution of white  $\text{BF}_3$  fumes ceased. The products distilled from the reaction mixture and condensed on the walls of the reaction vessel. The reaction mixture was extracted with ether, the extracts were washed with a solution of sodium carbonate (50 mL, 10%), and the solvent was removed. The residue was taken up in light petroleum and filtered through a column of alumina. Removal of the solvent afforded crude 4'-bromo-4-chloro-2,6-difluoro-

biphenyl (310 mg, 24%) of approximately 90% purity by NMR and GLC. A sample was purified further by preparative GLC at 160 °C (OV17, 3%, packed on Gas Chrom-Q, 45-60 mesh, 10 mm  $\times$  1.5 m) to give colorless needles ( $T_{\text{melt}} = 7$  min): mp 75-76 °C; UV (methanol) 249 (4.39) nm; IR (chloroform solution) 1700 (m b), 1620 (s s), 1590 (m s), 1570 (m s), 1510 (m s), 1465 (s s), 1425 (m s), 1410 (m s), 1360 (m b), 1260 (m b), 1190 (m b), 1090, (m b), 1040 (s s), 1010 (m s), 895 (m s), 850 (m s), 830 (m s)  $\text{cm}^{-1}$ ; NMR (acetone- $d_6$ ), see text; mass spectrum,  $m/e$  (relative intensity) 307 (2), 306 (24), 305 (18), 304 (100), 303 (14), 302 (73), 189 (11), 188 (91), 187 (8), 186 (7), 94 (25).

Anal. Calcd for  $\text{C}_{12}\text{H}_6\text{BrClF}_2$ : C, 47.5; H, 2.0; Br, 26.3; Cl, 11.7; F, 12.6. Found: C, 47.4; H, 2.15; Br, 0.0; Cl, 0.0; F, 12.6.

4'-Bromo-2,6-dichloro-4-nitrobiphenyl (1, X = Cl, Y =  $\text{NO}_2$ , Z = Br). A mixture of 4-bromiodobenzene (9.5 g), 2,6-dichloro-4-nitroiodobenzene (6.2 g), and copper powder (15 g) was heated in a sealed reaction bomb at 195 °C for 3 h. The mixture was cooled and extracted exhaustively with chloroform. The solvent was removed, and the crude product was purified by column chromatography (alumina, 100 g). Elution with light petroleum removed nonpolar components. Elution with light petroleum/ether (99:1) and crystallization from light petroleum gave 4'-bromo-2,6-dichloro-4-nitrobiphenyl as a pale yellow crystalline solid (2.6 g, 39%): mp 115-117 °C; UV (methanol) 221 (4.50), 278 (b, 3.92) nm; IR (chloroform solution) 3090 (m s), 1590 (m s), 1510-1540 (s b), 1490 (s s), 1420 (m s), 1400 (s s), 1360 (s s), 1190 (m s), 1160 (s s), 1080 (s s), 1020 (m s), 1010 (s s), 910 (m s), 895 (s s), 830 (m s), 810 (s s), 710 (m s)  $\text{cm}^{-1}$ ; NMR (acetone- $d_6$ ), see Table IV; mass spectrum,  $m/e$  (relative intensity) 349 (55), 348 (16), 347 (100), 345 (75), 222 (45), 220 (64), 185 (17), 173 (10), 150 (52), 75 (18).

Anal. Calcd for  $\text{C}_{12}\text{H}_6\text{BrCl}_2\text{NO}_2$ : C, 41.5; H, 1.7; Br, 23.0; Cl, 20.4; N, 4.0. Found: C, 41.8; H, 1.9; Br, 22.2; Cl, 20.2; N, 3.4.

2,6-Dichloro-4'-fluoro-4-nitrobiphenyl (1, X = Cl, Y =  $\text{NO}_2$ , Z = F). A mixture of 4-fluoroiodobenzene (4.5 g), 2,6-dichloro-4-nitroiodobenzene (3 g), and copper powder (10 g) was heated in a sealed reaction bomb at 195 °C for 3 h. The mixture was cooled and extracted exhaustively with chloroform. The solvent was removed, and the crude product was purified by column chromatography (alumina) with light petroleum/ether mixtures as eluant. Recrystallization from methanol afforded 2,6-dichloro-4'-fluoro-4-nitrobiphenyl as a pale yellow crystalline solid (600 mg, 22%): mp 108-110 °C; UV (methanol) 219 (4.38), 263 (4.14), 268 (4.16), 276 (4.16) nm; IR (chloroform solution) 3100 (m b), 3020 (w b), 1600 (s s), 1540-1500 (s b), 1450 (m s), 1425 (m s), 1395 (s s), 1360 (s b), 1250 (s s), 1180 (m s), 1100 (m s), 1020 (w s), 1010 (w s), 905 (w s), 890 (s s), 840 (s s), 810 (s s)  $\text{cm}^{-1}$ . NMR (acetone- $d_6$ ), see Table IV; mass spectrum,  $m/e$  (relative intensity) 289 (10), 288 (8), 287 (65), 286 (13), 285 (100), 257 (14), 255 (16), 229 (5), 227 (10), 206 (28), 205 (12), 204 (94), 169 (20), 168 (20).

Anal. Calcd for  $\text{C}_{12}\text{H}_6\text{Cl}_2\text{FNO}_2$ : C, 50.4; H, 2.1; Cl, 24.8; F, 6.6; N, 4.9; O, 11.2. Found: C, 50.2; H, 2.2; Cl, 25.0; F, 6.7; N, 4.7; O, 0.0.

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## Quantum Effects in Electron-Transfer Reactions

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**Abstract:** Classical, semiclassical, and quantum theories of outer-sphere electron-transfer reactions in polar media are discussed. For each, the Franck-Condon overlap factors for the hexaamminecobalt, hexaquoiron and hexaammineruthenium self-exchange rates and for the  $\text{Fe}^{2+}$ -Ru(bpy) $_3^{3+}$  cross-reaction are evaluated and compared. The quantum effect on the rates is relatively unimportant in the "normal"  $\Delta G^\circ$  region. Direct sum and saddle-point evaluations of the quantum Franck-Condon factors are made and compared.

### Introduction

An outer-sphere electron-transfer reaction in a polar solvent is characterized by changes in the force constants and bond lengths

and bond angles of the reactants and by fluctuations in the surrounding solvent. In many systems the inner-sphere changes are very small, so that the reaction is controlled by fluctuations in