running parallel to *b* along the screw axes located at the edges of the unit cell (through $0,\frac{1}{2},0$; $1,\frac{1}{2},0$; *etc.*) consists of alternating weak and strong hydrogen bonds, $\cdots[\mathrm{O}(16)\text{—}\mathrm{H}\cdots\mathrm{O}(23)\text{—}\mathrm{H}\cdots]_x\mathrm{O}(16)\text{—}$.

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Structures of Polyfluoroaromatic Compounds.
VII.* The Structure of 2,2′-Dibromooctafluorobiphenyl

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Abstract

$C_{12}Br_2F_8$ is monoclinic, space group $P2_1/c$, with $a = 12{\cdot}29\,(1)$, $b = 8{\cdot}20\,(1)$, $c = 12{\cdot}905\,(10)$ Å, $\beta = 102{\cdot}64\,(5)^\circ$, $Z = 4$. The structure was refined to $R = 4{\cdot}26\%$ for 1658 observed counter amplitudes. The inter-ring bond length is 1·489 (7) Å (uncorrected for thermal libration), and the inter-ring dihedral angle is 75·9 (5)°.

Introduction

The biphenyl system has been extensively studied by X-ray crystallography (*e.g.* Robertson, 1961; Charbonneau & Delugeard, 1976, 1977; Hamor & Hamor, 1978*a*,*b*), gas-phase electron diffraction (*e.g.* Rømming, Seip & Aanesen Øymo, 1974), spectroscopy (*e.g.* Schmid & Brosa, 1972), and theoretical calculations (*e.g.* Almlöf, 1974). Of particular interest in relation to bonding theory is the length of the central inter-ring bond and its variation (if any) with inter-ring dihedral angle. However, most crystal structures of biphenyls in the literature have inter-ring angles in the rather limited range 30–60°, and in only four structures, 2,2′-dichlorobiphenyl (Rømming, Seip & Aanesen Øymo, 1974), 2,2-′dibromo-4,4′-bis(*p*-methoxybenzylideneamino)biphenyl (Lesser, de Vries, Reed & Brown, 1975), 2-nitrononafluorobiphenyl (Hamor & Hamor, 1978*b*) and decachlorobiphenyl

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* Part VI: Goodhand & Hamor (1979).

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(Pedersen, 1975), are larger angles found. We now report the crystal structure of 2,2′-dibromooctafluorobiphenyl to provide further structural data for biphenyls having large inter-ring angles, and as part of a continuing study of highly fluorinated organic molecules.

Experimental

A sample of the title compound was kindly supplied by Dr P. L. Coe of this Department (Callander, Coe & Tatlow, 1966). Crystals in the form of thin plates were obtained from methanol. Intensities were measured with a Stoe computer-controlled two-circle diffractometer and graphite-monochromated Mo $K\alpha$ radiation from two crystals aligned about different axes, the two sets of data then being combined. Both crystals were sealed inside Pantak capillary tubes. The scan speed was 0·6° min^{-1} (in ω), and backgrounds were measured for 30 s at each end of the scan. Reflexions were scanned within the range $0{\cdot}1 < \sin\theta/\lambda < 0{\cdot}65$ Å^{-1} and those having $I > 2{\cdot}5\,\sigma(I)$ were considered to be observed and used in the analysis. Four standard reflexions were remeasured after each layer of data collection to monitor the stability of the system. For neither crystal was there any systematic variation in their intensities.

The first crystal, 0·6 × 0·5 × 0·1 mm, was set up about **c**. For layers 0–3 the scan range was 1·4°; for layers 4–13 it was calculated from $[A + (B \sin\mu/\tan\theta')]^\circ$ where μ is the equi-inclination angle, $2\theta'$ the azimuth angle and A and B were 1·0 and 0·6, respectively. 1329 reflexions were considered observed.

The second crystal, 0·75 × 0·5 × 0·15 mm, was set up about **b**. For layers 0–2 the scan range was 1·4° and for layers 3–8 the range was calculated by the same expression as for the first crystal. 1578 reflexions were observed.

In view of the high absorption coefficient (6·315 mm^{-1}) absorption corrections were applied in the conversion of intensities to structure amplitudes. These and subsequent calculations were carried out with *SHELX* (Sheldrick, 1976). The data from the two crystals were then combined to yield 1658 structure amplitudes.

Crystal data

$C_{12}Br_2F_8$, $M_r = 455{\cdot}9$, monoclinic, $a = 12{\cdot}29\,(1)$, $b = 8{\cdot}20\,(1)$, $c = 12{\cdot}905\,(10)$ Å, $\beta = 102{\cdot}64\,(5)^\circ$, $U = 1269$ Å^3, $Z = 4$, $D_c = 2{\cdot}386$ Mg m^{-3}, $F(000) = 856$; systematic absences: $h0l$, l odd; $0k0$, k odd; space group $P2_1/c$. Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo $K\alpha$) = 6·315 mm^{-1}.

Table 1. *Fractional atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

	x	y	z
C(1)	7508 (4)	−798 (6)	420 (4)
C(2)	8175 (4)	159 (7)	−93 (4)
C(3)	8923 (4)	1252 (7)	511 (4)
C(4)	9012 (5)	1403 (7)	1589 (5)
C(5)	8358 (5)	480 (7)	2092 (4)
C(6)	7612 (5)	−599 (7)	1499 (4)
C(1′)	6727 (4)	−2038 (7)	−173 (4)
C(2′)	6989 (4)	−3710 (7)	−85 (4)
C(3′)	6249 (5)	−4845 (8)	−623 (4)
C(4′)	5254 (5)	−4356 (9)	−1240 (4)
C(5′)	4982 (5)	−2745 (9)	−1347 (4)
C(6′)	5723 (5)	−1592 (7)	−814 (4)
F(3)	9582 (3)	2159 (4)	43 (3)
F(4)	9745 (3)	2457 (5)	2152 (3)
F(5)	8453 (4)	608 (5)	3135 (3)
F(6)	6980 (3)	−1502 (4)	2015 (2)
F(3′)	6484 (3)	−6447 (4)	−534 (3)
F(4′)	4529 (3)	−5487 (5)	−1734 (3)
F(5′)	4006 (3)	−2253 (5)	−1947 (3)
F(6′)	5436 (3)	3 (4)	−937 (3)
Br(2)	8100 (1)	−17 (1)	−1541 (0)
Br(2′)	8352 (1)	−4415 (1)	739 (1)

Structure determination

The positions of the two Br atoms were determined from a Patterson synthesis. From the electron-density map phased on the heavy-atom positions all the remaining atoms could be located. Least-squares refinement, first with isotropic then anisotropic temperature factors, was continued until all calculated shifts were $<0{\cdot}05\sigma$ and $R = 4{\cdot}26\%$ for the 1658 observed reflexions. Final atomic coordinates are in Table 1.* The weighting scheme was $w = 1/[\sigma^2(F) + 0{\cdot}0001F^2]$ where $\sigma(F)$ is the e.s.d. in the observed amplitude based on counting statistics.

Computations were carried out on the CDC 7600 computer at the University of Manchester Regional Computer Centre and on the Birmingham University ICL 1906A.

Results and discussion

Fig. 1 shows the molecule with the atom numbering. F and Br atoms take the numbers of the C atoms to which they are attached. Bond lengths and angles are in Table 2 and the results of mean-plane calculations in Table 3. The thermal parameters of the atoms were

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* Lists of thermal parameters and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35071 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

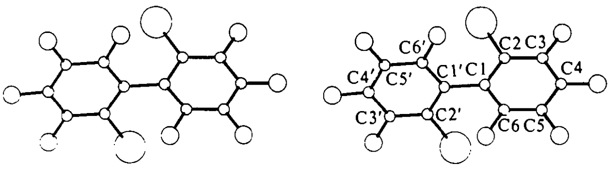

Fig. 1. Stereoscopic view of the molecule showing the atom labelling.

Table 2. *Molecular dimensions*

(*a*) Bond lengths (Å) with e.s.d.'s (×10³) in parentheses (*A*) and bond lengths corrected for thermal libration (*B*)

	A	*B*		*A*	*B*
C(1)–C(2)	1·401 (7)	1·408	C(1')–C(2')	1·407 (7)	1·414
C(2)–C(3)	1·394 (7)	1·400	C(2')–C(3')	1·378 (8)	1·383
C(3)–C(4)	1·377 (7)	1·384	C(3')–C(4')	1·365 (8)	1·372
C(4)–C(5)	1·366 (8)	1·373	C(4')–C(5')	1·362 (9)	1·369
C(5)–C(6)	1·380 (8)	1·385	C(5')–C(6')	1·387 (8)	1·392
C(6)–C(1)	1·380 (7)	1·386	C(6')–C(1')	1·376 (7)	1·383
C(1)–C(1')	1·489 (7)				
C(2)–Br(2)	1·857 (5)	1·866	C(2')–Br(2')	1·869 (5)	1·878
C(3)–F(3)	1·336 (6)	1·343	C(3')–F(3')	1·345 (7)	1·352
C(4)–F(4)	1·342 (6)	1·347	C(4')–F(4')	1·346 (7)	1·351
C(5)–F(5)	1·330 (6)	1·336	C(5')–F(5')	1·339 (6)	1·346
C(6)–F(6)	1·349 (7)	1·356	C(6')–F(6')	1·355 (6)	1·362

(*b*) Bond angles (°) with e.s.d.'s (×10) in parentheses

C(2)–C(1)–C(6)	118·4 (5)	C(2')–C(1')–C(6')	117·8 (5)
C(2)–C(1)–C(1')	121·2 (5)	C(2')–C(1')–C(1)	120·9 (5)
C(6)–C(1)–C(1')	120·4 (5)	C(6')–C(1')–C(1)	121·3 (5)
C(1)–C(2)–C(3)	118·6 (5)	C(1')–C(2')–C(3')	120·2 (5)
C(1)–C(2)–Br(2)	121·8 (4)	C(1')–C(2')–Br(2')	120·5 (4)
C(3)–C(2)–Br(2)	119·6 (4)	C(3')–C(2')–Br(2')	119·2 (4)
C(2)–C(3)–C(4)	121·3 (5)	C(2')–C(3')–C(4')	120·2 (6)
C(2)–C(3)–F(3)	119·7 (5)	C(2')–C(3')–F(3')	120·7 (5)
C(4)–C(3)–F(3)	119·0 (5)	C(4')–C(3')–F(3')	119·0 (6)
C(3)–C(4)–C(5)	120·3 (5)	C(3')–C(4')–C(5')	120·8 (5)
C(3)–C(4)–F(4)	120·0 (5)	C(3')–C(4')–F(4')	119·3 (7)
C(5)–C(4)–F(4)	119·7 (5)	C(5')–C(4')–F(4')	119·8 (6)
C(4)–C(5)–C(6)	118·7 (5)	C(4')–C(5')–C(6')	119·4 (5)
C(4)–C(5)–F(5)	120·4 (5)	C(4')–C(5')–F(5')	121·3 (5)
C(6)–C(5)–F(5)	120·8 (6)	C(6')–C(5')–F(5')	119·3 (6)
C(5)–C(6)–C(1)	122·6 (5)	C(5')–C(6')–C(1')	121·5 (5)
C(5)–C(6)–F(6)	117·6 (5)	C(5')–C(6')–F(6')	118·3 (5)
C(1)–C(6)–F(6)	119·8 (5)	C(1')–C(6')–F(6')	120·2 (5)

Table 3. *Mean-plane calculations*

Deviations (Å) of atoms from least-squares planes. Distances marked with an asterisk refer to atoms defining the plane. E.s.d.'s are *ca* 0·005 Å for C and F, and *ca* 0·003 Å for Br.

(I) Phenyl ring C(1)–(6)		(II) Phenyl ring C(1')–(6')	
C(1)	0·006*	C(1')	0·005*
C(2)	−0·002*	C(2')	−0·001*
C(3)	−0·002*	C(3')	−0·004*
C(4)	0·003*	C(4')	0·005*
C(5)	0·001*	C(5')	−0·001*
C(6)	−0·005*	C(6')	−0·004*
Br(2)	0·014	Br(2')	−0·037
F(3)	0·013	F(3')	0·008
F(4)	0·012	F(4')	0·041
F(5)	0·024	F(5')	0·014
F(6)	0·000	F(6')	−0·017
C(1')	0·064	C(1)	0·036
C(4')	0·164	C(4)	0·136

Interplanar angle (I)–(II) 75·9 (5)°

Table 4. *Rigid-body-motion analysis*

The eigenvectors of the libration tensor **L** and translation tensor **T** are referred, in terms of the corresponding direction cosines, to the orthogonal molecular system defined by the eigenvectors of the molecular tensor of inertia **I** with the origin shifted to symmetrize the screw tensor and reduce the trace of **T**. The eigenvectors of **I** are referred to axes *a*, *b*, *c**.

(i) C(1)–(6), Br(2), F(3)–(6)

	Eigenvalues	Eigenvectors		
	369 (at. wt Å^2)	−0·1797	0·0584	0·9820
I	1020	0·7098	0·6989	0·0883
	1390	−0·6811	0·7129	−0·1671
	72 × 10^{-4} rad^2	−0·5511	−0·8268	−0·1129
L	40	0·6786	−0·5228	0·5159
	36	−0·4855	0·2077	0·8492
	403 × 10^{-4} Å^2	0·6968	−0·7108	0·0960
T	344	0·7084	0·7030	0·0632
	230	−0·1124	0·0240	0·9934

R.m.s. discrepancy $\langle \Delta U^2 \rangle^{1/2}$ = 0·0036 Å^2
Mean e.s.d. in observed U_{ij} values = 0·0025 Å^2.

(ii) C(1')–(6'), Br(2'), F(3')–(6')

	Eigenvalues	Eigenvectors		
	373 (at. wt Å^2)	0·7587	−0·3399	0·5557
I	1014	−0·2362	−0·9386	−0·2517
	1387	0·6071	0·0597	−0·7924
	69 × 10^{-4} rad^2	0·5129	−0·8512	−0·1111
L	40	0·1747	−0·0231	0·9843
	34	−0·8405	−0·5243	0·1369
	376 × 10^{-4} Å^2	0·7205	0·6933	0·0176
T	352	0·6518	−0·6856	0·3241
	259	0·2368	−0·2220	−0·9459

R.m.s. discrepancy $\langle \Delta U^2 \rangle^{1/2}$ = 0·0032 Å^2.
Mean e.s.d. in observed U_{ij} values = 0·0026 Å^2.

analysed for rigid-body thermal motion (Schomaker & Trueblood, 1968). In these calculations the two ring systems were treated as independent units (Table 4). Bond lengths corrected for the effect of libration are also listed in Table 2.

The phenyl rings are planar to within ±0·006 Å and the angle between the rings is 75·9° (Table 3). This is slightly smaller than the inter-ring angle in 2,2'-dibromo-4,4'-bis(*p*-methoxybenzylideneamino)-biphenyl which is 80·1° (Lesser, de Vries, Reed & Brown, 1975). Here, however, Br···Br, rather than F···Br, interactions occur between the *ortho* substituents on the rings. In the latter structure, the Br atoms are orientated *cis* with a Br···Br separation of 3·96 Å, whereas in 2,2'-dibromooctafluorobiphenyl the relationship between them is *trans*, and the Br(2)···Br(2') distance is 4·62 Å, much larger than the sum of the van der Waals radii. The shortest distances between *ortho* substituents are Br(2)···F(6') and Br(2')···F(6), both 3·53 Å, still somewhat larger than the sum of the van der Waals radii of Br (1·85 Å) and F (1·5 Å) given by Bondi (1964). The distances Br(2)$\cdots$C(6′), 3·51 Å, and Br(2′)$\cdots$C(6), 3·46 Å, are, however, slightly smaller than the sum of the van der Waals radii, in this case 3·55 Å.

Although the inter-ring dihedral angle can be described essentially in terms of rotation about the central C(1)—C(1′) bond, the axis of the molecule defined by C(4), C(1), C(1′), C(4′) deviates significantly from collinearity (Table 3). If φ is defined as the angle of rotation of ring C(1)–(6) about an axis in its plane, passing through C(1) and perpendicular to C(1)—C(1′), and φ' the corresponding angle of rotation for ring C(1′)–(6′), then $\varphi = 2{\cdot}5°$ and $\varphi' = 1{\cdot}4°$.

There is some indication of repulsive interactions between *ortho* substituents and the neighbouring ring system. Thus C(1)—C(2)—Br(2) is 2·2° greater than C(3)—C(2)—Br(2); C(1)—C(6)—F(6) is 2·2° greater than C(5)—C(6)—F(6); C(1′)—C(2′)—Br(2′) is 1·3° greater than C(3′)—C(2′)—Br(2′); and C(1′)—C(6′)—F(6′) is 1·9° greater than C(5′)—C(6′)—F(6′). Bond angles within the rings range from 117·8 to 122·6°. As is generally found in biphenyls, the smallest angles, 118·4 and 117·8°, occur at C(1) and C(1′).

The aromatic C—C bonds range from 1·369 to 1·414, mean 1·387 Å (corrected for thermal libration), typical of highly fluorinated biphenyls. The C—F lengths are 1·336–1·362, mean 1·349 Å, intermediate between the means in 2-nitrononafluorobiphenyl (1·342 Å) (Hamor & Hamor, 1978*b*) and 2*H*-nonafluorobiphenyl (1·351 Å) (Hamor & Hamor, 1978*a*). The two C—Br lengths, 1·857 (5) and 1·869 (5) Å (uncorrected), are significantly shorter than the values observed in other biphenyls, *e.g.* 1·894 (5) and 1·904 (6) Å in 2,2′-dibromo-4,4′-bis(*p*-methoxybenzylideneamino)biphenyl (Lesser, de Vries, Reed & Brown, 1975), and 1·904 (9) and 1·908 (10) Å for the two independent molecules of 4-bromo-4′-cyanobiphenyl (Kronebusch, Gleason & Britton, 1976). An analogous bond shortening is found for the C—N-(nitro) bond in 2-nitrononafluorobiphenyl compared with unfluorinated nitrobiphenyls. This can be rationalized in terms of the hybridization changes which occur when highly electronegative F replaces H as the adjacent ring substituent (Bent, 1961).

The inter-ring bond length, C(1)—C(1′) = 1·489 (7) Å (uncorrected), is virtually identical to those in biphenyl (1·494 Å) (Robertson, 1961), 2*H*-nonafluorobiphenyl (1·486 Å), 2,2′-dichlorobiphenyl (1·489 Å), 2,2′-dibromo-4,4′-bis(*p*-methoxybenzylideneamino)-biphenyl (1·489 Å) and 2-nitrononafluorobiphenyl (1·492 Å). The inter-ring angles in these compounds range from near zero in crystalline biphenyl to 85·5° in 2-nitrononafluorobiphenyl so that once again one comes to the conclusion that there is very little, if any, correlation between inter-ring bond length and inter-ring angle (*cf.* Hamor & Hamor, 1978*b*). Decachlorobiphenyl (Pedersen, 1975) with inter-ring angle 86·7° has, however, a longer central bond (1·514 Å).

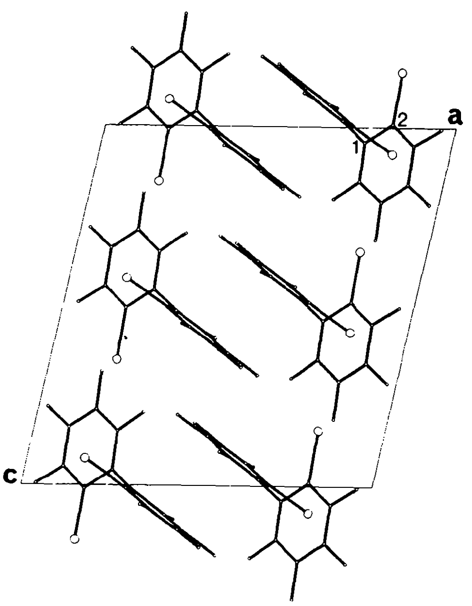

Fig. 2. The crystal structure projected along **b**.

The arrangement of the molecules in the unit cell is illustrated in Fig. 2. The shortest intermolecular contact distances within each category, F$\cdots$F, C$\cdots$F, F$\cdots$Br, C$\cdots$C, C$\cdots$Br and Br$\cdots$Br are 2·85, 3·20, 3·39, 3·40, 3·64 and 3·62 Å, respectively. Of these, only the F$\cdots$F distance, involving F(6′) of the reference molecule and the corresponding atom of the molecule at $(1-x, -y, -z)$, and the Br$\cdots$Br distance, Br(2)$\cdots$Br(2′) at $(x, -\frac{1}{2}-y, z-\frac{1}{2})$, are slightly smaller than the sum of the van der Waals radii.

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Chiral Mono-*N*-Substituted Primary Amides.
I. Molecular Packing Modes

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Abstract

Molecular packing modes of *R*CONHCH(CH_3)Ar, in which *R* are alkyl and Ar are aromatic residues, were determined and analysed in terms of molecular interactions to be used for the interpretation of chiral recognition phenomena involving these amides. The cell constants of a number of the amides as well as the crystal structures of (*R*)-*N*-trifluoroacetyl-1-(1-naphthyl)ethylamine, (*R*)- and (*RS*)-*N*-acetyl-1-(1-naphthyl)ethylamine were determined. Various molecular interactions are analysed and it is shown that the hydrogen-bonded 5 Å translation stack is particularly stable, sufficiently for the arrangement to be partially conserved in the melt.

1. Introduction

Our interest in chiral recognition stems from current work on the separation of enantiomers by chromatography (Weinstein, Feibush & Gil-Av, 1976) and crystallization (Lahav, Laub, Gati, Leiserowitz & Ludmer, 1976) and the resulting need to understand and control stereoselectivity. Chiral recognition involves differential interaction between a molecule, or an ensemble of molecules, with two enantiomorphs and can be expressed quantitatively by the difference in the stability constants of their diastereomeric association.

Here we are concerned with chiral secondary amides *R*CONHCH(CH_3)Ar with varying *R* and Ar groups, and the interactions between molecules within this series. In these systems, where the constituents are so similar in their chemical structure and the components contain an aromatic group, Ar, the stereoselective effects observed are relatively strong (Weinstein, Feibush & Gil-Av, 1976) and they are therefore suitable for the study of chiral recognition on the molecular level. The solid state has been chosen for this study since it represents minimum-energy arrangements of molecules. Thus, the relative stabilities of various interactions between chiral molecules can be recognized and evaluated.

In this work, the molecular packing modes of a series of enantiomerically pure and of racemic *N*-acyl-1-arylethylamines were determined from their cell constants and from detailed structure determination of three compounds. Evidence is produced for retention in the melt of some of the packing features observed in the crystalline state. In addition, an analysis of preferred conformations and intermolecular arrangements as carried out by energy computations is presented.

A model for chiral recognition based on the preferred modes of packing of these compounds derived here is presented in a separate publication (Weinstein, Leiserowitz & Gil-Av, 1980). It explains, on the molecular level, the stereoselectivity observed in both the solid and liquid states.

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