

Structures of Polyfluoroaromatic Compounds.

IV.* Crystal Structure of 2-Nitrononafluorobiphenyl

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(Received 23 March 1978; accepted 2 May 1978)

Crystals of $C_{12}F_9NO_2$ are monoclinic, space group $P2_1/c$, with $a = 11.30$ (1), $b = 7.79$ (1), $c = 15.22$ (1) Å, $\beta = 114.75$ (5)°, $Z = 4$. The structure was refined to $R = 4.7\%$ for 1407 observed counter amplitudes. The angle between the phenyl-ring planes is 85.5° and the nitro group is inclined at 56° to its phenyl ring. The inter-ring bond length is 1.492 Å (uncorrected for thermal libration). Estimated standard deviations are 0.004–0.005 Å for bond lengths and 0.3 – 0.4° for bond angles.

Introduction

The length of the central inter-ring bond in biphenyls and its variation with inter-ring dihedral angle is of interest in relation to bonding theory. Although the crystal structures of many biphenyls have been determined, in only two of these, 2,2'-dichlorobiphenyl (Rømming, Seip & Aanesen Øymo, 1974) and deca-chlorobiphenyl (Pedersen, 1975), is the inter-ring angle greater than 60° . In order to determine the full relationship between this angle and the inter-ring bond length, it is necessary to obtain further structural data for molecules in which the rings are near-perpendicular. 2-Nitrononafluorobiphenyl (Coe, Jukes & Tatlow, 1966) appeared to be a likely candidate for this role, and we now report its structure.

after each layer of data collection to check the stability of the system. In the conversion of intensities to structure amplitudes the polarization factor for monochromated radiation was used, but absorption corrections were not applied.

Crystal data

$C_{12}F_9NO_2$, $M_r = 361.1$, monoclinic, $a = 11.30$ (1), $b = 7.79$ (1), $c = 15.22$ (1) Å, $\beta = 114.75$ (5)°, $U = 1216.7$ Å³, $Z = 4$, $D_c = 1.971$ g cm⁻³, $F(000) = 704$; systematic absences: $h0l$, l odd; $0k0$, k odd; space group $P2_1/c$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(Mo K\alpha) = 1.65$ cm⁻¹.

Experimental

Suitable crystals were obtained from light petroleum. A crystal $0.6 \times 0.4 \times 0.4$ mm was sealed in a Pantak capillary tube and aligned about **b**. After preliminary photographic examination the intensities were measured with a Stoe computer-controlled two-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, and the ω -scan technique. For layers $h0l$ – $h2l$, 140 counts of 1 s at intervals of 0.01° were taken for each reflexion. For the higher layers the peak scan was defined by the expression $[A + (B \sin \mu / \tan \theta')]^\circ$ where μ is the equi-inclination angle and θ' is half the azimuth angle. The constants A and B were assigned the values 1.0 and 0.5. Backgrounds were measured for 30 s at each end of the scan. 3176 reflexions were scanned within the range $0.1 < \sin \theta / \lambda < 0.65$ Å⁻¹ of which 1407 having $I > 2.5\sigma(I)$ were considered to be observed. Three zero-layer reflexions were remeasured

Table 1. Fractional atomic coordinates ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	2638 (3)	4866 (4)	2838 (2)
C(2)	3927 (3)	4373 (4)	3342 (2)
C(3)	4268 (4)	3097 (5)	4025 (3)
C(4)	3334 (4)	2275 (4)	4222 (3)
C(5)	2060 (4)	2752 (4)	3735 (2)
C(6)	1723 (3)	4040 (4)	3056 (2)
C(1')	2236 (3)	6232 (4)	2082 (2)
C(2')	2259 (3)	7947 (4)	2313 (2)
C(3')	1900 (3)	9200 (4)	1619 (3)
C(4')	1537 (3)	8759 (5)	678 (3)
C(5')	1487 (4)	7071 (5)	419 (2)
C(6')	1825 (3)	5833 (4)	1115 (2)
F(3)	5515 (2)	2630 (4)	4508 (2)
F(4)	3665 (3)	1019 (3)	4867 (2)
F(5)	1137 (2)	1966 (3)	3908 (2)
F(6)	472 (2)	4466 (3)	2604 (2)
F(2')	2639 (3)	8393 (3)	3240 (1)
F(3')	1918 (2)	10842 (3)	1870 (2)
F(4')	1229 (2)	9977 (3)	2 (2)
F(5')	1119 (3)	6651 (3)	-510 (1)
F(6')	1769 (2)	4189 (3)	861 (2)
N(2)	4950 (3)	5217 (5)	3154 (3)
O(1)	4871 (3)	5218 (6)	2345 (3)
O(2)	5845 (3)	5842 (5)	3845 (3)

* Part III: Brock, Naae, Goodhand & Hamor (1978).

Structure determination

The structure was solved by direct methods (Karle & Karle, 1966; Germain & Woolfson, 1968) with *SHELX* (Sheldrick, 1975). Phases were found for 431 reflexions with $E > 1.2$ and from the E map all 24 atoms were located. Four cycles of isotropic full-matrix least-squares refinement reduced R to 15.2%. The atoms were then allowed to vibrate anisotropically and after a further six cycles all calculated shifts were $< 0.01\sigma$ and R was 4.71% for the 1407 observed amplitudes. The final atomic coordinates are listed in Table 1.* The weighting scheme was $w = 1/[\sigma^2(F) + 0.0002F^2]$, where $\sigma(F)$ is the standard deviation in the observed amplitudes 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 a stereoscopic view of the molecule and also the atomic numbering scheme. Bond lengths and angles are in Table 2. Estimated standard deviations are 0.004–0.005 Å for lengths and 0.3–0.4° for angles. Bond lengths corrected for the effect of rigid-body thermal libration (Cruickshank, 1956; Schomaker & Trueblood, 1968) are also listed in Table 2. In these calculations the two rings with their F and N substituents were treated as independent units (Hamor & Hamor, 1978) to give the results in Table 3.

The phenyl rings are planar to within ± 0.01 Å (Table 4), but the substituents are displaced by small (up to 0.04 Å) but significant amounts from their respective ring planes. It does not seem possible to rationalize these deviations on the basis of intramolecular interactions and they may well be due to the effect of packing forces. The nitro group is rotated at an angle of 56° to the phenyl ring to which it is bonded

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33602 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Molecular dimensions

(a) Bond lengths (Å). Values in the second column are corrected for thermal libration.

C(1)–C(1')	1.492 (4)		
C(1)–C(2)	1.386 (5)	1.396	
C(2)–C(3)	1.372 (5)	1.378	
C(3)–C(4)	1.370 (5)	1.377	
C(4)–C(5)	1.367 (5)	1.377	
C(5)–C(6)	1.375 (4)	1.382	
C(6)–C(1)	1.371 (4)	1.378	
C(2)–N(2)	1.458 (5)	1.466	
C(3)–F(3)	1.338 (4)	1.348	
C(4)–F(4)	1.324 (4)	1.331	
C(5)–F(5)	1.327 (4)	1.334	
C(6)–F(6)	1.330 (4)	1.339	
N(2)–O(1)	1.197 (4)		
N(2)–O(2)	1.215 (4)		
C(1')–C(2')	1.379 (4)	1.390	
C(2')–C(3')	1.369 (5)	1.376	
C(3')–C(4')	1.358 (5)	1.370	
C(4')–C(5')	1.368 (5)	1.380	
C(5')–C(6')	1.363 (5)	1.370	
C(6')–C(1')	1.381 (4)	1.393	
C(2')–F(2')	1.337 (4)	1.348	
C(3')–F(3')	1.333 (4)	1.344	
C(4')–F(4')	1.334 (4)	1.341	
C(5')–F(5')	1.337 (4)	1.348	
C(6')–F(6')	1.332 (4)	1.344	

(b) Bond angles (°)

C(2)–C(1)–C(6)	117.4 (3)	C(2')–C(1')–C(6')	116.9 (3)
C(2)–C(1)–C(1')	122.3 (3)	C(2')–C(1')–C(1)	121.8 (3)
C(6)–C(1)–C(1')	120.3 (3)	C(6')–C(1')–C(1)	121.3 (3)
C(1)–C(2)–C(3)	121.1 (3)	C(1')–C(2')–C(3')	121.7 (3)
C(1)–C(2)–N(2)	120.1 (3)	C(1')–C(2')–F(2')	119.0 (3)
C(3)–C(2)–N(2)	118.7 (3)	C(3')–C(2')–F(2')	119.3 (3)
C(2)–C(3)–C(4)	120.4 (3)	C(3')–C(3')–C(4')	119.7 (3)
C(2)–C(3)–F(3)	120.7 (4)	C(2')–C(3')–F(3')	119.9 (3)
C(4)–C(3)–F(3)	118.9 (3)	C(4')–C(3')–F(3')	120.4 (3)
C(3)–C(4)–C(5)	119.2 (3)	C(3')–C(4')–C(5')	120.4 (3)
C(3)–C(4)–F(4)	120.2 (4)	C(3')–C(4')–F(4')	120.0 (3)
C(5)–C(4)–F(4)	120.6 (4)	C(5')–C(4')–F(4')	119.7 (3)
C(4)–C(5)–C(6)	120.2 (3)	C(4')–C(5')–C(6')	119.4 (3)
C(4)–C(5)–F(5)	120.3 (3)	C(4')–C(5')–F(5')	119.9 (3)
C(6)–C(5)–F(5)	119.6 (3)	C(6')–C(5')–F(5')	120.7 (3)
C(5)–C(6)–C(1)	121.7 (3)	C(5')–C(6')–C(1')	121.9 (3)
C(5)–C(6)–F(6)	118.0 (3)	C(5')–C(6')–F(6')	119.4 (3)
C(1)–C(6)–F(6)	120.3 (3)	C(1')–C(6')–F(6')	118.7 (3)
C(2)–N(2)–O(1)	118.6 (4)		
C(2)–N(2)–O(2)	116.9 (3)		
O(1)–N(2)–O(2)	124.5 (4)		

and the angle between the planes of the phenyl rings is 85.5°. In this way energetically unfavourable interactions between *ortho* substituents are minimized. There is, however, some indication of repulsive interactions between the nitro group and the neighbouring C_6F_5 ring system. Thus angle C(2)–C(1)–C(1') is 2° greater than C(6)–C(1)–C(1'); C(1)–C(2)–N(2) is 1.4° greater than C(3)–C(2)–N(2); and C(2)–N(2)–O(1) is 1.7° greater than C(2)–N(2)–O(2). Nevertheless, one short contact, O(1)⋯C(1') = 2.94 Å, does

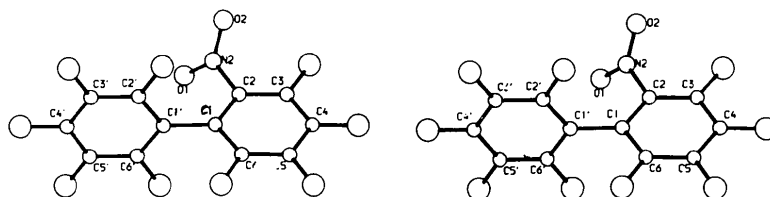


Fig. 1. Stereoscopic view of the molecule showing the atomic labelling.

Table 3. Results of 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**. The eigenvectors of **I** are referred to the unit-cell axes. The calculation is referred to the origin which symmetrizes the screw tensor and reduces the trace of **T**.

(i) C(1)–(6), N(2), F(3)–(6)

	Eigenvalues	Eigenvectors		
I	333 at. wt Å ²	0.9795	0.1371	0.1479
	493	-0.0021	-0.7265	0.6872
	825	0.2017	-0.6734	-0.7113
L	104 × 10 ⁻⁴ rad ²	0.4916	-0.8600	0.1371
	46	-0.6332	-0.2448	0.7343
	38	-0.5979	-0.4478	-0.6649
T	527 × 10 ⁻⁴ Å ²	0.9361	-0.2153	-0.2780
	388	-0.2851	-0.9276	-0.2416
	304	-0.2059	0.3054	-0.9297

Components of the origin shift, referred to the inertial frame, from the centre of mass ($x = 0.3081$, $y = 0.3278$, $z = 0.3691$) are -0.008, -1.172, -0.251 Å.

r.m.s. discrepancy $\langle \Delta U^2 \rangle^{1/2} = 0.0030 \text{ \AA}^2$.

Mean e.s.d. in observed U_{ij} values = 0.0017 Å².

(ii) C(1')–(6'), F(2')–(6')

	Eigenvalues	Eigenvectors		
I	329 at. wt Å ²	-0.1227	0.6974	0.7061
	482	-0.0429	-0.7146	0.6982
	810	0.9915	0.0554	0.1176
L	147 × 10 ⁻⁴ rad ²	0.0321	-0.9970	0.0703
	55	0.8215	-0.0138	-0.5700
	47	0.5693	0.0760	0.8186
T	480 × 10 ⁻⁴ Å ²	0.8209	-0.3084	0.4806
	372	-0.0380	-0.8693	-0.4929
	295	0.5698	0.3863	-0.7253

Components of the origin shift, referred to the inertial frame, from the centre of mass ($x = 0.1795$, $y = 0.7793$, $z = 0.1213$) are 0.030, 0.839, -0.002 Å.

r.m.s. discrepancy $\langle \Delta U^2 \rangle^{1/2} = 0.0027 \text{ \AA}^2$.

Mean e.s.d. in observed U_{ij} values = 0.0017 Å².

occur. Very similar angular distortions occur in 4-acetyl-2'-nitrobiphenyl (Sutherland, Hogg & Williams, 1974) and in 2'-nitro-4-aminobiphenyl (Fallon & Ammon, 1974) but not in the 4-substituted nitro derivative *p*-nitrobiphenyl (Casalone, Gavezzotti & Simonetta, 1973). The N(2)–O(1) bond length of 1.197 Å is shorter than the range of N–O bond lengths (1.213–1.222 Å) found in these nitrobiphenyls, but this difference is probably not significant.

The aromatic C–C bonds range from 1.370 to 1.396 Å, mean 1.381 Å (corrected for thermal libration). This compares well with means of 1.381 and 1.385 Å in perfluorobiphenyl (Gleason & Britton, 1976) and 2*H*-nonafluorobiphenyl (Hamor & Hamor, 1978), but is slightly smaller than in biphenyl itself (Charbonneau & Delugeard, 1976, 1977) where the corresponding mean is 1.391 Å. Slight shortening of

Table 4. Mean-plane calculations

Deviations (Å) of atoms from least-squares planes. Distances marked with an asterisk refer to atoms defining the plane.

(I) Phenyl ring C(1)–(6)		(II) Phenyl ring C(1')–(6')		(III) Nitro group	
C(1)	-0.005*	C(1')	0.008*	C(2)	0.002*
C(2)	0.001*	C(2')	0.002*	N(2)	-0.008*
C(3)	0.003*	C(3')	-0.011*	O(1)	0.003*
C(4)	-0.003*	C(4')	0.010*	O(2)	0.003*
C(5)	-0.001*	C(5')	0.000*		
C(6)	0.005*	C(6')	-0.010*		
N(2)	0.008	F(2')	0.007		
F(3)	0.008	F(3')	-0.036		
F(4)	-0.029	F(4')	0.044		
F(5)	-0.018	F(5')	0.012		
F(6)	0.014	F(6')	-0.026		
C(1')	-0.028	C(1)	0.035		

Interplanar angles (°)

(I)–(II) 85.5 (I)–(III) 55.9

Equations of planes (x , y and z are fractional coordinates relative to the cell axes)

$$(I) \quad 2.256x - 5.285y - 11.045z = -5.116$$

$$(II) \quad -11.209x - 0.460y + 4.772z = -1.791$$

$$(III) \quad -5.337x + 6.737y + 0.657z = 1.073$$

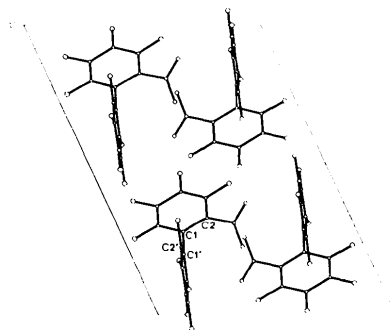


Fig. 2. Projection of the contents of the unit cell along **b**.

the aromatic bonds is consistent with the effect of hybridization changes induced by the electronegative F and nitro substituents (Bent, 1961; Domenicano, Vaciego & Coulson, 1975).

The C–F bonds range from 1.331 to 1.348 Å, mean 1.342 Å (corrected) – slightly shorter than in perfluorobiphenyl and 2*H*-nonafluorobiphenyl where mean values are 1.344 and 1.351 Å respectively. The C(2)–N(2) length [1.458 Å (uncorrected), 1.466 Å (corrected)] is slightly (0.007–0.017 Å) shorter than the C–N(nitro) bonds in 4-acetyl-2'-nitrobiphenyl, 2'-nitro-4-aminobiphenyl and *p*-nitrobiphenyl. These differences are not, however, significant.

Perhaps the most interesting result is that the inter-ring bond length, C(1)–C(1') = 1.492 Å (uncorrected), is virtually the same as that in perfluorobiphenyl and 2*H*-nonafluorobiphenyl (1.486 Å in both), notwith-

Table 5. Intermolecular contact distances (Å) <3.3 Å

F(4')...F(4 ^l)	2.77 ₅	O(2)...C(4 ^{vii})	3.06
F(5)...F(4 ⁱⁱ)	2.88	F(4')...O(2 ^{ix})	3.10
F(5)...F(6 ⁱⁱⁱ)	2.89	F(4)...F(6 ⁱⁱⁱ)	3.10
F(5)...F(5 ⁱⁱⁱ)	2.96	F(3')...C(6 ^v)	3.14
F(6)...F(5 ^{iv})	2.98	F(3')...O(2 ^{ix})	3.14
F(3')...F(8 ^v)	3.00	F(5')...F(6 ^{viii})	3.15
F(4')...C(4 ^l)	3.02	F(3')...C(5 ^v)	3.15
F(4)...F(3 ^{vi})	3.02	C(4')...O(2 ^{ix})	3.18
O(2)...F(4 ^{vii})	3.04	C(3')...O(2 ^{ix})	3.18
C(5)...F(4 ⁱⁱ)	3.04	O(1)...F(3 ^{ix})	3.26
F(2')...F(4 ^v)	3.04	F(2')...F(3 ^{vii})	3.28
F(5')...F(2 ^{vi})	3.05	F(4)...F(4 ^{vi})	3.28
F(5')...F(6 ^{viii})	3.06		

Symmetry code

(i)	\bar{x} , 2 - y, \bar{z}	(vi)	1 - x, \bar{y} , 1 - z
(ii)	x, 1½ - y, ½ + z	(vii)	1 - x, 1 - y, 1 - z
(iii)	x, ½ - y, ½ + z	(viii)	\bar{x} , 1 - y, \bar{z}
(iv)	\bar{x} , ½ + y, ½ - z	(ix)	1 - x, ½ + y, ½ - z
(v)	x, 1 + y, z		

standing the difference in inter-ring angle (59.6 and 59.5° in perfluoro- and 2H-nonafluorobiphenyl, compared with 85.5° in the present structure). This suggests that there is very little, if any, correlation between inter-ring bond length and inter-ring angle. However, in decachlorobiphenyl (Pedersen, 1975), where the dihedral angle between the rings is similar (86.7°), the C(1)–C(1') bond length is significantly longer (1.514 Å).

Fig. 2 shows the packing in the crystal viewed along *b*. Many close intermolecular contacts occur (Table 5), but none of these is substantially shorter than the sum of the van der Waals radii of the atoms concerned.

We thank Dr P. L. Coe and Professor J. C. Tatlow for suggesting this problem and providing suitable

crystals, Professor J. C. Robb for his interest, and the University of Birmingham for funds to purchase the diffractometer and for the award of a Research Studentship (to MJH).

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The Crystal and Molecular Structure of Tetrachloro-*o*-benzoquinone

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(Received 4 February 1978; accepted 4 May 1978)

Crystals of tetrachloro-*o*-benzoquinone (TOB) are monoclinic, with $a = 7.756(8)$, $b = 8.258(8)$, $c = 6.471(5)$ Å, $\beta = 90.3(1)^\circ$, $Z = 2$, space group $P2/a$ (after structure analysis) with required molecular symmetry C_2 . Intensity data were collected on a four-circle diffractometer with Mo $K\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least squares to a final conventional R value of 0.047 ($R_w = 0.049$) for the 826 observed reflexions with $I > 3\sigma(I)$. The quinoid ring adopts a shallow boat conformation with the Cl and O atoms significantly displaced from its mean plane. The molecular dimensions are in agreement with those found in *o*-benzoquinone and analogous compounds. In the crystal the molecules form layers, approximately parallel to $(\bar{2}01)$, whose mean separation is 3.33 Å.