Biphenylenes. Part XXIII.[1] Synthesis of Octafluorobiphenylene and its Conversion into Heptafluoro-1- and Heptafluoro-2-methoxybiphenylene

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Octafluorobiphenylene has been prepared by the pyrolysis of tetrafluorophthalic anhydride at 750°/0·6 ± 0·1 mm. Reaction of the biphenylene with sodium methoxide gave mixtures containing mono- and poly-methoxypolyfluorobiphenylenes. Treatment of the biphenylene with potassium hydroxide followed by diazomethane gave heptafluoro-1- and heptafluoro-2-methoxybiphenylene. The structure of the latter (and hence of the former) was shown by a detailed ^{19}F n.m.r. study. The orientations of both isomers are confirmed by the ^{1}H n.m.r. spectra. The ^{19}F n.m.r. spectrum of octafluorobiphenylene is discussed.

RECENTLY it was shown [2,3] that the pyrolysis of phthalic anhydride and of chloro- and methyl-phthalic anhydrides under reduced pressure is a useful method for the preparation of biphenylene and substituted biphenylenes. The use of this method for the preparation of octafluorobiphenylene (I) was described by one of us at an International Symposium on Aromaticity (Chemical Society, Sheffield) in July 1966. Since then, octafluorobiphenylene has been made by two other methods. Cohen and Massey [4] made the biphenylene (5%), m.p. 100—101·5°, by heating 3,3′,4,4′,5,5′,6,6′-octafluoro-2,2′-di-iodobiphenyl with copper powder at 200°. Sartori and Golloch [5] found that when mercury(II) tetrafluorophthalate was heated to 300°, it lost carbon dioxide and gave a cyclic compound, $(C_6F_4Hg)_3$, which when heated with silver powder gave octafluorobiphenylene (32%

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[1] Part XXII, J. F. W. McOmie, M. L. Watts, and D. E. West, *J. Chem. Soc.* (*C*), 1969, 646.

[2] M. P. Cava, M. J. Mitchell, D. C. De Jongh, and R. Y. Van Fossen, *Tetrahedron Letters*, 1966, 2947.

[3] R. F. C. Brown, D. V. Gardner, J. F. W. McOmie, and R. K. Solly, *Chem. Comm.*, 1966, 407; *Austral. J. Chem.*, 1967, **20**, 139.

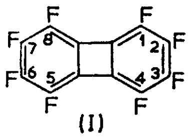
[4] S. C. Cohen and A. G. Massey, *Tetrahedron Letters*, 1966, 4393.

[5] P. Sartori and A. Golloch, *Chem. Ber.*, 1968, **101**, 2004.

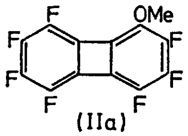
overall), m.p. 95—96°. In our method, the vapour of tetrafluorophthalic anhydride is passed through a silica tube (heated externally) at 750°/0·6 ± 0·1 mm.; the yield of crude octafluorobiphenylene is *ca.* 23%. The pure biphenylene, m.p. 99—100°, is almost colourless and its electronic spectrum (see Experimental section) is similar to that [6] of biphenylene itself except for a slight hypsochromic shift of all the maxima.

Polyfluoroaromatic compounds readily undergo substitution with nucleophilic reagents and the orientation of the products has been discussed by Tatlow and his co-workers [7] and by Burdon.[8] When the arguments of Tatlow and of Burdon are applied to octafluorobiphenylene they lead to different predictions, namely, that nucleophilic substitution should occur at the 1- and at the 2-position respectively. Our results support Burdon's thesis that the *para*-quinonoid transition state with the negative charge on a non-fluorine-bearing carbon atom is preferred.

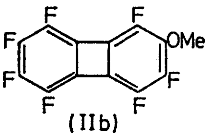
When octafluorobiphenylene was treated with sodium methoxide in methanol a complex reaction ensued. Under mild conditions a mixture of the two monomethoxy-compounds was isolated, whereas under vigorous conditions the major product was a mixture of tetrafluorotetramethoxybiphenylenes. Trace amounts of trifluoropentamethoxybiphenylenes were also detected (by mass spectrometry). When octafluorobiphenylene was treated with potassium hydroxide (1 equiv.) in t-butyl alcohol a mixture of two phenols was obtained. These, after separation, were treated with diazomethane, and gave the corresponding 1-methoxy- and 2-methoxy-biphenylenes (IIa and b), m.p. 73—75° (7%) and 66—68° (28%), respectively. The orientation of these isomers follows from the ^{19}F n.m.r. spectrum of the compound, m.p. 66—68°, which showed that this was the 2-isomer. The assignments are confirmed by the ^{1}H spectra of the isomers.



(I)



(IIa)



(IIb)

N.m.r. spectra.—The ^{19}F n.m.r. spectrum of the methoxy-compound (II), m.p. 66—68°, at 94·1 MHz consists of four well separated bands with $>$400 Hz between each band. Integration was not attempted, but the numbers of fluorine nuclei involved are apparently, in order of decreasing frequency, 1, 3, 1, and 2. In principle no two fluorine nuclei in (II) are equivalent, so it is clear that some second-order effects were to be expected. Moreover F–F coupling is well known to be rather long-ranged, and it is not surprising that each band has complex fine structure which could not be properly resolved. However some of the gross features are amenable to interpretation. We shall refer to the bands in order of decreasing frequency as A, B, C, and D. Band A (see Figure) is a doublet (J *ca.* 18 Hz) of doublets (J *ca.* 7 Hz); band C can be interpreted as an overlapping doublet (*ca.* 16 Hz) of 1 : 2 : 1 triplets (*ca.* 7 Hz). Double resonance experiments confirmed that bands A and C exhibited a common coupling of *ca.* 7 Hz. Band B consists of a 1 : 2 : 1 triplet (*ca.* 17 Hz) slightly to high frequency of a more intense doublet (*ca.* 12 Hz)—we shall refer to these bands as B′ and B″ respectively. Further decoupling experiments showed that bands A and B′ have a common coupling of *ca.* 17 Hz, as do bands B′ and C. Thus bands A, B′, and C are due to the three fluorine nuclei of the substituted ring. Abraham, Macdonald, and Pepper [9] have given the ranges of F–F coupling constants in simple fluoro-aromatic compounds as J_{ortho} −19 to −21, J_{meta} −20 to +20, and J_{para} +5 to +18 Hz.

There appear to be no reported coupling constants for compounds closely related to (II). However, consideration of the additive substituent effects in fluorobenzenes [9,10] makes it seem likely that the values of J_{meta} for the substituted ring of (IIa) and (IIb) will be small (probably between −4 and +6 Hz), whereas J_{para} is expected to be larger. There are several possible assignments of the coupling constants of the substituted ring of (II), but only two of these seem likely. Either the two large coupling constants (*ca.* 17 Hz) are of the same sign and are for *ortho*-fluorine atoms, in which case the compounds is (IIa); or these coupling constants are of opposite sign and one is for *ortho*-fluorine atoms while the other is for *para*-fluorine atoms—in this case the compound is (IIb). Partial decoupling experiments (see Figure) show unequivocally that $J_{AB'}$ and $J_{B'C}$ are opposite in sign, indicating that the structure is (IIb). Other double resonance experiments show that J_{AC} has the same sign as $J_{AB'}$.

Further definitive evidence for structure (IIb) is provided by the ^{1}H spectrum (100 MHz). This shows a doublet of doublets, centered at τ 5·853 (J 1·0 and 1·5 Hz). Lawrenson [11] found an H–F coupling of 1·1 Hz from the methoxy-protons to *ortho*-fluorine nuclei in pentafluoroanisole, and Burdon [12] has shown that in fluoroaromatic compounds the methoxy-protons couple only with fluorine atoms *ortho* to the side-chain (see also ref. 13); ^{1}H spectra therefore provide a count of the

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[6] W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J. Chem. Soc.*, 1954, 1476.

[7] B. Gething, C. R. Patrick, and J. C. Tatlow, *J. Chem. Soc.*, 1962, 186.

[8] J. Burdon, *Tetrahedron*, 1965, **21**, 3373.

[9] R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *J. Amer. Chem. Soc.*, 1968, **90**, 147.

[10] I. J. Lawrenson and R. G. Jones, *J. Chem. Soc.* (*B*), 1967, 797.

[11] I. J. Lawrenson, *J. Chem. Soc.*, 1965, 1117.

[12] J. Burdon, *Tetrahedron*, 1965, **21**, 1101.

[13] R. D. Chambers and D. J. Spring, *Tetrahedron*, 1969, **25**, 565.

number of *ortho*-fluorine atoms and in the present case two such nuclei are indicated. Long-range F–F coupling complicates the fluorine spectra, but double resonance experiments indicate that H–F coupling appears as splittings of 1·5 Hz in band C and 1·0 Hz in band A. The other isomer (m.p. 75—77°) shows a doublet in the ^{1}H spectrum (τ 5·84, $|J_{\mathrm{H,F}}|$ 1·3 Hz) which thus confirms that it is the 1-methoxy-compound.

The F–F coupling constants for (IIb) do not make it clear whether band A is due to F-1 and C to F-3 or *vice versa*. However, considerations of the substituent effects[10,11] of the methoxy-group in pentafluoroanisole suggest that the resonance of F-1 should be to high frequency of that of F-4 by 6·20 p.p.m.; band A is to high frequency of B′ by 6·33 p.p.m. Thus bands A, B′, and C may be assigned to F-1, F-4, and F-3, respectively, giving J_{ortho} *ca.* −16 (sign assumed), J_{para} *ca.* +18, and J_{meta} *ca.* +7 Hz for the substituted ring. The value of $|J_{para}|$ is unusually high and that of $|J_{ortho}|$ unusually low. This may be attributed to the effect of the four-membered ring (related cases are known[14]). Comparison of the shifts of bands A, B′, and C from those of octafluorobiphenylene (see Table) with the values expected on the basis of methoxy-substituent effects[11] enables us to suggest that the α fluorine nuclei of the parent molecule (I) resonate at higher frequency than the β nuclei; this leads to the complete chemical shift assignment (Table). Band B″, due to F-5 and F-8, appears as a doublet. This suggests that the chemical shift difference between F-5 and F-8 is negligibly small, and that the doublet splitting is approximately $|J_{ortho}\ (5,6) + J_{meta}\ (5,7)|$, with J_{ortho} *ca.* −18 and J_{meta} *ca.* +6 Hz. Observation of band C while irradiating band D shows that there is a large cross-ring coupling common to them, *ca.* 6 Hz; this contributes to the great complexity of band D (the chemical shift difference between F-6 and F-7 is clearly small, but by no means negligible). Other cross-ring coupling constants also affect the spectrum appreciably, but are probably typically 1—2 Hz.

The n.m.r. parameters for octafluorobiphenylene (I) and heptafluoro-2-methoxybiphenylene (IIb)

(I) Chemical shifts *	F_α −23·31
	F_β −12·78
	$|{}^3J_{\alpha\beta} + {}^4J_{\alpha\beta} + {}^6J_{\beta\alpha} + {}^7J_{\alpha\beta}| = 10{\cdot}8$ Hz
(IIb) Chemical shifts *	F-1 −28·64
	F-4 −22·31
	F-3 −17·11
	F-5, F-8 −22·11
	F-6, F-7 *ca.* −11·6
	OMe τ 5·853
Coupling constants †	${}^5J_{1,4}$ +18·6 Hz
	${}^4J_{1,3}$ +7·2 Hz
	${}^3J_{3,4}$ −16·1 Hz
	${}^3J_{5,6} + {}^4J_{5,7} = -11{\cdot}6$ Hz
	$|{}^5J_{1,\mathrm{Me}}|$ 1·0 Hz
	$|{}^5J_{3,\mathrm{Me}}|$ 1·5 Hz

* In p.p.m. from C_6F_6 (positive to low frequency). Lawrenson[11] gives ϕ^* (C_6F_6) 162·9, Boden and his co-workers[15] give ϕ^* (C_6F_6) 162·28. † F–F Coupling constants are only accurate to *ca.* ±0·8 Hz. It is assumed that the *ortho*-coupling constant is negative.[9]

Octafluorobiphenylene itself has an $[AX]_4$ spin system with D_{2h} symmetry; there are ten different coupling constants that affect the spectrum. It is not feasible to analyse the spectrum completely. However when the total component of spin of the X nuclei has an extreme value (±2), a single-line a_4 sub-spectrum is given. Thus one sixteenth of the A intensity lies in two lines separated by $|\Sigma J_{\mathrm{AX}_i}| = |{}^3J_{\mathrm{AX}} + {}^4J_{\mathrm{AX}} + {}^6J_{\mathrm{AX}} + {}^7J_{\mathrm{AX}}|$. This separation is found to be 10·8 Hz, and is presumably dominated by ${}^3J_{\mathrm{AX}}$(*ortho*) and ${}^4J_{\mathrm{AX}}$(*meta*), these being of opposite sign.

We were unable to measure the ^{19}F n.m.r. spectrum of heptafluoro-1-methoxybiphenylene because of the small quantity available.

EXPERIMENTAL

N.m.r. spectra of compounds (I), (IIa), and (IIb) were recorded at ambient temperature with a Varian HA100 spectrometer operating at 94·075 MHz for ^{19}F and 100 MHz for ^{1}H. Solutions in hexafluorobenzene were used, with internal tetramethylsilane for the proton resonance work. Spectra were obtained under frequency-sweep conditions in the HA mode. Double resonance frequencies were provided by Muirhead D-880-A and Schlumberger FSX-3005 frequency generators.

Pyrolysis of Tetrafluorophthalic Anhydride.—A horizontal silica tube (35 × 2·6 cm. i.d.) was heated by an external electric furnace. The temperature was measured by a chromel–alumel thermocouple in a silica sheath placed concentrically within the pyrolysis tube. Tetrafluorophthalic anhydride (994 mg.) was sublimed through the apparatus at 750°/0·6 ± 0·1 mm. during 70 min. A brown oil and a white solid collected in the exit tube and in the traps cooled in liquid nitrogen. The total product was sublimed at 45°/20 mm. and gave a light brown solid (160 mg., 24%), m.p. 85—90°. Recrystallisation of this solid from aqueous methanol, followed by resublimation at 45°/20 mm. gave octafluorobiphenylene as needles, m.p. 99—100° (lit.,[4] 100—101·5°; lit.,[5] 95—96°) (Found: C, 48·5; H, 0·0. Calc. for $C_{12}F_8$: C, 48·65; H, 0·0%). Similar pyrolyses of the acid or the anhydride at temperatures between 670 and 740° gave crude yields in the range 23—28%; $\lambda_{\mathrm{max.}}$ (EtOH) 235, 243, 315, 328, and 346 mμ (log ε 4·68, 4·79, 2·89, 2·93, and 2·85).

Reaction of Octafluorobiphenylene with Sodium Methoxide.—A solution of sodium methoxide [from sodium (1·4 g.) and dried methanol (100 ml.)] was used.

(*a*) A solution of octafluorobiphenylene (104 mg.) in methanolic sodium methoxide (1 ml.) was boiled under reflux for 2·75 hr. The yellow solution was poured into water and extracted twice with ether. The extract gave an oil which was separated, by preparative t.l.c. on silica with hexane as eluant, into three major products (in order of decreasing R_{F} value): (i) a solid (17 mg.) which, after sublimation at 40°/0·6 mm., had m.p. 38—40°; (ii) a solid (54·5 mg.) which, after sublimation at 50°/0·4 mm., had m.p. 55—102°; and (iii) a solid (23 mg.) which formed pale yellow needles, m.p. 90—112° (from aqueous ethanol). Molecular weight measurements (mass spectrometry) were consistent with the products being mixtures of hepta-

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[15] N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, 1964, **8**, 133.

fluoromethoxy-, hexafluorodimethoxy-, and pentafluorotrimethoxy-biphenylenes, respectively.

^{19}F N.m.r. spectrum of heptafluoro-2-methoxybiphenylene; band A: (*a*) single resonance, (*b*) partial decoupling due to irradiation at the high frequency side of band C, (*c*) partial decoupling due to irradiation at 17 Hz lower than for (*b*)

(*b*) In a similar experiment the biphenylene (99 mg.) and the sodium methoxide solution (3 ml.), were boiled for 2·75 hr. The major products were mixtures of hexafluorodimethoxy- and pentafluorotrimethoxy-biphenylenes (13 and 62 mg., respectively). The latter mixture gave green-yellow needles (27 mg.), m.p. 108—116° (from aqueous methanol).

(*c*) A mixture of the biphenylene (126 mg.), sodium methoxide (500 mg.), and methanol (10 ml.) was boiled for 6·25 hr. On cooling, long yellow needles (70 mg.), m.p. 114—127·5°, separated. These had m.p. 110—129° (from aqueous ethanol). This product was shown by mass spectrometry to contain mainly tetrafluorotetramethoxybiphenylene together with a small amount of the pentamethoxy-compound.

Reaction of Octafluorobiphenylene with Potassium Hydroxide.—A mixture of the biphenylene (448 mg.) and potassium hydroxide (120 mg.) in dried t-butyl alcohol (8 ml.) was boiled under reflux for 4·5 hr., then cooled; the solution was neutralised with dilute hydrochloric acid. The solvent was removed under reduced pressure and the residue was purified by preparative t.l.c. in benzene on silica gel. Two phenols with very similar R_F values were obtained and were separately methylated with an excess of diazomethane. The minor product (33 mg., 7%), obtained from the phenol of higher R_F value, was purified by t.l.c. in hexane, followed by sublimation at 55°/0·4 mm. and recrystallisation from aqueous methanol to give *heptafluoro*-1-*methoxybiphenylene*, m.p. 75—77° (Found: C, 50·5; H, 0·9. $C_{13}H_3F_7O$ requires C, 50·7; H, 1·0%).

The major product (131 mg., 28%) was purified by t.l.c. in hexane, followed by sublimation at 55°/0·4 mm., to give *heptafluoro*-2-*methoxybiphenylene*, m.p. 66—68° (Found: C, 51·1; H, 0·9%). A 1 : 1 mixture of the two ethers melted at *ca*. 38—40°.

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