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Structure of a phenylbis(pentafluorophenyl)benzofulvene isomer obtained from the reaction of $C_6H_5C{\equiv}CC_6F_5$ with palladium dichloride

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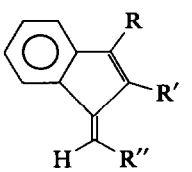
Abstract

Phenylpentafluorophenylacetylene reacts with $PdCl_2$ at room temperature to give several isomeric species. An X-ray study of one isomer has shown it to be 1,2-bis(pentafluorophenyl)-3-phenylbenzofulvene. The individual five- and six-membered rings are all planar, but the five-membered ring shows a significant dihedral angle of 5.4(2)° with the fused benzene ring. The fluorine atoms are displaced by no more than 0.09(1) Å from the least-squares ring-plane to which they are attached.

Introduction

Some years ago [1] we described the reaction which occurred between phenylpentafluorophenylacetylene and palladium dichloride in ethanol solution at room temperature. Three yellow or yellow-orange products could be isolated using TLC and these were assumed to be isomeric benzofulvenes from a study of their infrared and ultraviolet spectra. An X-ray structure of one product has now confirmed it to be a benzofulvene with the structure I.



(I: $R = C_6H_5$; $R' = R'' = C_6F_5$; II: $R = R' = R'' = C_6H_5$)

Maitlis has previously obtained triphenylbenzofulvene (II) by pyrolysis of a palladium complex formed by treating $PdCl_2$ with diphenylacetylene [2]; we were unable to isolate any intermediate metal complexes when using different polyfluorophenylphenylacetylenes. In all cases studied the presumed palladium intermediates were apparently unstable at room temperature and decomposed to form substituted benzofulvene isomers [1].

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Experimental

Phenylpentafluorophenylacetylene, prepared as described in a previous publication [3], was stirred for five days at room temperature in absolute ethanol with a slight excess of palladium dichloride. The solution gradually assumed an orange colour and began to deposit a reddish-grey solid. After filtration the solvent was removed under reduced pressure to leave a brown residue; the latter was separated into four bands on a preparative TLC plate developed using a 5% acetone–95% petroleum ether (60–80 °C) solvent mixture, but only the first two bands contained sufficient material for isolation; the first band (nearest the solvent front) contained two components which proved inseparable other than by crystal picking. Crystals from the second band were grown from petrol ether (60–80 °C) and used in the X-ray study: yellow needles, m.p. 123.5–126.5° [Found: C, 62.7; H, 2.0%; $m/e =$ 536; $C_{28}H_{10}F_{10}$ calcd.: C, 62.7; H, 1.9%; mol.wt., 536]. UV spectrum 325 (4.9×10^3) and 260 (7.9×10^3) nm.

Structure determination

D_m measured by flotation in aqueous $ZnCl_2$; yellow needle-like crystals; crystal $0.61 \times 0.39 \times 0.19$ mm; sealed in Lindemann glass capillary and mounted about c; preliminary lattice constants determined from oscillation and Weissenberg photographs, and the refined constants from a Stoe Stadi-2 two-circle diffractometer using axial-row reflections (θ range 5–21°); no corrections for absorption or extinction; $2\theta_{max} = 50°$; index range $-25 \leq h \leq 25$; $0 \leq k \leq 16$; $0 \leq l \leq 7$; one standard reflection taken every 50 reflections, no significant change noted; 2264 reflections measured, 2184 being unique and 1676 having $I > 3\sigma(I)$; C and F atoms

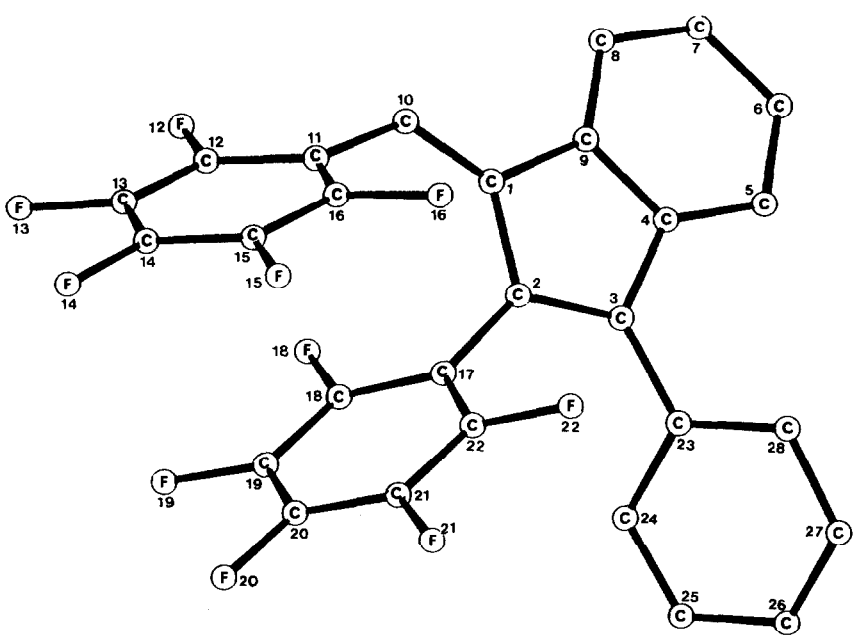

Fig. 1. ORTEP plot of I showing atom numbering (excluding H atoms).

Table 1

Atomic coordinates and isotropic thermal parameters (Å^2)

	x	y	z	B_{eq}		x	y	z	B_{eq}
C1	0.0340(3)	0.5896(2)	0.1639(8)	3.4(2)	F12	0.2098(2)	0.5266(2)	0.2942(8)	6.6(2)
C2	0.0198(3)	0.6866(3)	0.2152(8)	3.6(2)	F13	0.3064(2)	0.6373(3)	0.2548(8)	8.1(2)
C3	−0.0397(3)	0.6907(3)	0.2438(8)	3.8(2)	F14	0.2866(2)	0.7822(2)	0.0113(8)	8.3(2)
C4	−0.0676(3)	0.5946(3)	0.2185(8)	3.7(2)	F15	0.1685(3)	0.8145(2)	−0.1929(7)	7.3(2)
C5	−0.1258(3)	0.5611(3)	0.2427(8)	4.7(2)	F16	0.0720(2)	0.7060(2)	−0.1540(7)	5.6(1)
C6	−0.1361(3)	0.4634(4)	0.2300(9)	5.1(2)	F18	0.1377(2)	0.6888(2)	0.4673(7)	5.2(1)
C7	−0.0907(0)	0.4031(3)	0.1937(0)	4.8(2)	F19	0.2235(2)	0.8277(2)	0.4842(8)	7.7(2)
C8	−0.0330(3)	0.4370(3)	0.1645(8)	3.9(2)	F20	0.1954(3)	0.9833(2)	0.2697(9)	10.5(3)
C9	−0.0222(3)	0.5331(3)	0.1794(8)	3.5(2)	F21	0.0808(3)	0.9973(2)	0.0354(9)	10.6(3)
C10	0.0839(3)	0.5554(3)	0.1070(8)	3.9(2)	F22	−0.0029(2)	0.8562(2)	0.0078(7)	7.1(2)
C11	0.1373(3)	0.6124(3)	0.0729(8)	3.8(2)					
C12	0.1989(3)	0.5964(3)	0.1722(9)	4.8(2)					
C13	0.2485(3)	0.6525(4)	0.1513(10)	5.5(3)					B_{iso}
C14	0.2389(3)	0.7252(4)	0.0308(10)	5.7(3)	H5	−0.1622	0.6068	0.2720	7.1
C15	0.1791(3)	0.7425(3)	−0.0728(9)	5.2(2)	H6	−0.1815	0.4475	0.2597	7.1
C16	0.1299(3)	0.6856(3)	−0.0521(8)	4.3(2)	H7	−0.0995	0.3396	0.1826	7.1
C17	0.0647(3)	0.7670(3)	0.2355(8)	4.0(2)	H8	0.0020	0.3936	0.1319	7.1
C18	0.1226(3)	0.7643(3)	0.3578(8)	4.4(2)	H10	0.0882	0.4823	0.0961	7.1
C19	0.1669(3)	0.8353(4)	0.3686(10)	5.6(3)	H24	0.0013	0.8127	0.5207	7.1
C20	0.1528(3)	0.9130(4)	0.2615(11)	6.6(3)	H25	−0.0587	0.9428	0.6293	7.1
C21	0.0961(3)	0.9206(3)	0.1455(11)	6.6(3)	H26	−0.1558	0.9921	0.4513	7.1
C22	0.0523(3)	0.8481(3)	0.1305(9)	5.3(3)	H27	−0.2060	0.9033	0.1797	7.1
C23	−0.0717(3)	0.7734(3)	0.3004(8)	4.4(2)	H28	−0.1545	0.7606	0.0835	7.1
C24	−0.0436(3)	0.8265(3)	0.4526(10)	5.4(2)					
C25	−0.0738(4)	0.9049(4)	0.5049(10)	7.2(3)					
C26	−0.1329(4)	0.9303(4)	0.4062(12)	8.0(4)					
C27	−0.1614(3)	0.8786(4)	0.2555(11)	7.4(3)					
C28	−0.1317(3)	0.7991(3)	0.2006(9)	5.6(2)					

located by direct methods and 7H atoms from successive ΔF syntheses, the final 3H from calculated positions; anisotropic refinement of C and F by full-matrix least squares with unit weights gave a final $R = 0.034$ (H not refined); $\Delta/\sigma \leq 0.04$; $\Delta\rho$ excursions = +0.12 to −0.13 eÅ^{-3}; scattering factors were taken from Cromer and Mann [4]; structure solution and refinement used SHELXS [5] and SHELX76 [6] implemented at Loughborough University of Technology Computer Centre; drawing was performed by ORTEP [7] also implemented at LUTCC; geometry calculations by XTAL [8] at the University of Manchester Regional Computer Centre. A copy of the list of structure factors and anisotropic temperature-factors is available, on request from J. Bowen Jones. An ORTEP drawing of the molecule with hydrogen atoms omitted is given in Fig. 1 together with the atom numbering. Table 1 lists the atomic coordinates and isotropic thermal parameters for non-hydrogen atoms, and the bond lengths and angles are shown in Table 2.

Crystal data. $C_{28}H_{10}F_{10}$, $M_r = 536.372$, monoclinic, Cc, $a = 21.701(6)$; $b = 14.166(4)$; $c = 7.510(3)$ Å; $\beta = 102.61(1)°$; $V = 2252.99$ Å^3; $Z = 4$; $D_m = 1.590$; $D_x = 1.581$ g cm^{-3}; λ (Mo-K_α) = 0.71069 Å; $\mu = 1.03$ cm^{-1}; $F(000) = 1072$; $T = 298$ K; final $R = 0.034$ for 1676 observed reflections with $I > 3\sigma(I)$.

Table 2

Bond lengths (Å) and angles (°)

C(1)–C(2)	1.478(5)	C(5)–H(5)	1.080(5)
C(1)–C(9)	1.483(5)	C(6)–H(6)	1.080(6)
C(1)–C(10)	1.340(5)	C(7)–H(7)	0.920(4)
C(2)–C(3)	1.355(5)	C(8)–H(8)	1.047(5)
C(2)–C(17)	1.484(5)	C(10)–H(10)	1.045(4)
C(3)–C(4)	1.485(5)	C(24)–H(24)	1.016(6)
C(3)–C(23)	1.473(5)	C(25)–H(25)	1.065(7)
C(4)–C(5)	1.398(5)	C(26)–H(26)	1.097(6)
C(4)–C(9)	1.395(5)	C(27)–H(27)	1.069(6)
C(5)–C(6)	1.402(6)	C(28)–H(28)	1.062(6)
C(6)–C(7)	1.375(6)		
C(7)–C(8)	1.403(6)	C(12)–F(12)	1.333(5)
C(8)–C(9)	1.381(5)	C(13)–F(13)	1.343(5)
C(10)–C(11)	1.479(5)	C(14)–F(14)	1.346(5)
C(11)–C(12)	1.401(6)	C(15)–F(15)	1.347(6)
C(11)–C(16)	1.385(6)	C(16)–F(16)	1.351(5)
C(12)–C(13)	1.374(6)	C(18)–F(18)	1.345(5)
C(13)–C(14)	1.356(7)	C(19)–F(19)	1.344(6)
C(14)–C(15)	1.381(7)	C(20)–F(20)	1.351(5)
C(15)–C(16)	1.374(6)	C(21)–F(21)	1.362(6)
C(17)–C(18)	1.387(6)	C(22)–F(22)	1.346(5)
C(17)–C(22)	1.386(6)		
C(18)–C(19)	1.382(6)		
C(19)–C(20)	1.358(8)		
C(20)–C(21)	1.348(8)		
C(21)–C(22)	1.388(7)		
C(23)–C(24)	1.392(6)		
C(23)–C(28)	1.401(6)		
C(24)–C(25)	1.389(7)		
C(25)–C(26)	1.382(8)		
C(26)–C(27)	1.377(9)		
C(27)–C(28)	1.403(7)		
C(2)–C(1)–C(9)	105.2(3)	C(18)–C(19)–C(20)	119.4(5)
C(2)–C(1)–C(10)	130.4(3)	C(19)–C(20)–C(21)	120.2(5)
C(9)–C(1)–C(10)	124.4(3)	C(20)–C(21)–C(22)	120.4(5)
C(1)–C(2)–C(3)	109.8(3)	C(17)–C(21)–C(22)	121.1(5)
C(1)–C(2)–C(17)	124.9(3)	C(3)–C(23)–C(24)	121.1(4)
C(3)–C(2)–C(17)	125.3(4)	C(3)–C(23)–C(28)	119.6(4)
C(2)–C(3)–C(4)	108.5(3)	C(24)–C(23)–C(28)	119.2(4)
C(2)–C(3)–C(23)	127.3(4)	C(23)–C(24)–C(25)	121.0(5)
C(4)–C(3)–C(23)	124.1(3)	C(24)–C(25)–C(26)	119.7(5)
C(3)–C(4)–C(5)	130.5(4)	C(25)–C(26)–C(27)	120.0(5)
C(3)–C(4)–C(9)	108.2(3)	C(26)–C(27)–C(28)	121.0(5)
C(5)–C(4)–C(9)	121.0(4)	C(27)–C(28)–C(23)	119.0(5)
C(4)–C(5)–C(6)	117.5(4)		
C(5)–C(6)–C(7)	121.0(4)	C(4)–C(5)–H(5)	123.0(4)
C(6)–C(7)–C(8)	121.4(4)	C(6)–C(5)–H(5)	119.5(4)
C(7)–C(8)–C(9)	117.8(4)	C(5)–C(6)–H(6)	109.3(4)
C(1)–C(9)–C(4)	108.0(3)	C(7)–C(6)–H(6)	129.6(4)
C(1)–C(9)–C(8)	130.8(3)	C(6)–C(7)–H(7)	118.8(2)
C(4)–C(9)–C(8)	121.2(3)	C(8)–C(7)–H(7)	119.7(3)
C(1)–C(10)–C(11)	125.2(3)	C(7)–C(8)–H(8)	123.6(4)
C(10)–C(11)–C(12)	120.9(4)	C(9)–C(8)–H(8)	118.6(4)
C(10)–C(11)–C(16)	123.1(4)	C(1)–C(10)–H(10)	118.4(4)

Table 2 (continued)

C(12)–C(11)–C(16)	116.0(4)	C(11)–C(10)–H(10)	116.2(4)
C(11)–C(12)–C(13)	121.8(5)	C(23)–C(24)–H(24)	120.7(5)
C(12)–C(13)–C(14)	120.3(5)	C(25)–C(24)–H(24)	118.1(5)
C(13)–C(14)–C(15)	119.9(4)	C(24)–C(25)–H(25)	125.3(7)
C(14)–C(15)–C(16)	119.4(5)	C(26)–C(25)–H(25)	114.2(6)
C(11)–C(16)–C(15)	122.5(4)	C(25)–C(26)–H(26)	118.2(7)
C(2)–C(17)–C(18)	121.7(4)	C(27)–C(26)–H(26)	121.8(7)
C(2)–C(17)–C(22)	122.4(4)	C(26)–C(27)–H(27)	117.1(6)
C(18)–C(17)–C(22)	115.8(4)	C(28)–C(27)–H(27)	121.8(7)
C(17)–C(18)–C(19)	122.5(5)	C(23)–C(28)–H(28)	121.3(5)
C(17)–C(22)–C(21)	121.5(5)	C(27)–C(28)–H(28)	119.7(5)
C(11)–C(12)–F(12)	119.3(4)	C(17)–C(18)–F(18)	119.4(4)
C(13)–C(12)–F(12)	118.9(4)	C(19)–C(18)–F(18)	118.1(4)
C(12)–C(13)–F(13)	119.9(5)	C(18)–C(19)–F(19)	120.3(5)
C(14)–C(13)–F(13)	119.7(5)	C(20)–C(19)–F(19)	120.2(5)
C(13)–C(14)–F(14)	121.1(5)	C(19)–C(20)–F(20)	120.4(6)
C(15)–C(14)–F(14)	118.9(5)	C(21)–C(20)–F(20)	119.3(6)
C(14)–C(15)–F(15)	120.9(4)	C(20)–C(21)–F(21)	121.5(5)
C(16)–C(15)–F(15)	119.7(5)	C(22)–C(21)–F(21)	118.0(6)
C(11)–C(16)–F(16)	120.0(4)	C(17)–C(22)–F(22)	119.6(4)
C(15)–C(16)–F(16)	117.4(4)	C(21)–C(22)–F(22)	118.9(4)

Tables of hydrogen atom coordinates, thermal parameters, and structure factors are available from the authors.

Discussion

The X-ray study confirms that compound **2** of reference 1 page 431 is a benzofulvene and, taken in conjunction with spectroscopic data, strongly supports the suggestion that compounds **1A** and **1B** in reference 1 are two other isomers of I; at least four isomers of I are possible products of the reaction between phenylpentafluorophenylacetylene and palladium dichloride. The individual five- and six-membered rings in I are all planar with the five-membered ring making a dihedral angle of 5.4(2)° to the fused benzene ring. The bond C(2)–C(3) is significantly shorter than the other bonds in the five-membered ring in keeping with its assignment as a double-bond in the fulvene structure. From the ORTEP drawing of I it appears that the two pentafluorophenyl rings are almost parallel but in fact their dihedral angle is 17.3(2)°.

Table 3

The angles, in degrees, between the five rings of fulvene (I)

Ring	2	3	4	5
1	5.4(2)	55.0(2)	56.7(2)	58.5(2)
2		58.8(3)	59.0(3)	54.3(3)
3			17.3(2)	76.8(2)
4				62.0(3)

The fluorine atoms are displaced by no more than 0.09(1) Å from the least-squares plane of the ring to which they are attached. The angles between the five rings are quoted in Table 3.

Infrared spectrum (Nujol and hexachlorobutadiene; cm^{-1})

1577w, 1530s, 1502s, 1457m, 1163w, 1144w, 1134m, 1081s, 1075s, 1025w, 1009sh, 1000msh, 990s, 979s, 943w, 929s, 918w, 838m, 797m, 776w, 767m, 750m, 740m, 728m, 703s, 687w, 665w, 652w, 620w, 608m.

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