

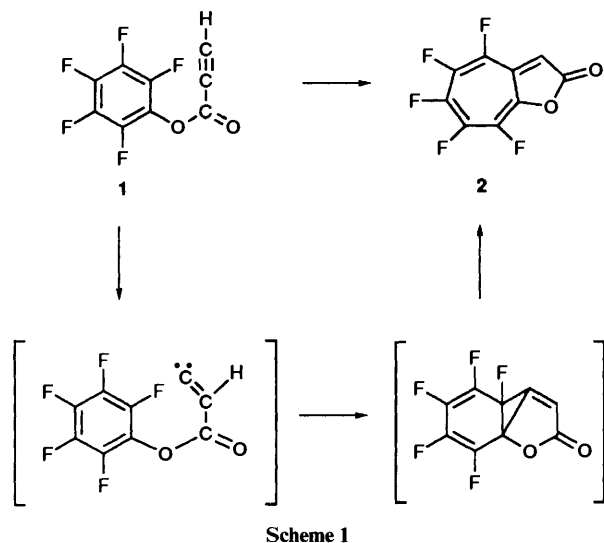
The Pyrolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Propynoate: Remarkable Products Obtained *via* an Internal Diels–Alder Reaction

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Flash vacuum pyrolysis of the ester 1,3,4,5,6,7,8-heptafluoro-2-naphthyl propynoate (**6**) at 550 °C/0.01 mmHg gave three products: **3** and **4** by an overall decarbonylation reaction, and **5** by a further decarbonylation of **3** and/or **4**. Isomerisation of **6** to 2-fluoropropynyl 2-naphthoate **8** by a Diels–Alder/retro-Diels–Alder sequence followed by decarbonylation and a series of 1,2-fluorine shifts offers a rationalisation for the formation of the products.

In a previous paper we described the flash vacuum pyrolysis of pentafluorophenyl propynoate **1** at 640 °C/0.01 mmHg to give 4,5,6,7,8-pentafluorocyclohepta[*b*]furan-2-one **2**, a golden yellow solid in 8% yield.¹ It has been proposed that the reaction, analogous to the original one carried out on phenyl propynoate,² proceeds *via* an alkyne–methylene carbene rearrangement³ (Scheme 1).

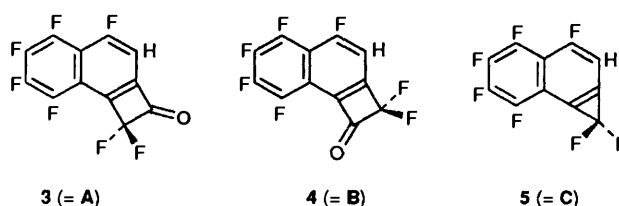


We now report a further investigation of this ring expansion using 1,3,4,5,6,7,8-heptafluoro-2-naphthyl propynoate **6** as a substrate of interest for two reasons: (i) there is the question of the orientation of the product since cyclisation could occur *via* the 1,2- and/or 2,3-bonds in the naphthalene ring; and (ii) the higher bond-order of the 1,2-position suggested the possibility of a more efficient and selective process.

The ester **6** was readily prepared from 1,3,4,5,6,7,8-heptafluoro-2-naphthol, propynyl chloride and potassium carbonate in water. Flash vacuum pyrolysis (FVP) of **6** through a silica tube packed with short pieces of silica under the conditions used with **1** produced a tarry product which showed no outstanding signals in its ¹⁹F NMR spectrum. However, when the reaction was carried out at 550 °C, although no yellow material was formed which would have been characteristic of a ring-expansion product, two major compounds, **A** and **B** and a minor compound **C**, all with characteristic singlets in their ¹⁹F NMR spectra at –97.0, –94.2 and –79.0 ppm and present in

the ratio 9:3:1 respectively, were isolated, albeit in an 8% combined yield. Compounds **A** and **B** were separated by a combination of chromatography on silica and recrystallisation, while further pyrolysis of **A** at 550 °C/0.01 mmHg gave recovery of **A** (58%), **B** (15%) and a significant amount of **C** (27%), a very volatile solid which was separated from **A** and **B** by sublimation.

The ¹⁹F NMR spectra of **A**, **B** and **C** all showed the presence of seven fluorines including two which were the singlets at the remote high frequency shifts characteristic of CF₂-groups, while the corresponding ¹H NMR spectra showed hydrogen attached to an aromatic ring, observations which indicated that very profound changes had taken place in the original naphthalene ring. The mass spectra of **A** and **B** both showed molecular ions at *m/z* 294 due to decarbonylation of the starting molecule (322 – 28), while the molecular ion of **C** *m/z* 266 resulted from a double decarbonylation process (322 – 2 × 28). Compounds **A**, **B** and **C** were characterised by X-ray single-crystal diffraction studies as **3**, **4** and **5**, respectively.



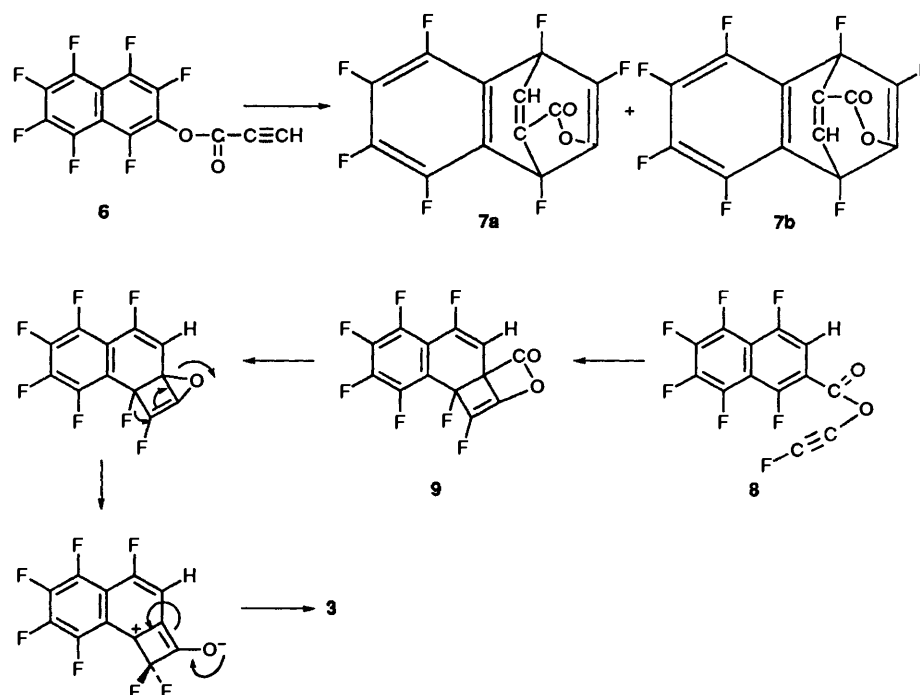
The 2,2-difluorocyclobutenone structural feature found in compounds **3** and **4** has a precedent: octafluorobicyclo[4.2.0]-octa-1,3,5-trien-7-one was prepared by Russian workers by treatment of decafluorobenzocyclobutene with SbF₅ followed by water.⁴ The 1,1-difluorocyclopropene fused ring found in **5** is known in 1,1-difluoro-1*H*-cyclopropa[*a*]naphthalene, formed *via* a carbene route.⁵

The formation of the three compounds **3**, **4** and **5** can be rationalised on the basis of an initial intramolecular Diels–Alder reaction. Two adducts are possible, **7a** and **7b**, both of which would undergo a retro Diels–Alder reaction to give the same key intermediate **8** which, in turn, can form **9** by a non-concerted 2 + 2 cycloaddition. Thereafter, it is a matter of some speculation as to the timing of the decarbonylation and fluorine shifts, one possibility is shown in Scheme 2.

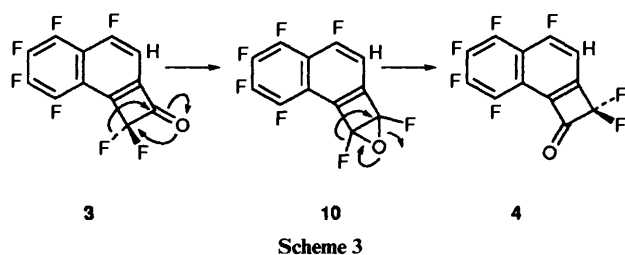
Compound **4** arises from the vapour phase isomerisation of **3** and could take place under the forcing conditions of the pyrolysis by two 1,2-fluorine shifts as shown in Scheme 3. Decarbonylation of either **3** and/or **4** is the obvious source of the cyclopropane derivative **5**.

The proposed intermediate **10** in the formation of **4** from **3**

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Scheme 2

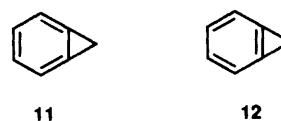


Scheme 3

has considerable credence since two research groups have found that hexafluorobenzene oxide rearranges spontaneously to hexafluorocyclohexa-2,4-dienone by a 1,2-fluorine shift.⁶ The opening of the benzene oxide ring to a zwitterion in polar solvents or to a related biradical in the case of a high temperature gas-phase pyrolysis, are plausible mechanisms for this reaction, and our observations under very vigorous conditions require merely that these processes are reversible. Re-aromatisation must be the driving force with conversion of 9 into 3.

Table 1 Selected bond lengths (Å) and angles (°) in 3–5

	3	4	5
C(1)–C(2)	1.376(3)	1.381(3)	1.338(3)
C(1)–C(9)	1.410(3)	1.416(3)	1.414(3)
C(2)–C(3)	1.400(4)	1.405(3)	1.406(3)
C(3)–C(4)	1.368(3)	1.367(3)	1.364(3)
C(4)–C(10)	1.439(3)	1.440(3)	1.437(3)
C(10)–C(5)	1.409(3)	1.410(3)	1.420(3)
C(5)–C(6)	1.372(3)	1.366(3)	1.370(3)
C(6)–C(7)	1.397(4)	1.403(3)	1.396(3)
C(7)–C(8)	1.366(3)	1.366(3)	1.362(3)
C(8)–C(9)	1.401(3)	1.403(3)	1.394(3)
C(9)–C(10)	1.435(3)	1.436(3)	1.434(3)
C(1)–C(11) ^a	1.508(4)	1.491(3)	1.437(3)
C(2)–C(12)	1.499(3)	1.505(3)	1.449(3)
C(11)–C(12)	1.584(3)	1.576(3)	
C–O	1.192(3)	1.201(2)	
C(sp ³)–F, average	1.355(3)	1.357(3)	1.364(2)
C(sp ²)–F, average	1.338(3)	1.339(3)	1.343(5)
C(9)C(1)C(2)	122.4(2)	122.1(2)	124.4(2)
C(9)C(1)C(11) ^a	142.5(2)	144.5(2)	172.4(2)
C(2)–C(1)–C(11) ^a	95.0(2)	93.4(2)	62.8(1)
C(1)C(2)C(3)	123.6(2)	124.0(2)	125.6(2)
C(1)C(2)C(12)	92.9(2)	94.0(1)	61.9(1)
C(3)C(2)C(12)	143.5(2)	142.0(2)	172.2(2)
C(2)C(3)C(4)	1149.(2)	114.2(2)	111.4(2)
C(3)C(4)C(10)	124.6(2)	125.4(2)	126.4(2)
C(1)C(11)C(12)	84.8(2)	87.0(1)	
C(2)C(12)C(11)	87.3(2)	85.5(2)	
C(1)C(12)C(2)			55.2(1)

^a For 5, C(12) instead of C(11).

X-Ray crystal structures of 3–5 are shown in Fig. 1(a)–(c); relevant bond lengths and angles are listed in Table 1. The crystal of 4, chosen for X-ray study, appeared to be a solid solution of *ca.* 10% of 3 in 4, so that the two F and one O atoms, bound to the 4-membered ring, are disordered over two positions each [Fig. 1(d)], and positions of the other atoms are coinciding. Molecules of 3–5 are approximately planar (except the CF₂-group fluorine atoms). Carbon atoms of the naphthalene moiety deviate from their mean plane, on average, by 0.006 Å in 3, 0.015 Å in 4 and 0.020 Å in 5; deviations of five fluorine substituents, F(4) to F(8), from the same plane average 0.021, 0.046 and 0.053 Å, respectively. The plane of the 4- or 3-membered ring is bent out of the naphthalene plane by 1.9° (3), 2.4° (4) and 4.3° (5). Thus, puckering of the molecules, though small, increases in the same order, (3) < (4) < (5), as the yield of the compounds decreases.

Structures of 3–5 give some insight into the effect of a small fused ring on the aromatic system. As far as we know, 5 is the first structurally studied cyclopropa[*a*]naphthalene, and only two structures of cyclobuta[*a*]naphthalenes have been studied before this work.⁷

Quantum chemistry has predicted long ago that fusion of a cyclopropane ring to an aromatic system must induce partial

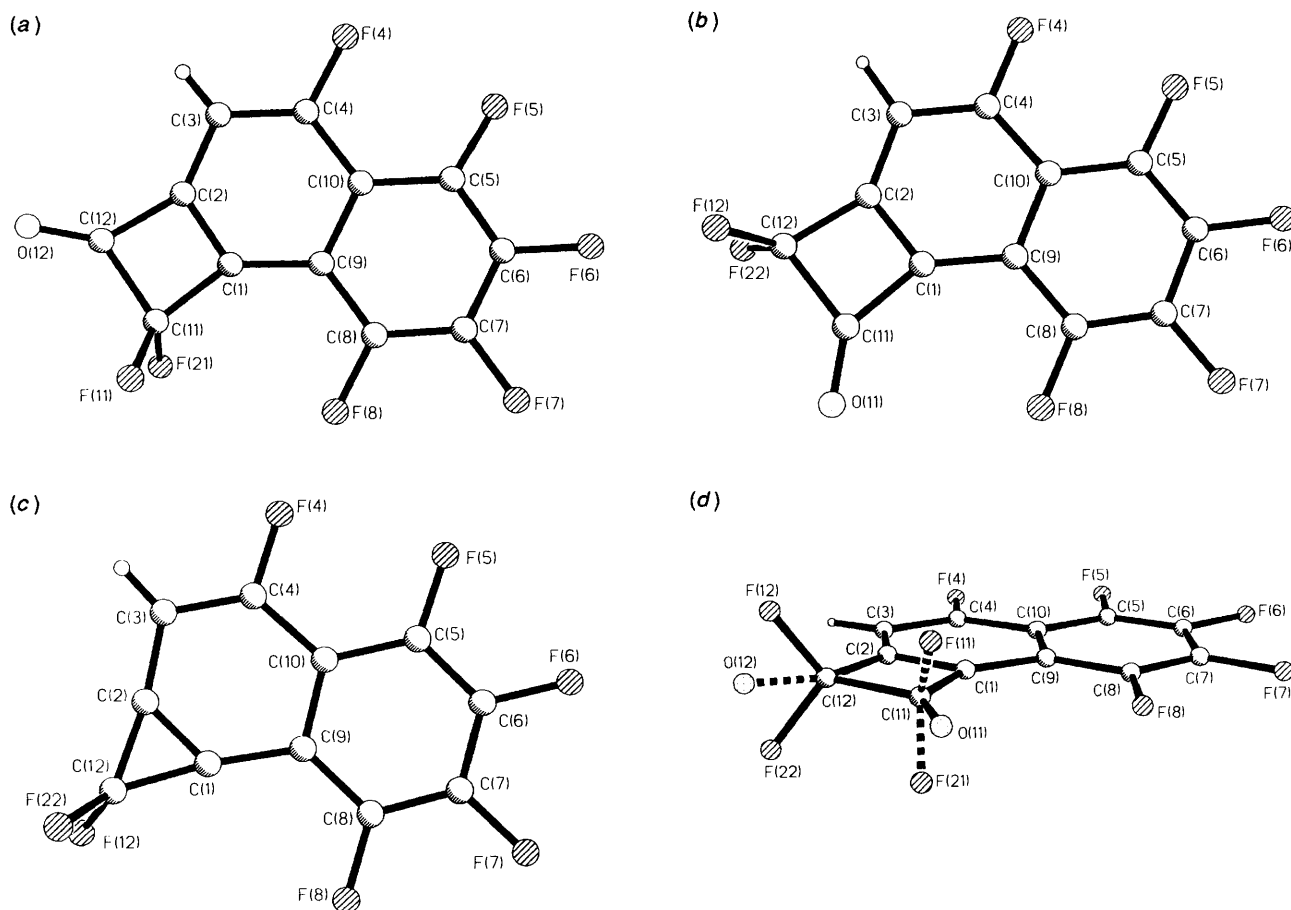


Fig. 1 (a) Molecular structure of **3**, (b) **4**, (c) **5**; (d) superposition of molecules **3** (dashed bonds) and **4** in the solid solution of **3** in **4**

localisation of the π -electron framework of the latter (Mills–Nixon effect, or bond fixation).⁸ However, theoretical models disagreed on the direction of bond localisation, *viz.* whether benzocyclopropene should tend to structure **11**,⁹ or **12**.¹⁰ X-Ray studies of benzocyclopropenes¹¹ have shown that though the fused C–C bond is shortened to 1.33–1.35 Å, the other bond distances in the benzene ring are almost unaffected. On the other hand, fusion with 4-membered rings is known to have little, if any, effect on the geometry of a benzene ring.¹²

In **3–5**, the overall geometry of the naphthalene moiety is similar to that of unsubstituted naphthalene,¹³ with significant localisation of double bonds in the 1–2, 3–4, 5–6 and 7–8 positions. Fluorine substituents have essentially no effect on this geometry, as had been proved earlier for perfluoronaphthalene.¹⁴ In **3** and **4**, the C(1)–C(2) bond is but marginally longer than three other localised bonds. In **5** it is shortened to the same length (1.338 Å) as in benzocyclopropenes, but the relative shortening is twice smaller. Thus, the effect of both 4- and 3-membered rings on a naphthalene system is similar to that on a benzene one, and similarly is essentially local (*i.e.* confined to the fused bond) and probably owes more to the steric strain in a 3-membered ring than to redistribution of π -electrons. The only other significant distortion of the D_{2h} symmetry of naphthalene in **3–5** is the lengthening of the C(4)–C(10) bond, which is common for naphthalenes, fused at the 1,2-positions, even with less strained rings, such as furan or azepine.¹⁵

Experimental

NMR spectra were recorded on the following instruments and at the frequencies listed: Bruker AC250 [¹H (250.133 MHz) and ¹⁹F (235.360 MHz)]; Varian 400 MHz [¹H (399.952 MHz) and

¹⁹F (376.33 MHz)]. Chemical shifts are quoted in ppm with respect to the following references: ¹⁹F (upfield from external CFC1₃) and ¹H (downfield from internal TMS). Mass spectra were recorded on a VG 7070E mass spectrometer with molecular ions M⁺, quoted for electron ionisation at 70 eV. Elemental analyses were performed on a Carlo ERBA C,H,N Elemental Analyser 1106.

Reaction of Propynoyl Chloride with Potassium 1,3,4,5,6,7,8-Heptafluoro-2-naphtholate.—Propionic acid (4.1 g, 0.059 mol) was added dropwise over 2 min to phosphorus pentachloride (20.6 g, 0.099 mol), cooled externally by an ice bath. The mixture was distilled at room temperature (0.05 mmHg) into a trap cooled with liquid air, and the distillate was dissolved in precooled (–30 °C) light petroleum (b.p. 40–60 °C) and shaken with iced water (15 cm³) to hydrolyse and remove POCl₃. The washing process was repeated twice, with the light petroleum layer being re-cooled to –30 °C between each washing. The organic layer was added to a solution of 1,3,4,5,6,7,8-heptafluoro-2-naphthol (5.27 g, 0.020 mol) and potassium carbonate (12.1 g, 0.088 mol) in water (50 cm³), cooled externally by an ice bath. The two-phase solution temperature was maintained at 2 °C for 30 min and then the organic layer was separated, dried (MgSO₄), filtered and the solvent evaporated to give the crude ester (4.53 g, 70% based on the 2-naphthol) which was virtually pure by ¹⁹F NMR spectroscopy (>95%). Recrystallisation gave heptafluoro-2-naphthyl propynoate **6** [from light petroleum (b.p. 60–80 °C)], m.p. 93.5–94.0 °C (Found: C, 48.75; H, 0.26%; M⁺, 322. C₁₃H₇F₇O₂ requires C, 48.47; H, 0.31%; M, 322); δ_F (CDCl₃) –134.0 (dd, 1-F), –144.8 (dt, 8-F), –145.7, –146.6 (both dt, unassigned 4-F and 5-F), –147.2 (s, 3-F), –153.1 (t, 6-F) and –154.6 (br s, 7-F); $J_{1-F,8-F}$ 62.4 Hz, $J_{4-F,5-F}$

Table 2 Crystal data

Compound	3		4		5	
Crystal size (mm)	0.11 × 0.40 × 0.40		0.02 × 0.25 × 0.30		0.05 × 0.27 × 0.60	
System	monoclinic		monoclinic		monoclinic	
Space group	P2 ₁ /c (No. 14)		C2/c (No. 15)		P2 ₁ /n (No. 14)	
T/K	290	155	290	125	150	150
a/Å	7.322(2)	7.282(2)	15.766(5)	15.578(5)	8.702(2)	8.702(2)
b/Å	12.377(2)	12.221(2)	13.027(3)	13.008(3)	11.364(2)	11.364(2)
c/Å	11.823(3)	11.709(2)	11.008(3)	10.788(3)	9.372(2)	9.372(2)
β/°	106.80(2)	106.76(3)	114.66(2)	114.34(3)	100.62(2)	100.62(2)
V/Å ³	1025.7(3)	997.7(2)	2054.6(1.1)	1991.5(1.0)	910.9(3)	910.9(3)
Refl. for unit cell	25	24	20	20	25	25
θ interval/°	6–11	13.5–14.5	12–14	12–14	10–15	10–15
Formula	C ₁₂ HF ₇ O		C ₁₂ HF ₇ O		C ₁₁ HF ₇	
M	294.1		294.1		266.1	
Z	4		8		4	
F(000)	1152		576		520	
D _c /g cm ⁻³	1.905	1.96	1.90	1.96	1.94	1.94
μ(Mo-Kα)/cm ⁻¹	2.1	2.1	2.1	2.1	2.1	2.1
Max. 2θ/°	50	55		60	50	50
Independent refls.	1793	2337		2837	1610	1610
Observed refls.						
I > 2σ(I)	795	1681		2084	1220	1220
No. of variables	121 ^a	185		197	167	167
R, observed data	0.044	0.039		0.045	0.031 ^b	0.031 ^b
wR, observed data	0.048	0.050		0.056	0.084 ^b	0.084 ^b
R, all data	0.132	0.063		0.069	0.055 ^b	0.055 ^b
wR, all data	0.056	0.052		0.112	0.094 ^b	0.094 ^b
Goodness of fit	1.64	1.64		1.86	1.075 ^b	1.075 ^b
Δρ/e Å ⁻³ , max.	0.27	0.38		0.41	0.21	0.21
min.	-0.22	-0.24		-0.24	-0.23	-0.23

^a Atoms in isotropic approximation. ^b Refinement based on F² (the rest on F).

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|} wR = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{\frac{1}{2}}, \text{ Goodness of fit} = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{n - p} \right]^{\frac{1}{2}}$$

58.6 Hz; δ_H(CDCl₃) 3.30 (s, alkylic CH). Unchanged heptafluoro-2-naphthol (0.54 g) was recovered from the aqueous phase by acidification (H₂SO₄, 2 mol dm⁻³) and subsequent extraction with ether.

Flash Vacuum Pyrolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Propynoate 6.—FVP of heptafluoro-2-naphthyl propynoate **6** (4.13 g) in separate experiments (approx. 500 mg each) at 550 °C/0.05 mmHg through a silica tube (50 cm × 2 cm) packed with silica tubing (5 mm × 5 mm) yielded a black oily product (3.48 g total), which was shown, by ¹⁹F NMR, to contain only three products present in significant proportion (8–9% total): compounds **3**, **4** and **5**, present in the ratio 9:3:1, respectively. Compounds **3** and **4** were separated together from tar by column chromatography on silica (7 in × 2.5 in)* with a mixture of CCl₄ and CHCl₃ as eluent (3:1, v/v) and were partially separated by further chromatography on silica (6.5 in × 1.5 in) using light petroleum (b.p. 40–60 °C) and diethyl ether (80:20, v/v) as eluent. The enriched faster moving component, compound **4**, was finally isolated pure by a combination of preparative TLC on silica with light petroleum (b.p. 40–60 °C) and diethyl ether (80:20, v/v) as eluent, followed by recrystallisation to give 1,2-dihydro-2,2,4,5,6,7,8-heptafluoro-cyclobuta[a]naphthalene-1-one (**4**) (1% based upon **6**), [from light petroleum (b.p. 60–80 °C)–diethyl ether (80:20, v/v)], m.p. 102.0–102.5 °C (Found: C, 49.2; H, 0.4%; M⁺, 294. C₁₂HF₇O requires C, 49.00; 0.34%; M, 294); δ_F(CDCl₃) –94.2 (dd, 4-F), –99.2 (s, CF₂), –139.8 (dt, 5-F), –135.0, –146.5 and –148.4 (all t, all unassigned); J_{4-F,5-F} 71 Hz; δ_H(CDCl₃) 7.60

(d, J_{H-4F}, 8.5 Hz). Sublimation (60 °C, 0.05 mmHg) of the enriched slower eluting component (0.29 g), followed by recrystallisation, gave 1,2-dihydro-1,1,4,5,6,7,8-heptafluorocyclobuta[a]naphthalen-2-one (**3**) (0.187 g, 5% based on **6** [from light petroleum (b.p. 60–80 °C)–diethyl ether (80:20, v/v)], m.p. 99.5–100.0 °C (Found: C, 49.1; H, 0.35%; M⁺, 294. C₁₂HF₇O requires C, 49.00; 0.34%; M, 294); δ_F(CDCl₃) –97.0 (s, CF₂), –101.3 (d, 4-F), –138.9 (dt, 5-F), –138.5, –146.5 and –148.2 (all t, all unassigned); J_{4-F,5-F} 69 Hz; δ_H(CDCl₃) 7.39 (d, J_{H-4F} 9 Hz).

Further Pyrolysis of 1,2-Dihydro-1,1,4,5,6,7,8-heptafluorocyclobuta[a]naphthalen-2-one (3).—FVP of **3** (26 mg) at 550 °C (0.01 mmHg), through the same pyrolysis tube as described above, gave recovery of starting material **3** (58%), accompanied by the isomer **4** (15%) and compound **5** (27%). Further quantities of **3** for characterisation were prepared by FVP of a 3:1 mixture of **3** and **4**. Compound **5** was separated from **3** and **4** by sublimation at 0 °C/0.05 mmHg into a liquid nitrogen cooled finger. The sublimate was identified by X-ray crystallography as 1,1,4,5,6,7,8-heptafluoro-1H-cyclopropa[a]naphthalene **5** (9.5 mg, 15% based on **3** and **4**), m.p. 53.5–54.0 °C (Found: M⁺, 266. C₁₁HF₇ requires M, 266); δ_F(CDCl₃) –79.0 (s, 1-F), –103.0 (d, 3-F), –138.8 (dt, 4-F), –140.1 (t, 7-F), –148.9 and –150.9 (both t, unassigned 5-F and 6-F); J_{3-F,4-F} 73 Hz; δ_H(CDCl₃) 7.36 (overlapping dt); J_{2-H,1-F} 3.6 Hz, J_{2-H3-F} 7 Hz.

X-Ray Crystallographic Study.—X-Ray single-crystal diffraction experiments were performed on a Rigaku AFC6S four-circle diffractometer (graphite monochromated Mo-Kα radiation, 2θ/ω scan mode), using Cryostream liquid nitrogen

* 1 inch = 2.54 cm.

open-flow gas cryostat¹⁶ for low-temperature studies. For **3**, the data were originally collected at room temperature, but the crystal was slowly decomposing during the exposure (three standard reflections showed 18% loss of intensities), thus affecting the quality of the data. No absorption correction was made for **3** and **4**; for **5** semi-empirical absorption correction¹⁷ was applied (108 ψ -scans of three reflections, $T_{\min}:T_{\max} = 0.9439$) using TEXSAN software,¹⁸ with insignificant effect. The structures were solved by direct methods, using SHELXS-86 programs.¹⁹ All non-hydrogen atoms were refined by full-matrix least-squares analysis with anisotropic displacement parameters, and H atoms were refined in isotropic approximation. The refinement of **3** and **4** was performed by SHELXLPLUS programs²⁰ and was based on F^2 's of the observed reflections [having $I > 2\sigma(I)$] with the $w = [\sigma^2(F) + 0.0002F^2]^{-1}$ weights; that of **5** was performed by SHELXL-93 programs²¹ and was based on F^2 's of all reflections, with the weights $w = [\sigma^2(F) + (0.0455P)^2 + 0.32P]^{-1}$, where $P = [\max(F^2, 0) + 2F^2]/3$. For **4**, difference Fourier map revealed additional peaks of electron density on bond distances from C(11) and C(12). Therefore we supposed the crystal to be a solid solution of **4** with a small amount of **3**, with the positions of all but O and two F atoms coinciding. The extra peaks were refined as atoms O(12), F(11) and F(21) in isotropic approximation. The refinement of occupancies yielded 90.2(5)% for **4** and 9.8(5)% for **3**. This assumption was later confirmed by chromatographic isolation of **3** from the crystals of **4** and its X-ray characterisation.

Crystal data and other experimental details are presented in Table 2. The additional material, available from the Cambridge Crystallographic Data Centre, comprises atomic coordinates and thermal parameters, full tables of bond distances and angles, and all the results of room temperature study of **3**, which exhibits no systematic differences from the low temperature results, apart from the higher thermal librations.

Acknowledgements

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