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Unsaturated nitrogen compounds containing fluorine. Part 20. Reactions of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene and hexafluoroacetone azine with cycloheptatriene ☆

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Abstract

Thermal reaction (70 °C) of the dichloroazine $CF_3CCl{=}NN{=}CClCF_3$, **1**, with cycloheptatriene (**7**) gave a complex mixture from which the major products were separated and identified as the dehydrochlorinated rearranged [3+2] cycloadducts **9** (28%) and **10** (23%) containing a $CF_3CHClN<$ group, a rearranged 1:1 adduct (**12** or **13**) (4%) and the amide **14** (18%) formed by hydrolysis on silica gel of the rearranged [3+6] cycloadduct **31** containing a $CF_3CCl_2N<$ group. At 100 °C in solvent CH_2Cl_2, the isolated products were the isomers **9** (4%), **10** (4%) and **11** (5.5%), amide **14** (1%) and the reduced compounds **15** (6%) and **16** (19%) containing a CF_3CH_2N group. Reaction between hexafluoroacetone azine $(CF_3)_2C{=}NN{=}C(CF_3)_2$ (**5**) and **7** at 70 °C was much cleaner and gave the bis[3+2] criss-cross cycloadduct **18** (15%), the bis-ene adduct **20** (17%) and the azo compound **19** (21%) together with the imine **17** (20%) formed from the oxidation of **20** by azine **5** and the [3+6] cycloadduct, the diaziridine **21** (7%).

Keywords: Unsaturated nitrogen compounds; Dichlorohexafluorodiazahexadiene; Hexafluoroacetone azine; NMR spectroscopy; IR spectroscopy; Mass spectrometry

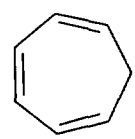
1. Introduction

1,3-Dipolar cycloaddition of the dichloroazine **1** to a range of cycloalkenes and cyclodienes has been reported recently [1,2]. The initial [3+2] cycloadducts, the azomethine imides **2a**, rearrange to adducts **3** containing a $CF_3CCl_2N<$ grouping and these are readily hydrolysed on silica gel to the corresponding amides **4** containing a $CF_3CON<$ grouping (Scheme 1).

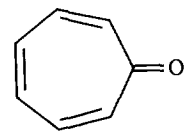
The corresponding azomethine imides **2b**, derived from [3+2] cycloaddition reactions of hexafluoroacetone azine (**5**) with alkenes, are isolable in certain cases, but they can react further with an excess of alkene to afford bis[3+2] criss-cross cycloadducts **6** (see, for example, Refs. [3,4]) (Scheme 2).

In a continuation of a study of the cycloaddition chemistry of azines **1** and **5**, their reactions have been investigated with cycloheptatriene (**7**), a dipolarophile for which concerted [3+2] and [3+6] cycloaddition are both thermally allowed processes. Although 1,3-dipolar cycloadditions to **7** have been little investigated, cycloadditions to the related compound cyclohepta-2,4,6-trienone (tropone) (**8**) are well documented, e.g. reactions with benzonitrile oxide ($PhC{\equiv}\overset{+}{N}{-}\overset{-}{O}$) [5] and diphenylnitrilimine ($PhC{\equiv}\overset{+}{N}{-}\overset{-}{N}Ph$) [6] both gave [3+2] and [3+6] cycloadducts in the ratio 89:6 and 89:11, respectively.

$CF_3CCl{=}NN{=}CClCF_3$ (**1**) $(CF_3)_2C{=}NN{=}C(CF_3)_2$ (**5**)



(**7**)



(**8**)

2. Results and discussion

The results obtained from the reactions of azines **1** and **5** with cycloheptatriene (**7**) are summarized in Table 1.

☆ For Part 19, see Ref. [1]; for preliminary communication, see Ref. [2].

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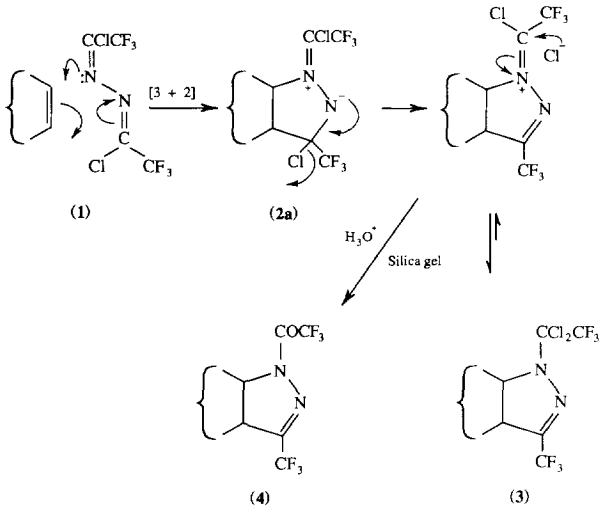
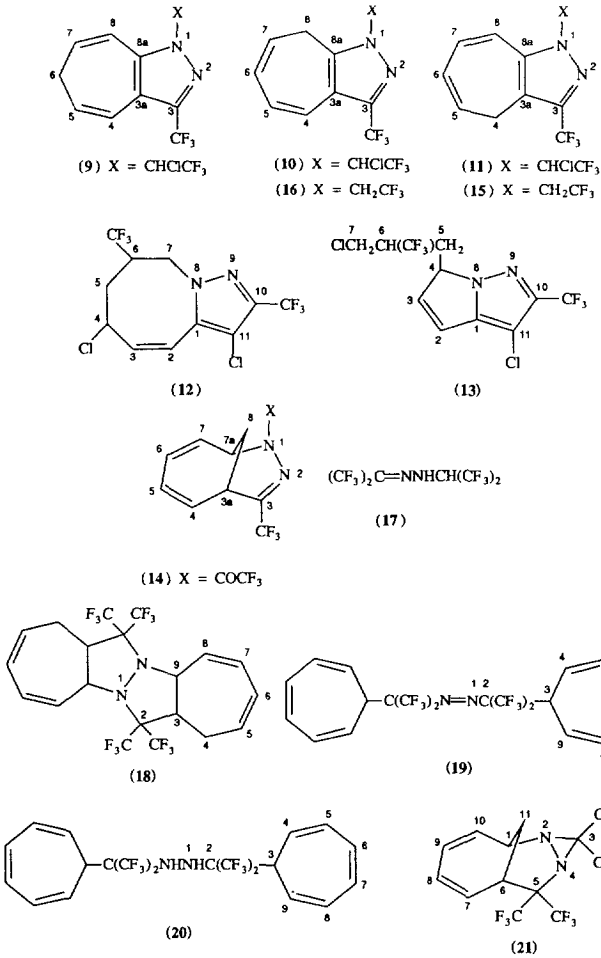


Scheme 1.



Both reactions involving the dichloroazine **1** gave complex mixtures of products from which only the major components could be isolated by chromatography.

The three isomers **9**–**11** are considered to have been formed via an initial [3+2] cycloaddition to give the azomethine imide **22**. Elimination of chloride ion from **22** afforded the immonium chloride **23**, which rearranged to the immonium chloride **24**. Dehydrochlororination of **24** then gave compound **11**. Isomers **9** and **10** could have arisen from **11** by acid-catalysed rearrangement, i.e. proton shifts, or by 1,5-[H] shifts. It is evident that rearrangement of the intermediate immonium chloride **23** to **24** is favoured over formation of the rearranged adduct **25** and hence the amide **26** (Scheme 3), as observed for the corresponding immonium chlorides derived from [3+2] cycloaddition of azine **1** to cycloalkenes and cyclodienes [1,2].

It has been observed that with azomethine imides derived from hexafluoroacetone azine **5** and C_5–C_7 cycloalkenes [7] or terminal alkenes containing bulky groups, e.g. Me_3C–, Me_2CH– [8,9], rearrangement to 1*H*-3-pyrazolines (analogous to the rearrangement of **23** to **24**) could compete with criss-cross adduct formation.

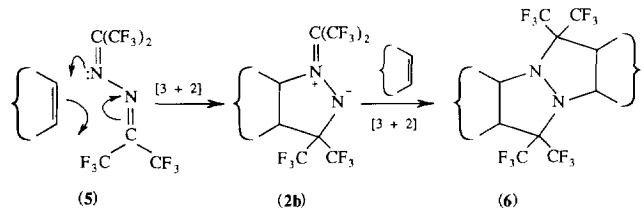
Compounds **15** and **16** were only detected in the products from reaction at 100 °C and are believed to have been formed from compound **11** via the intermediacy of the immonium chloride **27**. An intermolecular hydride shift from cycloheptatriene (**7**) to **27** would afford compound **15** and tropylium chloride (**28**). Rearrangement of **15** by acid catalysis or by a 1,5-[H] shift would then give its isomer **16** (Scheme 4). Cycloheptatriene (**7**) and its derivatives are reported to donate the hydride ion readily to a variety of carbocation acceptors [10,11].

A rearranged 1:1 adduct was isolated as a mixture of two diastereomers in the ratio 77:23 (NMR spectroscopy) from the reaction carried out at 70 °C. It was not possible to differentiate between structures **12** and **13** on the basis of the spectral data obtained (see later). The formation of compound **12** or **13** requires considerable skeletal rearrangement of any initial [3+2] or [3+6] cycloadduct and a satisfactory mechanism cannot be proposed.

The remaining isolated product, amide **14**, was formed by initial [3+6] cycloaddition to give the azomethine imide **29** which underwent rearrangement via the immonium chloride **30** to the adduct **31**. Hydrolysis of adduct **31** then took place during separation on silica gel (Scheme 5). The [3+6] cycloaddition was apparently more favoured at 70 °C than at 100 °C.

In both reactions, [3+2] cycloaddition was much favoured over [3+6] cycloaddition (ratio ca. 3:1 at 70 °C and ca. 40:1 at 100 °C), presumably because of the higher steric demand in the [3+6] transition state relative to that in the [3+2] process [12].

The reaction of azine **5** with **7** at 70 °C was much cleaner than the corresponding azine **1** reaction and the products were formed by three distinct mechanistic pathways, i.e. regio-

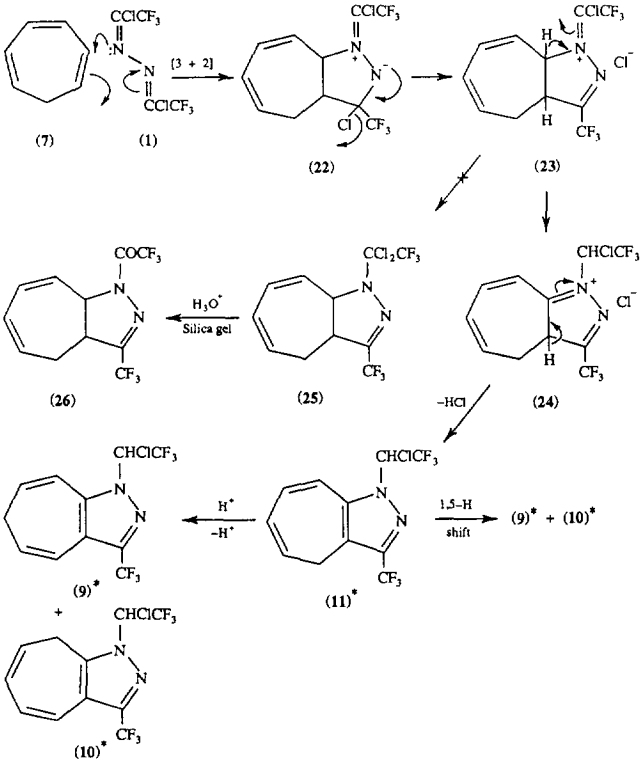


Scheme 2.

Table 1
Reactions of azines **1** and **5** with cycloheptatriene (**7**) (ca. 1:2 molar ratio)

Azine	Conditions		Recovered reactants		Products (%) [b]
	Temp. (°C)	Time (d)	Azine (%)	**7** (%)	
1	70	20	77	89	**9** (28); **10** (23); **12** or **13** (4) [c]; **14** (18)
1 [a]	100	14	82	91	**9** (4); **10** (4); **11** (5.5); **14** (1); **15** (6); **16** (19)
5	70	8	28	49	**17** (20); **18** (15); **19** (21); **20** (17) [d]; **21** (7)

[a] In solvent dichloromethane.
[b] Based on azine **1** or **5** reacted, i.e. not recovered.
[c] Mixture of two diastereomers in the ratio 77:23.
[d] Mixture of D,L and meso isomers in the ratio 1:1.



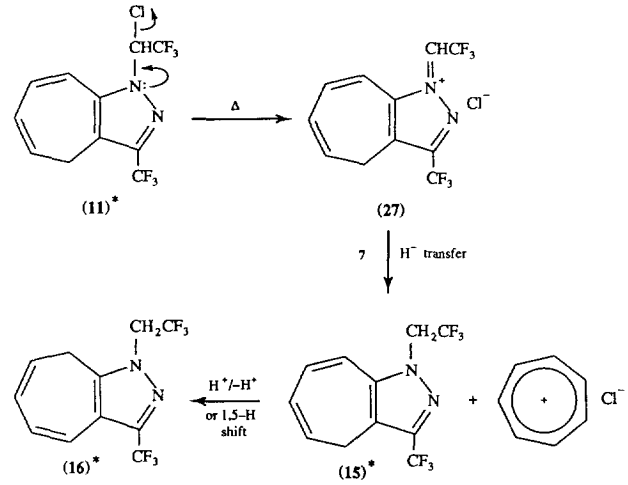
* Identified products.

Scheme 3.

selective [3+2] cycloaddition leading to the 'criss-cross' 2:1 adduct **18**, an ene reaction leading to the bis-ene adduct **20** and its oxidation product (the azo compound **19**) and [3+6] cycloaddition leading to the diaziridine **21**, in the ratio 15:38:7 (Scheme 6).

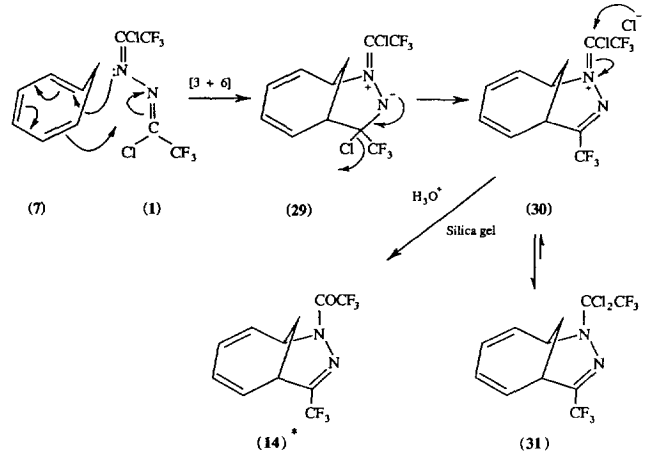
Initial [3+2] cycloaddition gave the azomethine imide **32** which underwent further reaction with **7** to afford the symmetrical bis[3+2] cycloadduct **18**. The direction of addition of both azine **5** and 1,3-dipole **32** to **7** is consistent with the two cycloadditions being LUMO (1,3-dipole)–HOMO (triene **7**) controlled, in agreement with the regioselectivity generally observed for other [3+2] cycloadditions of azine **5** and azomethine imides derived from **5** to unsymmetrical electron-rich alkenes (see, for example, Refs. [3,4,13]).

The favoured process was the ene reaction and, since only the bis-ene adduct **20** was detected, the initial mono-ene adduct **33** must undergo facile reaction with **7**. The ^{19}F NMR spectrum of compound **20** showed that it was a 1:1 mixture of the d,l (**20a**) and meso (**20b**) isomers in solution ($CDCl_3$) and it is believed that the two isomers are interconvertible by inversion at nitrogen, with the inversion being slow on the



* Isolated products.

Scheme 4.



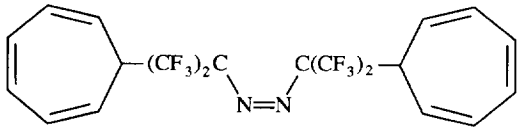
* Isolated product.

Scheme 5.

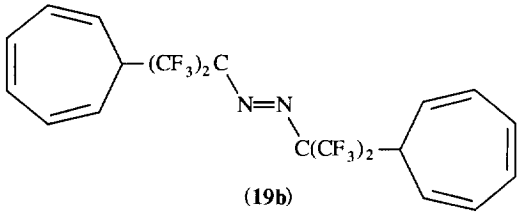
NMR time scale. Comparable slow nitrogen inversions in hydrazines are well documented [14–16].

A proportion of the bis-ene adduct **20** was oxidised to the corresponding azo compound **19** by azine **5** with the concomitant formation of the 1,2-reduction product of the azine, the imine **17**. The azo compound **19** was formed as a single isomer (NMR spectroscopy), but it is not known whether it is the (*E*)- or (*Z*)-isomer and attempts to obtain crystals suitable for an X-ray structural determination were unsuccessful. A concerted oxidation of **20** by azine **5** via a six-centre transition state would lead to the (*Z*)-isomer **19a**, while a non-concerted oxidation could lead to isomer **19a** or the (*E*)-isomer **19b**.

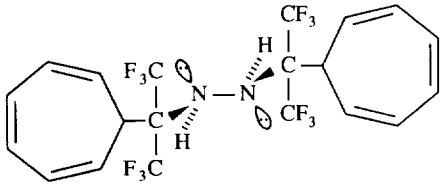
A noteworthy feature of the reaction was that the isolated [3+6] cycloadduct was not the azomethine imide **34** but its ring-closed isomer, diaziridine **21**. Azomethine imides formed by [3+2] cycloaddition between azine **5** and alkenes or dienes do not cyclise to diaziridines and this is considered to be a consequence of the greater stability of the bicyclo[3.1.0]diazaheptane system **35** relative to the bicyclo[2.1.0]diazahexane system **36**.



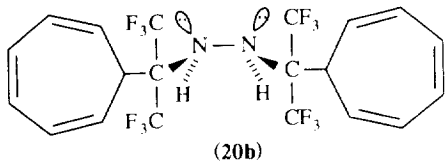
(19a)



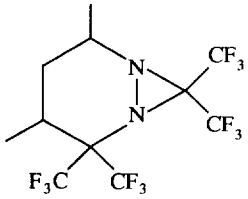
(19b)



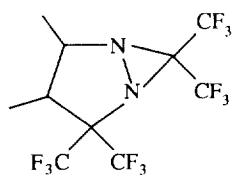
(20a)



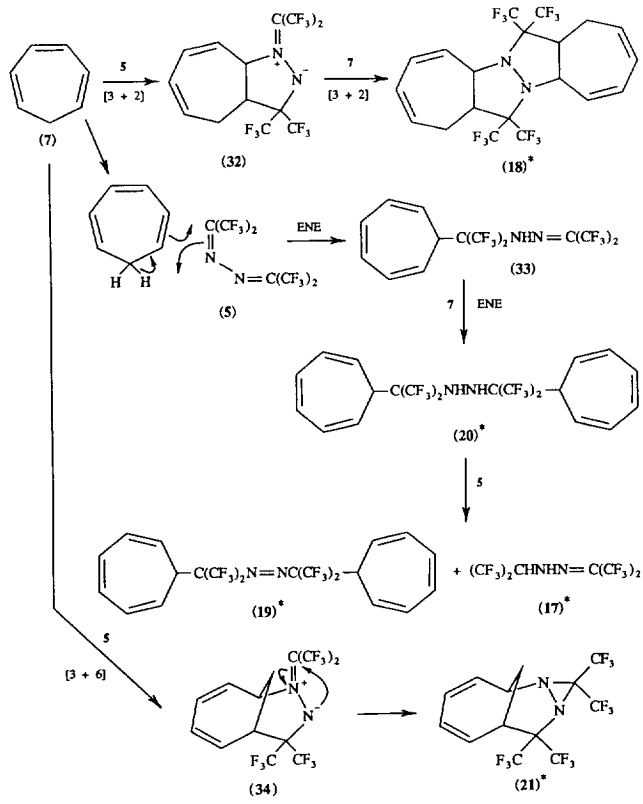
(20b)



(35)



(36)



* Isolated products.

Scheme 6.

In this reaction, [3+2] cycloaddition was less favoured relative to [3+6] cycloaddition (ratio ca. 2:1) than in the corresponding reaction of azine **1** with **7** at 70 °C (ratio ca. 3:1).

Satisfactory accurate mass measurements were obtained on all the new compounds except **17** and **19**, and an FAB mass spectrum of **19** showed a molecular ion peak as the highest mass peak. The structures were assigned on the basis of the following spectral evidence.

The ^1H and H,H COSY NMR spectra of compounds **9–11**, **15** and **16** showed that a $CH{=}CHCH_2CH{=}CH$ chain was present in compound **9**, while a $CH{=}CHCH{=}CHCH_2$ chain was present in the remaining compounds. Furthermore, the ^1H and ^{13}C NMR absorptions for the CH_2-8 group (δ_C: 24.6–24.8 ppm. δ_H: 3.25–3.45 ppm) in compounds **10** and **16** were at lower field (nearer to nitrogen) than the corresponding absorptions for the CH_2-4 group (δ_C: 21.8–22.0 ppm. δ_H: 3.10–3.18 ppm) in compounds **11** and **15**. A pyrazole ring $\overline{C{=}C{-}NRN{=}C}CF_3$ was also present in all the compounds [δ_C: 128–133 (C-3a in **9–11**); ca. 116.5 (C-3a in **15/16**); 138–143 (C-8a); ca. 140 (q, C-3, ^2J=37–38 Hz); ca. 121 (q, CF_3-3, ^1J=270–277 Hz) ppm] and the R group was identified as CF_3CHCl in compounds **9–11** [δ_H: ca. 6.5 (q, J_{CF-H}=ca. 5 Hz) ppm. δ_F: ca. +3 (d, J=ca. 5 Hz) ppm. δ_C: 125–121 (q, CF_3, ^1J=ca. 285 Hz); 68–67 (q, CHCl, ^2J=ca. 40 Hz) ppm] and CF_3CH_2 in compounds **15** and **16** [δ_H: ca. 4.7 (q, J_{CF-H}=ca. 8 Hz) ppm. δ_F: ca. +7.1 (t, J=ca. 8 Hz)

ppm. δ_C: 122.7 (q, CF_3, ^1J=ca. 280 Hz); ca. 51 (q, CH_2, ^2J=35.5 Hz) ppm].

The NMR spectra (including H, H COSY) of the 1:1 adduct, assigned structure **12** or **13** and present as a mixture of two diastereomers, showed that the chain $CH{=}CHCHXCH_2CH(CF_3)CH_2Y$ was present, where X and Y are N or Cl, together with a $CF_3C{=}NNC{=}CCl$ chain [δ_C: 120.6 (q, CF_3, ^1J=271 Hz); 142.0 (q, C=N, C-10, ^2J=37 Hz); 139.3 (NC=, C-1); 118.3 (ClC=, C-11) ppm]. It was not possible from the spectra to differentiate between structures **12** and **13**. The ^{1}H NMR splitting (tqd) of the methine proton (H-6) in the $CHCF_3$ group was due to coupling with the CH_2Y protons (H-7), the CF_3 fluorines and one proton in the CH_AH_B (H-5) group, respectively. This evidence is in favour of structure **12** where the H-5 group is in a ring, because for structure **13**, where the H-5 group is part of a side-chain, coupling of both protons in the H-5 group to the methine proton (H-6) would be expected. However, in the mass spectrum a peak was present at *m/z* 185 $(M-Cl-CF_3CHCH_2Cl)^+$, together with a base peak at *m/z* 49/51 (CH_2Cl^+), and these are better explained by structure **13**.

The NMR spectra (including H, H COSY) of amide **14** showed the presence of (i) the ring $\overline{CH{=}CHCH{=}CHCH}CH_aH_bCH$ containing four non-equivalent vinylic =CH groups, two coupled bridgehead CH groups, one adjacent to nitrogen (CH-7a: δ_H: 5.36 ppm. δ_C: 47.9 ppm) and the other adjacent to carbon (CH-3a: δ_H: 3.64 ppm. δ_C: 31.0 ppm), and a bridging CH_aH_b group (CH_2-8: δ_H: 2.21/2.07 ppm. δ_C: 22.4 ppm), (ii) a $CF_3C{=}N$ group [δ_C: 143.2 (q, C=N, C-3, ^2J=ca. 35 Hz); 119.9 (q, CF_3, ^1J=ca. 276 Hz) ppm] and (iii) a CF_3CON group [δ_C: 156.7 (q, NC=O, ^2J=39 Hz); 115.9 (q, CF_3, ^1J=287 Hz) ppm. IR (ν_{max}) (cm^{-1}): 1720 (s, C=O str.)]. This data confirmed that cycloaddition had taken place across the termini of the conjugated π-system in cycloheptatriene (**7**).

The imine **17** was identified in a mixture with azine **5** by spectral bands for the groups NH [δ_H: 9.89 ppm. IR (ν_{max}) (cm^{-1}): 3340 (m, N–H str.)], $(CF_3)_2CH$ [δ_H: 5.76 (septet, J_{CF-H}=6.5 Hz) ppm. δ_F: +8.0 (d, J_{H-CF}=6.5 Hz) ppm. δ_C: 118.0 (q, CF_3, ^1J=275 Hz); 63.2 (septet, CH–N, ^2J=32 Hz) ppm] and $(CF_3)_2C{=}N$ [δ_F: +13.0/+12.0 (2q, $2CF_3$, J=10 Hz) ppm. δ_C: 129.6 (septet, C=N, ^2J=38 Hz); 122.5/118.5 (2q, $2CF_3$, ^1J=282/280 Hz) ppm].

The NMR spectra (including H, H COSY) of compound **18** showed it was a symmetrical bis[3+2] cycloadduct containing the ring $N{-}\overline{CH{-}CH{=}CHCH{=}CHCH_2}{-}CH{-}C$ with absorptions for four non-equivalent vinylic =CH groups, an N–CH group (CH-9) [δ_H: 4.23 (d, J_{3-9}=ca. 10 Hz) ppm. δ_C: 62.8 ppm], the proton of which was coupled to an adjacent methine proton (H-3) bonded to CH_2 (CH-4) [δ_H: 3.55 (dt, H-3, J_{9-3}=ca. 10 Hz, J_{4-3}=ca. 5 Hz); 2.36 (t, H-4) ppm. δ_C: 55.2 (C-3); 25.7 (C-4) ppm]. The grouping $(CF_3)_2C$–N was also present [δ_F: +18.2/+8.9 (2q, $2CF_3$, J=ca. 10 Hz) ppm. δ_C: 123.7/122.8 (2q, $2CF_3$, ^1J=ca. 297/ca. 284 Hz); 67.3 (septet, C–N, ^2J=27.5 Hz) ppm].

The azo compound **19** and the hydrazine **20** were both shown by the spectral data (including H, H COSY NMR) to be 1-substituted cyclohepta-2,4,6-trienes with the methine proton (H-3) coupled equally to two adjacent vinylic protons (H-4/9). The ^{13}C chemical shift for C-3 (δ_C: ca. 40 ppm) in both compounds was consistent with a carbon atom adjacent to a $(CF_3)_2C$ group. The group $(CF_3)_2C{-}N{=}$ [δ_F: +11.9 ($2CF_3$) ppm. δ_C: 122.5 (q, $2CF_3$, ^1J=271 Hz); 81.2 (septet, C–N, C-2, ^2J=24 Hz) ppm] was present in compound **19**, while the group $(CF_3)_2C{-}NH$ [δ_H: 7.40 (br., N–H) ppm. δ_C: 69.0 (septet, C–N, C-2, ^2J=27.5 Hz) ppm. IR (ν_{max}) (cm^{-1}): 3400 (m, N–H str.)] was present in compound **20**. The ^{19}F and ^{13}C NMR spectra of hydrazine **20** showed that it was a 1:1 mixture of the d,l and meso isomers with absorptions for the non-equivalent CF_3 groups in the d,l isomer **20a** at δ_F: +13.9/+11.6 (2q, 2×3F, $2CF_3$, J=ca. 6 Hz) ppm and δ_C: 125.2/123.1 (2q, $2CF_3$, ^1J=271/272 Hz) ppm and for the equivalent CF_3 groups in the meso isomer **20b** at δ_F: +7.9 (s, 6F, $2CF_3$) ppm and δ_C: 117.8 (q, $2CF_3$, ^1J=281 Hz) ppm.

The 1:1 adduct, diaziridine **21**, showed NMR absorptions for a cycloheptadiene ring comparable to those observed for compound **14**, i.e. four non-equivalent =CH groups, two bridgehead CH groups, one of which was adjacent to nitrogen, and a bridging CH_aH_b group were present. This confirmed that the product was a [3+6] cycloadduct. A $(CF_3)_2C{-}N$ grouping was also present [δ_F: +14.3/+3.2 (2q, 2×3F, $2CF_3$, J=ca. 10 Hz) ppm. δ_C: 85.7 (septet, $\rangle C{-}N$, C-5, ^2J=27 Hz) ppm], together with a $(CF_3)_2C{=}N$ or $N{-}C(CF_3)_2{-}N$ grouping [δ_F: +19.4/+12.6 (2q, 2×3F, $2CF_3$, J=ca. 8 Hz) ppm. δ_C: 112.6 (septet, C=N or N–C–N, ^2J=36.4 Hz) ppm]. However, the absence of a strong IR absorption at ca. 1500 cm^{-1} ($\rangle C{=}\overset{+}{N}{-}\overset{-}{N}-$ str.), as expected for the azomethine imide **34** and observed for other azomethine imides derived from azine **5** [3,4], indicated that the product was the ring-closed diaziridine **21**.

3. Experimental details

3.1. Starting materials

The dichloroazine **1** was prepared by reaction of trifluoroacetic acid with hydrazine (2:1 molar ratio) to give the bishydrazide $CF_3CONHNHCOCF_3$ which was treated with phosphoryl chloride and *N,N*-dimethylaniline hydrochloride [17,18]. Hexafluoroacetone azine (**5**) was synthesised by reaction of hexafluoroacetone with hydrazine (2.5:1 molar ratio) to give the 2:1 adduct $(CF_3)_2C(OH)NHNHC(CF_3)_2OH$ which was dehydrated with phosphoryl chloride [19]. Cycloheptatriene (**7**) was a commercial sample (Aldrich) and its purity was checked (^{1}H and ^{13}C NMR spectroscopy) before use.

3.2. General techniques

The reactions were carried out in vacuo in sealed Pyrex ampoules fitted with Rotaflo Teflon taps and the volatile material was collected in vacuo in a conventional vacuum system and then analysed, where necessary, by analytical-scale gas–liquid chromatography using a column (2 m) packed with Celite impregnated with Silicone SE30 (15% w/w) at 60 °C. The non-volatile residue was then examined by ^{19}F NMR spectroscopy and the major products were separated by dry column flash chromatography (DCFC) using silica gel (Kieselgel 60 GF_{254}) and eluants as given in the text (light petroleum refers to the petroleum ether fraction, b.p. 30–40 °C) either directly or after a preliminary fractional distillation at low pressure (1–2 mmHg). Further separation or purification of the products was effected by preparative-scale thin layer chromatography (TLC) using plates coated with silica gel (Kieselgel 60 GF_{254}) and eluants as described in the text. The pure compounds were then examined by IR spectroscopy (Perkin-Elmer DE 783 instrument); ^1H NMR spectroscopy (including H, H COSY) [Bruker AC-300 (300 MHz) spectrometer; external reference Me_4Si]; ^{19}F NMR spectroscopy [Bruker AC-200 (188.3 MHz) instrument; external reference CF_3CO_2H]; ^{13}C NMR spectroscopy (including DEPT 135°) [Bruker AC-300 (75.0 MHz) instrument with broad-band proton-decoupling and D_2O as the deuterium lock signal; external reference Me_4Si]; and mass spectrometry [Kratos MS25 or MS45 instruments for low-resolution spectra under electron impact (EI) or fast atom bombardment (FAB) conditions and a Kratos Concept IS instrument for accurate mass measurement with all instruments operating at 70 eV]. The NMR spectra were run as solutions in $CDCl_3$ and chemical shifts to low field of reference are designated positive.

3.3. Reactions of cycloheptatriene (7)

(a) With 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diaza-hexa-2,4-diene (1) at 70 °C

A mixture of dichloroazine **1** (8.00 g, 30.65 mmol) and cycloheptatriene (**7**) (6.00 g, 65.21 mmol), heated at 70 °C (20 d), gave a volatile material (11.52 g) shown (GLC and ^1H and ^{19}F NMR spectroscopy) to be a mixture of unchanged dichloroazine **1** (6.17 g, 23.64 mmol, 77% recovered) and unchanged cycloheptatriene (**7**) (5.35 g, 58.15 mmol, 89% recovered), and a black non-volatile residue (2.42 g) which consisted of five major products and a number of minor products (^{19}F NMR spectroscopy).

The major products were separated by DCFC (eluant: light petroleum/CH_2Cl_2 2:1 v/v) to afford the following fractions: (i) a viscous oil (0.74 g), which was purified by preparative-scale TLC (eluant: light petroleum/Et_2O 10:1 v/v) to give 1-(1-chloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-1*H*,6*H*-cyclohepta[1,2-*c*]pyrazole (**9**) (nc) (0.61 g, 1.93 mmol, 28%) (Analysis: Found: M^+, 316.0217. $C_{11}H_7ClF_6N_2$ requires: M, 316.0202); (ii) a viscous oil (0.60 g), which was purified by preparative-scale TLC (eluant: light petroleum/CH_2Cl_2 2:1 v/v) to afford 1-(1-chloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-1*H*,8*H*-cyclohepta[1,2-*c*]-pyrazole (**10**) (nc) (0.49 g, 1.55 mmol, 23%) (Analysis: Found: M^+, 316.0216. $C_{11}H_7ClF_6N_2$ requires: M, 316.0202); (iii) a viscous oil (0.13 g), which was purified by preparative-scale TLC (eluant: light petroleum/CH_2Cl_2 2:1 v/v) to give a compound identified as either 4,11-dichloro-6,10-bis(trifluoromethyl)-8,9-diazabicyclo[6.3.$0^{1,8}$]-undeca-2,9,11-triene (**12**) or 2-chloro-6-[(3-chloro-2-trifluoromethyl)propyl]-3-trifluoromethyl-4,5-diazabicyclo-[3.3.$0^{1,5}$]octa-1,3,7-triene (**13**) (nc) (0.09 g, 0.25 mmol, 4%) (Analysis: Found: M^+, 351.9965. $C_{11}H_8Cl_2F_6N_2$ requires: M, 351.9965) as two diastereomers in the ratio 77:23 (^1H and ^{19}F NMR spectroscopy); and (iv) a viscous oil (0.47 g), which was purified by preparative-scale TLC (light petroleum/CH_2Cl_2 2:1 v/v) to afford 1-trifluoroacetyl-3-trifluoromethyl-3a,7a-dihydro-1*H*,8*H*-cyclohepta[1,3-*c*]pyrazole (**14**) (nc) (0.38 g, 1.27 mmol, 18%) (Analysis: Found: M^+, 298.0539. $C_{11}H_8F_6N_2O$ requires: M, 298.0541).

(b) With 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diaza-hexa-2,4-diene (1) in dichloromethane at 100 °C

A mixture of dichloroazine **1** (8.00 g, 30.65 mmol), cycloheptatriene (**7**) (5.60 g, 60.87 mmol) and dichloromethane (13.3 g, 10.0 cm^3), heated at 100 °C (14 d), gave a volatile material (24.98 g) shown (GLC and ^1H and ^{19}F NMR spectroscopy) to consist of unchanged dichloroazine **1** (6.56 g, 23.13 mmol, 82% recovered), unchanged cycloheptatriene (**7**) (5.09 g, 53.33 mmol, 91% recovered) and dichloromethane (13.3 g, 100% recovered), and a black non-volatile residue (1.93 g) which was shown (^{19}F NMR spectroscopy) to contain eight major products and a number of minor products.

The non-volatile residue was distilled at low pressure (ca. 1 mmHg) using a nitrogen inlet and a receiver connected to a cold trap (−78 °C) to give fraction A (0.36 g) which condensed at −78 °C, fraction B (0.049 g), b.p. 30 °C/1 mmHg, fraction C (0.38 g), b.p. 40–50 °C/1 mmHg, fraction D (0.71 g), b.p. 50–70 °C/1 mmHg, and a dark sticky residue (0.39 g).

The fractions were examined by ^{19}F NMR spectroscopy which showed that fractions A and B and the residue were complex mixtures which contained no major components, but fractions C and D contained the same 10 major components in different proportions. Fractions C and D were combined and separated by DCFC (eluant: light petroleum/CH_2Cl_2 2:1 v/v) to give the following products: (i) a viscous oil (0.02 g); (ii) a viscous mixture (0.35 g) which was separated by preparative-scale TLC (eluant: light petroleum/CH_2Cl_2 2:1 v/v) into its three components (ratio 31:39:30; ^{19}F NMR spectroscopy) identified as compound **9** (0.100 g, 0.32 mmol, 4%), 1-(1-chloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-1*H*,4*H*-cyclohepta[1,2-*c*]pyrazole (**11**) (nc) (0.125 g, 0.40 mmol, 5.5%) (Analysis: Found: M^+, 316.0217. $C_{11}H_7ClF_6N_2$ requires: M, 316.0202) and compound **10** (0.096 g, 0.30 mmol, 4%); (iii) a viscous mixture

Table 2
^{1}H, ^{19}F and ^{13}C NMR spectral data

Compound	NMR δ (ppm) [a]
9	δ_H: 6.73 (d, 1H, H-8, J_{7-8} = 10.0 Hz); 6.69 (d, 1H, H-4, J_{5-4} = 9.8 Hz); 6.48 (q, 1H, CF_3CHCl, J_{CF_3-H} = 5.3 Hz); 5.80 (dt, 1H, H-7, J_{8-7} = 10.0 Hz, J_{6-7} = 7.0 Hz); 5.63 (dt, 1H, H-5, J_{4-5} = 9.8 Hz, J_{6-5} = 7.0 Hz); 2.62 (ABt, 1H, H-6A, J_{6B-6A} = 14.0 Hz, J_{5-6A} = J_{7-6A} = 7.0 Hz); 2.52 (ABt, 1H, H-6B, J_{6A-6B} = 14.0 Hz, J_{5-6B} = 7.0 Hz). δ_F: +15.6 (d, 3F, CF_3-3, J = 1.2 Hz); +3.9 (d, 3F, CF_3CHCl, J_{H-CF_3} = 5.3 Hz). δ_C: 142.6 (C-8a); 141.8 (q, C-3, ^{2}J = 37.4 Hz); 129.1 (C-3a); 128.6 (C-8); 123.0 (C-4); 121.0 (q, CF_3CHCl, ^{1}J = 282.6 Hz); 120.8 (q, CF_3-3, ^{1}J = 273.0 Hz); 119.0 (C-7); 115.3 (C-5); 67.2 (q, CF_3CHCl, ^{2}J = 39.9 Hz); 26.6 (C-6).
10	δ_H: 6.83 (d, 1H, H-4, J_{5-4} = 11.0 Hz); 6.52 (q, 1H, CF_3CHCl, J_{CF_3-H} = 5.5 Hz); 6.46 (dd, 1H, H-5, J_{4-5} = 11.0 Hz, J_{6-5} = 5.8 Hz); 6.17 (dd, 1H, H-6, J_{7-6} = 11.0 Hz, J_{5-6} = 5.8 Hz); 5.58 (dt, 1H, H-7, J_{6-7} = 11.0 Hz, J_{8-7} = 6.5 Hz); 3.43 (ABd, 1H, H-8A, J_{8B-8A} = 15.0 Hz, J_{7-8A} = 6.5 Hz); 3.36 (ABd, 1H, H-8B, J_{8A-8B} = 15.0 Hz, J_{7-8B} = 6.5 Hz). δ_F: +15.7 (d, 3F, CF_3-3, J = 1.3 Hz); +3.3 (d, 3F, CF_3CHCl, J = 5.5 Hz). δ_C: 140.4 (q, C-3, ^{2}J = 38.1 Hz); 138.2 (C-8a); 132.7 (C-3a); 129.1 (C-4); 128.6 (C-5); 121.3 (C-6); 121.0 (q, CF_3CHCl, ^{1}J = 287.8 Hz); 120.8 (q, CF_3-3, ^{1}J = 275.2 Hz); 68.0 (q, CF_3CHCl, ^{2}J = 39.4 Hz); 24.6 (C-8).
11	δ_H: 6.90 (d, 1H, H-8, J_{7-8} = 11.5 Hz); 6.62 (q, 1H, CF_3CHCl, J_{CF_3-H} = 5.3 Hz); 6.47 (dd, 1H, H-7, J_{8-7} = 11.5 Hz, J_{6-7} = 6.0 Hz); 6.13 (dd, 1H, H-6, J_{5-6} = 10.5 Hz, J_{7-6} = 6.0 Hz); 5.82 (dt, 1H, H-5, J_{6-5} = 10.5 Hz, J_{4-5} = 6.2 Hz); 3.14 (ABd, 1H, H-4A, J_{4B-4A} = 15.0 Hz, J_{5-4A} = 6.2 Hz); 3.06 (ABd, 1H, H-4B, J_{4A-4B} = 15.0 Hz, J_{5-4B} = 6.2 Hz). δ_F: +16.1 (3F, CF_3-3); +3.6 (d, 3F, CF_3CHCl, J_{H-CF_3} = 5.3 Hz). δ_C: 141.3 (C-8a); 140.2 (q, C-3, ^{2}J = 37.3 Hz); 132.8 (C-8); 128.6 (C-7); 127.8 (C-3a); 127.6 (C-6); 124.6 (q, CF_3CHCl, ^{1}J = 283.7 Hz); 121.0 (q, CF_3-3, ^{1}J = 275.6 Hz); 117.6 (C-5); 67.5 (q, CF_3CHCl, ^{2}J = 39.6 Hz); 21.8 (C-4).
12 or **13** (major isomer)	δ_H: 6.36 (mult., 2H, H-2/3); 5.78 (dt, 1H, H-4, J_{5A-4} = 12.0 Hz, J_{3-4} = J_{5B-4} = 5.5 Hz); 4.51 (tqd, 2H, H-6, J_{7-6} = 6.0 Hz, J_{CF_3-6} = 5.2 Hz, J_{5A-6} = 4.0 Hz); 3.53 (d, 2H, H-7, J_{6-7} = 6.0 Hz); 2.95 (mult., 2H, H-5). δ_F: +16.05 (d, 3F, CF_3-10, J = 1.1 Hz); +4.0 (d, 3F, CF_3-6, J_{H-CF_3} = 5.2 Hz). δ_C: 142.0 (q, C-10, ^{2}J = 37.3 Hz); 139.3 (C-1); 126.9 (C-2); 120.8 (q, CF_3-6, ^{1}J = 282.2 Hz); 120.6 (q, CF_3-10, ^{1}J = 270.6 Hz); 118.1 (C-11); 117.5 (C-3); 66.9 (q, C-6, ^{2}J = 39.8 Hz); 52.8 (C-4); 39.8 (C-7); 36.2 (C-5).
12 or **13** (minor isomer)	δ_H: 6.36 (mult., 2H, H-2/3); 5.78 (dt, 1H, H-4, J_{5A-4} = 12.0 Hz, J_{3-4} = J_{5B-4} = 5.5 Hz); 4.51 (tqd, 1H, H-6, J_{7-6} = 6.0 Hz, J_{CF_3-6} = 5.2 Hz, J_{5A-6} = 4.0 Hz); 3.62 (AB mult., 1H, H-7A, J_{7B-7A} = 12.0 Hz); 3.46 (ABd, 1H, H-7B, J_{7A-7B} = 12.0 Hz, J_{6-7B} = 6.0 Hz); 3.04 (mult., 1H, H-5A); 2.87 (mult., 1H, H-5B). δ_F: +16.0 (d, 3F, CF_3-10, J = 1.2 Hz); +4.1 (d, 3F, CF_3-6, J_{H-CF_3} = 5.2 Hz). δ_C: 141.7 (q, C-10, ^{2}J = 37.6 Hz); 139.3 (C-1); 127.0 (C-2); 120.8 (q, CF_3-6, ^{1}J = 282.2 Hz); 119.9 (q, CF_3-10, ^{1}J = 276.2 Hz); 118.1 (C-11); 117.4 (C-3); 67.1 (q, C-6, ^{2}J = 39.9 Hz); 52.8 (C-4); 40.0 (C-7); 36.4 (C-5).
14	δ_H: 6.12 (mult., 4H, H-4/5/6/7); 5.36 (mult., 1H, H-7a); 3.64 (dd, 1H, H-3a, J_{7a-3a} = 7.0 Hz, J_{4-3a} = 2.5 Hz); 2.21 (d mult., 1H, H-8a, J_{8b-8a} = 14.0 Hz); 2.07 (d mult., 1H, H-8b, J_{8a-8b} = 14.0 Hz). δ_F: +7.9 (3F, CF_3-3); +7.6 (3F, CF_3CO). δ_C: 156.7 (q, C=O, ^{2}J = 39.2 Hz); 143.2 (q, C-3, ^{2}J = 34.7 Hz); 129.0/128.6/127.5/127.2 (C-4/5/6/7); 119.9 (q, CF_3-3, ^{1}J = 275.6 Hz); 115.9 (q, CF_3CO, ^{1}J = 287.3 Hz); 47.9 (C-7a); 31.0 (C-3a); 22.4 (C-8).
15	δ_H: 6.68 (d, 1H, H-8, J_{7-8} = 11.5 Hz); 6.53 (dd, 1H, H-7, J_{8-7} = 11.5 Hz, J_{6-7} = 6.0 Hz); 6.04 (dd, 1H, H-6, J_{5-6} = 10.5 Hz, J_{7-6} = 6.0 Hz); 5.79 (dt, 1H, H-5, J_{6-5} = 10.5 Hz, J_{4-5} = 6.5 Hz); 4.72 (q, 2H, CF_3CH_2, J_{CF_3-H} = 8.3 Hz); 3.18 (d, 2H, H-4, J_{5-4} = 6.5 Hz). δ_F: +16.6 (3F, CF_3-3); +7.1 (t, 3F, CF_3CH_2, J_{H-CF_3} = 8.3 Hz). δ_C: 141.2 (C-8a); 138.6 (q, C-3, ^{2}J = 37.0 Hz); 132.1 (C-8); 128.8 (C-7); 126.7 (C-6); 122.7 (q, CF_3CH_2, ^{1}J = 280.3 Hz); 121.2 (q, CF_3-3, ^{1}J = 276.5 Hz); 116.4 (C-3a); 115.7 (C-5); 51.1 (q, CF_3CH_2, ^{2}J = 35.5 Hz); 22.0 (C-4).
16	δ_H: 6.80 (d, 1H, H-4, J_{5-4} = 11.5 Hz); 6.34 (dd, 1H, H-5, J_{4-5} = 11.5 Hz, J_{6-5} = 6.0 Hz); 6.13 (dd, 1H, H-6, J_{7-6} = 10.5 Hz, J_{5-6} = 6.0 Hz); 5.52 (dt, 1H, H-7, J_{6-7} = 10.5 Hz, J_{8-7} = 6.3 Hz); 4.75 (q, 1H, CF_3CH_2, J_{CF_3-H} = 8.2 Hz); 3.25 (d, 2H, H-8, J_{7-8} = 6.3 Hz). δ_F: +16.2 (3F, CF_3-3); +6.9 (t, 3F, CF_3CH_2, J_{H-CF_3} = 8.2 Hz). δ_C: 139.2 (q, C-3, ^{2}J = 37.2 Hz); 138.8 (C-8a); 129.0 (C-4); 127.3 (C-5); 122.7 (q, CF_3CH_2, ^{1}J = 280.1 Hz); 121.2 (q, CF_3-3, ^{1}J = 276.0 Hz); 121.6 (C-6); 120.3 (C-7); 117.0 (C-3a); 51.4 (q, CF_3CH_2, ^{2}J = 35.6 Hz); 24.8 (C-8).
17	δ_H: 9.89 (br., 1H, NH); 5.76 [septet, 1H, $(CF_3)_2CH$, J_{CF_3-H} = 6.5 Hz]. δ_F: +13.0/+12.0 [2q, 2×3F, $(CF_3)_2C$=N, $J_{CF_3-CF_3}$ = 10.0 Hz]; +8.04 [d, 6F, $(CF_3)_2CH$, J_{H-CF_3} = 6.5 Hz]. δ_C: 129.6 (septet, C=N, ^{2}J = 37.7 Hz); 122.5/118.5 (2q, $2CF_3$, ^{1}J = 281.6/279.9 Hz); 118.0 [q, $(CF_3)_2CH$, ^{1}J = 275.4 Hz]; 63.2 [septet, $(CF_3)_2CH$, ^{2}J = 32.0 Hz].
18	δ_H: 6.12/5.97 (2 mult., 2×2H, H-5/6/7/8); 4.23 (d, 1H, H-9, J_{3-9} = 10.2 Hz); 3.55 (dt, 1H, H-3, J_{9-3} = 10.2 Hz, J_{4-3} = 5.2 Hz); 2.36 (t, 2H, H-4, $J_{3-4} \sim J_{5-4}$ = 5.5 Hz). δ_F: +18.2 (q, 3F, J = 9.9 Hz); +8.9 (q, 3F, J = 9.9 Hz). δ_C: 132.3 (C-8); 131.2 (C-7); 130.5 (C-6); 126.3 (C-5); 123.7 (q, CF_3, ^{1}J = 296.8 Hz); 122.8 (q, CF_3, ^{1}J = 284.2 Hz); 67.3 (septet, C-2, ^{2}J = 27.5 Hz); 62.8 (C-9); 55.2 (C-3); 25.7 (C-4).
19	δ_H: 6.82 (t, 2H, H-6/7, J_{5-6} = J_{8-7} = 3.0 Hz); 6.34 (mult., 2H, H-5/8); 5.47 (dd, 2H, H-4/9, J_{5-4} = J_{8-9} = 9.0 Hz, J_{3-4} = J_{3-9} = 6.3 Hz); 2.35 (t, 1H, H-3, J = 6.3 Hz). δ_F: +11.9 (CF_3). δ_C: 131.0 (C-6/7); 125.4 (C-5/8); 122.5 (q, CF_3, ^{1}J = 271.0 Hz); 114.9 (C-4/9); 81.2 (septet, C-2, ^{2}J = 24.3 Hz); 41.1 (C-3).
20	δ_H: 7.40 (br., 1H, NH); 6.72 (t, 2H, H-6/7, J = 3.2 Hz); 6.19 (mult., 2H, H-5/8); 5.29 (dd, 2H, H-4/9, J_{5-4} = J_{8-9} = 8.8 Hz, J_{3-4} = J_{3-9} = 6.6 Hz); 2.20 (t, 1H, H-3, J_{4-3} = J_{9-3} = 6.6 Hz). δ_F: +13.9 (qd, 3F, $J_{CF_3-CF_3}$ = 5.8 Hz, J_{H-CF_3} = 2.8 Hz)/+11.6 (q, 3F, CF_3, $J_{CF_3-CF_3}$ = 5.8 Hz) (d,l isomer); +7.9 (6F, $2CF_3$) (meso isomer). δ_C: 131.1 (C-6/7); 125.7 (C-5/8); 125.2 (q, CF_3, ^{1}J = 271.0 Hz)/123.1 (q, CF_3, ^{1}J = 272.2 Hz) (d,l isomer); 117.8 (q, $2CF_3$, ^{1}J = 281.3 Hz) (meso isomer); 116.7 (C-4/9); 69.0 (septet, C-2, ^{2}J = 27.5 Hz); 40.3 (C-3).
21	δ_H: 6.06 (mult., 4H, H-7/8/9/10); 4.83 (t, 1H, H-1, $J_{10-1} \sim J_{11a-1}$ = 6.5 Hz); 3.27 (mult., 1H, H-6); 2.95 (dt, 1H, H-11a, $J_{11b-11a}$ = 13.0 Hz, J_{1-11a} = J_{6-11a} = 6.3 Hz); 2.38 (d, 1H, H-11b, $J_{11a-11b}$ = 13.0 Hz). δ_F: +19.4 (q, 3F, CF_3-3, $J_{CF_3-CF_3}$ = 7.8 Hz); +14.3 (q, 3F, CF_3-5, $J_{CF_3-CF_3}$ = 9.8 Hz); +12.6 (q, 3F, CF_3-3, J = 7.8 Hz); +3.2 (q, 3F, CF_3-5, J = 9.8 Hz). δ_C: 131.0/130.2/128.3 (C-8/9/10); 127.5 (q, C-7, ^{4}J = 5.3 Hz); 122.5 (q, CF_3, ^{1}J = 278.2 Hz); 120.4 (q, CF_3, ^{1}J = 276.8 Hz); 118.8 (q, CF_3, ^{1}J = 277.8 Hz); 117.2 (q, CF_3, ^{1}J = 280.6 Hz); 112.6 (septet, C-3, ^{2}J = 36.4 Hz); 85.7 (septet, C-5, ^{2}J = 27.0 Hz); 60.8 (C-1); 38.7 (q, C-6, ^{3}J = 4.8 Hz); 29.4 (C-11).

[a] Singlet absorptions unless stated otherwise.

Table 3
Mass spectral data

Compound	MS[a]; *m/z* (%, assignment) [b]
9	316/318 (100, M^+); 297/299 [19, $(M-F)^+$]; 281 [61, $(M-Cl)^+$]; 261 (14, $C_{11}H_6F_5N_2^+$); 247/249 [94, $(M-CF_3)^+$]; 211 [31, $(M-CF_3-HCl)^+$]; 199 [17, $(M-CF_3CHCl)^+$]; 143 [21, $(M-2CF_3-Cl)^+$]; 116 (28, $C_8H_6N^+$); 89 (23, $C_7H_5^+$); 69 (35, CF_3^+); 63 (14, $C_5H_3^+/C_4HN^+$); 51 (12, $C_4H_3^+$); 39 (14, $C_3H_3^+/C_2HN^+$).
10	316/318 (84, M^+); 297/299 (80); 281 (61); 261 (12); 247/249 (100); 212 [21, $(M-CF_3-Cl)^+$]; 199 (33); 169 (8, $C_7F_3N_2^+$); 151 (33, $C_7HF_2N_2^+$); 143 (36); 136 (12, $C_4H_3F_3N_2^+$); 116 (47); 89 (36); 69 (56); 63 (30); 51 (26); 39 (31).
11	316/318 (100, M^+); 297/299 (16); 281 (35); 261 (4); 247/249 (34); 211 (5); 199 (9); 143 (5); 116 (4); 89 (3); 69 (4); 51 (8); 39 (2).
12 or **13**	352/354/356 (24, M^+); 333/335/337 [2, $(M-F)^+$]; 317/319 [33, $(M-Cl)^+$]; 298/300 [9, $(M-F-Cl)^+$]; 282 [3, $(M-2Cl)^+$]; 213 [5, $(M-2Cl-CF_3)^+$]; 201 (14, $C_9H_8F_3N_2^+$); 186 (11, $C_8H_5F_3N_2^+$); 116 (7, $C_8H_6N^+$); 69 (17); 49/51 (100, CH_2Cl^+).
14	298 (31, M^+); 201 [47, $(M-CF_3CO)^+$]; 187 [12, $(M-CF_3CON)^+$]; 186 (38, $C_9H_7F_3N^+$); 149 (18, $C_5H_4F_3N_2^+$); 133 (17, $C_4F_3N_2^+$); 116 (15); 91 (63, $C_7H_7^+$); 77 (26, $C_6H_5^+$); 69 (100); 66 (47, $C_3H_2N_2^+$); 58 (25, C_2HFN^+); 51 (42); 42 (13, NCO^+); 39 (53); 31 (11, CF^+); 29 (31, CHO^+).
15	282 (10, M^+); 213 [7, $(M-CF_3)^+$]; 88 (13, $C_7H_4^+$); 86 (31, $C_7H_2^+$); 69 (5); 51 (100, $C_4H_3^+$).
16	282 (21, M^+); 281 [11, $(M-H)^+$]; 263 [4, $(M-F)^+$]; 213 (22); 143 [7, $(M-H-2CF_3)^+$]; 116 (3, $C_8H_6N^+$); 88 (14); 86 (88); 69 (8); 51 (100); 41 (9); 38 (9, C_2N^+); 27 (3, $C_2H_3^+$).
18	512 (23, M^+); 91 (1, $C_7H_7^+$); 88 (8); 86 (46); 49 (100, C_4H^+); 37 (4, C_3H^+); 27 (6).
19 [c]	510 (100, M^+); 241 (17, $C_{10}H_7F_6^+$).
20	512 (100, M^+); 377 (8, $C_{14}H_{10}F_9N_2^+$); 297 (10, $C_{12}H_{11}F_6N_2^+$); 271 (15, $C_{10}H_9F_6N_2^+$); 256 (6, $C_{10}H_8F_6N^+$); 241 (28, $C_{10}H_7F_6^+$); 221 (41, $C_{10}H_6F_5^+$); 201 (43, $C_9H_8F_3N_2^+$); 173 (18, $C_9H_8F_3^+$); 69 (12).
21	420 (100, M^+); 401 [17, $(M-F)^+$]; 351 [26, $(M-CF_3^+$]; 270 {37, $[M-(CF_3)_2C]^+$}; 242 {16, $[M-(CF_3)_2CH_2]^+$}; 159 (18, $C_6H_2F_3N_2^+$); 69 (40).

[a] EI spectra unless stated otherwise.
[b] Expressed as percentage of base peak.
[c] FAB spectrum.

(0.12 g), which was separated by preparative-scale TLC (eluant: light petroleum/CH_2Cl_2 2:1 v.v) into the hydrolysed 1:1 adduct **14** (0.027 g, 0.09 mmol, 1%) and a mixture (0.085 g) of three unidentified compounds; (iv) a solid, identified as 1-(2,2,2-trifluoroethyl)-3-trifluoromethyl-1*H*,*4H*-cyclohepta[1,2-*c*]pyrazole (**15**) (nc) (0.13 g, 0.46 mmol, 6%) (Analysis: Found: M^+, 282.0568. $C_{11}H_8F_6N_2$ requires: M, 282.0592); and (v) a solid, identified as 1-(2,2,2-trifluoroethyl)-3-trifluoromethyl-1*H*,*8H*-cyclohepta[1,2-*c*]pyrazole (**16**) (nc) (0.41 g, 1.45 mmol, 19%) (Analysis: Found: M^+, 282.0570. $C_{11}H_8F_6N_2$ requires: M, 282.0592).

(c) With hexafluoroacetone azine (5)

A mixture of the azine **5** (4.00 g, 12.20 mmol) and cycloheptatriene (**7**) (2.24 g, 24.35 mmol), heated at 70 °C (8 d), gave a volatile material (2.80 g) and a dark brown, non-volatile residue (3.44 g).

The volatile material formed two immiscible layers which were carefully separated (micropipette). The upper layer was identified as unchanged cycloheptatriene (**7**) (1.105 g, 12.01 mmol, 49% recovered), while the lower layer (1.695 g) was shown (NMR spectroscopy) to be a mixture of unchanged azine **5** (1.115 g, 3.40 mmol, 28% recovered) and 1,1,1,6,6,6-hexafluoro-2,5-bis(trifluoromethyl)-3,4-diaza-hex-2-ene (**17**) (nc) (0.58 g, 1.76 mmol, 20%).

The residue was shown TLC (eluant: light petroleum) to contain four major components A–D (R_F = 0.58; 0.46; 0.41; 0.20) and it was separated by DCFC (same eluant) to afford the following fractions: (i) fraction 1, a mixture of compounds A–C (0.95 g), which on storage (4 d) gave a solid precipitate (component A). This was separated by filtration, washed ($CHCl_3$, 2×5 cm^3) and identified as 2,2,11,11-tetrakis(trifluoromethyl)-1,10-diazatetracyclo[8.8.0.^{1,10}.0.^{3,9}O^{12,18}]octadeca-8,6,14,16-tetraene (**18**) (nc) (0.66 g, 1.29 mmol, 15%) (Analysis: Found: M^+, 512.1116. $C_{20}H_{16}F_{12}N_2$ requires: M, 512.1122). The filtrate (0.27 g) was a mixture of components B and C; (ii) fraction 2, a mixture (1.75 g) of components B and C, which was combined with the filtrate from fraction 1 and separated by preparative-scale TLC (same eluant) to give component B, identified as 2,5-bis(cyclohepta-2,4,6-trien-1-yl)-1,1,1,6,6,6-hexafluoro-2,5-bis(trifluoromethyl)-3,4-diaza-hex-3-ene (**19**) (nc) (0.92 g, 1.80 mmol; 21%) (Analysis: Found: M^+, 510. $C_{20}H_{14}F_{12}N_2$ requires: M, 510), and component C, identified as 2,5-bis(cyclohepta-2,4,6-trien-1-yl)-1,1,1,6,6,6-hexafluoro-2,5-bis(trifluoromethyl)-3,4-diaza-hexane (**20**) (nc) (0.73 g, 1.43 mmol, 17%) (Analysis: Found: M^+, 512.1095. $C_{20}H_{16}F_{12}N_2$ requires: M, 512.1122) as a mixture of the d,l and meso isomers in the ratio 1:1 (^{19}F

NMR spectroscopy); and (iii) fraction 3, a liquid (component D), which was identified as 3,3,5,5-tetrakis-(trifluoromethyl)-2,4-diazatricyclo[4.4.1.^{1,7}0^{2,4}]undeca-7,9-diene (**21**) (nc) (0.24 g, 0.57 mmol, 7%) (Analysis: Found: M^+, 420.0498. $C_{13}H_8F_{12}N_2$ requires: M, 420.0496).

The ^1H, ^{19}F and ^{13}C NMR spectra of the new compounds **9–11**, **12** or **13** and **14–21** are given in Table 2 and the mass spectra are summarized in Table 3. All of the products, except compound **17**, showed IR absorptions (ν_{max}) (cm^{-1}): 3040–3020 (m, vinylic C–H str.); 2980–2940 (m, aliphatic C–H str.); 1650–1615 (s, C=C and/or C=N str.); 1260–1100 (s, C–F str.); 840–790 (m, =C–H out-of-plane bending); ca. 740 (m, CF_3 def.).

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References

[1] M.M. Abdul-Ghani and A.E. Tipping, *J. Fluorine Chem., 73* (1995) 189.

[2] M.M. Abdul-Ghani and A.E. Tipping, *J. Fluorine Chem., 63* (1993) 5.

[3] K. Burger, W. Thenn and A. Gieren, *Angew. Chem., 86* (1974) 481; A. Gieren, P. Naryanan, K. Burger and W. Thenn, *Angew. Chem., 86* (1974) 482.

[4] T.P. Forshaw and A.E. Tipping, *J. Chem. Soc. C,* (1971) 2404; S.E. Armstrong and A.E. Tipping, *J. Chem. Soc., Perkin Trans. 1,* (1975) 538, 1411.

[5] D. Mukherjee, C.R. Watts and K.N. Houk, *J. Org. Chem., 43* (1978) 817.

[6] K.N. Houk and C.R. Watts, *Tetrahedron Lett.,* (1970) 4025; M. Bonadeo, C. De Micheli and R. Gondolfi, *J. Chem. Soc., Perkin Trans. 1,* (1977) 939.

[7] S.E. Armstrong, T.P. Forshaw and A.E. Tipping, *J. Chem. Soc., Perkin Trans. 1,* (1975) 1902; K. Burger, H. Schickaneder, F. Hein and J. Elguero, *Tetrahedron, 35* (1979) 389.

[8] K. Burger, H. Schickaneder and J. Elguero, *Tetrahedron Lett.,* (1975) 2911.

[9] S.E. Armstrong and A.E. Tipping, *J. Chem. Soc., Perkin Trans. 1,* (1975) 538.

[10] G.A. Olah and P. von R. Schleyer (eds.), *Carbonium Ions,* Wiley-Interscience, New York, 1970.

[11] R.A.W. Johnstone, A.H. Wilby and I.D. Entwhistle, *Chem. Rev., 85* (1985) 129.

[12] C. De Micheli, R. Gondolfi and P. Gruenanger, *Tetrahedron, 30* (1974) 3765.

[13] D. Bell and A.E. Tipping, *J. Fluorine Chem., 66* (1994) 243.

[14] G.J. Bishop, B.J. Price and I.O. Sutherland, *Chem. Commun.,* (1967) 672; B.H. Korsh and N.V. Rigg, *Tetrahedron Lett.,* (1966) 5897.

[15] J.E. Anderson and J.M. Lehn, *J. Am. Chem. Soc., 89* (1967) 81; J.E. Anderson, D.L. Griffith and J.D. Roberts, *J. Am. Chem. Soc., 91* (1969) 6371.

[16] P. Ogden, *Chem. Commun.,* (1969) 1034.

[17] M.G. Barlow, D. Bell, N.J. O'Reilly and A.E. Tipping, *J. Fluorine Chem., 23* (1983) 293.

[18] D. Bell, A.O.A. Eltoum, N.J. O'Reilly and A.E. Tipping, *J. Fluorine Chem., 64* (1993) 151.

[19] K. Burger, J. Fehn and W. Thenn, *Angew. Chem., 85* (1973) 541.