Decisive Evidence for the Occurrence of Ring-expansion during Pyrolysis of Azidopentafluorobenzene: *X*-Ray Crystallographic Analysis of 'Pentafluorophenylnitrene Dimer'

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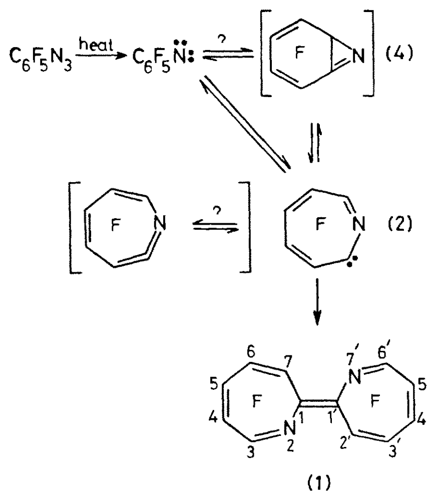
Summary Product analysis by *X*-ray crystallography has confirmed that gas-phase pyrolysis of azidopentafluorobenzene yields a diazaheptafulvalene [(*E*)-bi(pentafluoro-2-azacyclohepta-2,4,6-trien-1-ylidene) (**1**)], isolattion of which affords tangible evidence for an arylnitrene → 2-azepinylidene (direct ?) ring expansion

Resurgence of interest in mechanisms of thermal and photochemical transformations of aryl azides[1] prompts us to report that the orange solid (m p 118—120 °C) obtainable[2] in at least 10% yield by flow pyrolysis of nitrogen-diluted azidopentafluorobenzene in platinum at 300 °C and 760 mmHg has been shown by *X*-ray crystallography (see later) to be perfluoro-2,7'-diazaheptafulvalene (**1**) This work, which vindicates speculation[2] concerning the identity of 'pentafluorophenylnitrene dimer,' merits attention on several counts (i) from a mechanistic viewpoint, concrete evidence is available at last for ring-expansion of an aryl nitrene to an azacycloheptatrienylidene (**2**) (Scheme), as required in the Crow–Wentrup[3] pathway for high-temperature aromatic nitrene ⇌ carbene interconversions,[4] (ii) it should stimulate activity in the area of synthesis of diazaheptafulvalenes, membership of which class seems restricted to compound (**1**) at present, and (iii) further structural information on the theoretically interesting[5] non-alternant cross-conjugated 14 π-electron heptafulvalene system has become available As far as non-planarity is concerned, perfluoro-2,7'-diazaheptafulvalene (**1**) seems to be intermediate between heptafulvalene[6] and perchloroheptafulvalene,[7] all three molecules have S-shapes when viewed in the N(2)- or C(2)-to C(7) direction

Previously,[2] the compound isolated following vapour-phase pyrolysis of azidopentafluorobenzene was tentatively suggested to be the *Z*-isomer of (**1**) [*i e* perfluoro-2,2'-diazaheptafulvalene (**3**)] on the basis of elemental analysis, spectroscopic data (i r , ^{19}F n m r , and mass), and consideration of the literature dealing with nitrene ⇌ carbene[4] and carbene ⇌ carbene[4,8] interconversions of the aromatic class, particularly useful was a report[8a] dealing with the rearrangement of phenylcarbenes to cycloheptatrienylidenes, reorganizations which lead to the formation of heptafulvalenes

A scheme showing direct formation of perfluoro-2-azacyclohepta-2,4,6-trienylidene (**2**) from pentafluorophenylnitrene and its dimerisation [→ (**3**)] was deleted from the manuscript of ref 2(b) at the request of referees Even today the involvement of benzazirines[9] [*e g* (**4**)] in ring expansions of aryl azides remains hypothetical, and debate has also centred on the exact nature of the presumptive seven-membered heterocyclic species [*e g* (**2**)] generated [1,4]



SCHEME. 'F' within a ring indicates that hydrogen atoms have been replaced completely by fluorine.

That a dimerizable intermediate of the latter type can be produced *via* pyrolysis of an aryl azide is no longer in doubt following our identification of 'pentafluorophenylnitrene dimer' as perfluoro-2,7′-diazaheptafulvalene (**1**).

Crystal data: compound (**1**): $C_{12}F_{10}N_2$, triclinic, space group $P\bar{1}$, $a = 9{\cdot}63(1)$, $b = 9{\cdot}29(1)$, $c = 10{\cdot}50(1)$ Å, $\alpha = 46{\cdot}35(8)$, $\beta = 113{\cdot}71(8)$, $\gamma = 108{\cdot}47(5)°$, $Z = 2$. Intensities were measured with a Stoe two-circle diffractometer using monochromated Mo-K_α radiation within the range $0{\cdot}1 < \sin\,\theta/\lambda < 0{\cdot}6$ Å^{-1}. The structure was solved by direct methods with MULTAN[10] and refined by least-squares to $R = 9{\cdot}6\%$ for the 1161 reflections having $I > 3\sigma(I)$. There are two independent centrosymmetric molecules in the unit cell, the centres of the inter-ring bonds coinciding with crystallographic inversion centres.†

Each seven-membered ring adopts a boat-like conformation[11] with C(1) [or C(1′)] in a 'bow' position and C(4) and C(5) [or C(4′) and C(5′)] forming the 'stern'; ring shape can be described in terms of the three planes defined by atoms C(1), C(7), N(2); N(2),C(3),C(6),C(7); and C(3),C(4),C(5),C(6). These atomic groupings are each planar, and the angles which the first and third planes make with the second, the 'bow' and 'stern' angles, are 140 and 159°, respectively. Carbon–carbon bond lengths alternate in the sense predicted by the classical valence bond structure (**1**) (see Scheme). Carbon–fluorine bond lengths (mean 1·34 Å) are in good agreement with previous results.[11]

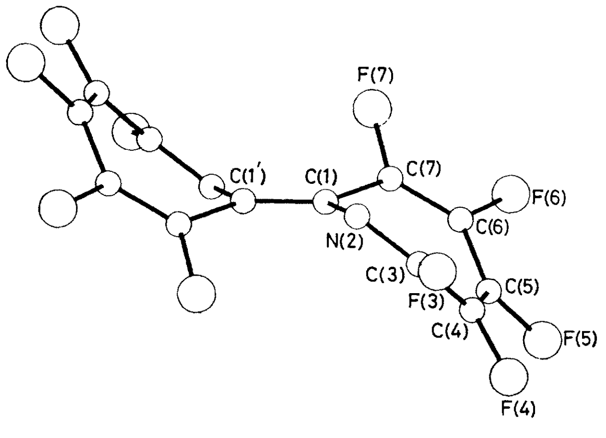


FIGURE. Conformation of the perfluoro-2,7′-diazaheptafulvalene molecule (**1**). Bond lengths (Å) averaged over the two independent centrosymmetric molecules are C(1)–C(1′), 1·35; C(1)–N(2), 1·41; N(2)–C(3), 1·27; C(3)–C(4), 1·42; C(4)–C(5), 1·33; C(5)–C(6), 1·43; C(6)–C(7), 1·34; C(7)–C(1), 1·46; C(3)–F(3), 1·33; C(4)–F(4), 1·34; C(5)–F(5), 1·33; C(6)–F(6), 1·34; C(7)–F(7), 1·35. Averaged intra-ring angles subtended at C(*n*) or N(2) are C(1), 117°; N(2), 124°; C(3), 130°; C(4), 126°; C(5), 127°; C(6), 125°; C(7), 126°. Estimated standard deviations are 0·01—0·025 Å for lengths and *ca.* 1° for angles.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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