

## A *para*-Bonded Isomer of an Aromatic Diazine

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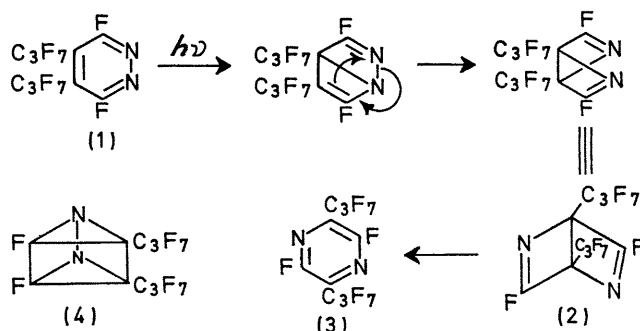
**Summary** Photolysis of perfluoro-(4,5-bis(isopropyl)pyridazine) (1) yields, in addition to perfluoro-(2,5-bis(isopropyl)pyrazine) (3), a *para*-bonded valence isomer (2).

In recent years there has been a number of surprising developments involving the isolation of valence isomers of benzene derivatives, and very recently *para*-bonded isomers of pyridine derivatives have been described.<sup>1</sup> We have previously observed<sup>2</sup> that fluorinated pyridazine derivatives undergo an unusual variety of rearrangement reactions and inferred the intermediacy of valence isomers. However, we now report the isolation of the first valence isomer of an aromatic diazine.

When perfluoro-(4,5-bis(isopropyl)pyridazine) (1) was irradiated in the gas phase (at 2537 Å) two major products were obtained, perfluoro-(2,5-bis(isopropyl)pyrazine) (3), which we have reported previously, and a component, of much shorter g.l.c. (di-isodecyl phthalate) retention time, to which we have assigned the structure (2). A ratio of 2:1, (2) to (3) respectively, has been observed, although the factors governing this ratio have not yet been fully established.

The i.r. spectrum of (2) shows a single strong absorption at 1680 cm<sup>-1</sup>, indicating either C=C or C=N, while the u.v. spectrum contains only end absorption. Nevertheless, a band in the <sup>19</sup>F n.m.r. spectrum at 37.05 p.p.m.† indicates -CF=N-, since the fluorine resonance of -CF=CF-, contained in a cyclic system, normally occurs in a much higher field region (>100 p.p.m.). Furthermore, since only one <sup>19</sup>F resonance arising from fluorine attached to unsaturated carbon (integrating for two fluorine atoms) is detected, there must be two equivalent, non-conjugated

-CF=N- groups. Only the *para*-bonded structure (2) fits these data, together with the fact that (2) slowly converts into (3) at room temperature and has a half-life of *ca.* 5 min at 100°. Consistent with structure (2) is the fact that no large coupling between -CF= (37.05 p.p.m.) and -CF(CF<sub>3</sub>)<sub>2</sub> (181.1 p.p.m.) is observed, although coupling would be expected if an arrangement, (CF<sub>3</sub>)<sub>2</sub>CF-C=CF- were present.<sup>3</sup> Also, two chemically shifted absorptions due to CF(CF<sub>3</sub>)<sub>2</sub> occur (74.2 and 75.7 p.p.m.) and it is probable that these arise from restricted rotation of the perfluoroisopropyl groups in (2), but this is difficult to confirm because of the limited temperature range before isomerisation to (3)



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becomes rapid. We have established that (2) is not produced from (3) under the reaction conditions.

† Chemical shifts are reported with reference to CFCl<sub>3</sub>.

We have previously described the photochemically-induced isomerisation of (1) to (3) and suggested the intermediacy of a diazaprismane (4) in order to account for the 1—3 shift in the relative positions of the nitrogen atoms.<sup>2</sup> Nevertheless, it is not possible to obtain (2) or (3) from the diazaprismane (4) without prior rearrangement and therefore isolation of the intermediate (2) confirms a mechanism

(see Scheme) put forward to explain a range of rearrangement reactions of polyfluoropyridazine derivatives.<sup>4</sup>

A trace of one other valence isomer has been detected which rearranges to (3) or (2) but it has not yet been identified.

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<sup>1</sup> K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, 1970, **92**, 2178; M. G. Barlow, J. G. Dingwall, and R. N. Haszeldine *Chem. Comm.*, 1970, 1580.

<sup>2</sup> C. G. Allison, R. D. Chambers, Yu. A. Cheburkov, J. A. H. MacBride, and W. K. R. Musgrave, *Chem. Comm.*, 1969, 1200.

<sup>3</sup> R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, 1970, **26**, 71.

<sup>4</sup> Paper presented by Dr. J. A. H. MacBride, Autumn Meeting of the Chemical Society, London, September, 1970.