X-Ray Crystal Structure Analysis of a 2*H*-Azirine. Unusually Long C–N Bond assuring Preferential C–N Bond Fission in Thermal Reactions

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Summary An *X*-ray crystal structure analysis of a 2*H*-azirine showed that its lopsided triangular structure, caused by an unusually long C–N bond, could explain the preferential C–N bond fission in thermal reactions of 2*H*-azirines.

It is well known that thermolysis of 2*H*-azirines proceeds by C–N bond fission to form vinyl nitrene intermediates which undergo intramolecular collapse into indoles, pyrroles, or isoxazoles, when a phenyl, an alkenyl, or an acyl group is substituted at the 2-position of the azirine ring.[1,2] Our recent investigation showed the versatility of 2*H*-azirines as starting materials for the synthesis of nitrogen-containing heterocycles in that pyridines and azepines were also formed *via* vinyl nitrenes.[3]

Our interest in this field, especially in easy and preferential C–N bond fission, prompted us to investigate the exact structure of the 2*H*-azirine ring system. Although an *X*-ray analysis was performed on the palladium(II) complex of 3-(*p*-methylphenyl)-2*H*-azirine by Hassner and his co-workers,[4] the molecular structure of 2*H*-azirine itself has not been determined.

We report here the molecular structure of 2,2-bis(*p*-methoxyphenyl)-3-methyl-2*H*-azirine (**1**), which was prepared by the thermal decomposition of the corresponding vinyl azide. Well-formed single crystals were grown from hexane.

Crystal data: $C_{17}H_{17}NO_2$, *M* 267·3, monoclinic, space group $P2_1/n$, $a = 9{\cdot}508(2)$, $b = 20{\cdot}226(4)$, $c = 8{\cdot}081(2)$ Å, $\beta = 109{\cdot}649(19)°$, $U = 1463{\cdot}5$ Å^3, $D_m = 1{\cdot}21$ g cm^{-3}, $D_c = 1{\cdot}21$ g cm^{-3} for $Z = 4$.

A Rigaku automated, four-circle diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0{\cdot}70926$ Å) was used for the measurement of lattice parameters and reflection intensities. Integrated intensities were measured by the θ–2θ scan method at a rate of 4° min^{-1} using a crystal with dimensions of *ca.* 0·25 × 0·30 × 0·30 mm. A total of 2598 (1764 non-zero) reflections were collected up to $2\theta = 50°$. Usual Lorentz and polarization corrections were made but no absorption correction was applied [μ(Mo-K_α) = 0·85 cm^{-1}].

The structure was solved by the direct method (MULTAN 74),[5] and refined anisotropically by the block-diagonal least-squares procedure (HBLS V).[6] All the hydrogen atoms were located in difference syntheses, and were included in the subsequent refinement with isotropic temperature factors. The final *R* value was 0·091 for the 1764 non-zero reflections. The atomic scattering factors used were taken from the International Tables for *X*-Ray Crystallography.[7]†

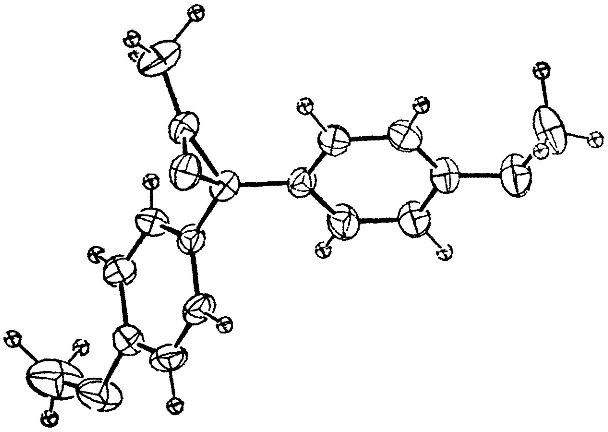

FIGURE 1. An ORTEP drawing of the molecular structure of 2,2-bis(*p*-methoxyphenyl)-3-methyl-2*H*-azirine (**1**). Thermal ellipsoids for non-hydrogen atoms are at 50% probability level. Hydrogen atoms are represented as spheres with diameter of 0·1 Å.

The molecular struture of (**1**) is shown in Figure 1.[8] Relevant bond lengths and bond angles are given in Figure 2. The skeleton of the molecule consists of a lopsided triangle, the asymmetry of which is more accentuated than that reported for the palladium(II) complex. The C(2)=N bond, 1·256(7) Å, is slightly shorter than normal non-conjugated C=N bonds, 1·29—1·31 Å.[9] It is worth comparing the two single bonds of (**1**) with those of cyclopropene and diazirine, which are also unsaturated 3-membered cyclic compounds. The C(1)–C(2) bond, 1·463(8) Å, is somewhat shorter than the corresponding C–C bond, 1·52 Å, in cyclopropene,[9] but the C(1)–N bond, 1·598(7) Å, is much longer than the C–N bond, 1·48 Å, in diazirine. The stretching of the C(1)–N bond and the shortening of the C(1)–C(2) bond would result from accommodation of the C(2)=N bond into the 3-membered ring and would reflect the weakness of the C–N bond, leading to easy and preferential C–N bond cleavage in the thermal reactions of 2*H*-azirines.

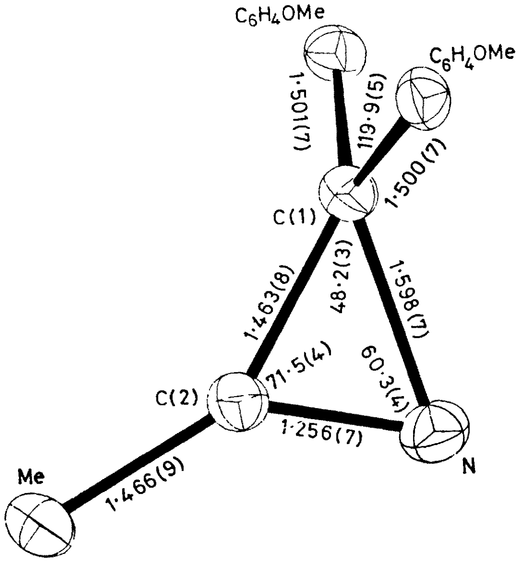

FIGURE 2. Selected bond lengths (Å) and bond angles (°) in the molecule. Estimated standard deviations in parentheses.

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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 Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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