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## A 1,5-Diazabicyclo[3.3.3]undecane Derivative with Almost Planar Bridgehead Nitrogens†

By ROGER W. ALDER\* and NIGEL C. GOODE

(School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS)

TREVOR J. KING

(Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD)

and JOHN M. MELLOR and BARRY W. MILLER

(Department of Chemistry, University of Southampton, Southampton SO9 5NH)

Summary The preparation, structure, and photoelectron spectrum of the naphtho-fused 1,5-diazabicyclo[3.3.3]-undecane, (1), are reported.

COMPOUNDS in which selected bond angles are expanded by strain are much less common than those with compressed bond angles, but derivatives of bicyclo[3.3.3]undecane show unusual properties due to this feature;<sup>1,2</sup> we report here an example with two bridgehead nitrogens.

The reaction of 1,3-dibromopropane with 1,8-diaminonaphthalene in DMF in the presence of Na<sub>2</sub>CO<sub>3</sub> gives (1) in *ca.* 5% yield, along with a number of other compounds; (1) is eluted first on Al<sub>2</sub>O<sub>3</sub> chromatography of the product mixture. (1) m.p. 66—68 °C is yellow,  $\lambda_{\max}$  380, log  $\epsilon$  2·35 in 2,2,4-trimethylpentane. The geometry of the molecule was determined by X-ray crystallography. Crystal data: orthorhombic,  $P2_12_12_1$  (from systematic absences) with a = 6.998(1), b = 8.546(1), c = 21.840(3) Å. Reflections were measured with Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71069$  Å) out to  $\theta = 30^{\circ}$  on a Hilger-Watt four circle diffractometer. 1726 planes were measured of which 1394 had net counts >3 $\sigma$ and were used in the refinement. The structure was solved routinely using MULTAN. Hydrogens (located from a difference map) were included and refined isotropically, the other atoms anisotropically. The variables were refined in three blocks and at convergence R was 0.047. The cal-

<sup>†</sup> No reprints available.

culated e.s.d.'s of bond lengths and angles not involving hydrogen were ca. 0.004 Å and  $0.27^{\circ}$ . The structure is shown in the Figure. It can be seen that the nitrogens (2.89 A apart) are almost planar; formally the lone pairs



have 98% p character. As expected the CH<sub>2</sub>-N bonds are significantly shorter than normal. In solution n.m.r. spectra are consistent with rapid boat-chair  $\rightleftharpoons$  chair-boat interconversion in the alicyclic eight-membered ring above −100 °C.

The photoelectron spectrum of (1) shows five ionisation potentials below 10.5 eV, at 6.90, 7.76, 8.13, 8.61, and 9.52 eV. The latter three bands are assigned to  $\pi$ -ionisations by comparison with naphthalene (8.15, 8.90, and 10.02 eV) and several other 1,8-diaminonaphthalenes we have examined. For comparison (2) (m.p. 83-85 °C, first absorption band at 323 nm, log  $\epsilon$  3.25, in 2,2,4-trimethylpentane, prepared in good yield from 1,2-dibromoethane and 1,8-diaminonaphthalene) has photoelectron ionisation peaks at 7.56, 8.01, ca. 8.8 (double intensity) and 9.70 eV. We assign  $n_+$  at 7.56 and  $n_{-}$  at ca. 8.8 eV, giving an  $n_{+}/n_{-}$  splitting of ca. 1.2 eV in good agreement with that (1.22 eV) reported<sup>3</sup> for 1,5diazabicyclo[3.2.2]nonane. The average lone-pair ionisation potential for (1), 7.3 eV, is therefore considerably lower than that for (2)  $(8\cdot 2 \text{ eV})$  or the reported<sup>4</sup> n ionisation potential for benzoquinuclidine (8.35 eV). We ascribe this difference to the nearly pure p character of the lone pairs in (1). Of the two n ionisation bands for (1), only that at



FIGURE. Structure of the naphtho-fused 1,5-diazabicyclo[3.3.3]undecane. Selected bond lengths (Å); N(1)–C(1), 1·430; N(2)–C(8), 1·421; N(1)–C(11), 1·454; N(2)–C(13), 1·447; N(1)–C(14), 1·461; N(2)–C(16), 1·456. Selected bond angles (°); C(1)–N(1)–C(11), 116·7; C(1)–N(1)–C(14), 118·5; C(11)–N(1)–C(14), 120·2; C(8)–N(2)–C(13), 118·7; C(8)–N(2)–H(16), 118·6; C(13)–N(2)–C(16), 118·6; C(13)–C(16), 118·2; C(16), 118·6; C(16), 118·2; C(16), 118/2; C(16), 118/2; C(16), 118/2; C(16), 118.9.

7.76 eV shows vibrational structure and a strong 0.0 band similar to that reported<sup>2</sup> for 1-azabicyclo[3.3.3]undecane. The radical cation formed is probably in the  $n_{+}(\uparrow)$   $n_{-}(\uparrow\downarrow)$ state and has an equilibrium geometry close to that of the parent amine. The ground state of the radical cation (formed in the 6.90 ev ionisation) is then  $n_{+}(1 \downarrow) n_{-}(1)$  and probably has an equilibrium geometry with inward pyramidalised nitrogens.

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