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

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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;[1,2] 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_2CO_3 gives (**1**) in *ca.* 5% yield, along with a number of other compounds; (**1**) is eluted first on Al_2O_3 chromatography of the product mixture. (**1**) m.p. 66—68 °C is yellow, λ_{max} 380, log ϵ 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 $a = 6{\cdot}998(1)$, $b = 8{\cdot}546(1)$, $c = 21{\cdot}840(3)$ Å. Reflections were measured with Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å) out to $\theta = 30°$ 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-

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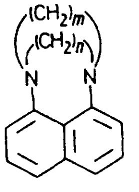
† No reprints available.

culated e.s.d.'s of bond lengths and angles not involving hydrogen were *ca.* 0·004 Å and 0·27°. The structure is shown in the Figure. It can be seen that the nitrogens (2·89 Å apart) are almost planar; formally the lone pairs have 98% *p* character. As expected the CH_2–N bonds are significantly shorter than normal. In solution n.m.r. spectra are consistent with rapid boat–chair ⇌ chair–boat interconversion in the alicyclic eight-membered ring above −100 °C.



(1); $m = n = 3$

(2); $m = n = 2$

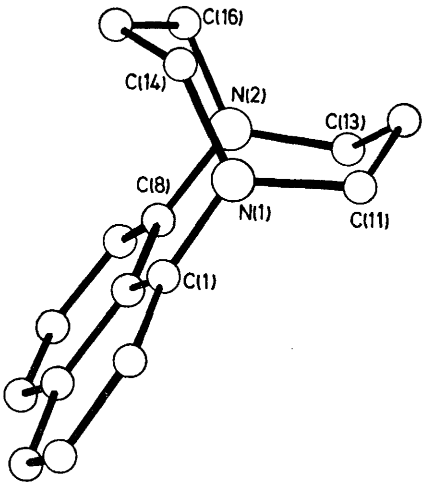


FIGURE. Structure of the naphtho-fused 1,5-diazabicyclo[3.3.3]-undecane. Selected bond lengths (Å); N(1)–C(1), 1·430; N(2)–C(8), 1·421; N(1)–C(11), 1·454; N(2)–C(13), 1·447; N(1)–C(14), 1·461; N(2)–C(16), 1·456. Selected bond angles (°); C(1)–N(1)–C(11), 116·7; C(1)–N(1)–C(14), 118·5; C(11)–N(1)–C(14), 120·2; C(8)–N(2)–C(13), 118·7; C(8)–N(2)–H(16), 118·6; C(13)–N(2)–C(16), 118·9.

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 π-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 ϵ 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[3] for 1,5-diazabicyclo[3.2.2]nonane. The average lone-pair ionisation potential for (**1**), 7·3 eV, is therefore considerably lower than that for (**2**) (8·2 eV) or the reported[4] *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 7·76 eV shows vibrational structure and a strong 0,0 band similar to that reported[2] 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 $n_+(\uparrow\downarrow)$ $n_-(\uparrow)$ and probably has an equilibrium geometry with inward pyramidalised nitrogens.

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