A Novel Carboxylic Acid Azide Decomposition to yield 1,1,7-Trimethylindazol-3-ylio Oxide

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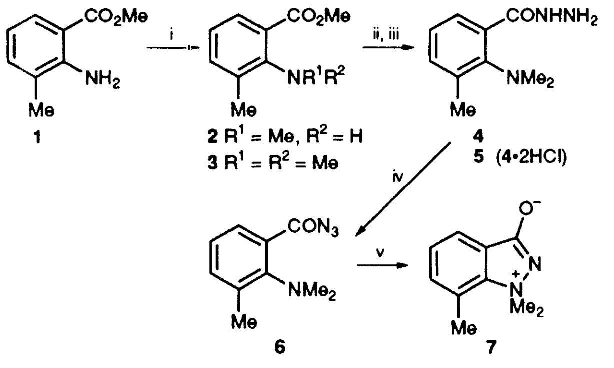
Thermal decomposition of 2-dimethylamino-3-methylbenzazide produced, instead of the expected isocyanate, a high yield of the isomeric cyclised product 1,1,7-trimethylindazol-3-ylio oxide; a single-crystal X-ray diffraction study shows delocalisation of the negative charge though little conjugation of the unsaturation of the five-membered ring with the benzene ring.

In attempting to make the corresponding isocyanate from the azide **6** by Curtius rearrangement, an extremely rapid loss of nitrogen occurred with almost complete conversion of the azide into the cyclic zwitterion **7**. This novel cyclisation probably takes place by the trapping of the intermediate nitrene by the lone pair of electrons on the nearby amino group. The monohydrate of the product was obtained in 81% yield from the hydrazide hydrochloride **5**, as cream coloured crystals, partially dissolving in its own water of crystallisation at 60–70 °C and finally melting as the anhydrous material at 221–223 °C. The monohydrate had satisfactory elemental analysis, IR, ^{1}H and ^{13}C NMR.†

A few examples of corresponding substituted but not fused rings of this type (pyrazol-3-ylio oxides) have been made previously where the structure is presented with a delocalised negative charge[1] or with a localised negative charge on the nitrogen atom.[2] In both cases protonation of these structures by hydrochloric acid is indicated on the nitrogen atom. The only known examples of the fused ring indazol-3-ylio oxide system[3] have been shown with a delocalised negative charge and protonation on oxygen. The crystal structures presented here confirm the latter arrangements.

The synthetic procedure for obtaining the zwitterion **7** is outlined in Scheme 1. Methylation of the amino group of **1** was achieved in two stages by the use of excess methyl iodide in methanol, with yields of 87 and 82% of the methylated oils **2** and **3**, having boiling points of 134 °C/18 mm Hg and 143 °C/16 mm Hg, respectively. The yield of crude hydrazide **4** was 100% which was crystallised for analysis from light petroleum (bp 100–120 °C) with mp 80–81 °C. The crude hydrazide was dissolved in hot ethanol which was saturated with HCl gas and then cooled to give a 73% yield of white crystals of the dihydrochloride **5**. Conversion of the dihydrochloride into the azide **6** was effected with $NaNO_2$ at −10 °C in water–diethyl ether followed by a final neutralisation of excess acid with NaOH. The diethyl ether solution of the azide was already slowly decomposing at this temperature so that it could not easily be purified. The solution was diluted with benzene and heated to 50 °C to complete the decomposition into the zwitterion **7** and remove the ether when the product crystallised out. On one occasion, a small amount (≈ 1 g) of azide **6** was obtained as a colourless oil by rotary evaporation of the ether solution at −10 °C. When the azide was allowed to warm to near 0 °C, a spontaneous violent explosion occurred.



Scheme 1 *Reagents and conditions*: i, MeI–MeOH, 50 °C, 24 h; ii, $N_2H_4 \cdot H_2O$ 100 °C, 3 days; iii, HCl gas–EtOH, 20 °C; iv, $NaNO_2$, −10 °C, 30 min; v, C_6H_6, 50 °C, 30 min

The ^{1}H NMR spectrum [$(CD_3)_2SO$] of the zwitterion **7** had an aromatic multiplet at δ 7.46, a six proton singlet at δ 3.32 for the two methyl groups on the quaternary nitrogen atom and a three proton singlet at δ 2.63 for the methyl group on the benzene ring. The ^{13}C NMR spectrum [$(CD_3)_2SO$] confirmed the presence of the methyl groups on a quaternary nitrogen atom with a resonance at δ 54.86 and the carbon bearing the negatively charged oxygen atom [C(1)] by the δ 171.30 peak. The other resonances were at δ 15.55 [C(8), Ar–Me], 152.06 [C(3)], 121.02 [C(2)] and 127.02, 131.01, 131.21, 133.16 [C(4)(5)(6)(7)].

The X-ray crystal structure determination‡ of **7** (Fig. 1) confirmed its zwitterionic nature, the negatively charged oxygen atom being hydrogen-bonded to two water molecules which in turn were hydrogen-bonded to a further molecule of **7**. The C–O bond length was short, being 1.254(2) Å which is similar to the carboxylate C–O bond length in aromatic acids (1.255 Å[4]). Delocalisation of the charge to the nitrogen atom is therefore indicated. In consequence the C=N bond length at 1.321(2) Å is longer than the usual bond length in similar situations (*e.g.* *p*-methoxybenzaldehyde oxime, 1.275 Å[5]) but still slightly shorter than the fully delocalised C=N (*e.g.* pyridine, 1.337 Å[4]). The C(1)–C(2) bond was only slightly shorter at 1.485(2) Å than the usual singly bonded carbon to the benzene ring and similar to that in substituted benzoic acids and benzoates. Thus the delocalised negatively charged N–C–O system does not appear to be appreciably conjugated to the benzene ring.

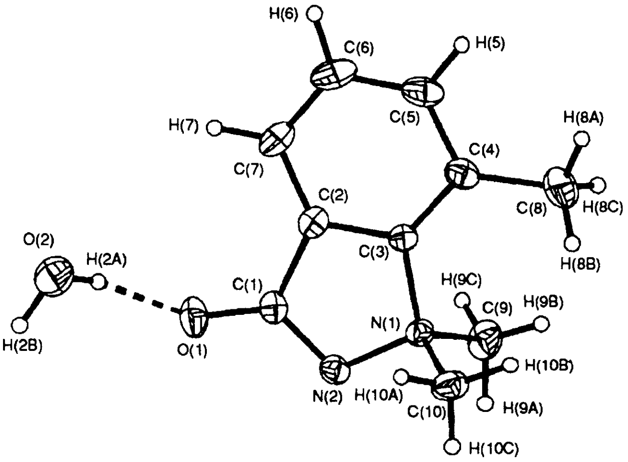


Fig. 1 X-ray crystal structure of the hydrate of compound **7**. Selected bond lengths (Å) and angles (°): N(1)–N(2) 1.475(2), N(2)–C(1) 1.321(2), C(1)–C(2) 1.485(2), C(2)–C(3) 1.372(2), C(3)–N(1) 1.485(2), C(3)–N(1)–N(2) 107.04(10), N(1)–N(2)–C(1) 107.21(11), N(2)–C(1)–C(2) 111.24(13), C(1)–C(2)–C(3) 107.62(12), C(2)–C(3)–N(1) 106.89(12), C(3)–C(4)–C(5) 113.3(2), C(6)–C(7)–C(2) 117.2(2).

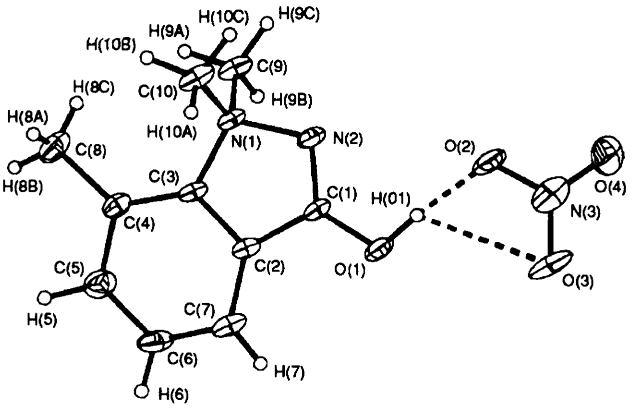


Fig. 2 X-ray crystal structure of the nitrate salt of compound **7**. Selected bond lengths (Å) and angles (°): N(1)–N(2) 1.476(3), N(2)–C(1) 1.294(3); C(1)–C(2) 1.459(4), C(2)–C(3) 1.370(3), C(3)–N(1) 1.484(3), C(3)–N(1)–N(2) 106.6(2), N(1)–N(2)–C(1) 106.1(2), N(2)–C(1)–C(2) 114.0(2), C(1)–C(2)–C(3) 106.3(2), C(2)–C(3)–N(1) 107.2(2), C(3)–C(4)–C(5) 113.5(3), C(6)–C(7)–C(2) 116.2(3).

During the preparation of the zwitterion **7**, if the neutralisation with alkali at the end of the procedure for azide formation was omitted, the product of azide decomposition was not the zwitterion itself but the nitrate salt, H $7^+NO_3^-$. X-Ray crystal structure determination (Fig. 2) of this material gave very similar bond lengths and bond angles to the zwitterion **7** except as expected for those associated with C(1). Protonation of the oxygen atom increased the C–O bond length to 1.300(3) Å a similar value to those found for the C–O of substituted benzoic acids. The C=N bond length is shorter in the salt [1.294(3) Å] showing an increase in double bond character reflecting loss of conjugation with the oxygen atom. The length of the C(1)–C(2) bond [1.459(4) Å] compared with that in the zwitterion itself shows that in the salt also there is only a small amount of conjugation with the benzene ring. The interior angles of the benzene ring at C(4) in both the zwitterion and its salt were considerably less (113.3 and 113.5°) than the regular hexagonal value.

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Footnotes

† Similar satisfactory characterisations of all the compounds in the synthetic sequence were obtained.

‡ *Crystal data* for (hydrate of **7**): $C_{10}H_{12}N_2O{\cdot}H_2O$; M = 194.23, monoclinic, space group $P2_1/a$, a = 15.801(3), b = 7.856(2), c = 8.231(1) Å, β = 94.43(1)°, U = 1508.6 Å^3, Z = 4, D_c = 1.266 g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å), μ = 0.9 cm^{-1}, F = 416, S = 1.071, 2219 independent reflections on θ range 2.48–26.98° and index range $-20 \leqslant h \leqslant 20$, $-1 \leqslant k \leqslant 10$, $0 \leqslant l \leqslant 10$. The final R indices [$F^2 > 2\sigma(F^2)$] was 0.0413 and $R_w(F^2)$ = 0.1137. *Crystal data* for (nitrate salt of H 7^+): $C_{10}H_{12}N_2O{\cdot}HNO_3$; M = 239.23, triclinic, space group $P\bar{1}$, a = 7.346(1), b = 7.881(1), c = 10.997(2) Å, α = 74.38(1), β = 94.43(1), γ = 67.84(1)°, U = 567.9(2) Å^3, Z = 2; D_c = 1.399 g cm^{-3}, Mo-Kα radiation (λ = 0.710 69 Å), μ = 0.11 cm^{-1}, F = 252, S = 0.976, 1568 independent reflections on θ range 1.92–22.97° and index range $0 \leqslant h \leqslant 8$, $-8 \leqslant k \leqslant 8$, $-12 \leqslant l \leqslant 12$. The final R indices [$F^2 > 2\sigma(F^2)$] were 0.0446 and R_w (F^2) = 0.1113. The intensity data were collected by a CAD4 diffractometer using ω–2θ scans. The unit-cell parameters were determined by a least-squares refinement on diffractometer angles for 25 automatically centred reflections with $10 \leqslant \theta \leqslant 13°$. The structures were solved by direct methods using the SHELXS program package (G. M. Sheldrick),[6] and refined anisotropically by full-matrix least squares on F^2, using the SHELXL-93 program package (G. M. Sheldrick).[7] The H atom positions were calculated geometrically by using the AFIX command on SHELXL-93. The program SNOOPI (K. Davis)[8] was used for drawing the molecules. Atomic coordinates, bond lengths and bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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