Observation of a Stable Monomeric *N*-Methylene Aromatic Amine†

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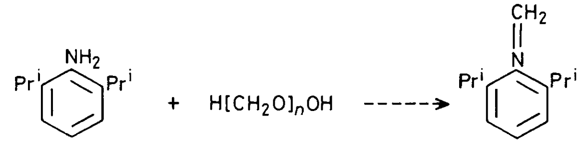
The first free *N*-methyleneaniline stable under ordinary conditions was authenticated by spectroscopic and analytical data and some of its reactions were observed; a room temperature equilibrium between another free *N*-methylene aromatic amine and its oligomeric species is reported.

We have recently defined many of the structural details of the monomer, dimer,[1] trimer,[2] and tetramer[3] of the Schiff base derived from aniline and formaldehyde. However, there is no literature report to date about any free monomeric *N*-methylene aromatic amine stable under ordinary conditions in the solid or liquid state, authenticated by analytical and spectroscopic data.[4]

We report the preparation and reactions of *N*-methylene-2,6-di-isopropylaniline (**1**), the first stable characterised monomeric *N*-methylene aromatic amine. It is easily prepared by heating equimolar amounts of polyoxymethylene (**2**) and 2,6-di-isopropylaniline (**3**) until the former has completely dissolved at *ca.* 100 °C.‡ Product (**1**), which correctly analysed for $C_{13}H_{19}N$, is a colourless liquid, its positive ion electron impact mass spectrum showed a parent ion at *m/z* 189, with sequential losses of a methyl group (*m/z* 174) and propene§ (*m/z* 132, base peak) at 70 eV. The i.r. spectrum exhibited a practically identical pattern in the aromatic out-of-plane bending region of CH bonds (756s and 785m cm^{-1}) as compared with (**3**) (740s and 782 cm^{-1}) and two of the strongest bands in the finger-print region were almost coincidental in position [1042m and 1460s shouldered unresolved multiplet, in (**1**)]; the bands of (**3**) at 1620m and the NH_2 stretching doublet centred at 3440m—w disappeared. A sharp band appeared at 1647s cm^{-1} for (**1**). The ^{1}H n.m.r. spectrum of (**1**) ($CDCl_3$) showed resonances of the non-equivalent methylene protons at very low field, δ 7.72 and 7.35 (AB-quartet, $^{2}J_{H-H}$ 18.3 Hz), beyond the aromatic complex multiplet, centred at δ 7.10 (3H), in addition to the expected aliphatic pattern, δ 2.93 (CH, 2H, septet, *J* 6.9 Hz), 1.15 (CH_3, 12H, doublet).¶ Space filling molecular models clearly evidenced the impossibility of positioning the methylene group atoms in the plane of the ring and the nitrogen atom; the two hydrogen atoms as a result end up in different environments, and rotation about the C–N bond is hindered.

The nature of the methylene group is confirmed by ^{13}C n.m.r. spectroscopy: we found that the resonance of the methylene carbon falls some 646 Hz *below* the resonance of the highest field aromatic carbon; the corresponding signal for



(**3**) (**2**) (**1**)

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† Part of the series: 'Revisitation of the Reaction between Aniline and Formaldehyde.'

‡ Water formed and any excess of (**2**) can be eliminated by evaporation *in vacuo*. The colourless reaction product is then distilled under reduced pressure (*ca.* 50 °C/0.1 Torr; quantitative yield). G.c. analysis (capillary column, 25 m long, 0.1 mm i.d., SE 30; H_2 carrier, injector temp. 200 °C, flame ionisation detector, column temp. from 80 to 200 °C, 10 °C/min) combined with electron impact mass spectrometry reveals the presence of some (less than 3%) unreacted (**3**), which appears difficult to remove either by conventional separation methods or further reaction with excess of (**2**).

§ The formal loss of 57 units from the parent ion of (**1**) may be either a C_4H_9 or a C_3H_7N fragment. We prepared *N*-dideuteriomethylene-2,6-di-isopropylaniline, which upon electron impact at 70 eV lost both 59 units ($M^{+\cdot}-$ Et, then $-CD_2N$) and to a larger extent 57 units ($M^{+\cdot}-$ -Me, then $-C_3H_6$). These observations indicated deep skeletal rearrangements of the parent ion not involving the $N{=}CD_2$ function prior to fragmentation.

¶ The ^{2}J value for the methylene protons is very close to the figures reported for an aliphatic *N*-methyleneimine.[6]

trimeric *N*-methyleneaniline (1,3,5-triphenylhexahydro-*sym*-triazine) is located some 1006 Hz *above* the resonance of the highest field aromatic carbon (respectively 436.9 and 1541 Hz below the ^{13}C resonance of dimethyl sulphoxide, used as solvent), and the ^{1}H methylene singlet appears at δ 4.87,[2] in strict analogy with the ^{13}C and ^{1}H spectra of aniline and dimethylaniline.

N-Methylenation deeply affects the u.v. spectrum of freshly distilled (**3**).|| Steam distillation at atmospheric pressure of (**1**) caused its complete hydrolysis to (**3**). Whereas the reduction of (**1**) in aqueous acidic medium with $NaBH_4$ led to partial hydrolysis to (**3**) and both *N*-methyl-2,6-di-isopropylaniline and *N*,*N*-dimethyl-2,6-di-isopropylaniline, a result expected on the basis of the known *N*-permethylation reaction,[5] $LiAlH_4$ rapidly converted (**1**) into the monomethylated compound quantitatively in tetrahydrofuran.

Addition of acetic anhydride across the azomethine bond of (**1**) was effected by the action of acetic acid and acetic anhydride at 130 °C (oil bath) during 90 min, followed by neutralization with aqueous alkali and diethyl ether extraction, to produce *N*-acetyl-*N*-acetoxymethyl-2,6-di-isopropylaniline and *N*,*N*-diacetyl-2,6-di-isopropylaniline in a 3:2 ratio. Imine (**1**) was converted into *N*-trifluoroacetyl-*N*-trifluoroacetoxymethyl-2,6-di-isopropylaniline by treatment with an equivalent of trifluoroacetic anhydride at room temperature during 60 min. Reaction of (**1**) with either n-butylamine or n-octylamine at 75 °C for 60 min caused complete reversion to the free amine (**3**).

A preliminary investigation of the system generated under analogous conditions by the reaction of (**2**) with 2,6-dimethylaniline allowed the observation of the equilibrium between the free *N*-methylene derivative and an oligomeric species with equivalent methylene groups at room temperature by ^{13}C n.m.r. spectroscopy.

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6 B. L. Shapiro, S. J. Ebersole, G. J. Karabatsos, F. M. Vane, and S. L. Mannat, *J. Am. Chem. Soc.*, 1963, **85**, 4041 for two monomeric tertiary alkyl methyleneamines and C. F. Chang, B. J. Fairless, and M. R. Willcott, *J. Mol. Struct.*, 1967, **22**, 112, who also reported the position of the chemical shifts (δ 6.90—7.55), for methyl methyleneamine.

|| Compound which showed maxima in hexane at 208 (log ε 4.32), 235 (3.86), and 284 nm (3.43), with definite maxima at 206 (log ε 4.34) and 278 nm (2.95) and shoulders at 223 (log ε 3.91), 232 (3.77), 298 (2.88), and 309 nm (2.62).