An NMR observation of the *N*-methylideneamine–hexahydrotriazine equilibrium

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The first trimeric *N*-methylideneamine from a heterocyclic amine (4-aminoantipyrine, **1**) has been fully characterized and its X-ray diffraction structural determination carried out; also the equilibrium between the trimer **2** and the monomer **3** has been studied by ^{1}H and ^{13}C NMR spectroscopy.

Systematic work in the last decade[1] has clarified many facets of the reaction between primary aromatic amines and formaldehyde. Free monomeric *N*-methylideneamines[1b,1e] were for the first time obtained as distillable liquids; the ETS and UPS spectra of gaseous *N*-methylidene aniline[1h] were recorded and interpreted and a theoretical study of the molecule has been carried out. The dimeric species, most likely in the form of a zwitterion in equilibrium with the four-membered ring structure, is most elusive but was proposed both in the above study and in a thermochemical study, where the transformation of the trimeric species into the more stable tetrameric species was observed at the pseudo-melting point of the former by IR and Raman spectroscopy.[1g] X-Ray structural data are now available for a few trimeric[1a,f] structures and tetramers.[1c]

In this general picture there was a lack of observation of the *N*-methylideneamines derived from heterocyclic amines and their oligomers. A spectroscopic study of the dynamic interconversion between a monomer and trimer of this type is now presented.

Results and discussion

4-Amino-1,5-dimethyl-2-phenylpyrazol-3(2*H*)-one (**1**) reacted with paraformaldehyde in boiling toluene to yield a solid, mp 153 °C, which analysed as $C_{12}H_{13}N_3O$. The IR spectrum of a carefully recrystallized and dried sample exhibited no NH absorption, weak aromatic peaks for Ar-C–H bonds and sharp ν_{CH} peaks for the aliphatic substituents. No likely $\nu_{C=N}$ absorption appeared below 1660 cm^{-1}.

A dilute solution of 1,3,5-tri(4-antipyrinyl)hexahydro-*sym*-triazine (**2**) in CH_2Cl_2 was admitted at high temperature into the injection port (kept at 260 °C) of a GC-MS system. The volatilized material was passed through a suitable column, from which it emerged as monomer **3**, thus showing the reversibility of the trimer formation reaction for this system.

When solid **2** was slowly evaporated into the ion source of a mass spectrometer, we observed that some material reached the source when the temperature of the solid inlet was *ca.* 150 °C. In the range of evaporation temperatures 150–160 °C a gaussian type curve was generated by the total ion monitor, at any point the whole spectrum at 70 eV being absolutely identical (Fig. 1) and corresponding to that obtained in the GC-MS experiment.

The evaporation process is consistent with the slow formation of monomeric **3** from **2** and, possibly, some dimeric species **4**; it is **3** which was admitted into the ion source. As no more material was admitted into the ion source (arrowed position of the curve of Fig. 2), the temperature was quickly raised (*ca.* 230 °C) until fresh material reached the ion source to generate a second gaussian, the MS pattern of which was throughout identical with the one generated from the former gaussian.

The trimer **2** showed an endothermal transition at 153.12 °C in a DSC experiment carried out with a scanning rate of 2.0 °C min^{-1}. The shape of the curve was such that the phenomenon could well be interpreted as a relatively slow decomposition causing fusion of the sample. At a slightly higher temperature (*ca.* 158 °C) the inception of a slightly exothermic reaction was observed in this experiment. Visual observation of the melting characteristics of **2** in a classical apparatus for the determination of melting points confirmed that a rather slow transition with fusion of the sample took place between 153 and 154.5 °C.

A likely rationale for these observations is the following. The pure trimer **2** undergoes slow decomposition to the monomeric species according to the elementary steps **a** and, possibly, also **b** (Scheme 1), which involves dimeric form **4** decomposing into **3**. The monomer **3** is ionized in the ion source to generate its mass spectrum (Fig. 1). The area below the two gaussian curves was a function of the temperature at which the first one was produced, the higher the temperature the lower the area of the second gaussian: this is a confirmation that reaction **b** is favoured over the alternative association process **c**.

Dimeric *N*-methylideneamines are elusive species, none of them being obtained as a separated compound: their high reactivity was ascribed to their zwitterionic nature (possibly in fast equilibrium with a ring structure). Moreover, in electron impact mass spectrometry experiments their parent ions also appeared highly prone to decomposition to the monomeric ion and molecule even at low ionization energy. Thermal decomposition to the monomer can also very likely occur on the multiple collisions on the hot metal surface of the ion source before ionization. Melts of trimers are known[1g] often to generate high melting tetramers, at least in the aromatic cases. Thus we may expect that a high melting tetramer **5** is formed from dimer **4** (reaction **c**, Scheme 1). Eventually, at much higher temperature this may revert to **4** and subsequently to **3**, which can be directly admitted into the ion source, obviously producing the usual mass spectral pattern of **3**. We consider highly unlikely the direct admission of **5** into the ion source, due to its expected extremely low volatility.

On the other hand, solutions of **2** in dimethyl [$^2H_6$]sulfoxide ([$^2H_6$]DMSO) and CD_2Cl_2 showed a ^{1}H NMR spectrum of an equilibrated system, where the starting material and a monomeric species were simultaneously present. We could record the spectrum of pure **2** in CD_2Cl_2 below 233 K: two sharp singlets for the methyl groups at 2.44 and 2.89 ppm, a

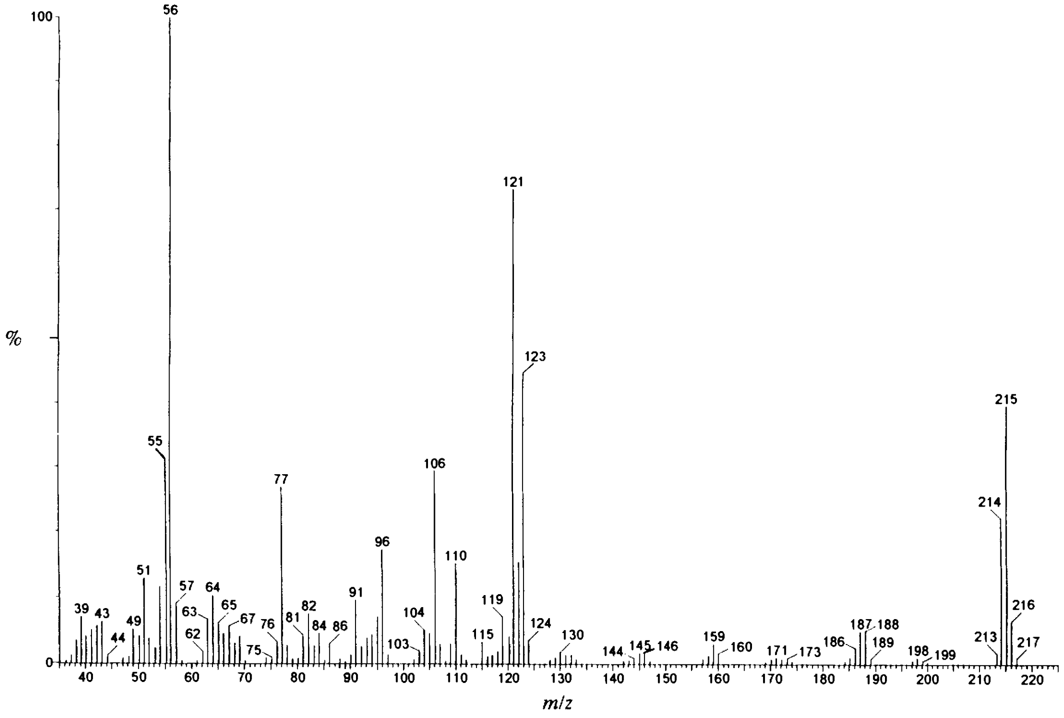
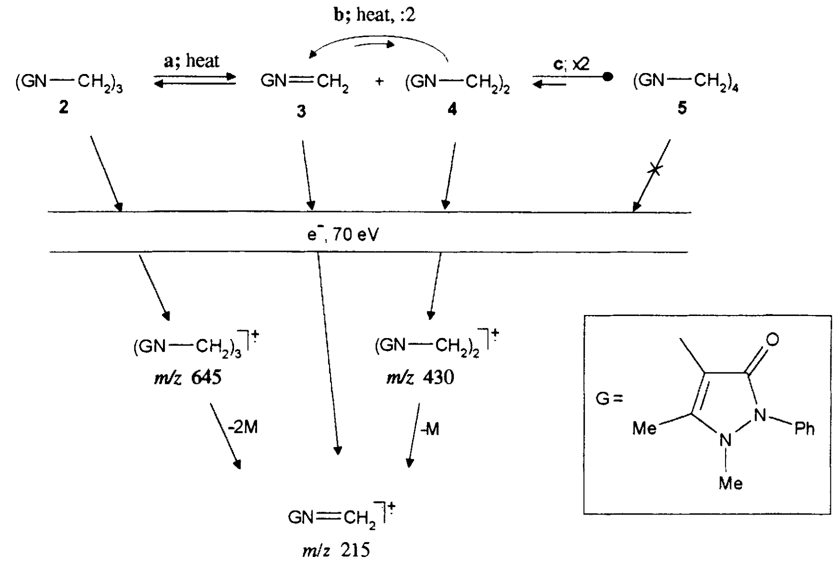


Fig. 1 Electron impact (70 eV) mass spectrum of vaporized **2** and monomer **3**

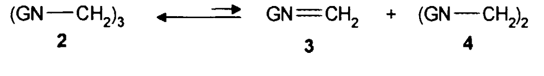


Scheme 1

slightly broad singlet for the methylene at 4.74 ppm and a complex multiplet for the aromatic protons between 7.15–7.50 ppm with the expected integral ratios. When the spectrum of the same solution was recorded at 273 K two new resonances appeared: the intensity of the C-methyl group peak decreased while a new singlet showed up at 3.16 ppm, also a well separated doublet appeared at 8.73 ppm, whose position and coupling constant value (J_{AA} = 17.3 Hz), was in excellent agreement with literature[1b,1e] reports for *N*-methylideneamines [Fig. 3(*a*) and 3(*b*)].

Recording the spectrum of **2** at different temperatures in [$^2H_6$]DMSO offered two advantages: it was possible to expand the temperature range of our observations and the more basic solvent caused a substantial high field shift of both methylene protons of **3**, thus allowing a clear observation of the high field proton. In fact, the methylene end of the molecule **1** is expected to be positively charged and therefore able to coordinate strongly the solvent molecules at their negative end [Fig. 4(*a*)].

Interestingly none of the spectra showed any evidence for other species, an evidence for instantaneous disappearance of any dimer in detectable concentrations. The equilibrium may thus be described in Scheme 2.



Scheme 2

The spectrum of the monomer **3** in practically pure form could be observed at 363 K in [$^2H_6$]DMSO [Fig. 4(*b*)]; at 233 K in CD_2Cl_2 only the trimer **2** was present. The equilibrium

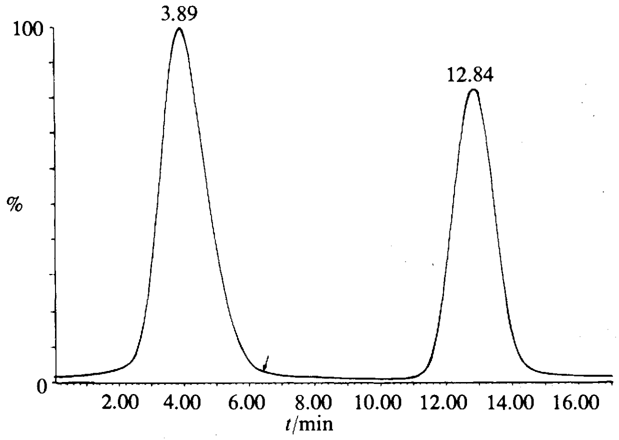


Fig. 2 EI-MS monitoring of the evaporation behaviour of **2**

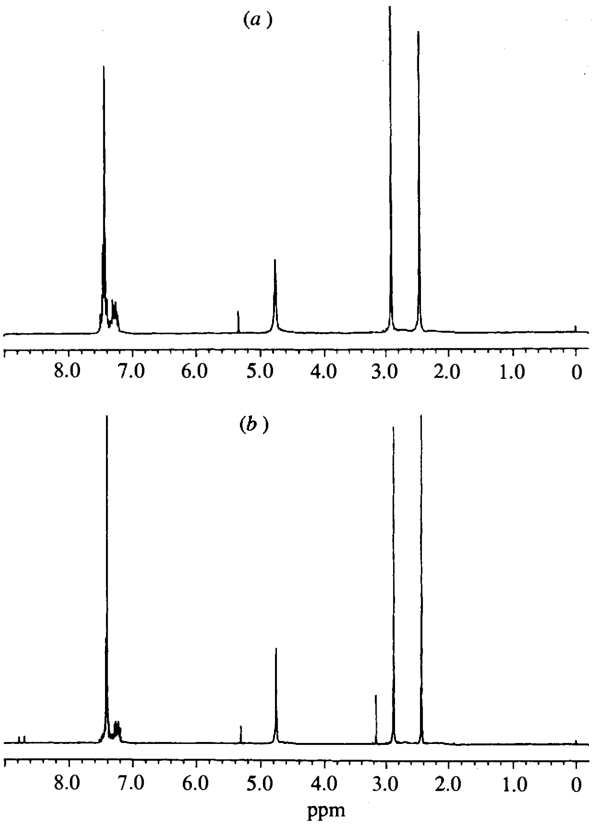


Fig. 3 ^{1}H NMR spectra of $(GN\text{–}CH_2)_n$ at 233 K, $n = 3$ (*a*) and 273 K, $n = 1$ and 3 (*b*) in CD_2Cl_2

constant ($K_{eq} = 0.0177$ mol^2 dm^{-6}) for the equilibrium (1) in [$^2H_6$]DMSO at 323 K was determined.

$$\underset{\mathbf{3}}{3\,GN{=}CH_2} \rightleftharpoons \underset{\mathbf{2}}{(GN\text{–}CH_2)_3} \qquad (1)$$

^{13}C NMR spectra recorded in CD_2Cl_2 and [$^2H_6$]DMSO at different dilutions and temperatures permitted us tentatively to ascribe all observed peaks to the different carbon nuclei of either species **2** or **3** as indicated in Fig. 5.

X-Ray diffraction data of crystalline **2** were obtained. A perspective view of the molecule and the crystallographic numbering scheme are shown (Fig. 6). In the triazacyclohexane ring the torsion angles around the N–C bonds are in the range 51.9(3)–59.3(3)° averaging 55.5° (referred to the absolute values), which is lower than the ideal value of 54.7° for a *pure* chair conformation. The molecules adopt the *eaa* conformation

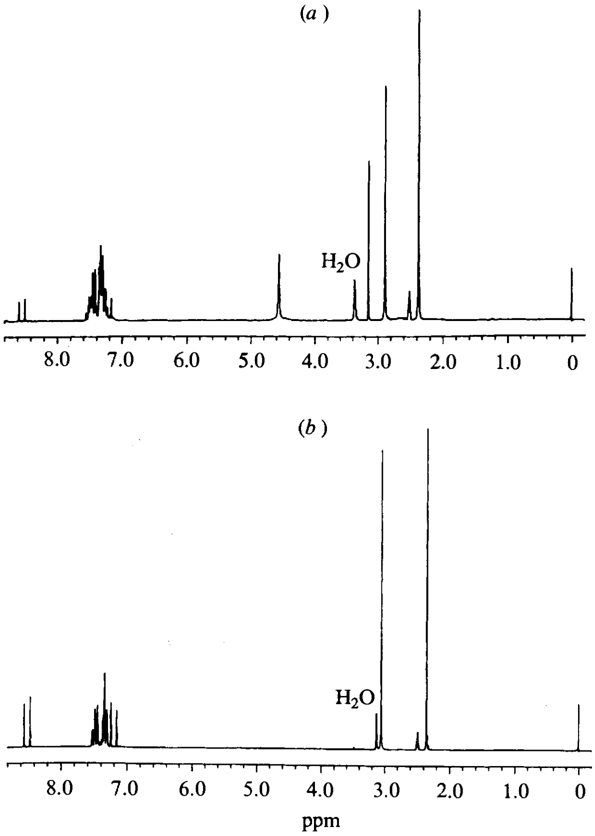
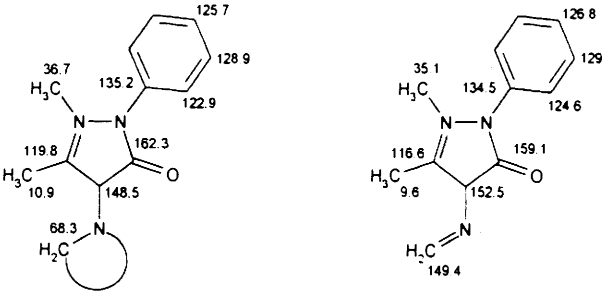


Fig. 4 ^{1}H NMR spectra of $(GN\text{–}CH_2)_n$ at 303 K, $n = 1$ and 3 (*a*) and 363 K, $n = 1$, (*b*) in [$^2H_6$]DMSO



2 **3**

Fig. 5 ^{13}C Chemical shifts of trimer **2** (CD_2Cl_2, 233 K) and monomer **3** ([$^2H_6$]DMSO, 363 K)

with diaxial repulsion between the phenazone groups preferred to that of lone-pairs of electrons. The triazine ring N atoms have different pyramidal conformation with the N–C exocyclic bond inclined at 50.5(2)°, 53.2(2)° and 139.8(2)° to the CH_2–N–CH_2 planes at N(1), N(2) and N(3), respectively. The out of plane angle for the equatorial N(3)–C(26) bond is distinctly smaller than the value of 54.7° for a pure tetrahedral geometry, while those of the axial N(1)–C(4) and N(2)–C(15) bonds are closer to the ideal value (4.2° and 1.5° of difference, respectively). The bond angles around N(3), having the substituent in an equatorial position, are very close to each other [range 110.2(2)–112.9(2)°] while those around N(1) and N(2) with the substituent in the axial position range from 108.3(2)° to 119.5(2)°. The C–N ring bond lengths [1.449(4)–1.479(4) Å] are in the range of those observed for 1,3,5-tribenzoylperhydro-1,3,5-triazine[2] and 1,3,5-triphenylhexahydro-*sim*-triazine.[1a] The C–N–C and N–C–N ring bond angles are also comparable [the average values are 109.4(3)° and 113.0(3)°, respectively]. The pentatomic moieties (all of envelope conformation) of the

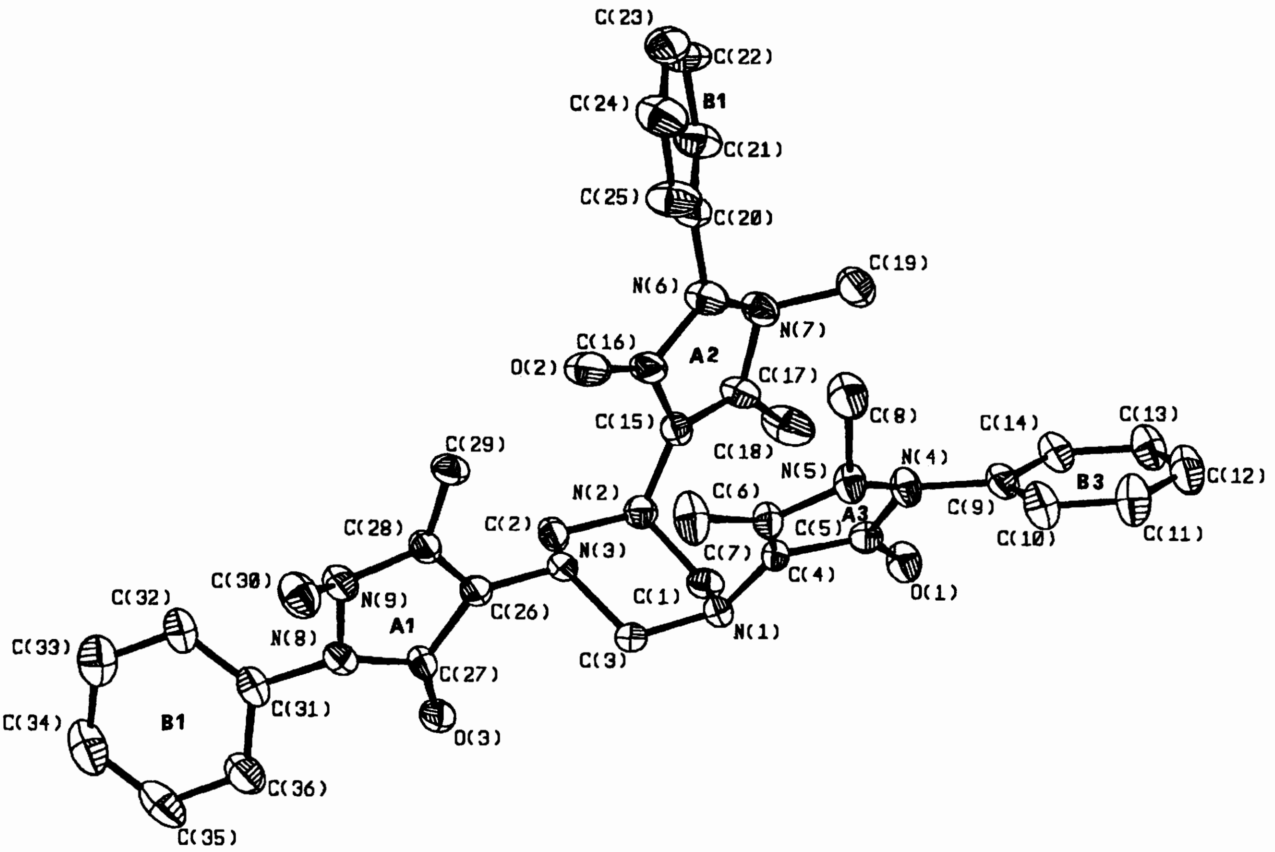


Fig. 6 Perspective view of the trimer **2** and the crystallographic numbering scheme

phenazone are differently inclined with respect to the chair plane of the triazine ring here considered [C(1), N(2), N(3), C(3)] independently from their axial or equatorial positions [C–A1 93.2(1)°, C–A2 57.2(1)° and C–A3 71.2(1)° represent the angles between the respective best mean planes (Fig. 6)]. The benzene rings are rotated rather regularly to the respective pentatomic ring with values of 45.5(1)°, A1 ^ B1, 140.0(1)° A2 ^ B2 and 43.2(1)° A3 ^ B3. The shortest intramolecular separation present in the molecule is O(1) ••• H(1B) 2.31 Å where H(1B) is the equatorial H atom in C(1) [C(1)–H(1B) ••• O(1) is 130°] and it is comparable to the values of 2.3 Å found for similar interactions in the 1,3,5-tribenzoylperhydro-1,3,5-triazine.[2] In the crystal cell the presence of a disordered dichloromethane molecule (see Experimental) does not affect the molecular conformation as in the case of 1,3,5-tri(4-nitrobenzene)hexahydro-1,3,5-triazine,[3] where the presence of associated pyridine molecules was considered responsible for the observed twist-boat conformation of the hexahydro-1,3,5-triazine ring.

Experimental

Materials and equipment

4-Aminoantipyrine (**1**) was purchased from Fluka (Switzerland) and used as received, polyoxymethylene (paraformaldehyde) was obtained from BDH (Milano, Italy). ^{1}H and ^{13}C NMR spectra were recorded in CD_2Cl_2 for analytical purposes at room temperature and in [$^2H_6$]DMSO in the variable temperature experiments with a Bruker AC-F 200 spectrometer equipped with a variable temperature probe. The equilibrium constant was calculated from ^{1}H NMR data obtained using a Bruker AM 500 spectrometer equipped with a precisely programmable temperature probe, by electronically scanning the spectrum after careful temperature equilibration (10 h). The data for the evaluation of the equilibrium constant were obtained from a simple experiment at 50 °C using a solution containing 12.1 mg cm^{-3} of **2**. NMR peaks locations are reported as δ-values from Me_4Si (^{1}H NMR) and benzene (^{13}C NMR). IR spectra were obtained with a Nicolet FT-IR Magna 550 spectrophotometer. MS were obtained using the solid probe of a Fisons TRIO-200 mass spectrometer by slowly increasing the probe temperature until a spectrum could be recorded (*ca.* 120 °C). DSC experiment was performed on a DCS 7 Perkin Elmer instrument. Elemental analysis data was obtained with a Carlo Erba Mod. 1106 elemental analyser.

Crystal data

1,3,5-Tri(4-antipyrinyl)hexahydro-*sym*-triazine (**2**), $C_{36}H_{42}N_9O_3$, M = 648.79, monoclinic, space group $P2_1/n$, a = 13.024(3), b = 11.753(2), c = 23.599(4) Å, β = 100.98(3)°, V = 3546(1) Å^3, Z = 4, D_x = 1.215 g cm^{-3}, μ(Mo-Kα) = 0.805 cm^{-1}, F(000) = 1380, T = 295 K, R = 0.0464 for 3957 observations with $I \geq 3\sigma(I)$.

A crystal of dimensions 0.26 × 0.38 × 0.52 mm was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW1100 (Febo System) diffractometer with graphite-monochromated radiation. The orientation matrix and preliminary unit-cell dimensions were determined from 25 reflections found by mounting the crystal at random, varying the orientation angles χ and φ over a range of 120°, with $6 \leq \theta \leq 9°$. For the determination of precise lattice parameters, 40 strong reflections with $10 \leq \theta \leq 13°$ were considered. Integrated intensity for *hkl* reflections ($h = \pm 16, k = 0$–$14, l = 0$–29 were measured in the interval θ = 3–26°), using $\theta/2\theta$ scans. Three standard reflections (1,1,14, 1,−1, 5 and 3,2,2) were collected every 180 reflections. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects but not for absorption.

The structure was solved using the direct methods program

Table 1 Selected bond lengths (Å) and angles (°) for $C_{36}H_{42}N_9O_3$ (**2**)

O(1)–C(5)	1.230(4)	O(2)–C(16)	1.228(4)
O(3)–C(27)	1.234(4)	N(1)–C(1)	1.458(3)
N(1)–C(3)	1.449(4)	N(1)–C(4)	1.420(4)
N(2)–C(1)	1.458(4)	N(2)–C(2)	1.451(4)
N(2)–C(15)	1.409(4)	N(3)–C(2)	1.476(3)
N(3)–C(3)	1.479(4)	N(3)–C(26)	1.429(4)
N(4)–N(5)	1.408(4)	N(4)–C(5)	1.384(4)
N(4)–C(9)	1.424(4)	N(5)–C(6)	1.400(4)
N(5)–C(8)	1.464(5)	N(6)–N(7)	1.410(4)
N(6)–C(16)	1.393(4)	N(6)–C(20)	1.415(4)
N(7)–C(17)	1.392(4)	N(7)–C(19)	1.475(5)
N(8)–N(9)	1.409(4)	N(8)–C(27)	1.403(4)
N(8)–3(31)	1.436(4)	N(9)–C(28)	1.378(4)
N(9)–C(30)	1.467(4)	C(4)–C(5)	1.450(4)
C(4)–C(6)	1.350(4)	C(6)–C(7)	1.491(5)
C(15)–C(16)	1.451(4)	C(15)–C(17)	1.346(4)
C(17)–C(18)	1.482(5)	C(26)–C(27)	1.447(4)
C(26)–C(28)	1.352(4)	C(28)–C(29)	1.487(5)
C(3)–N(1)–C(4)	119.5(2)	C(1)–N(1)–C(4)	114.1(2)
C(1)–N(1)–C(3)	108.3(2)	C(2)–N(2)–C(15)	119.1(2)
C(1)–N(2)–C(15)	115.8(2)	C(1)–N(2)–C(2)	109.7(2)
C(3)–N(3)–C(26)	112.9(2)	C(2)–N(3)–C(26)	110.4(2)
C(2)–N(3)–C(3)	110.2(2)	C(5)–N(4)–C(9)	124.4(2)
N(5)–N(4)–C(9)	118.1(2)	N(5)–N(4)–C(5)	109.5(2)
N(4)–N(5)–C(8)	111.9(3)	N(4)–N(5)–C(6)	106.0(2)
C(6)–N(5)–C(8)	118.5(3)	C(16)–N(6)–C(20)	125.8(3)
N(7)–N(6)–C(20)	119.1(2)	N(7)–N(6)–C(16)	110.3(2)
N(6)–N(7)–C(19)	113.0(3)	N(6)–N(7)–C(17)	104.9(2)
C(17)–N(7)–C(19)	117.1(3)	C(27)–N(8)–C(31)	123.7(3)
N(9)–N(8)–C(31)	117.5(3)	N(9)–N(8)–C(27)	109.2(2)
N(8)–N(9)–C(30)	114.4(3)	N(8)–N(9)–C(28)	106.7(2)
C(28)–N(9)–C(30)	120.0(3)	N(1)–C(1)–N(2)	113.4(2)
N(2)–C(2)–N(3)	113.6(2)	N(1)–C(3)–N(3)	111.9(2)
N(1)–C(4)–C(6)	132.9(3)	N(1)–C(4)–C(5)	118.5(2)
C(5)–C(4)–C(6)	108.0(3)	N(4)–C(5)–C(4)	105.6(2)
O(1)–C(5)–C(4)	130.6(3)	O(1)–C(5)–N(4)	123.7(3)
N(5)–C(6)–C(4)	110.0(3)	C(4)–C(6)–C(7)	133.1(3)
N(5)–C(6)–C(7)	116.9(3)	N(4)–C(9)–C(14)	119.5(3)
N(2)–C(15)–C(16)	127.9(3)	C(16)–C(15)–C(17)	107.6(3)
N(6)–C(16)–C(15)	105.0(3)	O(2)–C(16)–C(15)	131.6(3)
O(2)–C(16)–N(6)	123.3(3)	N(7)–C(17)–C(15)	111.7(3)
C(15)–C(17)–C(18)	129.3(3)	N(7)–C(17)–C(18)	119.1(3)
N(3)–C(26)–C(28)	126.3(3)	N(3)–C(26)–C(27)	124.9(2)
C(27)–C(26)–C(28)	108.4(3)	N(8)–C(27)–C(26)	104.8(2)
O(3)–C(27)–C(26)	130.9(3)	O(3)–C(27)–N(8)	124.2(3)
N(9)–C(28)–C(26)	110.4(3)	C(26)–C(28)–C(29)	129.5(3)
N(9)–C(28)–C(29)	120.0(3)		

SHELX-86[4] and refined by the full-matrix least squares method with anisotropic thermal parameters for all non-hydrogen atoms. The H atoms were placed in calculated positions with fixed, isotropic thermal parameters (U_{equiv} of the parent carbon atom). In the last stages of refinement, the difference Fourier map showed electron density residuals of about 1.5–3 e $Å^{-3}$, these were interpreted as disordered dichloromethane molecules (two per cell content, each distributed on three different positions). Refinement was carried out by full-matrix least-squares; the function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, with weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.0418P)^2 + 2.36\ P^*]$, where $P = \max\ (F_o^2 - F_c^2)/3$. Conventional $R = 0.0464$, based on F values of 3597 reflections having $F_o^2 \leq 3\sigma(F_o^2)$ and $S = 1.141$ (wR on $F^2 = 0.156$). Scattering factors were taken from ref. 5. Structure refinement and final geometrical calculations were carried out with SHELXL-93[6] and PARST[7] programs, drawings were produced using ORTEP II.[8] Selected bond lengths and angles are given in Table 1.†

Reaction between 4-aminoantipyrine (1) and paraformaldehyde
To the amine **1** (2.00 g, 14.8 mmol) in refluxing heptane or toluene (40 cm^3) paraformaldehyde (0.53 g, 17.7 mmol) was added portionwise and refluxed for an additional 60 min. Excess paraformaldehyde was removed by filtration of the cold solution and the solvent was distilled off under a slightly reduced pressure. Recrystallization of the solid residue from toluene–$CHCl_3$ or hexane–CH_2Cl_2 yielded (72%) pure **2**: mp 153 °C; ν_{max}(KBr)/cm^{-1} 3300w, 3050m, 3040m, 3020m, 2985s, 2910s, 2890s, 2845s, 1660vs, 1620s, 1590s, 1495s, 1450s, 1350s, 1310s, 1295s, 1260s, 1155s, 1140s, 765s and 700s; δ_H(CD_2Cl_2, 233 K) 2.44 (s, 9 H, CH_3), 2.89 (s, 9 H, N-CH_3), 4.74 (s, 6 H, CH_2) and 7.15–7.50 (m, 15 H, ar-H); δ_C(CD_2Cl_2, 233 K) 10.9, 36.7, 68.3, 119.8, 122.9, 125.7, 128.9, 135.2, 148.5 and 162.3; *m/z* 215 (40%), 214 (22), 123 (44), 121 (73), 110 (15), 106 (29), 96 (17), 91 (10), 77 (27), 65 (6), 56 (100), 55 (31) and 51 (13) (Calc. for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.9; H, 6.1; N, 19.5).

3: δ_H([$^2H_6$]DMSO, 363 K) 2.34 (s, 3 H, CH_3), 3.12 (s, 3 H, N-CH_3), 7.21 (d, *J* 18.0 Hz, 1 H, N=CH_2), 7.28–7.55 (m, 5 H, ar-H) and 8.52 (d, *J* 18.0 Hz, 1 H, N=CH_2); δ_C([$^2H_6$]DMSO, 363 K) 9.6, 35.1, 116.6, 124.6, 126.8, 129.1, 134.5, 149.4, 152.5 and 159.1.

Acknowledgements

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