Barsilowsky's base and Perkin's base: two products from the oxidation of *p*-toluidine

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The oxidation of *p*-toluidine in H^+/H_2O can give mainly a tetramer, a trimer, or a mixture of both. The outcome is dependent upon the oxidant, the pH and the concentration of *p*-toluidine. Both the trimer and tetramer are definitively characterised by X-ray single crystal structure determination.

Keywords: Barsilowsky's base, Perkin's base, *p*-toluidine, potassium dichromate, potassium permanganate

A number of studies have focussed on unravelling the products formed from the oxidation of *p*-toluidine. In 1873, Barsilowsky first reported the oxidation of *p*-toluidine with $KMnO_4$ or $K_3Fe(CN)_6$ to give a tetramer of molecular formula $C_{28}H_{28}N_4$.[1–6] In 1879, Perkin studied the oxidation of *p*-toluidine hydrosulfate with $K_2Cr_2O_7$ and reported a trimer of molecular formula $C_{21}H_{21}N_3$ and some tetramer of molecular formula $C_{28}H_{27}N_3$.[7–9] In 1884, the oxidation was examined by Klinger and Pitschke who followed Barsilowsky's method.[10] They obtained a tetramer of molecular formula $C_{28}H_{28}N_4$. In 1893, Green studied the oxidation of *p*-toluidine with $K_2Cr_2O_7$ in dilute sulfuric acid, characterised the product with the molecular formula $C_{21}H_{21}N_3$ and drew the correct structure.[11] The empirical formula of C_7H_7N was suggested from previous studies[12] and a molecular weight determination showed that the substance was formed from 3 moles of *p*-toluidine. In 1901 and 1910, Börnstein studied the oxidation of *p*-toluidine in dilute sulfuric acid and reported a trimer and a tetramer analogous to Perkin's work.[13,14] In 1901, Börnstein drew the structure of the trimer and tetramer[13] and suggested the names for these compounds as Barsilowsky's base and Perkin's base respectively.[13] Reported melting points for these compounds vary considerably suggesting the two compounds were difficult to separate.[11] The trimer and tetramer and other by-products were also isolated by Saunders from the action of the enzyme peroxidase upon *p*-toluidine.[15–17] The oxidation of *p*-toluidine with $K_3Fe(CN)_6$ in liquid NH_3 gave the trimer.[18] The above studies were done before X-ray crystallography and NMR spectroscopy became available, apart from work by Kametani,[18] so we have carried out further experiments to confirm the structure of these products and to be sure of the identity of Barsilowsky's base. The trimer, as proposed by Green,[11] was recently reported as the product of the oxidation of *p*-toluidine with $FeCl_3$.[19]

Discussion

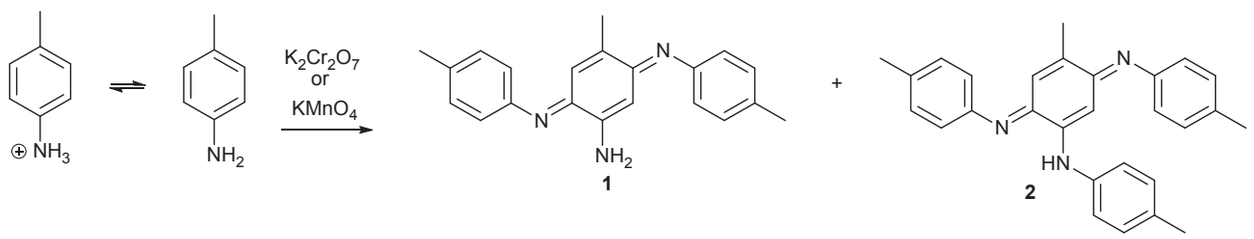
Scheme 1 shows the structure of the trimer **1** and tetramer **2** correctly drawn by Bornstein in 1901. Table 1 summarises our results from the oxidation of *p*-toluidine with either $KMnO_4$ or $K_2Cr_2O_7$ at different pHs, concentrations and temperatures. The oxidation of *p*-toluidine with aqueous alkaline $K_3Fe(CN)_6$ was unsatisfactory in our hands.

In summary, the oxidation of either *p*-toluidine in dilute sulfuric acid at 60 °C with $KMnO_4$ or the oxidation of *p*-toluidine hydrochloride in H_2O at 60 °C with $KMnO_4$ gave exclusively the trimer 2-amino-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine) **1** (entries 1 and 2). TLC analysis showed that the trimer was also formed exclusively by performing both these reactions at room temperature and a concentration of 10 mg mL^{-1}. The trimer was characterised spectroscopically and by X-ray crystallography and the data correspond to the correct structure suggested by Green (Fig. 1).[11] This suggests that Barsilowsky's compound is indeed a trimer and not a tetramer because he worked with $KMnO_4$ as oxidant.[1] However, the oxidation of *p*-toluidine in dilute sulfuric acid with $K_2Cr_2O_7$ at 60 °C gives a different less polar product (entry 3). This was characterised spectroscopically and by X-ray crystallography as the tetramer 2-(4-methylphenylamino)-5-methyl-1,4-

Table 1 Yields of trimer **1** and tetramer **2** isolated by oxidising *p*-toluidine with either $KMnO_4$ or $K_2Cr_2O_7$ under different conditions

Entry	Conditions	Trimer **1**/%[a]	Tetramer **2**/%[a]
1	*p*-Toluidine (10 mg/mL) $KMnO_4$/dil H_2SO_4/60 °C	9	0
2	*p*-Toluidine HCl (7.2 mg mL^{-1}) $KMnO_4$/60 °C	11	0
3	*p*-Toluidine (10 mg mL^{-1}) $K_2Cr_2O_7$/dil H_2SO_4/60 °C	2	12
4	*p*-Toluidine (10 mg mL^{-1}) $K_2Cr_2O_7$/dil H_2SO_4/rt	1	6
5	*p*-Toluidine (5 mg mL^{-1}) $K_2Cr_2O_7$/dil H_2SO_4/60 °C	14	6
6	*p*-Toluidine HCl (3.4 mg mL^{-1}) $K_2Cr_2O_7$/60 °C	16	0

[a]Yields calculated from the mass of isolated material purified by flash column chromatography.



Scheme 1 Formation of either a trimer **1**, a tetramer **2** or both from the oxidation of *p*-toluidine in dilute H_2SO_4 or *p*-toluidine hydrochloride.

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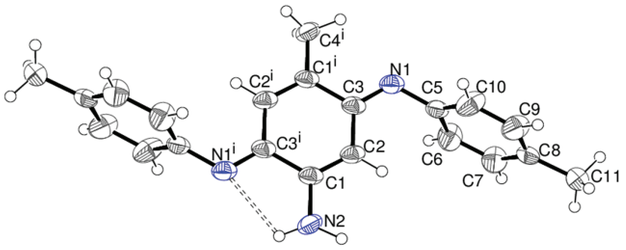


Fig. 1 The molecular structure of **1** showing 50% displacement ellipsoids [symmetry code (i) = 1–*x*, 1–*y*, 1–*z*]. The intramolecular N2–H2aN1^{i} hydrogen bond [N–H = 0.89 Å, HN = 2.32 Å; N–HN = 109°] is shown as a double-dashed line. Only one disorder component for C4 and N2 is shown. Selected geometrical data (Å,°): C1–C2 = 1.337 (4); C2–C3 = 1.456 (4); C1–C3^{i} = 1.483 (4); C3–N1 = 1.289 (4); C3–N1–C5 = 118.8 (3). The dihedral angle between the central ring and the pendant ring is 87.33 (12)°. In the crystal, an N2–H2bN1^{ii} (ii = *x*–*y*+1/3, *x*–1/3, 2/3–*z*) hydrogen bond occurs, but there are no aromatic π–π stacking interactions. For the results of, and our comments on, on a previous crystallographic study see the experimental section.[19]

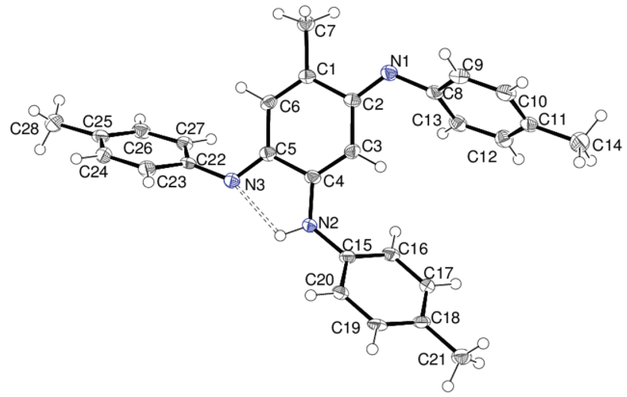


Fig. 2 The molecular structure of **2** showing 50% displacement ellipsoids. The intramolecular N2–H1N3 hydrogen bond [N–H = 0.88 (3) Å, HN = 2.19 (2) Å; N–HN = 110.6 (19)°] is shown as a double-dashed line. Selected geometrical data (Å,°): C1–C2 = 1.481 (3); C2–C3 = 1.453 (3); C3–C4 = 1.353 (3); C4–C5 = 1.480 (3); C5–C6 = 1.461 (3); C6–C1 = 1.345 (3); C2–N1 = 1.306 (3); C4–N2 = 1.377 (3); C5–N3 = 1.295 (3); C2–N1–C8 = 120.7 (2); C4–N2–C15 = 126.3 (2); C5–N3–C22 = 122.1 (2). The dihedral angles between the central ring and the C8, C15 and C22 rings are 58.02 (8), 52.03 (9) and 67.62 (8)°, respectively. There are no π–π stacking interactions in the crystal and only possible directional interactions are very weak C–Hπ bonds with Hπ > 2.75 Å.

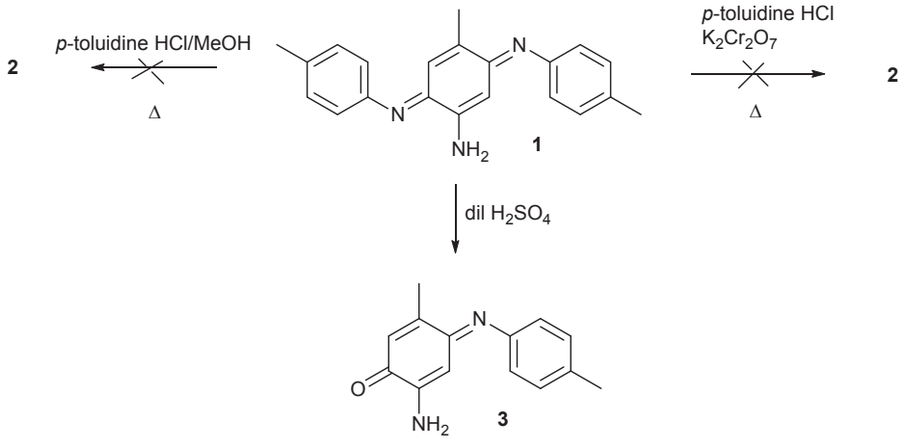
benzoquinone-1,4-(4-methylphenylimine) **2** (Fig. 2). A small amount of the trimer **1** was also isolated in this reaction.

The contrast of these two reactions using different oxidants at approximately the same pH is striking. Both solutions, *p*-toluidine in dil H_2SO_4 and *p*-toluidine hydrochloride, turn blue litmus red. Using pH indicator paper the first is estimated to have a pH of 4.0–5.0 and the second 6.0. If the same reaction with $K_2Cr_2O_7$ is performed at room temperature, rather than at 60 °C, after work-up a mixture of the trimer **1** and tetramer **2** was present but in lower yield (entry 4). The product ratio was not significantly altered by a change in temperature, but halving the concentration of *p*-toluidine favoured the trimer **1** (entry 5). This may explain Green's result. He carried out the oxidation of *p*-toluidine in dilute sulfuric acid with $K_2Cr_2O_7$ at 5 °C and obtained the trimer **1.**[11] Perkin performed this reaction at room temperature and obtained trimer **1** and some tetramer **2.**[8] Saunders also showed, using peroxidase and hydrogen peroxide as oxidant, that the tetramer is only produced when the concentration of *p*-toluidine is greater than 1 g L^{-1}.[16] The oxidation of *p*-toluidine hydrochloride in H_2O at 60 °C with $K_2Cr_2O_7$ also gave exclusively the trimer **1** (entry 6). The milder acidic conditions change the selectivity from tetramer **2** to trimer **1**. In summary, using $K_2Cr_2O_7$ as oxidant a higher pH (6.0) and a lower concentration of *p*-toluidine favour the trimer **1** or a mixture of trimer **1** and tetramer **2** rather than the tetramer **2**. Likewise a lower pH (4.0–5.0) and a greater concentration of *p*-toluidine favours the tetramer **2**.

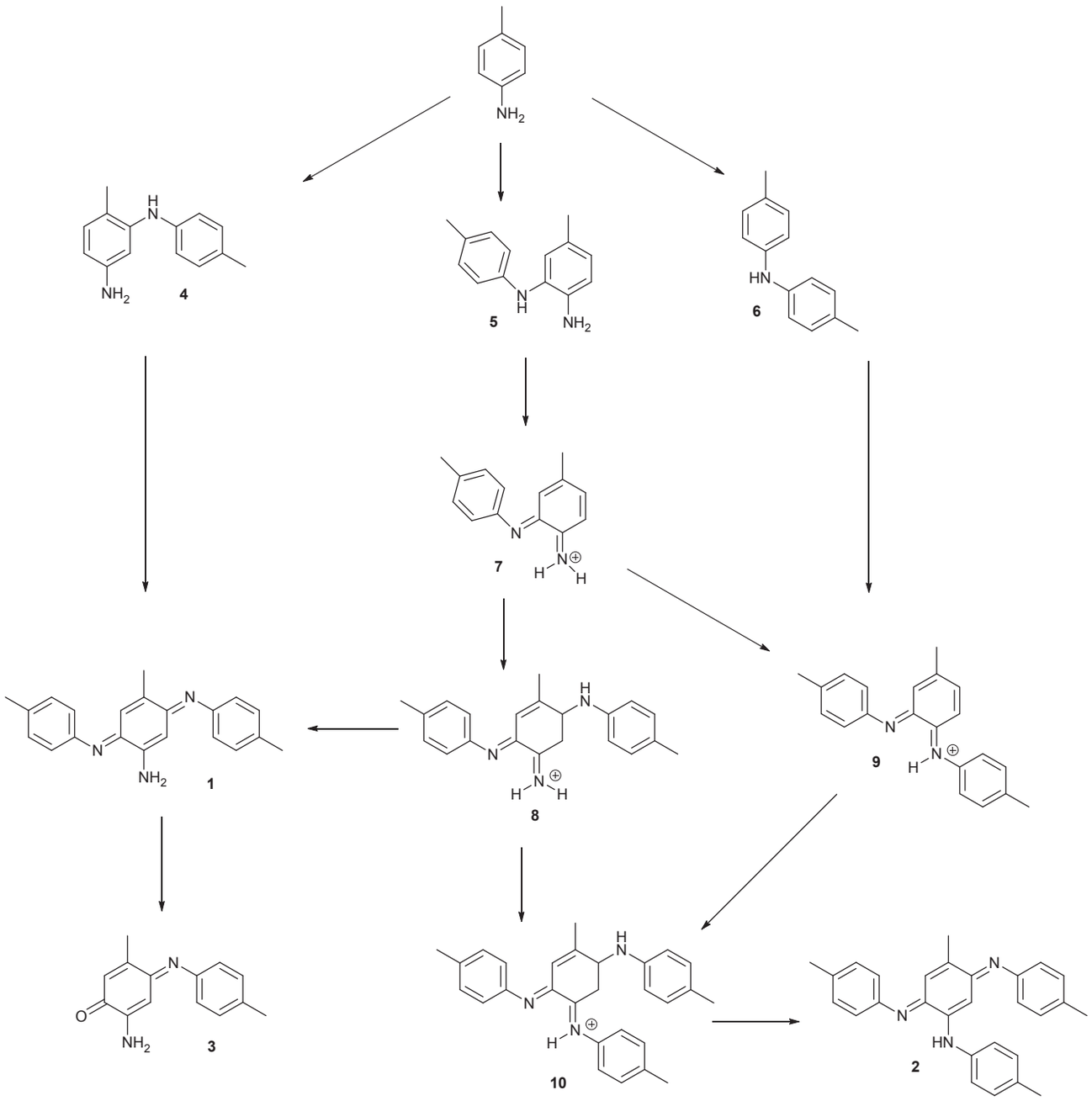
Some experiments were performed to investigate the mechanistic pathways to these two products (Scheme 2). Treatment of the trimer **1** with *p*-toluidine hydrochloride in refluxing MeOH for 2 h or with *p*-toluidine hydrochloride and $K_2Cr_2O_7$ in H_2O gave none of the tetramer **2**. This showed that the trimer **1** is not an intermediate on route to the tetramer **2**. These were small scale reactions. Hydrolysis and attempted oxidative degration of the tetramer **2** does not give the dimer **3**. The tetramer **2** is therefore not an intermediate on route to the trimer **1**. Hydrolysis of the trimer **1** to the dimer **3** has already been reported by Green[11] and we verified this. The dimer **3** has previously been made by us at low pH and by independent synthesis.[15]

Proposed mechanistic pathways

Scheme 3 summarises some possible mechanistic pathways that might lead to the trimer **1** and tetramer **2**. The selectivity of the reaction with different oxidants, concentrations of reagents and solution pHs is unusual. The diarylamine linkage in tetramer **2**, formed in relatively high yield, is also unprecedented in this chemistry. Since the product mixtures formed using either $KMnO_4$ or $K_2Cr_2O_7$ are different their pathways may also be



Scheme 2 The reactivity of trimer **1**.



Scheme 3 Proposed routes leading to the trimer **1**, tetramer **2** and dimer **3.**

different. For example, the oxidation of *p*-toluidine with $KMnO_4$ may proceed through intermediate **4** to trimer **1** or through intermediates **5**, **7** and **8** to trimer **1**. Intermediates **5**, **7** and **8** should however also give tetramer **2**, which does not form so intermediate **5** is less likely with $KMnO_4$ as oxidant. Oxidation with $K_2Cr_2O_7$ could proceed *via* the same intermediates **5**, **7** and **8** to trimer **1**, through intermediates **5** and **7**, then **8** or **9** and **10** to tetramer **2**, or through intermediates **6**, **9** and **10** to tetramer **2**. To form trimer **1**, intermediate **7** would firstly require condensation with *p*-toluidine by a Michael addition reaction to give intermediate **8**, then oxidation, to give trimer **1**. To form tetramer **2** intermediate **7** could react in two ways. It could add *p*-toluidine by a Michael addition to give intermediate **8**, followed by an imine exchange reaction with *p*-toluidine to give intermediate **10**, or it could undergo an imine exchange reaction with *p*-toluidine to give intermediate **9**, followed by a Michael addition of *p*-toluidine to give intermediate **10**. These reactions explain how the unusual diarylamine structure might form.

At higher pH (6.0) the Michael addition reaction alone and oxidation is favoured leading to trimer **1**, but at a lower pH (4.0–5.0) and with a higher concentration of *p*-toluidine the imine exchange reaction on either compound **7** or **8** is favoured, so the tetramer **2** forms. A change of temperature did not change the product ratio so increasing the temperature may accelerate both Michael addition, oxidation and imine exchange reactions. Imminium salt **8** should be more electrophilic than imminium salt **7**, so may condense more readily with *p*-toluidine, but it would also be easily oxidised. Both imminium salts would also be easily hydrolysed. We considered ditolylamine **6** as another intermediate that might follow a new reaction pathway leading to tetramer **2**, although we have no evidence for this intermediate. However, Saunders has previously shown that

ditolylamine **6** with *p*-toluidine can be oxidised to tetramer **2** by hydrogen peroxide and the enzyme peroxidase.[16] The evidence was based on an improved yield of tetramer **2** with ditolylamine **6** present. The oxidation of *p*-toluidine and ditolylamine **6** with $K_2Cr_2O_7$ gave recovered ditolylamine **6** (67%) and a yield of tetramer **2** of 14%. The high yield of recovered starting material suggests that ditolylamine **6** is not an intermediate, although at the *p*-toluidine concentration of 2.14 mg/mL the trimer had been expected to form spontaneously and not the tetramer. Since the coupling of intermediate **4** with *p*-toluidine should give exclusively the trimer **1** the tetramer **2** must arise exclusively *via* intermediate **5** from the oxidation of *p*-toluidine.

The exclusive formation of dimer **3** at lower pH[20] could result from the hydrolysis of trimer **1**[11] arising from a more facile oxidation of intermediate **8** at a lower pH. The conversion of intermediate **5** into trimer **1** with $K_2Cr_2O_7$ was reported by Green who typically worked with dilute H_2SO_4 in the cold.[11] Aromatic amine oxidations are complex, as is mauveine synthesis, and we cannot be sure if the amines couple by standard reactions, such as Michael addition and imine exchange, or by the coupling of aminyl radicals. *p*-Toluidine works well and the methyl group can stabilise aminyl radicals which may facilitate the reactions indicated in Scheme 3.

Conclusion

X-ray crystal structure determinations have verified the structure of trimer **1** formed from the oxidation of *p*-toluidine with $KMnO_4$ in hot, dilute H_2SO_4 and tetramer **2** formed from the oxidation of *p*-toluidine with $K_2Cr_2O_7$ in hot, dilute H_2SO_4. Spectroscopic methods have also been used to confirm the structures of both trimer **1** and tetramer **2**. The oxidation of *p*-toluidine with either $K_2Cr_2O_7$ or $KMnO_4$ shows unusual selectivity enabling predominantly trimer **1**, tetramer **2**, or a mixture of both to form depending upon the oxidant, the pH and the concentration. In summary, proposed mechanistic pathways suggest that trimer **1** can form *via* intermediates **4** or **5** depending upon the choice of oxidant, but tetramer **2** can only form *via* intermediate **5**. Barsilowsky's base is believed to be the trimer **1**[1] and not the tetramer **2** although the two syntheses are closely related and the product ratio is easily affected. Some possible mechanistic pathways have been discussed.

Experimental

IR spectra were recorded on an ATI Mattson FTIR spectrometer using potassium bromide discs. UV spectra were recorded using a Perkin-Elmer Lambda 25 UV-VIS spectrometer with CH_2Cl_2 as the solvent. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100.5 MHz respectively using a Varian 400 spectrometer. Chemical shifts, δ are given in ppm relative to the residual solvent and coupling constants, *J* are given in Hz. Low resolution and high resolution mass spectra were obtained at the University of Wales, Swansea using electron impact ionisation and chemical ionisation. Melting points were determined on a Kofler hot-stage microscope. Solutions were evaporated to dryness with gentle warming or *in vacuo*. Dichloromethane can bump when heated in beakers.

X-ray crystallographic characterisation of trimer **1** *tetramer* **2**

The X-ray intensity data were collected on a Rigaku CCD diffractometer (graphite monochromated MoKα radiation, λ = 0.71073 Å, *T* = 100 K).[21] The structures were solved by direct methods with SHELXS-97[22] and the atomic models were refined against $|F|^2$ with SHELXL-97.[22] We modelled the structure of **1** in space group $R\bar{3}$ with half a molecule in the asymmetric unit, which necessitates statistical disorder of the methyl (C4) and amine (N2) groups attached to the central benzene ring. The recent report[19] of the structure of **1** modelled the space group as *R*3. This resolved the disorder of the methyl and amine groups, but resulted in unrealistic anisotropic displacement and geometrical parameters and our own attempts at modelling the structure in *R*3 led to the same problems. We therefore prefer the centrosymmetric space group, but the non-centrosymmetric space group (possibly with merohedral twinning) cannot be ruled out. The C-bound hydrogen atoms for **1** and **2** were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding atoms; the methyl groups were allowed to rotate, but not to tip, to best fit the electron density. The N-bound hydrogen atoms in **1** were located in a difference map and refined as riding atoms. The N-bound hydrogen atom in **2** was located in a difference map and its position was freely refined.

1: $C_{21}H_{21}N_3$, M_r = 315.41, red block, 0.36 × 0.18 × 0.08 mm, trigonal, space group $R\bar{3}$ (no. 148), *Z* = 9, *a* = 20.9896 (8), *c* = 10.0985 (4) Å, *V* = 3853.0 (3) Å^3 at 100 K. Number of measured and unique reflections = 12736 and 1686, respectively ($-25 \le h \le 22$, $-25 \le k \le 25$, $-12 \le l \le 12$; $2\theta_{max} = 52.0°$; $R_{int} = 0.054$). Final $R(F) = 0.089$, $wR(F^2) = 0.167$ for 112 parameters and 1620 reflections with $I > 2\sigma(I)$ (corresponding *R*-values based on all 1686 reflections = 0.092 and 0.168, respectively), CCDC reference number 988298.

2: $C_{28}H_{27}N_3$, M_r = 405.53, ruby-red block, 0.08 × 0.06 × 0.02 mm, monoclinic, space group $P2_1/n$ (No. 14), *Z* = 4, *a* = 13.5019 (7), *b* = 6.3512 (3), *c* = 25.918 (2) Å, β = 95.425 (7)°, *V* = 2212.6 (2) Å^3 at 100 K. Number of measured and unique reflections = 20455 and 3902, respectively ($-16 \le h \le 16$, $-7 \le k \le 7$, $-30 \le l \le 30$; $2\theta_{max} = 50.2°$; $R_{int} = 0.097$). Final $R(F) = 0.052$, $wR(F^2) = 0.096$ for 288 parameters and 2375 reflections with $I > 2\sigma(I)$ (corresponding *R*-values based on all 3902 reflections = 0.115 and 0.119, respectively), CCDC reference number 982643.

Entry 1: *2-Amino-5-methyl-1,4-benzoquinone-1,4-(4-methyl phenylimine)* (**1**): *p*-Toluidine (1.0 g, 0.009 mol) and $KMnO_4$ (2.95 g, 0.019 mol) in dilute sulfuric acid (10 drops, 0.5 mL of cH_2SO_4 in 200 mL of H_2O) were heated for 45 min at 60 °C. After cooling the reaction was filtered through a fine pore sinter and washed with H_2O (100 mL) then extracted with MeOH (50 mL) and CH_2Cl_2 (50 mL × 4). The combined fractions were evaporated to dryness and purified by chromatography on silica gel. Dichloromethane eluted the title compound (89 mg, 9%) as an orange solid, m.p. > 225 °C from dichloromethane/light petroleum ether 40–60. λ_{max} (CH_2Cl_2)/nm 440 (log ε 3.99) and 295 (4.37); ν_{max} (KBr disc) 3306br, 3022w, 2914w, 1646s, 1603vs, 1572vs, 1501vs, 1433s, 1369s, 1310s, 1258s, 1230s, 1208s, 1168w, 1017w, 844s, 807s, 736w, 715w and 480s; δ_H(400 MHz; $CDCl_3$) 2.18 (s, 3H), 2.32 (s, 3H), 2.37 (s, 3H), 4.80–5.20 (s, br, 2H), 5.86 (1H, s), 6.58 (s, 1H), 6.78–6.84 (m, 4H), 7.14 (d, 2H, *J* = 8.0) and 7.20 (d, 2H, *J* = 7.6); δ_C(100.1 MHz; $CDCl_3$) 18.4, 20.9, 21.0, 95.5, 120.6, 120.8, 129.4, 129.6, 133.5, 134.7, 144.0, 146.7, 153.3 and 159.6 (3 resonances are missing), *m/z* (orbitrap ASAP) 316.1808 (M^+ + H, 100%) $C_{21}H_{22}N_3$ requires 316.1808. The same reaction at room temperature gave exclusively the trimer by TLC analysis (25 : 75 Et_2O/light petrol 40–60).

Entry 2: *2-Amino-5-methyl-1,4-benzoquinone-1,4-(4-methyl phenylimine)* (**1**): *p*-Toluidine hydrochloride (1.43 g, 0.01 moles) and $KMnO_4$ (2.95 g, 0.019 moles) in H_2O (200 mL) were heated at 60 °C for 45 min. After cooling the reaction was filtered, washed with H_2O, then extracted with MeOH (50 mL) followed by dichloromethane (50 mL × 4). The combined fractions were evaporated to dryness and purified by chromatography on silica gel. Dichloromethane eluted the title compound (114 mg, 11%) as an orange solid with identical spectroscopic properties to previous material.

Entry 3: *2-(4-Methylphenylamino)-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine)* (**2**) and *2-amino-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine)* (**1**)**:** *p*-Toluidine (2.0 g, 0.0187 mol) in dilute H_2SO_4 (1.0 mL of cH_2SO_4 in 200 mL H_2O) was treated with $K_2Cr_2O_7$ (5.49 g, 0.0187 mol) and heated at 60–70 °C for 1.5 h. The reaction was allowed to cool and a brown precipitate was filtered off. This was extracted with MeOH (50 mL) and CH_2Cl_2 (50 mL × 4) and the combined extracts evaporated to dryness in a beaker. The product was purified by chromatography on silica gel. Elution with

dichloromethane gave the title compound **2** (232 mg, 12%) as a red solid, m.p. 201–202 °C (lit.[11] 175, 227, 244–245, 216–220, 220–225 °C) from dichloromethane/light petroleum ether 40–60. λ_{max} (CH_2Cl_2)/nm 453 (log ε 3.7) and 301 (4.1); ν_{max} (KBr disc) 3340vs, 3109–2819vs, 1636vs, 1507vs, 1500vs, 1346vs, 1306vs, 1282vs, 1254vs, 1168s, 1109s, 1017s, 936w, 875vs, 850vs, 822s, 810s, 671w, 585w and 560w; δ_H(400 MHz; $CDCl_3$) 2.24 (3H, s), 2.30 (3H, s), 2.36 (3H, s), 2.41 (3H, s), 6.36 (1H, s), 6.68 (1H, d, *J*=1.6), 6.83 (2H, d, *J*=8.0), 6.86 (2H, d, *J*=8.4), 7.00 (2H, d, *J*=8.4), 7.07 (2H, d, *J*=8.0), 7.16 (2H, d, *J*=8.0), 7.23 (2H, d, *J*=8.0) and 7.76 (1H, s); δ_C(100.1 MHz; $CDCl_3$) 18.5, 20.8, 20.9, 21.0, 94.3, 120.6, 120.7, 120.8, 120.9, 129.3, 129.7, 129.8, 132.8, 133.5, 134.6, 137.0, 144.8, 146.6, 153.6 and 159.4 (two resonances are overlapping); *m/z* (orbitrap ASAP) 406.2270 (M^++H, 100%) $C_{28}H_{28}N_3$ requires 406.2278. Elution with Et_2O/light petrol (25 : 75) gave title compound **1** (32 mg, 2%) with identical spectroscopic properties to previous material.

Entry 4: *2-(4-Methylphenylamino)-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine)* (**2**) and *2-amino-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine)* (**1**)**:** *p*-Toluidine (2.0 g, 0.0187 mol) in dilute H_2SO_4 (1.0 mL of cH_2SO_4 in 200 mL H_2O) was treated with $K_2Cr_2O_7$ (5.49 g, 0.0187 mol) at room temperature for 1.5 h. The reaction was allowed to cool and a brown precipitate was filtered off. This was extracted with MeOH (50 mL) and CH_2Cl_2 (50 mL × 4) and the combined extracts evaporated to dryness in a beaker. The product was purified by chromatography on silica gel. Elution with dichloromethane gave the title compound **2** (112 mg, 6%). Elution with Et_2O/light petrol (25 : 75) gave title compound **1** (20 mg, 1%) with identical spectroscopic properties to previous material.

Entry 5: *2-(4-Methylphenylamino)-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine)* (**2**) and *2-amino-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine)* (**1**): *p*-Toluidine (1.0 g, 0.00935 mol) in dilute H_2SO_4 (0.5 mL of cH_2SO_4 in 200 mL H_2O) was treated with $K_2Cr_2O_7$ (2.75 g, 0.0094 mol) and heated at 60–70 °C for 1.5 h. The reaction was allowed to cool and a brown precipitate was filtered off. This was extracted in the sinter with MeOH (50 mL) and CH_2Cl_2 (50 mL × 4) and the combined extracts evaporated to dryness in a beaker. The product was purified by chromatography on silica gel. Elution with dichloromethane gave the title compound **2** (54 mg, 6%). Elution with Et_2O/light petrol (25 : 75) gave the title compound **1** (136 mg, 14%). Both products had identical spectroscopic properties to previous material.

Entry 6: *2-Amino-5-methyl-1,4-benzoquinone-1,4-(4-methyl phenylimine)* (**1**): *p*-Toluidine hydrochloride (0.67 g, 0.0047 mol) and $K_2Cr_2O_7$ (1.37 g, 0.0047 mol) in H_2O (200 mL) were heated at 60 °C for 1.5 h. After cooling, the reaction was filtered, washed with H_2O, then extracted with MeOH (50 mL) followed by CH_2Cl_2 (50 mL × 4). The combined extracts were evaporated to dryness and purified by chromatography on silica gel. Dichloromethane eluted the title compound (78 mg, 16%) with identical spectroscopic properties to previous material.

2-Amino-5-methyl-1,4-benzoquinone-4-(4-methyl)phenylimine (**3**): 2-Amino-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine) **1** (50 mg, 0.16 mmol) in dilute sulfuric acid (2 mL of cH_2SO_4 in 20 mL H_2O) was heated at 60 °C for 30 min. The reaction was cooled, neutralised with KOH, then extracted with CH_2Cl_2. The product was purified by chromatography on silica gel. Elution with Et_2O/light petrol (25 : 75) gave the title compound as an orange/red solid with identical spectroscopic properties to material prepared previously by the $K_2Cr_2O_7$ oxidation of *p*-toluidine at a similar pH.[15]

Attempted synthesis of 2-(4-methylphenylamino)-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine) (**2**): 2-Amino-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine) **1** (10 mg, 0.032 mmol) and *p*-toluidine hydrochloride (20 mg, 0.14 mmol) in MeOH (30 mL) were refluxed for 2 h. TLC analysis (25 : 75 Et_2O/light petrol) showed some baseline decomposition and only starting material.

Attempted synthesis of 2-(4-methylphenylamino)-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine) (**2**): 2-Amino-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine) **1** (10 mg, 0.032 mmol), *p*-toluidine hydrochloride (20 mg, 0.14 mmol) and $K_2Cr_2O_7$ (41 mg, 0.14 mmol) were heated in H_2O (20 mL) at 60 °C for 1 h. The reaction was cooled, neutralised with KOH, then extracted with CH_2Cl_2. TLC analysis (25 : 75 Et_2O/light petrol) showed only the starting material to be present.

Attempted synthesis of 2-amino-5-methyl-1,4-benzoquinone-4-(4-methyl)phenylimine (**3**): 2-(4-Methylphenylamino)-5-methyl-1,4-benzoquinone-1,4-(4-methylphenylimine) **2** (30 mg, 0.074 mmol) in dilute sulfuric acid (2 mL of cH_2SO_4 in 20 mL of H_2O) was treated with $K_2Cr_2O_7$ (50 mg, 0.17 mmol) and heated at 60 °C for 1 h. The reaction was cooled, neutralised with KOH, then extracted with CH_2Cl_2. TLC analysis (25 : 75 Et_2O/light petrol) showed no starting material and none of the dimer **3** to be present.

Attempted oxidation of p-toluidine and ditolylamine **6** *with* $K_2Cr_2O_7$*: p*-Toluidine (214 mg, 2.0 mmol) and ditolylamine **6** (200 mg, 1.0 mmol) were heated in water (100 mL) at 60 °C acidified with cH_2SO_4 (0.1 mL, 2 drops) and treated with $K_2Cr_2O_7$ (298 mg, 1.0 mmol). After 1.5 h the mixture was cooled, filtered and extracted with MeOH (50 mL) then CH_2Cl_2 (50 mL × 4). The products were purified by chromatography on silica gel. Dichloromethane eluted the recovered starting material **6** (134 mg, 67%) then Et_2O/light petrol (25 : 75) eluted the tetramer **2** (28 mg, 14%) with identical spectroscopic properties to previous material.

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References

1 J. Barsilowsky, *Chem. Ber.*, 1873, **6**, 1207.
2 J. Barsilowsky *Chem. Ber.*, 1875, **8**, 693.
3 J. Barsilowsky and G. Wagner, *Chem. Ber.*, 1878, **11**, 2148.
4 J. Barsilowsky, *Chem. Ber.*, 1881, **14**, 2073.
5 J. Barsilowsky, *J. Liebigs Ann. Chem*., 1881, **207**, 102.
6 J. Barsilowsky, *J. Russ. Phys. Chem*., 1881, **1**, 450.
7 W.H. Perkin, *J. Chem. Soc., Trans*., 1879, **35**, 717.
8 W.H. Perkin, *J. Chem. Soc., Trans*., 1880, **37**, 546.
9 W.H. Perkin, *Chem. Ber.*, 1880, **13**, 1874.
10 H. Klinger and R. Pitschke, *Chem. Ber.*, 1884, **17**, 2439.
11 A.G. Green, *J. Chem. Soc., Trans*., 1893, **63**, 1395.
12 F. Klingemann, *J. Liebigs Ann. Chem*., 1893, **275**, 92.
13 E. Börnstein, *Chem. Ber.*, 1901, **34**, 1274.
14 E. Börnstein, *Chem. Ber.*, 1910, **43**, 2380.
15 B.C. Saunders and P.J.G. Mann, *J. Chem. Soc*., 1940, 769.
16 V.R. Holland and B.C. Saunders, *Tetrahedron*, 1966, **22**, 3345.
17 V.R. Holland and B.C. Saunders, *Tetrahedron*, 1969, **25**, 4153.
18 T. Kametani and K. Ogasawara, *Chem. Pharm. Bull*., 1968, **16**, 1843.
19 K.-S. Peng, Q.-L. Zeng and W. Zhang, *Chin. J. Syn. Chem*., 2010, **18**, 239; (Chem. Abtrs., 2010, **153**, 579858).
20 M.J. Plater, *J. Chem. Res*., 2011, **35**, 304.
21 S.J. Coles and P.A. Gale, *Chem. Sci*., 2012, **3**, 683.
22 G.M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112.