3-Hydroxypyrroles and 1*H*-Pyrrol-3(2*H*)-ones. Part 9.[1] Diazo-coupling Reactions of 1-Substituted-1*H*-pyrrol-3(2*H*)-ones

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Reaction of the 1-substituted 1*H*-pyrrol-3(2*H*)-ones **6** and **7** with diazonium salts under acidic conditions gives rise to 2-coupled products, which are shown by X-ray crystallography to adopt the ketohydrazone structures **9–11K**.

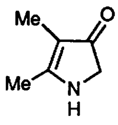
Although the reactions of 3-hydroxypyrroles [1*H*-pyrrol-3(2*H*)-ones] **1** with diazonium salts have been known since the beginning of this century,[2] early examples employed heavily substituted substrates, and the constitution of the products was poorly defined.[3] More recently, Bauer has shown that the coupling product of the 4,5-dimethylpyrrolone **2** with benzenediazonium salts exists as the hydrazone tautomer **3**, by comparison of its UV spectrum with that of the related azo compound **4**,[4] and we have obtained 4-substituted azo derivatives from the 2,2-dimethylpyrrolone **5**.[1] In the work described here, we sought to resolve the question of regiochemistry for the azo coupling reactions of simple 1-alkyl- and 1-aryl-pyrrolones **6** and **7**, in which all three ring carbon positons are unsubstituted, and also to identify unambiguously the tautomeric form of the products both in solution and in the solid state. It is of interest that Momose *et al.* obtained the hydrazone **8K** by Jaap–Klingemann-like reaction of the corresponding pyrrolone-2-carboxylic ester with diazonium salts under basic conditions; ring expansion reactions took place at lower pH.[5] The tautomeric structure of **8** followed from its ^{1}H NMR spectrum, which showed peaks at δ_H 5.37 and 7.45 (^3J 4 Hz) characteristic of the 4- and 5-protons of a pyrrolone system.[6]

Treatment of the *N*-phenylpyrrolone **6** with aryl diazonium chlorides under acidic conditions gave the coupling products **9** and **10** as orange–brown precipitates. The product **11** from the *N*-alkylpyrrolone **7** was more soluble, but was obtained in 71% yield after extraction. The ^{1}H NMR spectra of compounds **9–11** are closely similar to that of **8**[5] with mutually coupled one-proton doublets (^3J *ca.* 4 Hz) in the range δ_H 5–6 and 7–8. The possibility of reaction at the 4- or 5-positions of the pyrrolone is excluded by these data, since the keto forms of such products would show a 2-proton peak due to the 2-position, and the enol forms would be expected to have much smaller coupling constants (in general, $^4J_{2,4}$ and $^4J_{2,5}$ *ca.* 2.0 and 2.7 Hz, respectively).[7]

These results suggest that the diazo-coupling reaction takes place *via* the 3-hydroxypyrrole tautomer, since in this form the 2-position is activated by both the 3-substitutent and the nitrogen heteroatom. The complete absence of 4-substituted product is of interest, especially in the 1-t-butyl case where steric effects are known to deactivate pyrrole α-positions substantially.[8] Although reaction at the 4-position would be expected of the 1*H*-pyrrol-3(2*H*)-one tautomer,[1] it is likely that this would be deactivated under the acidic conditions used in the coupling.[1,9]

In an attempt to establish the tautomeric form of the products **9–11** in solution, a detailed comparison of their NMR spectra with those of the keto[6] and enol[7] forms of the precursors **6** and **7** was carried out (Table 1). The ^{1}H NMR data proved surprisingly equivocal; although the size of $^3J_{4,5}$ for **9** and **11** generally favours the keto form, the chemical shift of 5-H in particular may be more consistent with conjugative deshielding induced by the 2-azo function present in the enol form. Clearly, assignment of tautomeric form based solely on ^{1}H NMR data should be treated with caution. In the ^{13}C NMR spectra (Table 1), neither the C-4 chemical shift nor the coupling data allow discrimination between the tautomers, but the chemical shifts of C-3 and C-5 both show substantial differences. In particular, that of C-5 in the coupled products **9–11** (δ_C 148–150) is clearly

1E **1K**



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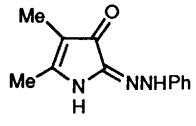

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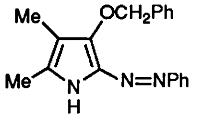

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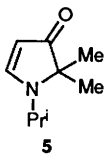

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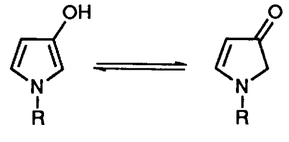


E **K**

6 R = Ph
7 R = Bu^t

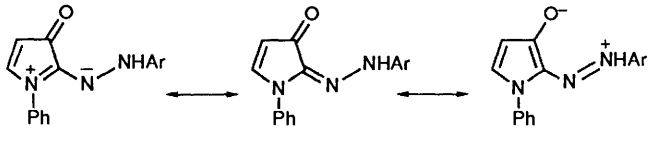
Table 1 NMR parameters of the pyrrolones **6** and **7**, and of the coupled products **9–11**[a]

Compound	4-H	5-H	$^3J_{4,5}$	C-2	C-3	C-4	C-5	$^1J_{C-4,4-H}$	$^1J_{C-5,5-H}$	$^2J_{C-4,5-H}$	$^2J_{C-5,4-H}$
6E[7,b]	5.85	7.06	3.1	101.54	146.07	102.18	115.96	170.9	186.5	7.0	6.6
6K[6,c]	5.46	8.40	3.6	55.65	198.71	103.81	158.31	179.2	176.7	6.2	9.4
9[c]	5.66	7.87	4.0	133.38	179.25	101.29	149.44	179.5	183.2	5.6	7.7
10[c]	5.70	7.84	4.0	132.58	178.47	101.19	148.64				
10[b]				132.99	178.55	100.64	151.53				
10[d]				132.53	*e*	99.71	150.00				
7E[7,b]	5.50	6.49	2.9	101.16	143.37	97.60	114.18				
7K[6,c]	5.09	7.93	3.4	54.19	199.76	99.13	162.58				
11[c]	5.33	7.63	3.9	134.48	178.86	97.47	148.93				

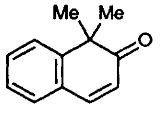
[a] Coupling constants are in Hz. [b] [$^2H_6$]DMSO solution. [c] [^{2}H]Chloroform solution. [d] [$^2H_4$]Methanol solution. [e] Very low solubility, quaternary not detected.

Table 2 Atomic co-ordinates with esd's

	x	y	z	U_{iso}
N(1)	0.374 2(4)	0.9399(5)	0.1692(8)	0.046(4)
C(2)	0.354 2(4)	0.8270(6)	0.1713(10)	0.044(5)
C(3)	0.425 9(4)	0.7688(7)	0.2800(10)	0.043(5)
O(3)	0.428 0(3)	0.6658(4)	0.3083(7)	0.059(4)
C(4)	0.485 2(5)	0.8537(7)	0.3366(12)	0.060(6)
C(5)	0.454 2(4)	0.9522(7)	0.2653(11)	0.057(5)
N(6)	0.285 2(4)	0.786 5(5)	0.0807(8)	0.044(4)
N(7)	0.276 9(4)	0.6761(5)	0.0953(8)	0.046(4)
C(11)	0.328 4(3)	1.0249(3)	0.0670(6)	0.043(5)
C(12)	0.243 3(3)	1.0337(3)	0.0617(6)	0.047(5)
C(13)	0.198 9(3)	1.1216(3)	−0.0323(6)	0.055(5)
C(14)	0.239 8(3)	1.200 6(3)	−0.1209(6)	0.061(6)
C(15)	0.324 9(3)	1.1917(3)	−0.1156(6)	0.061(6)
C(16)	0.369 2(3)	1.1039(3)	−0.0216(6)	0.053(5)
C(71)	0.206 29(22)	0.6226(3)	0.0037(6)	0.039(4)
C(72)	0.199 79(22)	0.5092(3)	0.0400(6)	0.053(5)
C(73)	0.130 92(22)	0.4490(3)	−0.0461(6)	0.055(5)
C(74)	0.068 56(22)	0.5022(3)	−0.1684(6)	0.049(5)
C(75)	0.075 06(22)	0.6155(3)	−0.2047(6)	0.054(5)
C(76)	0.143 93(22)	0.6757(3)	−0.118 7(6)	0.050(5)
C(74M)	−0.006 0(5)	0.4352(7)	−0.2628(12)	0.065(6)



Scheme 1



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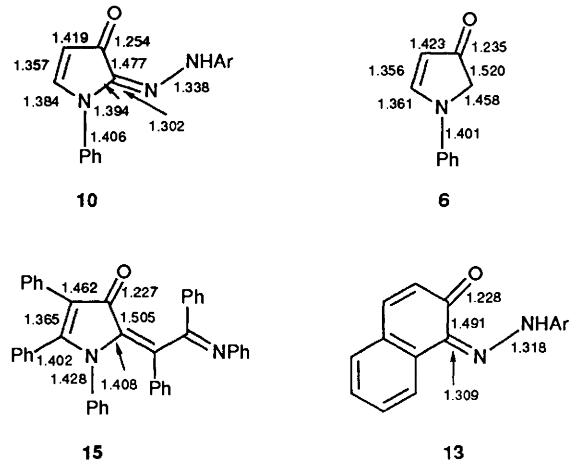
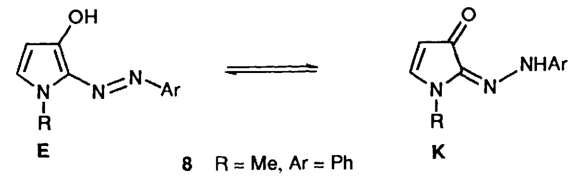
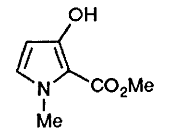


Fig. 1 Selected bond lengths (Å) for **10** and related compounds



8 R = Me, Ar = Ph
9 R = Ar = Ph
10 R = Ph, Ar = p-MeC_6H_4
11 R = Bu^t, Ar = Ph



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much closer to the range expected for a 1*H*-pyrrol-3(2*H*)-one enaminone-type system[6] (δ_C *ca.* 160) than for the 5-position of a 3-hydroxypyrrole[7] (δ_C *ca.* 115). The effect of a 2-azo (electron-withdrawing) group in **9–11E** would be expected to cause some deshielding of C-5, but it is highly unlikely that this should be as large as 45 ppm: for example δ_C (C-5) of the ester **12**[10] is 128.02, corresponding to a shift of just 14 ppm from the model compound **7E**. Conversely, a 2-hydrazono group in **9–11K** might be expected to act predominantly by electron donation [*cf.* structure **10K2** (Scheme 1)] and therefore lead to a low frequency shift at C-5, as observed. Although the chemical shift of the 3-position in **9–11** (δ_C *ca.* 180) is intermediate between those of the pyrrolones[6] (δ_C *ca.* 200) and 3-hydroxypyrroles[7] (δ_C *ca.* 145) (Table 1), a 2-electron-withdrawing group would again be expected to cause deshielding of a hydroxypyrrole resonance by only *ca.* 10 ppm [*eg* **12** δ_C (C-3) 155.24[10]], whereas a β-hydrazono group causes substantial shielding of carbonyl signals. Indeed, the observed shielding of this resonance in the naphthalenone **13**[11] relative to its 1,1-dimethyl analogue **14**[12] (24.1 ppm) is quantitatively similar to the pyrrolone examples.

Overall, we believe that the ^{13}C NMR data are fully in accord with the ketohydrazone tautomers **9–11K** being the dominant forms in solution. We cannot exclude the presence of a small amount of the hydroxyazo forms **9–11E** in rapid tautomeric equilibrium, as found for some 1-(arylazo)-2-naphthols.[11] However, the ^{13}C NMR spectra of **10**, recorded in a non-polar solvent ([^{2}H]chloroform), a hydrogen-bond acceptor solvent ([$^2H_6$]DMSO) and a hydrogen-bond donor solvent ([$^2H_4$]-methanol) are all closely similar (Table 1), which suggests that the position of any such equilibrium in these compounds is remarkably insensitive to external factors.

In order to confirm the structure and tautomerism of these coupling products in the solid state, an X-ray crystal structure

Table 3 Bond lengths °, angles and torsion angles with standard deviations

Bond length (Å)		Bond angle (°)		Torsion angle (°)	
N(1)–C(2)	1.394(9)	C(2)–N(1)–C(5)	107.5(6)	C(5)–N(1)–C(2)–C(3)	1.7(8)
N(1)–C(5)	1.384(10)	C(2)–N(1)–C(11)	127.4(6)	C(5)–N(1)–C(2)–N(6)	−174.6(7)
N(1)–C(11)	1.406(7)	C(5)–N(1)–C(11)	124.5(6)	C(11)–N(1)–C(2)–C(3)	172.7(6)
C(2)–C(3)	1.477(10)	N(1)–C(2)–C(3)	107.5(6)	C(11)–N(1)–C(2)–N(6)	−3.6(11)
C(2)–N(6)	1.302(9)	N(1)–C(2)–N(6)	122.8(6)	C(2)–N(1)–C(5)–C(4)	−2.9(9)
C(3)–O(3)	1.254(9)	C(3)–C(2)–N(6)	129.6(7)	C(11)–N(1)–C(5)–C(4)	−174.3(6)
C(3)–C(4)	1.419(11)	C(2)–C(3)–O(3)	123.6(7)	C(2)–N(1)–C(11)–C(12)	46.9(8)
C(4)–C(5)	1.356(12)	C(2)–C(3)–C(4)	104.9(6)	C(2)–N(1)–C(11)–C(16)	−136.3(6)
N(6)–N(7)	1.338(8)	O(3)–C(3)–C(4)	131.4(7)	C(5)–N(1)–C(11)–C(12)	−143.4(6)
N(7)–C(71)	1.390(7)	C(3)–C(4)–C(5)	108.7(7)	C(5)–N(1)–C(11)–C(16)	33.3(8)
C(74)–C(74M)	1.525(10)	N(1)–C(5)–C(4)	111.3(7)	N(1)–C(2)–C(3)–O(3)	−179.9(7)
		C(2)–N(6)–N(7)	114.8(6)	N(1)–C(2)–C(3)–C(4)	0.1(8)
		N(6)–N(7)–C(71)	120.4(5)	N(6)–C(2)–C(3)–O(3)	−3.9(13)
		N(1)–C(11)–C(12)	120.3(4)	N(6)–C(2)–C(3)–C(4)	176.1(8)
		N(1)–C(11)–C(16)	119.6(4)	N(1)–C(2)–N(6)–N(7)	178.7(6)
		N(7)–C(71)–C(72)	116.2(4)	C(3)–C(2)–N(6)–N(7)	3.3(11)
		N(7)–C(71)–C(76)	123.8(4)	C(2)–C(3)–C(4)–C(5)	−1.9(9)
		C(73)–C(74)–C(74M)	119.5(5)	O(3)–C(3)–C(4)–C(5)	178.1(8)
		C(75)–C(74)–C(74M)	120.5(5)	C(3)–C(4)–C(5)–N(1)	3.0(10)
				C(2)–N(6)–N(7)–C(71)	−179.4(6)
				N(6)–N(7)–C(71)–C(72)	−174.5(5)
				N(6)–N(7)–C(71)–C(76)	5.5(8)
				N(1)–C(11)–C(12)–C(13)	176.7(5)
				N(1)–C(11)–C(16)–C(15)	−176.8(5)
				N(7)–C(71)–C(72)–C(73)	179.9(4)
				N(7)–C(71)–C(76)–C(75)	−179.9(4)
				C(72)–C(73)–C(74)–C(74M)	179.4(5)
				C(74M)–C(74)–C(75)–C(76)	−179.4(5)

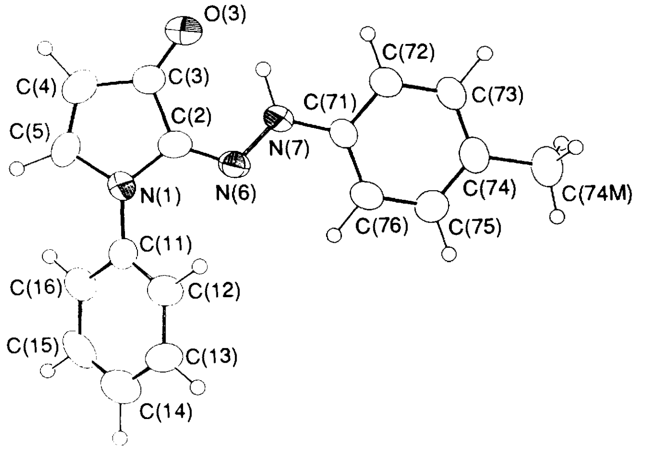

Fig. 2 ORTEP plot of **10** showing the crystallographic numbering scheme

determination was carried out. Attempts to obtain suitable crystals of the *N*-phenyl derivative **9** were unsuccessful, but careful recrystallisation of the *p*-tolyl derivative **10** from cyclohexane gave long needles which were of barely adequate diffraction quality. Atomic co-ordinates, bond lengths and angles are given in Tables 2–3 and are summarised in Fig. 1 along with data for some relevant model compounds: Fig. 2 is an ORTEP plot of **10** showing the crystallographic numbering system. The results confirm that coupling has taken place in the 2-position, and they clearly support the hydrazone tautomer of the product. Thus the C–O bond length [1.254(9) Å] is very similar to that of the pyrrolone **6** [1.235(2) Å],[13] and much shorter than expected for a phenol-type C–O [1.362(15) Å].[14] The length of the C(2)–C(3) ring bond [1.477(10) Å], though significantly shorter than that of the model compound **6** [1.520(2) Å][13] (see below), is much longer than the mean value for the formal C(2)–C(3) double-bond in pyrroles [1.374(17) Å].[15] Similarly, the geometry of the exocyclic group [C(2)–N(6) 1.302(9) Å; N(6)–N(7) 1.338(8) Å] suggests a hydrazone function hydrogen bonded to a carbonyl group (mean values for C=N and N–N in such structures are 1.313 and 1.307 Å, respectively)[16] rather than an azo group [typical values for C–N 1.431(20) Å and for N=N 1.240(12) Å].[14] The overall similarity in bond lengths between **10** and the corresponding section of the β-naphthol derivative **13** (Fig. 1), which is known to adopt the hydrazone tautomer,[17] is also noteworthy.

A comparison of the geometry of the three pyrrolones **6**, **10** and **15**[18] is also of interest. The N(1)–C(2) bonds of the 2-double bonded derivatives **10** and **15** are significantly shorter than that of the parent compound **6**, presumably because of some delocalisation of the ring-nitrogen atom's lone pair (*cf.* resonance structure **10K**). Alternatively, the lengths of the C(2)–C(3) and C(3)–O(3) bonds are significantly shorter and longer, respectively, in the hydrazone **10** than in either **6** or **15**. This may be explained by delocalisation of the ketohydrazone moiety (structure **10K2**), a feature which may also contribute to the ^{13}C NMR chemical shift of C-3 (see above). The increase in steric crowding around the ring nitrogen atom is reflected in the dihedral angles (**6**, 7.5°; **10** 33.3°; **15** 73.0°) between the pyrrolone and its *N*-phenyl group. Whereas the geometry around this nitrogen atom is essentially trigonal in **6** and **10** it is distinctly pyramidal in the case of **15**. The change in hybridisation at C(2) from sp^3 in **6** to sp^2 in **10** and **15** is accompanied by a slight increase in N(1)–C(2)–C(3) bond angle (**6**, 103.4°; **10**, 107.5°; **15**, 106.5°).

In summary, therefore, the X-ray structure of the coupling product **10** clearly shows that it exists in the hydrazone tautomer **10K** in the solid state. Modifications of the geometry from that of model compounds can be rationalised by delocalisation as shown in Scheme 1.

The UV spectra of **10** and **11** in methanol solution showed peaks at λ_{max}/nm 469, 376 and 265; and 463, 376 and 258, respectively. These data compare favourably with Bauer's results[4] for the 4,5-dimethyl derivative **3** (λ_{max}/nm 444, 388 and 255), and further support the hydrazone structure for the coupling products in solution.

Experimental

^1H And ^{13}C NMR spectra were recorded at 80 or 200, and 20 or 50 MHz, respectively, for solutions in [^2H]chloroform. All J values are in Hz.

*2-Arylhydrazono-*1H*-pyrrol-*3(2H)*-ones*.—A solution of the aryl diazonium chloride (1 mmol) in water (0.75 cm^3) was added to a stirred solution of the pyrrol-3-one[19] (1 mmol) in methanol (5 cm^3) at room temperature, and was stirred for 20 min. The 1-phenyl compounds precipitated from solution and were collected. The 1-t-butyl product was obtained by extraction of the reaction mixture with methylene chloride (3 × 15 cm^3), drying ($MgSO_4$), evaporation of the solvent under reduced pressure and bulb-to-bulb distillation of the residue. The following title compounds were obtained: *1-phenyl-2-phenylhydrazono-*1H*-pyrrol-*3(2H)*-one* (158 mg, 60%), m.p. 159–160 °C (from methanol) (Found: C, 72.85: H, 4.85; N, 15.8. $C_{16}H_{13}N_3O$ requires C, 73.0; H, 4.95; N, 15.95%); δ_H 13.57 (1 H, br s), 7.87 (1 H, d, ^3J 4.0), 6.9–7.6 (10 H, m) and 5.66 (1 H, d, ^3J 4.0); δ_C 179.25(q), 149.44, 142.60(q), 137.51(q), 133.38(q), 129.29, 129.22, 126.10, 123.07, 122.69, 114.29 and 101.29; m/z 263 (M^+, 100%), 234(16), 206(10), 186(16), 171(61), 158(52), 146(58), 145(42), 130(45), 117(48) and 104(74): *1-phenyl-2-*p*-tolylhydrazono-*1H*-pyrrol-*3(2H)*-one* (260 mg, 98%), m.p. 139–140 °C (from methanol) (Found: C, 72.3; H, 5.35; N, 14.8. $C_{17}H_{15}N_3O$. 0.25 H_2O requires C, 72.45; H, 5.5; N, 14.9%); δ_H 14.82 (1 H, br s), 7.84 (1 H, d, ^3J 4.0), 7.0–7.5 (9 H, m), 5.70 (1 H, d, ^3J 4.0) and 2.30 (3 H, s); δ_C 178.47(q), 148.64, 140.06(q), 137.49(q), 132.99(q), 132.85(q), 129.80, 129.14, 125.99, 122.60, 114.26, 101.19 and 20.67; m/z 277 (M^+, 100%), 171(23), 146(26), 104(24), 91(42), 77(63), and 51(21): *1-t-butyl-2-phenylhydrazono-*1H*-pyrrol-*3(2H)*-one* (172 mg, 71%), m.p. 70–72 °C (from methanol) (Found: C, 68.85; H, 6.75; N, 17.05. $C_{14}H_{17}N_3O$ requires C, 69.15; H, 7.0; N, 17.3%); δ_H 7.63 (1 H, d, ^3J 3.9), 6.8–7.4 (5 H, m), 5.33 (1 H, d, ^3J 3.9) and 1.59 (9 H, s); δ_C 178.86(q), 148.93, 142.89(q), 134.48(q), 129.26, 122.58, 114.04, 97.47, 56.69(q) and 28.89; m/z 243 (M^+, 90%), 187(100), 110(37), 95(67) and 93(49).

*Crystal Structure Determination on 1-Phenyl-2-*p*-tolylhydrazono-*1H*-pyrrol-*3(2H)*-one.—Crystal data.* $C_{17}H_{15}N_3O$, M = 277.32. Monoclinic, space group $P2_1/c$ (No. 14), a = 7.4573(11), b = 12.0023(12), c = 16.4114(18) Å, β = 100.513(10)°, V = 1444 Å^3 [from 2θ values of 37 reflections measured at ±ω (2θ = 24–26°, λ = 0.71073 Å)], Z = 4, D_{calc} = 1.275 g cm^{-3}, T = 298 K, $F(000)$ = 584, deep red needle, 0.077 × 0.12 × 0.77 mm, μ = 0.08 mm^{-1}.

Data collection and processing. Stoë STADI-4 four-circle diffractometer, graphite-monochromated Mo-K_α X-radiation, T = 298 K, ω-2θ scans with ω scan width (1.20 + 0.347tanθ)°. Of 2039 data measured ($2\theta_{max}$ 45°, $\pm h$, $+k$, $+l$), 1478 were unique (R_{int} 0.11) and of these 1045 with $F \geqslant 2\,\sigma(F)$ were used in all calculations. The intensities of three standard reflections measured every 2 h varied by only ±1%, indicating no significant crystal decay or movement had occurred.

Structure analysis and refinement. Automatic direct methods[20] located all non-H atoms and H atom positions were identified from a difference Fourier synthesis. The structure was then refined (by least-squares on F^2[21]) with anisotropic thermal parameters for all non-H atoms, with phenyl rings constrained to be rigid idealised hexagons and with H atoms in fixed, calculated positions or as part of a rigid methyl group. At final convergence R, R_w = 0.0910, 0.1088, respectively, S = 0.902 for 169 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 0.33 or below −0.37 eÅ^{-3}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.00879F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max}$ was 0.027. Atomic scattering factors were inlaid,[21] Fig. 2 was generated using ORTEPII[22] and molecular geometry calculations were performed using CALC.[23]

Thermal parameters, calculated H-atom positions and full structural parameters are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for the paper.*

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