Structural Studies of Arylazo and Arylimino Compounds. ^{15}N NMR and X-Ray Crystallographic Studies of Azo–Hydrazo Tautomerism

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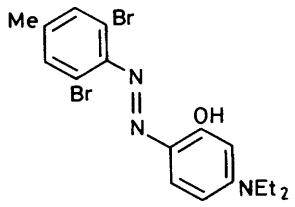
^{15}N NMR measurements on several diarylazo, arylhydrazonopyrazolone, diarylazomethine and arylaminomethylidenepyrazolone compounds are reported. The presence of hydrazo tautomers is recognised by NOE experiments. The crystal structures of 4-(2,6-dibromo-4-methylphenylazo)-3-hydroxy-*N*,*N*-diethylaniline (**12**) and 4-(2-bromophenylhydrazono)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (**15**) have been determined from X-ray diffraction data. Both of these molecules contain a six-membered NNCCOH ring as a result of intramolecular hydrogen bonding. Whereas (**12**) exists as the azo–phenol tautomer, the pyrazolone (**15**) is in the hydrazo–ketone form. The implication of these results for copper-assisted nucleophilic substitution of the halogen in these aryl bromides is discussed.

Studies of copper-assisted nucleophilic substitution in aryl halides have shown that charge distribution in the substrate is important.[1] Many of the substrates of interest to us[2] contain azo and imino linkages. We were particularly interested by the observation that 2-halo-2-hydroxydiarylazo compounds react when heated with potassium acetate in the presence of tetra(acetato)dicopper(II) in *N*,*N*-dimethylformamide solvent to give the corresponding 2,2-dihydroxodiarylazo compound after treatment with concentrated acid. Under identical conditions, 4-(2-haloarylhydrazono)-3-alkyl-1-aryl-(1*H*)-pyrazol-5(4*H*)-ones are unreactive. In contrast with this, 4-(4-nitroarylhydrazono)-3-alkyl-1-aryl-(1*H*)-pyrazol-5-(4*H*)-ones will react with hydrogen peroxide in the presence of tetra(acetato)dicopper(II) at 273 K to form the 2-hydroxy-derivative, but 2-(4-nitrophenylazo)-phenol is unreactive under identical conditions.[3] In order to understand this remarkable difference in reactivity and gain further insight into the mechanism of copper-promoted nucleophilic aromatic substitution, we have compared some of the physical properties of a range of diarylazo compounds, arylhydrazonopyrazolones and their imino analogues in detail.[4] Some of the results which indicate the differences in electron density in these compounds are presented here.

Results and Discussion

Azobenzene Derivatives.—(i) ^{15}N NMR. The presence of a *N*,*N*-diethylamino group *para* to the azo link in the compounds we have measured (Table 1) causes the azo-nitrogen resonances to be more shielded than in azobenzene (δ_N 128.47 ppm[5]) itself, and the contribution of the quinonoid canonical form in these molecules causes a clear distinction between the two azo-nitrogen atoms. Consistent with this, the resonance of the amino-nitrogen is deshielded relative to *N*,*N*-dimethylaniline (−335.63 ppm).[6] The inductive effect of the dialkylamino group is recognised in the low frequency shift (11.85 ppm) of N(2) in (**1**) relative to azobenzene.[5] The presence of an electron-withdrawing substituent *ortho* to N(1) in (**2**) produces a low frequency shift in N(1), whereas N(2) shifts to high frequency relative to (**3**). This inverse relationship continues when an electron-donating substituent is *ortho* to N(1) in (**4**). Azo compounds which do not have a substituent, X, *ortho* to N(2) generally show a difference in the chemical shift of N(1) and N(2) which is in the range 10–25 ppm, except for (**5**), where the presence of two nitro groups increases the separation (to 73.51 ppm) and shifts the amino-nitrogen resonance to higher frequency relative to (**1**). This shows that the interaction between the amino-nitrogen lone pair and the azobenzene π-system increases in the presence of two strong acceptor substituents in (**5**). Consistent with this, the nitro groups are slightly more shielded than in nitrobenzene (−9.90 ppm[7]).



(**12**)

When the substituent X (OH, NHAc) *ortho* to N(2) is capable of H-bonding interaction with N(1), there is a significant shift of the N(1) resonance to lower frequency [X = H(**1**) < NHAc (**6**) ≪ OH(**9**)]; the change in the chemical shift of N(2) in the same direction is much smaller. This interaction can be compared to the protonation of azobenzene for which the ^{15}N shift is 150.4 ppm.[7] Solubility problems prevented a more extensive investigation.

(ii) *Crystal structure of* 4-(2,6-*dibromo*-4-*methylphenylazo*)-3-*hydroxy*-N,N-*diethylaniline* (**12**). The molecular structure is illustrated in Figure 1. Fractional atomic co-ordinates for the

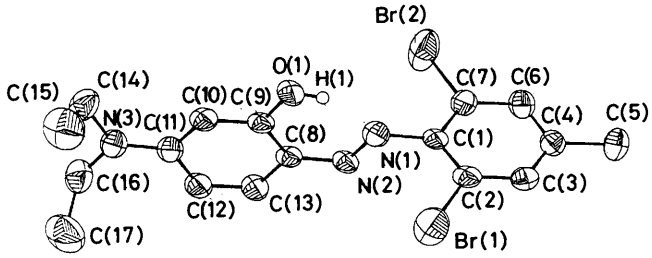
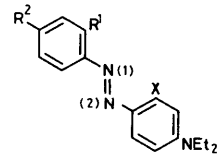


Figure 1. ORTEP view of compound (**12**) showing the atomic numbering.

Table 1. ^{15}N Chemical shifts [δ/(ppm)] of diarylazo compounds in $CDCl_3$ solution.



Compound	X	R_1	R_2	N(1)	N(2)	NEt_2	X	NS[b]
(1)	H	H	H	93.12	116.62	−295.91		3 002
(2)	H	Br	Me	90.63	115.89	−295.16		3 244
(3)	H	H	Me	92.99	112.28	−296.81		2 150
(4)	H	Me	Me	96.02	109.65	−297.69		2 086
(5)	H	NO_2	NO_2[a]	127.60	54.09	−282.67		11 092
(6)	NHAc	H	H	63.80	103.64	−289.28	−253.40	16 217
(7)	NHAc	Br	H	51.39	114.61	−286.10	−251.50	28 800
(8)	NHAc	Br	Me	53.90	112.26	−287.84	−251.86	2 293
(9)	OH	H	H	−23.72	81.31	−285.44		21 508
(10)	OH	H	Me	−11.73	84.22	−286.86		4 515
(11)	OH	Me	Me		71.18	−285.97		2 976

[a] δ(NO_2) −13.87, −16.92 ppm. [b] NS = number of scans recorded.

Table 2. Fractional atomic co-ordinates (× 10^4) for compound (**12**).

Atom	x	y	z
Br(1)	−962(1)	5 654(1)	7 564(1)
Br(2)	4 519(1)	3 541(1)	6 396(1)
O(1)	1 103(7)	734(5)	7 511(4)
N(1)	1 812(6)	3 563(6)	7 489(4)
N(2)	2 648(6)	3 952(5)	8 556(4)
N(3)	3 544(7)	−492(6)	11 052(4)
C(1)	1 818(7)	4 798(6)	6 934(5)
C(2)	645(7)	5 816(7)	6 860(5)
C(3)	602(9)	6 922(7)	6 258(6)
C(4)	1 716(8)	7 056(7)	5 711(5)
C(5)	1 695(11)	8 274(8)	5 050(7)
C(6)	2 875(9)	6 033(8)	5 751(6)
C(7)	2 896(7)	4 918(7)	6 362(5)
C(8)	2 736(7)	2 803(6)	9 111(5)
C(9)	2 015(7)	1 218(6)	8 622(5)
C(10)	2 261(8)	154(7)	9 267(5)
C(11)	3 225(7)	577(7)	10 434(5)
C(12)	3 872(8)	2 183(7)	10 933(6)
C(13)	3 635(8)	3 214(7)	10 282(5)
C(14)	2 917(9)	−2 172(8)	10 536(7)
C(15)	1 381(12)	−2 603(13)	10 660(9)
C(16)	4 487(10)	−41(8)	12 272(6)
C(17)	3 547(13)	638(12)	13 072(8)

Table 3. Selected bond lengths/Å and bond angles/° for compound (**12**).

(*a*) Bond lengths

C(2)–Br(1)	1.886(8)	N(1)–N(2)	1.278(7)
C(7)–Br(2)	1.901(8)	C(1)–N(1)	1.438(7)
C(9)–O(1)	1.341(8)	C(8)–N(2)	1.363(7)
O(1)–H(1)	0.782(81)	C(8)–C(9)	1.421(9)
C(11)–N(3)	1.355(8)	C(14)–N(3)	1.480(9)

(*b*) Bond angles

C(8)–N(2)–N(1)	116.3(5)	C(2)–C(1)–N(1)	122.0(6)
C(1)–N(1)–N(2)	114.1(5)	C(7)–C(1)–N(1)	120.6(6)
C(9)–O(1)–H(1)	113.1(70)	C(13)–C(8)–N(2)	117.0(6)
C(1)–C(2)–Br(1)	119.7(5)	C(9)–C(8)–N(2)	126.8(6)
C(1)–C(7)–Br(2)	119.8(5)		

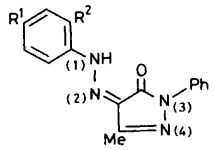
(*c*) Torsion angles

N(2)–N(1)–C(1)–C(2)	−91.4
N(2)–N(1)–C(1)–C(7)	94.9

refined structure and a selection of the resultant bond lengths and angles are given in Tables 2 and 3. The halogen-bearing ring plane of this molecule is effectively perpendicular to the plane defined by the azo group and the aminophenol ring (dihedral angle = 93°). This conformation reduces the interaction between the electron pair on N(2) and the two bromine atoms. The phenol ring and the C(14)–N(3)–C(16) plane are effectively coplanar (dihedral angle = 2°). The conformation of the molecule is such that the azo linkage and the hydroxy group participate in a six-membered ring. The short N(1)···H(1) (1.919 Å) and N(1)···O (2.567 Å) distances suggest the presence of a hydrogen bond. These values are comparable to those in 3-acetylamino-4-(2-chloro-4-methanesulphonylphenylazo)-*N*,*N*-diethylaniline[8] (1.89 and 2.663 Å respectively), and 1-(1-naphthylazo)-2-naphthol[9] (N···O 2.529 Å). The N(1)–N(2) bond length in (**12**) (1.278 Å) is similar to that in 3-acetylamino-4-(2-chloro-4-methanesulphonylphenylazo)-*N*,*N*-diethylaniline[8] (1.279 Å). The N(1)–N(2)–C(8)–C(9)–O(1)–H(1) ring, completed by the H(1)···N(1) hydrogen bond is essentially planar, with a maximum deviation from the least squares plane defined by all atoms of 0.04 Å [H(1)]. The H(1)···N(1) distance is 1.9(1)Å and the O(1)–H(1)···N(1) angle is 140(3)°. The N(2)–N(1)–H(1) angle is 103(1)°. A MNDO calculation[10] on the experimentally determined geometry of (**12**) provides an estimate of the heat of formation, $\Delta H_f^{\ominus}$ (**12**)$_g$ −831.9 kJ mol^{-1}. The electronic charges on N(1) and N(2) are calculated as −0.19 and 0.00 respectively. The Pariser–Pople–Parr method[11] estimates the energy of the maximum UV absorption (373 nm) to be in fair agreement with the experimental value (392 nm in ethanol). Solubility problems prevented measurement of the ^{15}N NMR spectrum of this compound.

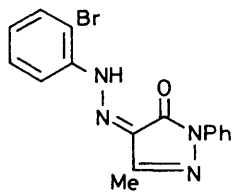
(*b*) *Arylhydrazonopyrazolone Derivatives.*—The strong negative NOE observed for N(1) due to the close proximity of the proton in (**13**) and (**14**) (Table 4) demonstrates the presence of the N–H bond in these compounds and confirms the hydrazo–ketone structure in chloroform solution, in agreement with previous evidence[12] from ^1H NMR spectroscopy. Solubility problems prevented a more extensive investigation of the ^{15}N NMR spectra of this class of compound. Assignment of

Table 4. ^{15}N Chemical shifts of arylhydrazonopyrazolones.



Compound	R^1	R^2	N(1)	N(2)	N(3)	N(4)	NS[a]
(**13**)	Me	H	−205.95	−19.65	−193.34	−78.74	26 114
(**14**)	Me	Me	−205.67	−19.36	−193.02	−79.23	16 642

[a]NS = number of scans recorded.



(**15**)

the four signals observed in the ^{15}N spectra of (**13**) and (**14**) is straightforward. Measurements on 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one have been reported.[13]

Crystal structure of 4-(2-*bromophenylhydrazono*)-3-*methyl*-1-*phenyl*-1H-*pyrazol*-5(4H)-*one* (**15**). The molecular structure is illustrated in Figure 2. The fractional atomic co-ordinates for the refined structure and a selection of the resulting bond lengths and bond angles are given in Tables 5 and 6. The halogen-bearing ring plane is effectively coplanar with the azo group and the pyrazolone ring. The slight distortion (6°) out of the plane may be attributed to the conflict between the largely sp^3-character of N(1) and the participation of its electron pair in the delocalised π-system. The conformation of the molecule places N(2) *anti* with respect to the bromine-bearing C(1). The O···H(1) (2.011 Å) and N(1)···O (2.714 Å) distances are both slightly longer than in (**12**), but the *syn* orientation suggests that there is a hydrogen bond completing the six-membered ring. The C(10)–O (1.234 Å) and the N(2)–C(7) (1.312 Å) bond lengths are consistent with partial double bond character expected in the hydrazone tautomer. Comparison with the corresponding bonds in (**12**) indicates that they are significantly longer (1.341 and 1.363 Å, respectively) in the latter. The O(1)–C(10)–C(7)–N(2)–N(1)–H(1) ring is also planar with the hydrogen atom deviating 0.03 Å from the least-squares plane. The C(10)–O(1)···H(1) angle is 91(1)° and the O(1)···H(1)–N(1) angle 141(2)°. A MNDO calculation[10] on the experimentally determined geometry of this molecule provided an estimate of the heat of formation, ΔH_f° (**15**)$_g$ − 1 436.5 kJ mol^{-1}. The electronic charges on N(1) and N(2) are calculated as −0.18 and 0.06 respectively.

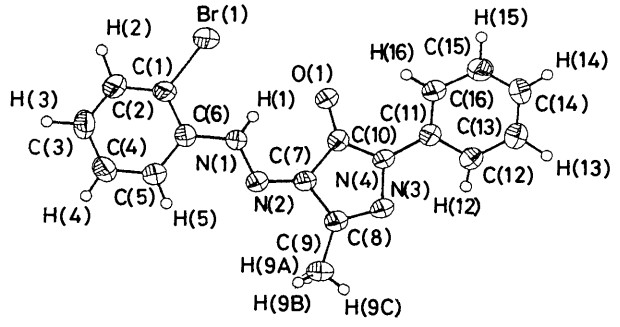


Figure 2. ORTEP view of compound (**15**) showing the atomic numbering.

Table 5. Fractional atomic co-ordinates (× 10^4) for compound (**15**).

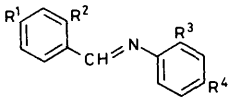
Atom	*x*	*y*	*z*
Br(1)	3 831(1)	474(.5)	3 816(.5)
C(1)	3 627(5)	1 376(4)	2 989(2)
C(2)	3 905(5)	2 043(2)	3 549(3)
C(3)	3 652(6)	2 703(2)	2 959(3)
C(4)	3 152(6)	2 693(2)	1 824(3)
C(5)	2 923(5)	2 023(2)	1 259(3)
C(6)	2 185(5)	1 357(2)	1 830(2)
N(1)	2 994(4)	664(1)	1 281(2)
N(2)	2 644(4)	627(1)	184(2)
C(7)	2 408(4)	−46(2)	−238(2)
C(8)	1 989(5)	−239(2)	−1 400(2)
C(9)	1 780(8)	288(2)	−2 372(3)
C(10)	2 452(5)	−752(2)	372(2)
O(1)	2 792(4)	−847(1)	1 390(2)
N(3)	1 764(4)	−954(1)	−1 519(2)
N(4)	2 043(4)	−1 273(1)	−439(2)
C(11)	1 833(5)	−2 060(2)	−324(2)
C(12)	2 207(5)	−2 521(2)	−1 219(3)
C(13)	1 988(6)	−3 285(2)	−1 112(3)
C(14)	1 393(6)	−3 585(2)	−140(3)
C(15)	1 017(6)	−3 128(2)	738(3)
C(16)	1 225(5)	−2 363(2)	656(3)

Table 6. Selected bond lengths/Å and bond angles/° for compound (**15**).

(*a*) Bond lengths			
C(1)–Br(1)	1.895(5)	N(1)–N(2)	1.317(4)
C(6)–C(1)	1.396(5)	N(2)–C(7)	1.312(4)
C(6)–N(1)	1.405(5)	C(7)–C(10)	1.461(5)
N(1)–H(1)	0.836(35)	C(10)–O(1)	1.234(4)
(*b*) Bond angles			
N(1)–C(6)–C(1)	119.5(4)	C(7)–N(2)–N(1)	115.9(3)
N(2)–N(1)–C(6)	120.9(3)	C(10)–C(7)–N(2)	127.3(3)
O(1)–C(10)–C(7)	127.5(4)		

(*c*) ^{15}N NMR *Spectra of Azines*.—The presence of a hydroxy group *ortho* to the azomethine link in the *N*-(2-hydroxyphenylmethylene)benzeneamines (**16**)–(**19**) (Table 7) causes a low frequency shift of *ca.* 30 ppm in the ^{15}N resonance compared with the de-hydroxy analogues,[14] consistent with an increase in the concentration of the ketenimine tautomer. Substitution in the aromatic ring adjacent to nitrogen does not influence the ^{15}N resonance frequency very much, as was observed previously[14] in *N*-(phenylmethylene)benzeneamines. The presence of a hydroxy group *ortho* to the azomethine link in 2-hydroxy-*N*-(arylmethylene)benzeneamines (**20**)–(**22**) also causes a low frequency shift of *ca.* 30 ppm in the ^{15}N resonance

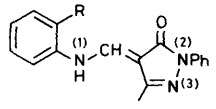
Table 7. ^{15}N Chemical shifts of Schiff bases in $CDCl_3$ solution.



Compound	Substituent R¹	R²	R³	R⁴	δ(ppm)	NS[c]
(16)	H	OH	Br	H	−87.74	18 357
(17)	H	OH	H	Me	−85.75	1 859
(18)	H	OH	Me	Me	−87.75	4 234
(19)	H	OH	H	NO_2[a]	−89.96	21 188
(20)	H	H	OH	H	−83.61	3 013
(21)	H	Br	OH	H	−78.52	24 686
(22)	NO_2[b]	H	OH	H	−71.04	22 934

[a] δ(NO_2) −12.95 ppm. [b] δ(NO_2) −12.95 ppm. [c] NS = number of scans recorded.

Table 8. ^{15}N Chemical shifts of arylaminomethylenepyrazolones in $CDCl_3$ solution.



Compound	R	δ(ppm) N(1)	N(2)	N(3)	NS[a]
(23)	H	−255.81	−189.83	−87.46	22 512
(24)	Br	−253.37	−189.83	−91.31	32 560

[a] NS = number of scans recorded.

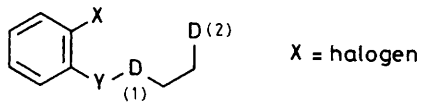
compared with the azines without a hydroxy substituent.[14] Substituents on the aromatic ring remote from nitrogen exert a greater influence on the ^{15}N resonance of 2-hydroxy-*N*-(arylmethylene)benzeneamines than on that of *N*-(2-hydroxyphenylmethylene)benzeneamines. There is no evidence of NOE in these spectra, particularly the spectra of (**16**)–(**19**), which might indicate a significant contribution from the hydrazoketone tautomer. In contrast to this, the ^{15}N NMR spectra of two arylhydrazonopyrazolones (**23**) and (**24**) (Table 8), reveal a negative NOE on the signal assigned to N(1) at δ *ca.* −255 which is consistent with the presence of an N–H bond in the hydrazo ketone tautomer.

Conclusions

The existence of an essentially planar six-membered NXCCYH ring (X = N, C; Y = O, N) in the appropriately substituted molecules is clearly established by the crystal structures and supported by the ^{15}N NMR measurements. The presence of a pyrazol-5-one ring shifts the prototropic equilibrium decisively in favour of the hydrazo tautomer. The shift in the resonance of the protonated nitrogen atom, N(1), as a result of replacement of the 2-hydroxyphenyl group by a oxopyrazol-2-yl group is *ca.* 175 ppm to low frequency in both the azo and the azine systems.

The crystal structures of the two azo compounds show interesting points of comparison. The halogen-bearing ring is nearly perpendicular to the NNCCO plane in (**12**), but it is effectively coplanar with it in (**15**). The greater inter-annular distance C(6)···N(2) (2.368 Å) in the azopyrazolone (**15**) than the corresponding distance C(1)···N(2) (2.281 Å) in the azophenol (**12**) is attributable to the significantly greater angle at N(1) in the former [C(6)N(1)N(2) 120.9°] than in the latter [C(1)N(1)N(2) 114.1°].

Copper-assisted nucleophilic substitution of aryl halides is assisted[1,2] when the aryl halide contains two donor atoms, D, as in structure (**A**).



(**A**)

Contrary to expectation, the presence of a donor heteroatom Y—the position of N(1) in compounds (**2**), (**7**), (**8**), (**12**), (**16**), and (**24**)—is not required for effective substitution of halogen.[2] If D(1) is absent substitution does not occur under normal conditions. If D(1) is present but not D(2), substitution is slower than if both are present. It is reasonable to suggest that these donor atoms play an important role in the mechanism, probably by (weak) co-ordination to copper at some intermediate stage. We have shown[2] that copper(I) [rather than copper(II) or copper metal] is involved initially. Whereas (**12**) reacts with CuCN/pyridine at reflux to substitute cyanide for bromide, (**15**) does not undergo substitution. Stable copper(II) complexes of 2-haloarylhydrazonopyrazolones are easily formed. It is assumed that co-ordination to the metal atom occurs through N(1) and O(1) in these complexes. However, attempts to force these azopyrazolone complexes to react with nucleophiles were uniformly unsuccessful.

Experimental

The compounds (**1**)–(**24**) were prepared by standard methods and characterised by microanalysis and NMR (^1H, ^{13}C) spectrometry. ^{15}N NMR spectra were measured at a frequency of 40.55 MHz on saturated solutions of the compounds in deuteriochloroform solution at 303 K by Dr. E. H. Curzon with a Bruker WH400 spectrometer at the University of Warwick. All chemical shifts are related to $CH_3{}^{15}NO_2$ as an external standard. The relaxation agent tris(pentane-2,4-dionato)chromium(III) was added to the solutions (*ca.* 0.04 mol dm^{-3}). The broad-band decoupled spectra were based on a FID of 16 000 with a pre-pulse delay of 2 s, a pulse width of 10^{-5} s and a dwell time of 2×10^{-5} s. The spectral width was usually 25 kHz (616.52 ppm). The number of scans accumulated for each spectrum is shown in the Tables.

All X-ray measurements were made using a CAD4 diffractometer with Ni-filtered Cu radiation (λ Cu-K_α = 1.54178 Å), operating in the ω/2θ scan mode following previously detailed procedures.[15] The structures were solved and developed *via* standard heavy atom methods and refined by least squares. Experimental and other details are given below.

Compound (**12**): $C_{17}H_{19}Br_2N_3O$, M = 440.8, triclinic, a = 8.683(1), b = 8.867(1), c = 12.669(1) Å, α = 103.96(1), β = 107.65(1), γ = 92.41(1)°, V = 895.0 Å^3, space group = $P\bar{1}$, Z = 2, D_x = 1.635 g cm^{-3}, $F(000)$ = 440. μ(Cu-K_α) = 54.4 cm^{-1}. Total unique data collected = 3 399, total observed = 2 405 [$I > 1.5\sigma(I)$]. Refinement with anisotropic displacement factors for non-hydrogen atoms; organic hydrogens in idealised positions, with group U_{iso} values for CH_3 and CH_2 hydrogens, hydroxy hydrogen refined freely. Data were corrected for

absorption empirically. Final R, R_w values = 0.067, 0.081 for 247 variables with weights = $[\sigma^2(F_0) + 0.000\,45F_0^2]^{-1}$.

Compound (**15**): $C_{16}H_{13}BrN_4O$, M = 357.21, monoclinic, a = 6.919(1), b = 17.914(1), c = 11.973(1) Å, β = 94.74(1)°, V = 1 478.9 Å^3, space group = $P2_1/c$, Z = 4, D_x = 1.604 g cm^{-3}, $F(000)$ = 720, μ(Cu-K_α) = 35.96 cm^{-1}. Total unique data collected = 2 808, total observed = 2 037 [$I > 1.5\sigma(I)$]. Refinement with anisotropic displacement factors for non-hydrogen atoms, isotropic for hydrogens. Data corrected for absorption empirically. Final R, R_w values = 0.0375, 0.0443 for 251 parameters with weights = $[\sigma^2(F_0) + 0.0004F_0^2]^{-1}$.*

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* Tables of temperature factors and hydrogen atom co-ordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of this Scheme, see 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

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