1-Benzazepines. Novel Ring Transformations occurring during the Reactions of 5-Methyl- and 5-Phenyl-1,3-dihydro-2*H*-1-benzazepin-2-ones with Phosphoryl Chloride

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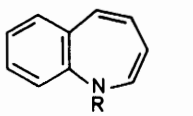
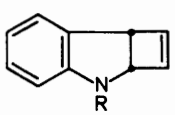
Treatment of 8-substituted (H, Me, MeO) 5-methyl-1,3-dihydro-2*H*-1-benzazepin-2-ones with phosphoryl chloride under reflux produces two products. *X*-Ray structure determination of the products from the 8-methoxy derivative shows them to be 2,12-dimethoxy-5,9-dimethyl-7*H*-[1]benzazepino-[1′,2′:1,2]pyrrolo[5,4-*b*]quinoline (major product) and 5-chloromethyl-2,11-dimethoxy-5,8-dimethyl-5,6-dihydroquino[1′,2′:1,2]pyrrolo-[5,4-*b*]quinoline (minor product). The corresponding reaction of 8-methoxy-5-phenyl-1,3-dihydro-2*H*-1-benzazepin-2-one yields 2,12-dimethoxy-5,9-diphenyl-7*H*-[1]benzazepino[1′,2′:1,2]pyrrolo[5,4-*b*]quinoline as the sole product.

A mechanistic pathway is proposed in which the first step involves condensation of two molecules of the appropriate 2-chloro-5-methyl-1*H*-1-benzazepine or its 3*H* analogue.

The chemistry of the 1*H*-1-benzazepine system (**1**; R = H) has been little explored, although a number of substituted 1-benzazepines have been reported.[1-12] In particular, (**1**; R = Bz) is stable at room temperature but at *ca.* 300 °C undergoes rearrangement to yield (**2**) and (**3**) (R = Bz).[12] Neither the stability of the parent (**1**; R = H) nor its relative stability when compared with 3*H*-1-benzazepine is known. In contrast, Vogel[13] has reported that the ^{1}H n.m.r. spectrum of 1*H*-1-azepine (**4**) can be measured at −78 °C, but on warming, the molecule undergoes tautomerism and polymerises. Treatment of (**4**) with trimethylamine gives the more stable 3*H*-1-azepine.[13]



(**1**)



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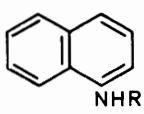

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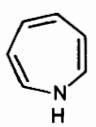

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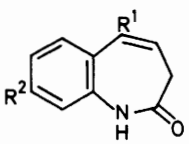
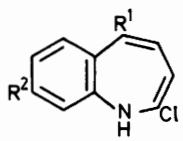
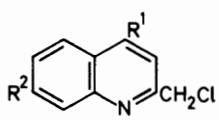


(**5**)



(**6**)

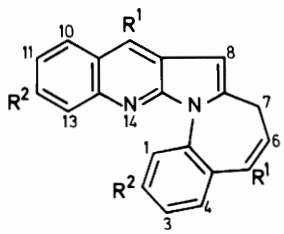


(**7**)

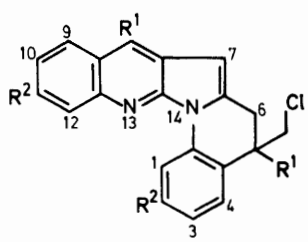
One-step syntheses of (**5**; R^1 = Me; R^2 = H)[14,15] and (**5**; R^1 = Me or Ph; R^2 = MeO)[15] may be effected by condensation of the appropriate aniline derivative with laevulinic acid (R^1 = Me) or β-benzoylpropionic acid (R^2 = Ph). Such compounds should be direct precursors to the 1*H*-1-benzazepine ring system. Treatment of (**5**) with phosphoryl chloride should yield (**6**). We did not expect to isolate compounds corresponding to (**6**), instead we hoped that such species would rearrange and that the structures of the rearrangement products should give an insight into the chemistry of the 1*H*-1-benzazepine system. We predicted the formation of quinolines, *e.g.* (**7**); in the event, the products do contain quinoline nuclei but the structures bear only a fleeting resemblance to (**7**).

Results and Discussion

The reactions between (**5**; R^1 = Me; R^2 = H, Me and MeO) and phosphoryl chloride under reflux for 1 h produced two products: (i) a major product (formed in 40—60% yield) corresponding formally to dimerisation of (**6**) minus two molecules of hydrogen chloride, and (ii) a minor product (0.5—6%) corresponding formally to 2 × (**6**) − HCl. No other products were obtained and no starting material remained in any case. The reactions were repeated under a variety of temperature conditions (−50 to 110 °C) and reaction times (5 min to 20 h) using various concentrations of phosphoryl chloride, neat or in dichloromethane. No other products were isolated, and no intermediates were detected. *X*-Ray analysis (see below) of the products from 8-methoxy-5-methyl-1,3-dihydro-2*H*-1-benzazepin-2-one (**5**; R^1 = Me, R^2 = MeO), showed the major product to be 2,12-dimethoxy-5,9-dimethyl-7*H*-[1]benzazepino[1′,2′:1,2]pyrrolo[5,4-*b*]quinoline (**8**; R^1 = Me; R^2 = MeO), and the minor product to be 5-chloromethyl-2,11-dimethoxy-5,8-dimethyl-5,6-dihydroquino-[1′,2′:1,2]pyrrolo[5,4-*b*]quinoline (**9**; R^1 = Me; R^2 = MeO). Comparison of spectroscopic data indicate that it is probable that the products from (**5**; R^1 = Me; R^2 = H), and (**5**; R^1 = Me; R^2 = Me) correspond to (**8**; R^1 = Me; R^2 = H and Me) and (**9**; R^1 = Me; R^2 = H and Me).



(**8**)



(**9**)

Table 1. Non-hydrogen atom co-ordinates

	(8)			(9)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
N(1)	0.229 9(5)	0.175 1(8)	0.163 4(11)	0.593 8(6)	0.001 7(12)	−0.336 1(9)
C(2)	0.281 0(6)	0.142 8(10)	0.088 6(13)	0.563 3(9)	0.102 2(14)	−0.407 6(12)
N(3)	0.295 8(5)	0.032 6(9)	0.058 6(11)	0.610 6(7)	0.142 0(13)	−0.480 9(9)
C(4)	0.349 0(6)	0.023 1(10)	−0.027 1(12)	0.560 0(9)	0.239 5(16)	−0.536 5(12)
C(5)	0.364 0(6)	−0.094 7(11)	−0.069 3(13)	0.600 0(10)	0.292 7(17)	−0.615 7(12)
C(6)	0.415 7(7)	−0.110 3(11)	−0.153 8(15)	0.559 5(12)	0.387 1(18)	−0.674 7(12)
O(6)	0.436 8(4)	−0.221 0(8)	−0.207 2(11)	0.593 1(7)	0.443 2(11)	−0.756 6(8)
C(61)	0.400 3(7)	−0.322 6(12)	−0.170 3(16)	0.679 9(12)	0.405 0(21)	−0.775 8(12)
C(7)	0.456 5(6)	−0.013 3(11)	−0.190 7(13)	0.475 5(11)	0.432 6(18)	−0.659 5(14)
C(8)	0.441 2(6)	0.099 7(12)	−0.145 9(15)	0.439 1(10)	0.384 1(19)	−0.581 6(15)
C(9)	0.387 8(6)	0.123 0(11)	−0.056 9(13)	0.475 6(11)	0.284 3(16)	−0.516 5(13)
C(10)	0.369 5(6)	0.239 8(10)	−0.016 4(13)	0.437 3(9)	0.237 9(17)	−0.433 1(12)
C(101)	0.406 1(6)	0.350 0(10)	−0.064 7(14)	0.351 2(9)	0.284 9(17)	−0.406 4(12)
C(11)	0.315 1(6)	0.250 8(11)	0.057 5(12)	0.479 6(8)	0.139 9(16)	−0.375 1(12)
C(12)	0.279 8(6)	0.347 9(9)	0.120 8(13)	0.464 8(9)	0.067 4(16)	−0.287 6(13)
C(13)	0.228 6(6)	0.303 5(10)	0.177 9(12)	0.532 4(9)	−0.014 1(15)	−0.265 6(10)
C(14)	0.172 4(6)	0.357 0(10)	0.244 1(14)	0.550 7(8)	−0.117 6(15)	−0.186 7(10)
C(15)	0.110 8(6)	0.331 2(11)	0.140 4(14)	0.649 3(8)	−0.139 5(17)	−0.143 5(12)
C(16)	0.085 4(6)	0.222 5(13)	0.115 2(13)	0.684 6(9)	−0.025 4(16)	−0.075 3(10)
C(161)	0.023 7(6)	0.203 2(13)	0.001 7(15)	0.658 3(9)	−0.255 9(17)	−0.076 7(13)
Cl(16)				0.631 7(3)	0.001 3(6)	0.037 3(3)
C(17)	0.116 3(7)	0.114 7(12)	0.198 2(13)	0.701 1(9)	−0.136 8(14)	−0.231 4(10)
C(18)	0.078 2(9)	0.024 8(13)	0.246 0(15)	0.785 1(10)	−0.193 5(15)	−0.225 4(11)
C(19)	0.104 1(9)	−0.080 1(15)	0.323 6(17)	0.835 5(9)	−0.190 1(14)	−0.299 6(13)
C(20)	0.170 3(9)	−0.096 2(13)	0.348 2(16)	0.809 8(9)	−0.120 5(14)	−0.388 3(12)
O(20)	0.207 4(6)	−0.196 5(9)	0.417 3(13)	0.856 2(6)	−0.104 8(10)	−0.468 7(7)
C(201)	0.175 7(11)	−0.287 6(19)	0.471 1(23)	0.943 9(9)	−0.156 1(19)	−0.457 9(12)
C(21)	0.209 4(6)	−0.008 5(12)	0.297 2(13)	0.729 2(10)	−0.059 7(14)	−0.401 1(10)
C(22)	0.183 3(7)	0.097 0(10)	0.222 7(13)	0.677 0(7)	−0.064 0(13)	−0.325 1(11)

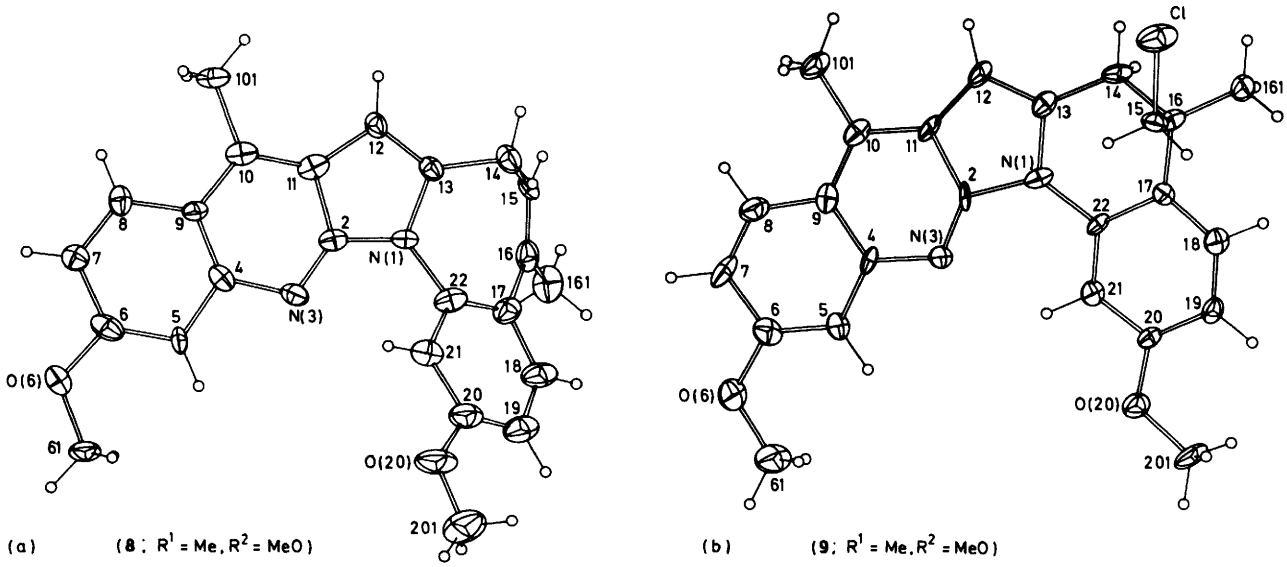


Figure. Molecular projections of (a) (**8**) and (b) (**9**) (R^1 = Me; R^2 = MeO) normal to the fused aromatic system plane. Twenty percent thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have an arbitrary radius of 0.1 Å. Non-hydrogen atom labelling is shown.

The corresponding reaction between 8-methoxy-5-phenyl-1,3-dihydro-2*H*-1-benzazepin-2-one (**5**; R^1 = Ph; R^2 = MeO) and phosphoryl chloride produced (**8**; R^1 = Ph; R^2 = MeO) in 51% yield. No product corresponding to (**9**; R^1 = Ph; R^2 = MeO) was detected.

Crystallography.—Both specimens were small (*ca.* 0.1 mm) and diffracted poorly with wide line widths; the structure determinations in consequence are of limited precision and suffice only to establish broad general stereochemistry and connectivity. Atom identity is generally made on the basis of chemical assignment.

Unique data sets were measured to $2\theta_{max.}$ 45° (**8**; R^1 = Me; R^2 = MeO), 40° (**9**; R^1 = Me; R^2 = MeO) using a Syntex $P\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode, yielding N independent reflections, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement without absorption correction after solution of the structure by direct methods. Monochromatic Mo-$K\alpha$ radiation was used (λ = 0.7106$_9$ Å); T was 295 K. Anisotropic thermal

Table 2. Molecular non-hydrogen geometry

Atoms	(8)	(9)
Distance (Å)		
N(1)–C(2)	1.35(2)	1.44(2)
N(1)–C(13)	1.43(1)	1.42(2)
N(1)–C(22)	1.44(2)	1.44(2)
C(2)–N(3)	1.30(2)	1.26(2)
C(2)–C(11)	1.43(2)	1.47(2)
N(3)–C(4)	1.41(2)	1.36(2)
C(4)–C(5)	1.40(2)	1.39(2)
C(4)–C(9)	1.41(2)	1.44(2)
C(5)–C(6)	1.38(2)	1.35(2)
C(6)–C(7)	1.43(2)	1.42(3)
C(6)–O(6)	1.40(2)	1.38(2)
O(6)–C(61)	1.41(2)	1.45(2)
C(7)–C(8)	1.36(2)	1.33(2)
C(8)–C(9)	1.45(2)	1.41(2)
C(9)–C(10)	1.41(2)	1.40(2)
C(10)–C(11)	1.37(2)	1.38(2)
C(10)–C(101)	1.52(2)	1.50(2)
C(11)–C(12)	1.45(2)	1.41(2)
C(12)–C(13)	1.32(2)	1.35(2)
C(13)–C(14)	1.48(2)	1.49(2)
C(15)–C(16)	1.32(2)	1.54(2)
C(15,16)–C(161)	1.51(2)	1.50(2)
C(15,16)–C(17)	1.49(2)	1.49(2)
C(14)–C(15)	1.48(2)	1.54(2)
C(17)–C(18)	1.36(2)	1.36(2)
C(17)–C(22)	1.37(2)	1.43(2)
C(18)–C(19)	1.41(2)	1.36(2)
C(19)–C(20)	1.36(3)	1.36(2)
C(20)–C(21)	1.37(2)	1.38(2)
C(20)–O(20)	1.43(2)	1.36(2)
O(20)–C(201)	1.32(2)	1.44(2)
C(21)–C(22)	1.41(2)	1.36(2)
Angles (°)		
C(2)–N(1)–C(13)	109.3(9)	108.4(11)
C(2)–N(1)–C(22)	127.6(9)	127.9(12)
C(13)–N(1)–C(22)	123.1(10)	123.2(11)
N(1)–C(2)–N(3)	124.3(11)	125.7(13)
N(1)–C(2)–C(11)	107.4(10)	103.3(13)
N(3)–C(2)–C(11)	128.2(11)	131.0(14)
C(2)–N(3)–C(4)	113.4(10)	114.4(13)
N(3)–C(4)–C(5)	115.0(10)	118.2(14)
N(3)–C(4)–C(9)	122.5(10)	121.1(14)
C(5)–C(4)–C(9)	122.3(11)	120.7(14)
C(4)–C(5)–C(6)	118.0(11)	119.9(15)
C(5)–C(6)–C(7)	122.8(11)	121.4(16)
C(5)–C(6)–O(6)	125.5(11)	123.9(16)
C(7)–C(6)–O(6)	111.6(12)	114.7(15)
C(6)–O(6)–C(61)	115.2(11)	118.4(13)
C(6)–C(7)–C(8)	117.7(12)	118.3(16)
C(7)–C(8)–C(9)	122.6(12)	124.4(16)
C(8)–C(9)–C(4)	116.4(11)	115.1(15)
C(8)–C(9)–C(10)	123.1(11)	123.2(16)
C(4)–C(9)–C(10)	120.1(11)	121.5(15)
C(9)–C(10)–C(11)	117.6(11)	117.7(14)
C(9)–C(10)–C(101)	120.7(11)	123.6(15)
C(11)–C(10)–C(101)	121.5(10)	118.7(14)
C(10)–C(11)–C(2)	117.7(11)	114.0(14)
C(10)–C(11)–C(12)	136.7(11)	136.1(14)
C(2)–C(11)–C(12)	105.5(10)	109.8(13)
C(11)–C(12)–C(13)	109.4(10)	107.6(13)
C(12)–C(13)–C(14)	134.4(10)	132.2(14)
C(12)–C(13)–N(1)	108.3(10)	110.9(13)
N(1)–C(13)–C(14)	117.3(10)	116.8(12)
C(13)–C(14)–C(15)	109.2(10)	114.9(12)
C(14)–C(15)–C(16)	124.3(11)	108.4(12)
C(15,16)–C(17)–C(18)	120.7(12)	122.7(12)
C(15,16)–C(17)–C(22)	122.6(12)	123.7(12)
C(18)–C(17)–C(22)	116.6(12)	113.3(13)
C(17)–C(18)–C(19)	123.7(14)	126.5(13)
C(18)–C(19)–C(20)	119.1(15)	118.4(13)
C(19)–C(20)–C(21)	118.1(14)	119.0(14)
C(19)–C(20)–O(20)	129.1(15)	126.1(13)
C(21)–C(20)–O(20)	112.8(15)	114.9(13)
C(20)–O(20)–C(201)	119.0(15)	118.6(11)
C(20)–C(21)–C(22)	122.5(13)	121.2(13)
C(21)–C(22)–N(1)	115.9(11)	121.9(12)
C(21)–C(22)–C(17)	119.9(12)	121.4(12)
N(1)–C(22)–C(17)	123.9(10)	116.7(12)

(**8**): C(15)–C(16)–C(17), 121.3(11); C(15)–C(16)–C(161), 120.9(12); C(17)–C(16)–C(161), 117.8(12)°.
(**9**): C(14)–C(15)–C(17), 109.8(11); C(14)–C(15)–C(161), 108.9(12); C(17)–C(15)–C(16), 103.6(12); C(17)–C(15)–C(161), 116.1(14); C(16)–C(15)–C(161), 109.6(12); C(15)–C(16)–Cl(16), 114.9(11)°. C(16)–Cl(16), 1.80(2) Å.

Table 3. Torsion angles (°) in the seven-membered ring, (**8**). Atoms are denoted by number only.

Atoms	Angle
22–1–13–14	−6.1
1–13–14–15	−63.5
13–14–15–16	66.9
14–15–16–17	3.1
15–16–17–22	−41.9
16–17–22–1	−3.7
17–22–1–13	48.0

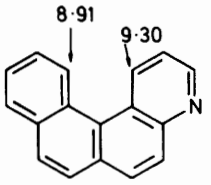
parameters were refined for the non-hydrogen atoms; (x, y, z, $U_{iso})_H$ were constrained at idealized values. Residuals R, R' on $|F|$ at convergence are quoted, reflections weights being $(\sigma^2(F_0) + 0.0003(F_0)^2)^{-1}$. Neutral complex scattering factors[16] were used; computation used the X-RAY 76 program system[17] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Results are given in the Figure and Tables, the former showing non-hydrogen atom labelling. No significant features were observed in final difference maps.

Structural Commentary.—Although of modest precision, the structure determinations, taken in conjunction with the chemical evidence, establish connectivity and establish the identity of compounds (**8**; R^1 = Me; R^2 = MeO) and (**9**; R^1 = Me; R^2 = MeO) to be as shown. The fused ring systems defined by atoms 1—13 form good planes as expected [σ, 0.042, (**8**); 0.027 Å, (9)] with the methoxy groups at C(6) also substantially coplanar [δC(61) 0.08, 0.14 Å respectively] as expected and similarly directed. The dihedral angle of the phenyl ring (C(17—22) to the main plane is 46.9°, (**8**); 13.6°, (**9**), the substantial difference being occasioned by the presence of the seven-membered ring in (**8**). Atom deviations from the main plane of (**8**) are [C(14,15,16,17,22)] 0.22, 1.52, 1.82, 0.81, −0.04 Å, while for (**9**), deviations are [C(14,15,17,22,161)] −0.04, 0.71, 0.39, 0.08, 0.42 Å. Within the limits of error, bond lengths and angles within the two molecules are consistent with the norms for the assigned formulae.

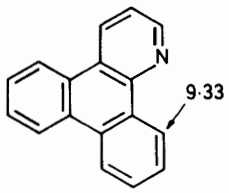
Spectroscopic Evidence.—Spectroscopic data are listed in the Experimental section. Although the various spectra of the two products from (**5**; R^1 = Me; R^2 = MeO) do not by themselves allow unequivocal structural assignments, they are entirely consistent with structures (**8**) and (**9**) (R^1 = Me; R^2 = MeO) defined by *X*-ray structure determination. The spectroscopic data obtained for all other products are also consistent with structures (**8**) and (**9**). The minor product from (**5**; R^1 = Me, R^2 = H) was isolated in very small yield; its mass spectrum is consistent with structure (**9**; R^1 = Me; R^2 = H).

There are certain aspects of the spectra that are worthy of mention, since these are characteristic of particular structural features. The ^1H n.m.r. spectra are most diagnostic for compounds (**8**). For example, the singlet near δ 6.15 is due to the hydrogen of the pyrrole ring,[18] whereas the triplet centred near δ 5.85 (6-H) is characteristic of the particular azepine functionality in this series of compounds.

The spectra of (**9**) show a number of diagnostic features including the following: (i) a major peak in the mass spectra is produced by the 'benzylic' cleavage $M^{+\bullet} \longrightarrow (M^{+\bullet} - {}^{\bullet}CH_2Cl)$; (ii) the ^{13}C n.m.r. spectra show the presence of a quaternary carbon (C-5) which resonates at highfield (δ 37.6); (iii) the ^1H n.m.r. spectra contain the characteristic singlet at δ 6.15 arising from the pyrrole hydrogen, but lack the 'azepine' triplet at δ 5.85; and (iv) the ^1H n.m.r. spectra show a lowfield doublet at δ 9.2 (1-H).



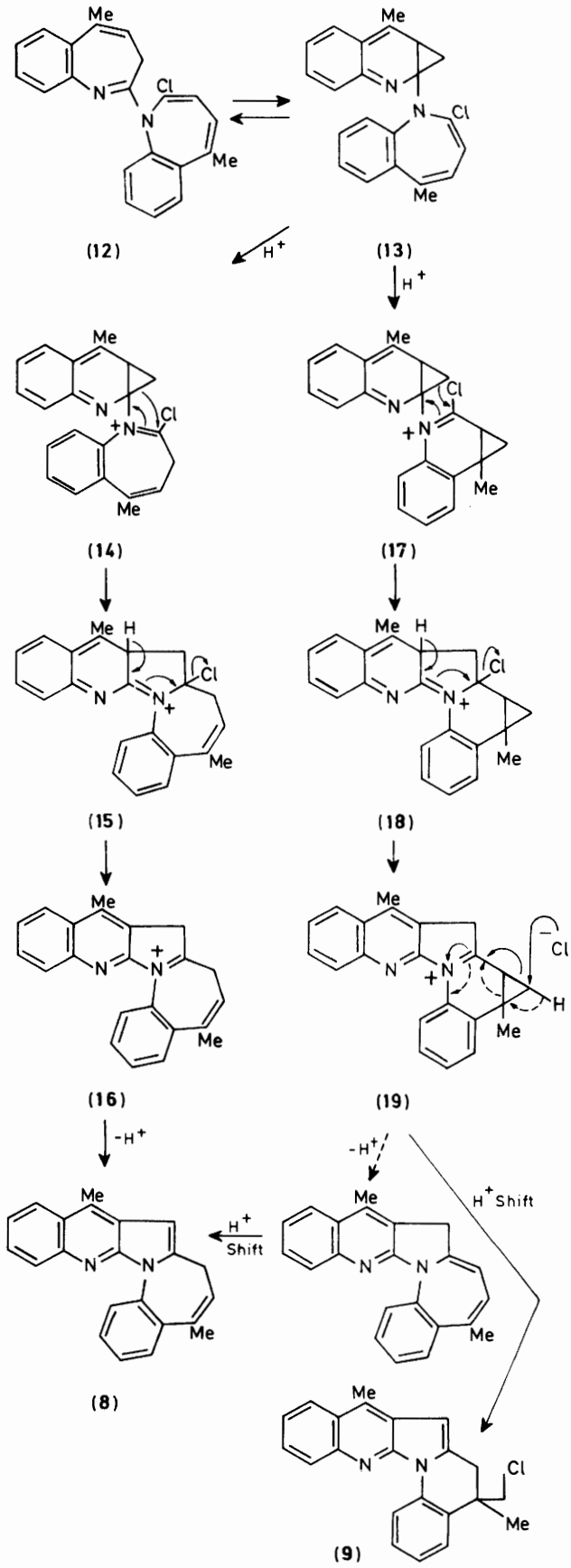
(**10**)



(**11**)

The observation of the lowfield signal at δ 9.2 in the ^1H n.m.r. spectra of compounds (**9**; R^1 = Me) is of particular significance, suggesting that the aromatic systems in (**9**; R = Me) are close to coplanar, a feature substantiated by *X*-ray data [Figure (b)]. As a consequence, the field at 1-H is strongly influenced by the ring currents of both aromatic systems thus causing strong deshielding. For comparison, the chemical shifts of the analogous systems (**10**) and (**11**)[19] are shown above.

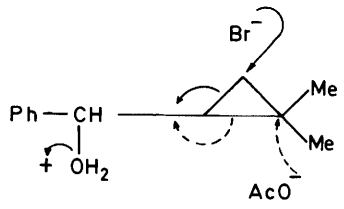
The Mechanisms of the Rearrangement Reactions.—A number of possible mechanistic pathways may be drawn for compounds (**8**), but we can only suggest one pathway for the formation of compounds (**9**). The most plausible reaction sequence is that shown [for the products from (**5**; R^1 = Me; R^2 = H] in the Scheme. The precursor to the rearrangement products must be (**6**; R^1 = Me; R^2 = H) or its 3*H* isomer. Condensation of two such molecules could form the initial intermediate (**12**) which should isomerise to (**13**),[20] the key intermediate to both products. Protonation of (**13**) may form both (**14**) and (**17**)[21] which undergo 'vinylcyclopropane' rearrangements to (**15**) and (**18**) respectively.* These species should be converted into (**8**) and (**19**) as shown. The intermediate (**19**) is a cyclopropylcarbinyl ion in which ring opening by a nucleophile can be unimolecular or concerted bimolecular.[26] Thus it has been shown that more nucleophilic reagents (*e.g.* Br^-) attack at the less hindered carbon while less nucleophilic reagents (*e.g.* AcO^-) attack at the more hindered position [*cf.* (**20**)].[27] Similar instances are found in the chemistry of i-steroids.[28] It is therefore possible that (**19**) acts as an intermediate to both (**8**) and (**9**), the major pathway involving the most favourable ring opening and proton loss to (**8**), the minor



Scheme

* While some argument continues as to whether these reactions have a biradical-like transition state[22] or are concerted symmetry-allowed suprafacial [1,3]migrations,[23] they have been shown to occur with inversion at the migrating centre,[24] consistent with the latter hypothesis. Although temperatures near 300 °C are often necessary,[25] the charge on the nitrogen atom in (**17**) may account for the facility of the rearrangement observed here.

pathway involving the S_N2' attack at the least-substituted carbon by Cl^- to give (**9**). Compounds (**8**) and (**9**) are quite stable under the reaction conditions, indeed they are not interconvertible even when heated under reflux with phosphoryl chloride for 20 h.



(**20**)

In conclusion, we believe that reaction of (**5**) with phosphoryl chloride yields (**6**) (or its 3*H*-isomer) and that oxidative dimerisation of this unstable system is responsible for the formation of the novel rearrangement products.

Experimental

Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. U.v. spectra (in cyclohexane) and i.r. spectra were recorded respectively on Pye Unicam SP 8–100 and Jasco IRA-1 spectrometers. ^{1}H N.m.r. spectra were recorded at 60 MHz on a JEOL JMN-PMX 60 instrument (unless specifically indicated to the contrary); ^{13}C spectra with a Bruker WP 80 spectrometer. Mass spectra were determined at 70 eV, by direct insertion, with an AEI MS 3074 instrument. Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Light petroleum refers to the fraction of b.p. 50—60 °C.

5-Methyl-1,3-dihydro-2*H*-1-benzazepin-2-one (**5**; R^1 = Me; R^2 = H), 8-methoxy-5-methyl-1,3-dihydro-2*H*-1-benzazepin-2-one (**5**; R^1 = Me; R^2 = MeO), and 8-methoxy-5-phenyl-1,3-dihydro-2*H*-1-benzazepine-2-one (**5**; R^1 = Ph; R^2 = MeO) were available from a previous study.[15]

5,8-*Dimethyl*-1,3-*dihydro*-2H-1-*benzazepin*-2-*one* (**5**; R^1 = R^2 = Me).—A mixture of laevulinic acid (10 g), *m*-toluidine (50 ml), and *m*-toluidine hydrochloride (25 g) was heated under reflux, in a nitrogen atmosphere, for 8 h. The excess of *m*-toluidine was removed under reduced pressure, the residue acidified with aqueous hydrogen chloride (2M; 100 ml) and continuously extracted with diethyl ether for 24 h. The residue from the ether extract was crystallised from methanol to yield 5,8-*dimethyl*-1,3-*dihydro*-2H-1-*benzazepin*-2-*one* (3.68 g, 23%) as colourless needles, m.p. 143—143.5 °C (Found: C, 77.0; H, 7.1; N, 7.3. $C_{12}H_{13}NO$ requires C, 77.0; H, 7.0; N, 7.5%); $\nu_{max.}$ (CCl_4) 1 690 cm^{-1}; δ ($CDCl_3$) 9.75 (1 H, br s, 1-H), 7.35—6.72 (3 H, m, ArH), 5.68 (1 H, br t, *J* 7 Hz, 4-H), 2.72 (2 H, br d, *J* 7 Hz, CH_2), 2.30 (3 H, s, ArMe), 2.10 (3 H, s, vinyl Me); *m/z* 187 ($M^{+\bullet}$, 86%), 172 (*M*—CH_3, 32), 158 (*M*—CHO, 88), 145 (*M*—CH_2CO, 100), and 144 (*M*—CH_3CO, 94).

Reactions with Phosphoryl Chloride.—(i) 8-*Methoxy*-5-*methyl*-1,3-*dihydro*-2H-1-*benzazepin*-2-*one* (**5**; R^1 = Me; R^2 = MeO).—A solution of 8-methoxy-5-methyl-1,3-dihydro-2*H*-1-benzazepin-2-one (8 g) in phosphoryl chloride (25 ml) was heated under reflux for 45 min. The reaction mixture was cooled to 0 °C, poured into aqueous sodium carbonate (saturated; 300 ml), and extracted with dichloromethane (3 × 100 ml). The organic extract was washed with aqueous sodium carbonate (10%; 50 ml), water (50 ml), and aqueous sodium chloride (saturated; 50 ml), dried (K_2CO_3), and the solvent evaporated to give a yellow-brown foam (7.2 g). This foam was chromatographed on silica gel (300 g) in light petroleum–dichloromethane. Gradient elution gave 5-*chloromethyl*-2,11-*dimethoxy*-5,8-*dimethyl*-5,6-*dihydroquino*[1′,2′:1,2]*pyrrolo*[5,4-b]*quinoline* (**9**; R^1 = Me; R^2 = MeO) (405 mg, 5.6%) which crystallised from dichloromethane–light petroleum (1:9) as pale yellow needles, m.p. 181—182·5 °C (Found: C, 70.8; H, 5.8; N, 7.1%; $M^{+\bullet}$, 406.1148. $C_{24}H_{23}{}^{35}ClN_2O_2$ requires C, 70.8; H, 5.7; N, 6.9%; $M^{+\bullet}$, 406.1147); $\lambda_{max.}$ (cyclohexane) 235, 247sh, 270sh, 279, 291, 297sh, 330.5, 345.5, and 363 nm (log ε 4.46, 4.33, 4.35, 4.59, 4.68, 4.45, 3.93, 4.04, and 3.81); δ (80 MHz, $CDCl_3$) 9.12 (1 H, d, *J* 2.7 Hz, 1-H), 7.88 (1 H, d, *J* 9.3 Hz, 9-H), 7.39 (1 H, d, *J* 2.5 Hz, 12-H). 7.22 (1 H, d, *J* 8.7 Hz, 4-H), 7.08 (1 H, dd, *J* 9.3 and 2.5 Hz, 10-H), 6.67 (1 H, dd, *J* 8.7 and 2.7 Hz, 3-H), 6.38 (1 H, s, 7-H), 3.93 (6 H, s, MeO), 3.32 (2 H, s, $ClCH_2$), 3.27 and 2.78 (2 H, ABq, *J* 15.4 Hz, 6- and 6′-H), 2.72 (3 H, s, ArMe) 1.45 (3 H, s, Me); ^{13}C {^{1}H} n.m.r. δ ($CDCl_3$) 159.6, 159.3 (C-2, C-11), 148.7 (C), 146.2 (C), 136.7 (C), 134.2 (C), 126.4 (CH), 124.7 (CH), 123.0 (C), 120.8 (C), 119.7 (C), 116.4 (CH), 108.9 (CH), 107.2 (CH), 106.1 (CH), 97.8 (C7), 55.3 (2 MeO), 51.7 ($ClCH_2$), 37.6 (C-5), 33.3 (C6), 23.1 (ArMe), and 14.4 (Me); *m/z* 408, 406 ($M^{+\bullet}$, 31%, 89%), 370 (*M*—HCl, 63), 357 (*M*—CH_2Cl, 100), 355 (*M*—HCl—CH_3, 23), 342 (*M*—CH_3—CH_2Cl, 50), and 327 (*M*—2CH_3—CH_2Cl, 18).

Further elution gave 2,12-*dimethoxy*-5,9-*dimethyl*-7H-[1]-*benzazepino*[1′,2′:1,2]*pyrrolo*[5,4-b]*quinoline* (**8**; R^1 = Me; R^2 = MeO) (4.46 g, 61%) which crystallised from dichloromethane–light petroleum (1:9) as pale yellow crystals, m.p. 167—168 °C (Found: C, 77.7; H, 6.3; N, 7.8%, $M^{+\bullet}$, 370.1675. $\lambda_{max.}$ (cyclohexane) 218, 236, 249sh, 271, 290sh, 328sh, 336sh, 342, 351, and 368 nm (log ε 4.65, 4.73, 4.64, 4.55, 4.44, 3.96, 4.02, 4.09, 3.99, and 3.89); δ [80 MHz, $(CD_3)_2CO$] 8.03 (1 H, d, *J* 9.5 Hz, 10-H), 7.88 (1 H, d, *J* 2.6 Hz, 1-H), 7.53 (1 H, d, *J* 8.8 Hz, 4-H), 7.31 (1 H, d, *J* 2.5 Hz, 13-H), 7.09 (1 H, dd, *J* 9.5 and 2.5 Hz, 11-H), 6.97 (1 H, dd, *J* 8.8 and 2.6 Hz, 3-H), 6.36 (1 H, s, 8-H), 6.00 (1 H, br t, *J* 7.5 Hz, 6-H), 3.91 (6 H, s, MeO), 3.38 (2 H, br d, *J* 7.5 Hz, CH_2), 2.82 (3 H, s, ArMe), 2.06 (3 H, s, vinyl Me); ^{13}C {^{1}H} n.m.r. δ ($CDCl_3$) 159.4, 158.8 (C-2, C-12), 149.8 (C), 148.4 (C), 146.4 (C), 136.8 (C), 135.6 (C), 134.6 (C), 128.8 (CH), 127.4 (C), 124.9 (CH), 124.6 (CH), 121.7 (C), 120.1 (C), 116.5 (CH), 112.7 (CH), 111.7 (CH), 107.3 (CH), 93.5 (C-8), 55.6 (2 MeO), 27.1 (C-7), 22.7 (ArMe), and 14.8 (vinyl Me); *m/z* 370 ($M^{+\bullet}$, 100%), 355 (*M*—CH_3, 49), 185 (M^{2+}, 22).

(ii) 5,8-*Dimethyl*-1,3-*dihydro*-2H-1-*benzazepin*-2-*one* (**5**; R^1 = R^2 = Me). A solution of 5,8-dimethyl-1,3-dihydro-2*H*-benzazepin-2-one (2.6 g) in phosphoryl chloride (10 g) was treated as described in (i) above. The residue (2.74 g) remaining after extraction was chromatographed on silica gel (150 g) in dichloromethane–light petroleum. Gradient elution gave 5-*chloromethyl*-2,5,8,11-*tetramethyl*-5,6-*dihydroquino*[1′,2′:1,2]-*pyrrolo*[5,4-b]*quinoline* (**9**; R^1 = R^2 = Me) (14 mg, 0.5%) which crystallised from methanol as pale yellow needles, m.p. 173—175 °C (Found: C, 76.6; H, 5.9; N, 7.3%; $M^{+\bullet}$, 374.1551. $C_{24}H_{23}{}^{35}ClN_2$ requires C, 76.9; H, 6.2; N, 7.5%; $M^{+\bullet}$, 374.1550); $\lambda_{max.}$ (cyclohexane) 232, 243sh, 252sh, 277, 288, 303sh, 316, 335sh, 341, 362, 414sh, and 432sh nm (log ε 4.34, 4.31, 4.26, 4.48, 4.60, 3.96, 3.86, 3.78, 3.78, 3.72, 2.97, and 2.89); δ (80 MHz, $CDCl_3$) 9.29 (1 H, br s, 1-H), 8.04—7.94, 7.35—7.25, and 7.06—6.95 (5 H, 3 m, 3-, 4-, 9-, 10-, 12-H), 6.52 (1 H, br s, 7-H), 3.41 (2 H, s, $ClCH_2$), 3.40 and 2.92 (2 H, ABq, *J* 15.6 Hz, 6-, 6′-H), 2.86, 2.59, and 2.53 (9 H, 3 s, ArMe), 1.54 (3 H, s, Me); *m/z* 376, 374 ($M^{+\bullet}$, 23 and 68%), 338 (*M*—HCl, 100), 325 (*M*—CH_2Cl, 51), 323 (*M*—HCl—Me, 41), and 310 (*M*—CH_2Cl—Me, 40).

Further elution gave 2,5,9,12-*tetramethyl*-7H-[1]*benzazepino*[1′,2′:1,2]*pyrrolo*[5,4-b]*quinoline* (**8**; R^1 = R^2 = Me) (1.33 g, 57%) which crystallised from methanol as colourless microcrystals, m.p. 148—150 °C (Found: C, 85.0; H, 6.8%; $M^{+\bullet}$,

338.1775. $C_{24}H_{22}N_2$ requires C, 85.2; H, 6.6%; $M^{+\bullet}$ 338.1782); $\lambda_{max.}$ (cyclohexane) 236, 242sh, 247.5, 269, 286sh, 328, 341.5, 351, and 365 nm (log ε 4.49, 4.49, 4.50, 4.46, 4.35, 3.79, 3.86, 3.78, and 3.70); δ ($CDCl_3$) 8.03—6.90 (6 H, m, Ar), 6.13 (1 H, s, 8-H), 5.85 (1 H, br t, *J* 7 Hz, 6-H), 3.17 (2 H, br d, *J* 7 Hz, CH_2), 2.73, 2.45, and 2.40 (9 H, 3 s, ArMe), and 2.00 (3 H, s, vinyl Me); ^{13}C {^1H} n.m.r. δ ($CDCl_3$) 149.4, 145.0, 137.7, 137.0, 135.9, 135.6, 133.9, 131.9, 128.3, 127.7, 127.4, 125.6, 125.3, 123.5, and 122.9 (Ar and vinyl C), 93.3 (C-8), 27.2 (C-7), 22.6, 21.7, and 21.5 (ArMe), 14.7 (vinyl Me); *m/z* 338 ($M^{+\bullet}$, 100%), 323 (*M*—CH_3, 38), and 169 (M^{2+}, 14).

(iii) 5-*Methyl*-1,3-*dihydro*-2H-1-*benzazepin*-2-*one* (**5**; R^1 = Me; R^2 = H).—5-Methyl-1,3-dihydro-2*H*-1-benzazepin-2-one (173 mg) was treated with phosphoryl chloride (1 g) as described in (i) above. The residue (180 mg) remaining after extraction was subjected to thick layer chromatography on silica (35 g) using dichloromethane–light petroleum (7:3) as eluant. Extraction of the higher R_F fluorescent band gave 5-*chloromethyl*-5,8-*dimethyl*-5,6-*dihydroquino*[1′,2′:1,2]-*pyrrolo*[5,4-*b*]*quinoline* (**9**; R^1 = Me; R^2 = H) as a yellow solid (1 mg, 0.6%) (Found: $M^{+\bullet}$ 346.1237. $C_{22}H_{19}{}^{35}ClN_2$ requires $M^{+\bullet}$ 346.1237); *m/z* 348, 346 ($M^{+\bullet}$, 3 and 9%), 310 (*M*—HCl, 100), 297 (*M*—CH_2Cl, 14), 295 (*M*—HCl—Me, 39), 282 (*M*—CH_2Cl—Me, 12). Insufficient material was available for further characterisation.

Extraction of the lower R_F fluorescent band gave 5,9-*dimethyl*-7H-[1]*benzazepino*[1′,2′:1,2]*pyrrolo*[5,4-b]*quinoline* (**8**; R^1 = Me, R^2 = H) (70 mg, 45%) which crystallised from methanol as pale yellow needles, m.p. 195—196 °C (Found: C, 85.0; H, 6.1%, $M^{+\bullet}$, 310.1464. $C_{22}H_{18}N_2$ requires C, 85.1; H, 5.9%; $M^{+\bullet}$ 310.1469); $\lambda_{max.}$ (cyclohexane) 214, 221sh, 230sh, 244, 266, 284, 320.5, 337, 351.5, and 368 nm (log ε 4.54, 4.50, 4.45, 4.49, 4.50, 4.38, 3.72, 3.79, and 3.72); δ ($CDCl_3$) 8.25—7.03 (8H, m, ArH), 6.15 (1 H, s, 8-H), 5.85 (1 H, br t, *J* 6.7 Hz, 6-H), 3.22 (2 H, br d, *J* 6.7 Hz, CH_2), 2.77 (3 H, s, ArMe), 2.03 (3 H, s, vinyl Me); ^{13}C {^1H} n.m.r. δ ($CDCl_3$) 149.9, 149.6, 144.7, 135.9, 134.6, 134.1, 129.3, 127.8, 127.1, 125.9, 124.7, 123.8, and 123.2 (Ar and vinyl C), 93.5 (C-8), 27.1 (C-7), 22.6 (ArMe), and 14.8 (vinyl Me); *m/z* 310 ($M^{+\bullet}$, 100%), 295 (*M*—CH_3, 37), and 155 (M^{2+}, 4).

(iv) 8-*Methoxy*-5-*phenyl*-1,3-*dihydro*-2H-1-*benzazepin*-2-*one* (**5**; R^1 = Ph; R^2 = MeO). 8-Methoxy-5-phenyl-1,3-dihydro-2*H*-1-benzazepin-2-one (750 mg) was treated with phosphoryl chloride as described in (i) above. The residue (748 mg) remaining after extraction was subjected to thick layer chromatography on silica gel (70 g) using dichloromethane–light petroleum (7:3) as eluant. Extraction of the only fluorescent band gave 2,12-*dimethoxy*-5,9-*diphenyl*-7H-[1]*benzazepino*-[1′,2′:1,2]*pyrrolo*[5,4-b]*quinoline* (**8**; R^1 = Ph; R^2 = MeO) (355 mg, 51%) crystallised from dichloromethane–methanol as pale yellow microcrystals, m.p. 179—181 °C (Found: $M^{+\bullet}$, 494.1986. $C_{34}H_{26}N_2O_2$ requires $M^{+\bullet}$, 494.1994);* $\lambda_{max.}$ (cyclohexane) 240, 280, 296sh, 329sh, 344, 366sh, and 440sh nm (log ε 4.93, 4.49, 4.29, 3.90, 3.99, 3.85, and 2.56); δ (80 MHz, $CDCl_3$) 8.09—6.71 (16 H, m, ArH), 6.25 (1 H, br t, *J* 6.9 Hz, 6-H), 6.12 (1 H, br s, 8-H), 3.98 and 3.95 (6 H, 2 s, 2 MeO), 3.56—3.23 (2 H, m, 7-H, 7′-H); ^{13}C {^1H} n.m.r. δ ($CDCl_3$) 160.1 (C-2, C-12), 149.5 (C), 143.9 (C), 133.0 (CH), 131.1, 129.5, 129.0, 128.3, 127.7, 126.3, 117.7 (CH), 113.3 (CH), 112.1 (CH), 107.6 (CH), 95.6 (C-8), 56.2 (2 MeO), and 28.2 (C-7); *m/z* 494 ($M^{+\bullet}$, 100%), 479 (*M*—CH_3, 14), and 247 (M^{2+}, 14).

Crystal Data.—Compound (**8**; R^1 = Me; R^2 = MeO). $C_{24}H_{22}N_2O_2$, *M* = 370.4, Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), *a* = 20.49(2), *b* = 11.09(1), *c* = 8.72(1) Å, β = 97.8(1)°, *U* = 1 963(4) Å^3, D_m = 1.23(1), D_c(*Z* = 4) = 1.25 g cm^{-3}, *F*(000) = 784, μ_{Mo} = 0.87 cm^{-1}, *N* = 2 578, N_o = 1 495, *R* = 0.096, *R*′ = 0.11.

Compound (**9**; R^1 = Me; R^2 = MeO). $C_{24}H_{23}ClN_2O_2$, *M* = 406.9, Monoclinic, space group $P2_1/n$ (variant of No. 14), *a* = 15.316(9), *b* = 10.665(9), *c* = 12.859(9) Å, β = 99.51(5)°, *U* = 2 072(2) Å^3, D_m = 1.29(1), D_c(*Z* = 4) = 1.30 g cm^{-3}, *F*(000) = 856, μ_{Mo} = 2.1 cm^{-1}, *N* = 1 937, N_o = 1 275, *R* = 0.10, *R*′ = 0.12.

Supplementary data available [*No.* SUP. 56055 (7 pp.)]: hydrogen and thermal parameters, least-squares planes. See Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1, Section 4.0. Structure factors are available from the editorial office on request.

* This compound is pure by spectroscopic standards. It occludes solvent, particularly halogenated solvents, which cannot be fully removed without decomposing the compounds. Analytical results are repeatedly low and non-reproducible.

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