Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	−0.03036 (13)	0.1485 (3)	0.67626 (7)	0.0426 (5)
C2	−0.0407 (2)	0.0483 (3)	0.72444 (8)	0.0552 (6)
C3	−0.1144 (2)	0.0748 (4)	0.75841 (10)	0.0645 (7)
C4	−0.1780 (2)	0.2022 (4)	0.74550 (10)	0.0662 (7)
C5	−0.1689 (2)	0.3031 (4)	0.69802 (10)	0.0624 (7)
C6	−0.09588 (14)	0.2745 (3)	0.66298 (9)	0.0518 (6)
C7	0.04832 (13)	0.1191 (3)	0.64003 (7)	0.0402 (5)
C8	0.12805 (13)	0.0491 (3)	0.65484 (8)	0.0462 (5)
C9	0.19999 (14)	0.0180 (3)	0.61580 (8)	0.0446 (5)
C10	0.17788 (12)	0.0676 (3)	0.55896 (7)	0.0402 (5)
C11	0.23877 (14)	0.0361 (3)	0.51489 (8)	0.0486 (6)
C12	0.21800 (14)	0.0840 (3)	0.46266 (9)	0.0515 (6)
C13	0.13430 (13)	0.1676 (3)	0.45022 (8)	0.0436 (5)
C14	0.1110 (2)	0.2213 (3)	0.39597 (8)	0.0516 (6)
C15	0.0293 (2)	0.2977 (3)	0.38491 (9)	0.0544 (6)
C16	−0.0333 (2)	0.3254 (3)	0.42700 (8)	0.0503 (6)
C17	−0.01359 (14)	0.2764 (3)	0.48018 (8)	0.0431 (5)
C18	0.07033 (12)	0.1979 (2)	0.49290 (7)	0.0369 (5)
C19	0.09558 (12)	0.1444 (2)	0.54715 (7)	0.0360 (5)
O1	0.03107 (8)	0.1720 (2)	0.58699 (5)	0.0420 (4)
O2	0.27408 (9)	−0.0452 (2)	0.62897 (6)	0.0613 (5)

Table 2. *Selected geometric parameters* (Å, °)

C1—C6	1.388 (3)	C10—C19	1.375 (3)
C1—C2	1.393 (3)	C10—C11	1.415 (3)
C1—C7	1.473 (3)	C11—C12	1.348 (3)
C2—C3	1.380 (3)	C12—C13	1.419 (3)
C3—C4	1.374 (4)	C13—C14	1.415 (3)
C4—C5	1.380 (4)	C13—C18	1.418 (3)
C5—C6	1.389 (3)	C14—C15	1.363 (3)
C7—C8	1.338 (3)	C15—C16	1.391 (3)
C7—O1	1.367 (2)	C16—C17	1.368 (3)
C8—C9	1.441 (3)	C17—C18	1.407 (3)
C9—O2	1.235 (2)	C18—C19	1.422 (3)
C9—C10	1.461 (3)	C19—O1	1.371 (2)
C6—C1—C2	118.8 (2)	C11—C10—C9	121.6 (2)
C6—C1—C7	121.0 (2)	C12—C11—C10	121.1 (2)
C2—C1—C7	120.2 (2)	C11—C12—C13	120.9 (2)
C3—C2—C1	120.5 (3)	C14—C13—C18	117.9 (2)
C4—C3—C2	120.3 (2)	C14—C13—C12	122.3 (2)
C3—C4—C5	120.0 (2)	C18—C13—C12	119.8 (2)
C4—C5—C6	120.0 (3)	C15—C14—C13	121.1 (2)
C1—C6—C5	120.4 (2)	C14—C15—C16	120.6 (2)
C8—C7—O1	121.9 (2)	C17—C16—C15	120.4 (2)
C8—C7—C1	126.5 (2)	C16—C17—C18	120.3 (2)
O1—C7—C1	111.6 (2)	C17—C18—C13	119.7 (2)
C7—C8—C9	122.5 (2)	C17—C18—C19	123.4 (2)
O2—C9—C8	123.2 (2)	C13—C18—C19	116.9 (2)
O2—C9—C10	122.6 (2)	O1—C19—C10	122.2 (2)
C8—C9—C10	114.2 (2)	O1—C19—C18	115.0 (2)
C19—C10—C11	118.4 (2)	C10—C19—C18	122.8 (2)
C19—C10—C9	119.9 (2)	C7—O1—C19	119.1 (1)

Data collection: *P*4 diffractometer software. Cell refinement: *XSCANS* (Siemens, 1991). Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including H-atom geometry, have been deposited with the IUCr (Reference: KA1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Pair Stacking of 10-(4-Nitrophenyl)-5(10*H*)-phenazinyl Radicals

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Abstract

The title radicals, $C_{18}H_{12}N_3O_2.0.5C_6H_6$, are arranged in radical pairs along the *a* axis with specific overlap of the π systems, leading to short intermolecular contacts between atoms with large spin populations.

Comment

Like Wurster's blue radical cation salts (Hausser, 1956; Yamauchi & Fujita, 1990), 10-ethyl-5(10*H*)-phenazinyl, (1) (McIlwain, 1937) shows an anomalous temperature (T) dependence of the static magnetic susceptibility (χ) in the solid state, with χT falling off with decreasing temperature (Hausser 1956; Serafimov & Zimmermann, 1972). Therefore, crystal structures of 5(10*H*)-phenazinyl radicals, which can provide some insight into this phenomenon, are of particular interest. Recently, we succeeded in determining the crystal

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structures of the α- and β-modifications of 10-phenyl-5(10*H*)-phenazinyl, (2) (Barth, Kanellakopulos, Krieger & Neugebauer, 1993). In both the radical-chain pattern of α-(2) (3.29 Å) and the radical-pair arrangement of β-(2) (3.50 Å), short interplanar distances are found. Moreover, all short intermolecular contacts [α-(2): C(2)···N(5) 3.315 (2), C(4)···C(10a) 3.347 (2) Å; β-(2): C(2)···N(5) 3.554 (3), C(4)···C(10a) 3.539 (3) Å] occur between atoms bearing large spin populations, *i.e.* C(2), C(4), N(5), C(6), C(8), C(9a), N(10), C(10a) (Peraus & Neugebauer, 1994). The results of α- and β-(2) can be taken as evidence that the magnetic anomalies of 5(10*H*)-phenazinyl radicals are due to specific π–π interactions (Kosower, 1983; Geuder, Hünig & Suchy, 1986). The crystal structures obtained, however, could also represent a chance packing arrangement. Therefore, studies of further crystal structures of 5(10*H*)-phenazinyl radicals are necessary to confirm the specific π–π interactions in the crystalline state. Now 10-(4-nitrophenyl)-5(10*H*)-phenazinyl, (3), has become available and has afforded crystals suitable for X-ray structure analysis.

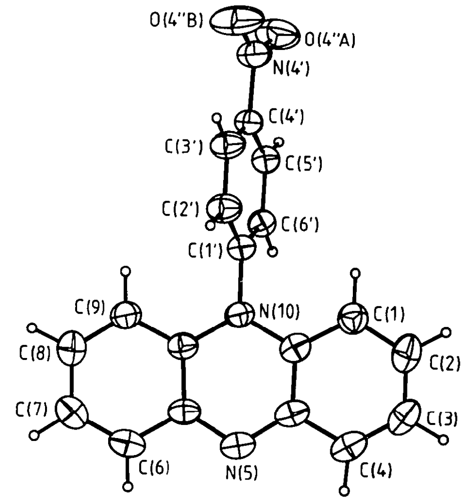
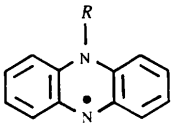


Fig. 1. A view of the 5(10*H*)-phenazinyl radical (3) with the atom-labelling scheme. Displacement ellipsoids are plotted at the 50% probability level.



(1) $R = CH_3CH_2$
(2) $R = C_6H_5$
(3) $R = 4\text{-}NO_2C_6H_4$

A view of (3) is shown in Fig. 1. The crystal structure reveals an almost planar 5(10*H*)-phenazinyl skeleton, in which the hydropyrazinyl ring takes on a very flat boat conformation, with both N(5) and N(10) being displaced out of the C(4a), C(5a), C(9a), C(10a) plane by +0.017 and +0.028 Å, respectively. Owing to steric requirements, the 4-nitrophenyl ring is distorted out of the 5(10*H*)-phenazinyl plane by about 67° [C(10a)—N(10)—C(1′)—C(2′) −112.7 (2), C(10a)—N(10)—C(1′)—C(6′) 66.6 (2)°]. The distortion is less than that in α- and β-(2) with an almost perpendicular arrangement of the phenyl substituent with regard to the 5(10*H*)-phenazinyl plane [α-(2) 87, β-(2) 86°]. The smaller torsion angle of (3) probably indicates that there is some electronic interaction between the electron-attracting 4-nitro substituent and the electron-donating 5(10*H*)-phenazinyl system, which also shows up in a comparison of the electron-spin resonance and ENDOR results of (2) and (3) (Peraus & Neugebauer, 1994).

Bond lengths and angles in (3) (Table 2) agree well with those of α- and β-(2). Compared with phenazine [C—N 1.355, 1.335 Å, C—N—C 116.6° (Herbstein & Schmidt, 1955) or C—N 1.341 (1), 1.342 (1) Å, C—N—C 116.72 (8)° (Wozniak, Kariuki & Jones, 1991)], in the C(4a), N(5), C(5a) segment of (3) only the C—N bond lengths are slightly increased [C(4a)—N(5) 1.356 (3), N(5)—C(5a) 1.362 (3) Å, C(4a)—N(5)—C(5a) 117.0 (1)°], whereas in the C(9a), N(10), C(10a) segment both the N—C bond lengths [C(9a)—N(10) 1.395 (2), N(10)—C(10a) 1.400 (3) Å] and the C—N—C angle [C(9a)—N(10)—C(10a) 120.4 (1)°] are significantly enlarged.

Unlike α- and β-(2) ($Z = 4$), the unit cell of (3) consists of two 5(10*H*)-phenazinyl molecules and one benzene solvate molecule which lies on the inversion centre at the origin (Fig. 2). The 5(10*H*)-phenazinyl radicals are stacked along the *a* axis; the stacking axis and 5(10*H*)-phenazinyl plane enclose an angle of 26°. Each 5(10*H*)-phenazinyl is related to its direct neighbour by inversion centres (Fig. 2), shifted by $a/2$ ($-x, 1-y, 1-z$; $1-x, 1-y, 1-z$).

Alternating interplanar distances between the 5(10*H*)-phenazinyl systems (3.43 and 3.45 Å) and different transverse displacements (1.2 and 4.5 Å) provide evidence of radical-pair formation. As in the case of α- and β-(2), there is a specific overlap of the π systems in the radical pair of (3) leading to short contacts between atoms bearing large spin populations: N(5)···C(10a^{ii}) 3.434 (3), C(4)···C(9a^{ii}) 3.429 (3) Å (Table 2) [(ii) = $-x, 1-y, 1-z$]. On the other hand, the overlap between the radical pairs is restricted to the outer C(1), C(2), C(3), C(4), C(4a), C(10a) ring, giving rise to short intermolecular contacts between C(1)···C(4^{iii}) 3.482 (3), C(2)···C(4a^{iii}) 3.463 (3) and C(3)···C(10a^{iii}) 3.506 (3) Å (Fig. 2, Table 2) [(iii) = $1-x, 1-y, 1-z$]. In agreement with α- and β-(2), the radical-pair arrangement in the crystal structure of (3) with the short interplanar distance of 3.43 Å (phenazine 3.49 Å; Herbstein & Schmidt, 1955) and the short intermolecular contacts between atoms bearing large spin populations also provide evidence of specific intermolecular π–π interactions in the crystal, which now seems to be a typical characteristic of 5(10*H*)-phenazinyl radicals substituted only at N(10). It is feasible that further substitution, particularly with space-demanding substituents, *e.g.* in the 3,7-positions, may completely suspend the specific intermolecular π–π interactions.

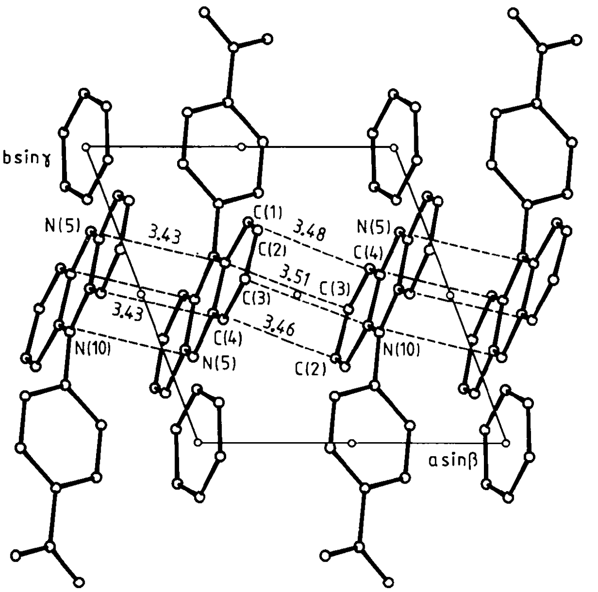


Fig. 2. Packing diagram of (3) projected down the *c* axis showing the radical pairs with shortest intermolecular contacts.

Experimental

To 5-(4-nitrophenyl)phenazinium tetrafluoroborate (1.00 g, 2.57 mmol) (Peraus & Neugebauer, 1994) dissolved in water (200 ml) and covered by a benzene layer (50 ml) was added a solution of potassium ferrocyanide trihydrate (5.40 g, 13 mmol) in water (50 ml) under slow stirring. The resulting 5(10*H*)-phenazinyl radical was repeatedly extracted into benzene (4 × 50 ml). The combined benzene extracts were dried ($MgSO_4$) and evaporated *in vacuo* (= 10^{-1} Torr) at room temperature. Crystallization of the residue from acetonitrile/benzene (2:3) at 255 K afforded 52 mg (7%) black crystals, m.p. 455 K (decomp.).

Crystal data

$C_{18}H_{12}N_3O_2.0.5C_6H_6$
$M_r = 341.37$
Triclinic
$P\bar{1}$
$a = 7.735\ (1)$ Å
$b = 8.066\ (1)$ Å
$c = 14.319\ (2)$ Å
$\alpha = 103.94\ (2)°$
$\beta = 98.20\ (2)°$
$\gamma = 107.83\ (2)°$
$V = 802.4\ (6)$ Å^3
$Z = 2$
$D_x = 1.413$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 12$–$16°$
$\mu = 0.0871$ mm^{-1}
$T = 300$ K
Isometric prism
0.2 × 0.2 × 0.2 mm
Black

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3280 measured reflections
3145 independent reflections
1561 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.026$
$\theta_{\rm max} = 26°$
$h = 0 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 17$
3 standard reflections frequency: 90 min intensity decay: <3%

Refinement

Refinement on F
$R = 0.033$
$wR = 0.035$
$S = 1.14$
1516 reflections
295 parameters
H-atom U's refined isotropically
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.09$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
C(1)	0.4316 (3)	0.7431 (3)	0.5238 (2)	0.0444 (6)
C(2)	0.4526 (3)	0.7158 (3)	0.4284 (2)	0.0526 (6)
C(3)	0.3508 (3)	0.5511 (3)	0.3563 (2)	0.0535 (6)
C(4)	0.2318 (3)	0.4142 (3)	0.3800 (2)	0.0489 (6)
C(4a)	0.2056 (2)	0.4337 (2)	0.4771 (1)	0.0396 (6)
N(5)	0.0888 (2)	0.2897 (2)	0.4971 (1)	0.0436 (5)
C(5a)	0.0718 (3)	0.3142 (2)	0.5924 (1)	0.0376 (5)
C(6)	−0.0447 (3)	0.1668 (3)	0.6165 (2)	0.0474 (6)
C(7)	−0.0733 (3)	0.1838 (3)	0.7098 (2)	0.0514 (7)
C(8)	0.0151 (3)	0.3493 (3)	0.7830 (2)	0.0487 (6)
C(9)	0.1316 (3)	0.4963 (3)	0.7635 (1)	0.0420 (6)
C(9a)	0.1627 (2)	0.4816 (2)	0.6690 (1)	0.0349 (5)
N(10)	0.2787 (2)	0.6277 (2)	0.6450 (1)	0.0377 (4)
C(10a)	0.3068 (2)	0.6054 (2)	0.5490 (1)	0.0370 (5)
C(1′)	0.3591 (3)	0.8067 (2)	0.7157 (1)	0.0352 (5)
C(2′)	0.5016 (3)	0.8440 (3)	0.7966 (2)	0.0542 (6)
C(3′)	0.5796 (3)	1.0171 (3)	0.8622 (2)	0.0466 (6)
C(4′)	0.5145 (3)	1.1496 (3)	0.8452 (1)	0.0383 (5)
C(5′)	0.3712 (3)	1.1146 (2)	0.7658 (1)	0.0365 (5)
C(6′)	0.2929 (3)	0.9413 (3)	0.7007 (1)	0.0365 (5)
N(4′)	0.6009 (2)	1.3363 (2)	0.9134 (1)	0.0511 (5)
O(4″*A*)	0.7214 (2)	1.3648 (2)	0.9856 (1)	0.0886 (6)
O(4″*B*)	0.5499 (2)	1.4552 (2)	0.8935 (1)	0.0717 (5)
C(1*B*)	0.0553 (3)	−0.0451 (3)	−0.0861 (2)	0.556 (7)
C(2*B*)	0.1158 (3)	0.1344 (3)	−0.0290 (2)	0.0527 (6)
C(3*B*)	0.0604 (3)	0.1789 (3)	0.0573 (2)	0.0525 (7)

Table 2. *Selected geometric parameters* (Å, °)

C(1)—C(2)	1.372 (3)	N(10)—C(10a)	1.400 (3)
C(1)—C(10a)	1.389 (3)	N(10)—C(1′)	1.436 (2)
C(2)—C(3)	1.385 (2)	C(1′)—C(2′)	1.383 (3)
C(3)—C(4)	1.352 (3)	C(1′)—C(6′)	1.381 (3)
C(4)—C(4a)	1.413 (3)	C(2′)—C(3′)	1.374 (2)
C(4a)—N(5)	1.356 (3)	C(3′)—C(4′)	1.368 (3)
C(4a)—C(10a)	1.418 (2)	C(4′)—C(5′)	1.377 (3)
N(5)—C(5a)	1.362 (3)	C(4′)—N(4′)	1.469 (2)
C(5a)—C(6)	1.405 (3)	C(5′)—C(6′)	1.372 (2)
C(5a)—C(9a)	1.416 (2)	N(4′)—O(4″*A*)	1.212 (2)
C(6)—C(7)	1.366 (3)	N(4′)—O(4″*B*)	1.220 (3)
C(7)—C(8)	1.382 (2)	C(1*B*)—C(2*B*)	1.374 (3)
C(8)—C(9)	1.368 (3)	C(1*B*)—C(3*B*$^{\rm i}$)	1.365 (3)
C(9)—C(9a)	1.392 (3)	C(2*B*)—C(3*B*)	1.368 (3)
C(9a)—N(10)	1.395 (2)		

C(4)···C(9a^{ii})	3.429 (3)	C(2)···C(4a^{iii})	3.463 (3)
N(5)···C(10a^{ii})	3.434 (3)	C(3)···C(10a^{iii})	3.506 (3)
C(1)···C(4^{iii})	3.482 (3)		

C(2)—C(1)—C(10a)	120.1 (2)	C(8)—C(9)—C(9a)	120.3 (2)
C(1)—C(2)—C(3)	120.6 (2)	C(5a)—C(9a)—C(9)	119.8 (2)
C(2)—C(3)—C(4)	120.0 (2)	C(5a)—C(9a)—N(10)	117.6 (2)
C(3)—C(4)—C(4a)	122.0 (2)	C(9)—C(9a)—N(10)	122.6 (1)
C(4)—C(4a)—N(5)	119.3 (1)	C(9a)—N(10)—C(10a)	120.4 (1)
C(4)—C(4a)—C(10a)	117.0 (2)	C(9a)—N(10)—C(1′)	120.7 (2)
N(5)—C(4a)—C(10a)	123.7 (2)	C(10a)—N(10)—C(1′)	118.7 (2)
C(4a)—N(5)—C(5a)	117.0 (1)	C(1)—C(10a)—C(4a)	120.2 (2)
N(5)—C(5a)—C(6)	118.6 (1)	C(1)—C(10a)—N(10)	122.2 (1)
N(5)—C(5a)—C(9a)	123.7 (2)	C(4a)—C(10a)—N(10)	117.5 (2)
C(6)—C(5a)—C(9a)	117.7 (2)	C(4′)—N(4′)—O(4″*A*)	118.3 (2)
C(5a)—C(6)—C(7)	121.7 (2)	C(4′)—N(4′)—O(4″*B*)	118.3 (2)
C(6)—C(7)—C(8)	119.6 (2)	O(4″*A*)—N(4′)—O(4″*B*)	123.4 (2)
C(7)—C(8)—C(9)	121.0 (2)		

C(5a)—C(9a)—N(10)—C(1′)	173.1 (1)
C(1′)—N(10)—C(10a)—C(4a)	−171.6 (1)
C(9a)—N(10)—C(1′)—C(2′)	72.3 (2)
C(10a)—N(10)—C(1′)—C(6′)	66.6 (2)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, 1-y, 1-z$.

The phase problem was solved by direct methods: 259 reflections with $E > 180$ were included and four starting reflections, in addition to the three origin-fixing reflections, were used. An initial difference Fourier map revealed the half benzene molecule located on the inversion centre at the origin. All H atoms could be found in a further difference map. In the refinement, several cycles of a full-matrix least-squares procedure lead to a convergence at $R = 0.034$; positions of non-H atoms were included with anisotropic and H-atom positions with isotropic displacement parameters.

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1992). Data reduction: *DATA* (Enraf–Nonius, 1990). Structure refinement: *LSFM* (Enraf–Nonius, 1990). Structure solution: *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori & Viterbo, 1989). Molecular graphics: *ORTEP*II (Johnson, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: JZ1027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Intermediate for Chloroquine Analogs: (*E*)-2-(4,7-Dichloro-2-quinolinyl)-3-(dimethylamino)-2-propenal

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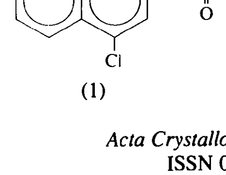
Abstract

The title compound, $C_{14}H_{12}Cl_2N_2O$, has been shown to have an *E* configuration about the double bond in the propenal moiety. Significant delocalization of the lone pair on the N atom of the dimethylamino group into the π system of this moiety is indicated by the planarity about this N atom.

Comment

The increasing resistance observed in *Plasmodium falciparum* to the traditional antimalarial chloroquine [4-(7-chloro-4-quinolinylamino)-1-(diethylamino)-pentane] (Krogstad, Gluzman, Kyle, Oduoula, Martin, Milhous & Schlesinger, 1987; Peters, 1990) has stimulated a search for more effective analogs. As part of our effort in this area, we required chemically reactive derivatives of 4,7-dichloroquinoline that could be used for the synthesis of heterocyclic chloroquine analogs. An attractive intermediate is (1) which has been synthesized in good yield (De, Mague, Byers & Krogstad, 1995).



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