Solid-state Interactions in Radicals: Crystal Structures of α- and β-10-Phenyl-5(10*H*)-phenazinyl

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Crystallization of 10-phenyl-5(10*H*)-phenazinyl affords two modifications in which the radicals are arranged in a chain pattern along the *a*-axis (α) or in radical pairs along the *c*-axis (β) giving rise to considerable spin pairing.

Solid-state properties of organic free radicals, in particular anomalies in the temperature (T) dependence of the static magnetic susceptibility (χ) attract considerable interest, an example being Wurster's blue radical cation salts.[1,2] Similarly the uncharged 10-ethyl-5(10*H*)-phenazinyl **1**[3] shows no Curie-Weiss behaviour, $\chi \cdot T$ falls off with decreasing temperature.[1,4] A determination of its crystal structure, however, is not feasible owing to experimental difficulties in isolating **1** in a pure state. Further studies, therefore, require a more stable derivative. We report here the synthesis and the crystal structure of 10-phenyl-5(10*H*)-phenazinyl **2** and comment upon some of its properties.

Reaction of phenazine with phenyl lithium followed by oxidation of the intermediate 5,10-dihydro-5-phenylphenazine with silver tetrafluoroborate afforded 5-phenylphenazinium tetrafluoroborate [7% yield, m.p. 290 °C (decomp.)]. Reduction of this salt with potassium ferrocyanide in water led to **2**, which after careful recrystallization gave black needles [α-**2**, 6%, m.p. 156–157 °C (decomp.)] accompanied by very few prisms [β-**2**, m.p. 156 °C (decomp.)]. Microhydrogenation (5% Pd/BaSO$_4$, 0.48 mol H$_2$) and spin concentration determinations in toluene (EPR, 298 K, 98%) confirmed the pure radical nature of **2**.

The well-resolved EPR spectrum of **2** in toluene was analysed by ENDOR† and ^{1}H NMR[5] studies. Unexpectedly the π-SOMO (singly occupied molecular orbital) of **2** with large positive spin populations at N-5, 2,8-C (*para*) and 4,6,9a,10a-C (*ortho*) and small negative spin populations at 1,3,7,9-C (*meta*) is similar to that of diphenylaminyl.[6] Determination of spin concentration of **2** in toluene in the 300–220 K temperature range ($c = 10^{-3}$ mol dm^{-3}) clearly shows that **2** is monomeric in solution, whereas magnetic measurements in

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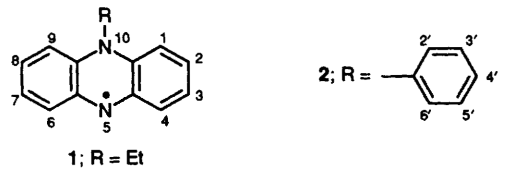
† ENDOR (toluene, 260 K): a(5-N) = 6.79, a(10-N) = 4.29 G (1G = 10^{-4} T); (230 K) a(2,8-H) = −3.47, a(4,6-H) = −2.70, a(H) ≈ 0.21G. ^{1}H NMR (CD$_2$Cl$_2$, 295 K): a(2′,6′-H) = −0.22, a(3′,5′-H) = +0.24, a(4′-H) = −0.06 G; additionally a(H) = +0.24 and a(H) = +0.13 G are found for the hydrogens in 1,9- and 3,7-positions. All assignments are deduced from EPR results of selectively substituted derivatives (G. Peraus, unpublished results). The observed EPR spectrum (toluene, 300 K) is well simulated with the data a(N) = 6.80, a(N) = 4.23, a(H) = 3.50 (2H), a(H) = 2.74 (2H) and a(H) = 0.25 G (8H).



1; R = Et

the solid state using the Faraday method indicate a radical content of only 43% at 294 K which further decreases at lower temperatures to reach a limit value of 2% at 70–4 K. The temperature dependence of χ was analysed by the triplet-singlet model[7] yielding a singlet-triplet separation energy of ΔE = 1.1 kcal mol^{-1} (1 cal = 4.184 J). In comparison with **1** (ΔE = 0.9 kcal mol^{-1})[4] the magnetic behaviour of solid **2** is similar. The striking spin pairing in solid 5(10*H*)-phenazinyl radicals points to a specific radical pair interaction which may be discernible from the crystal structure.

The molecular structures of α- and β-**2** were established by X-ray diffraction.‡ In both modifications approximate C_{2v} symmetry is found for the molecules. Owing to spatial requirements the phenyl substituent is forced into an almost perpendicular arrangement with regard to the 5(10*H*)-phenazinyl plane [Fig. 1(*a*), torsion angle α-**2**: C(10a)–N(10)–C(1′)–C(2′) 93.0(1)°; β-**2**: [C(10a)–N(10)–C(1′)–C(2′) 94.0(2)°]. Corresponding bond lengths and angles in α- and β-**2** show no significant deviation. As compared to phenazine[8] (C–N 1.345 Å, C–N–C 116.6°), in the C(4a), N(5), C(5a) segment of α- and β-**2** [Fig. 1(*a*)] the C–N bond lengths are slightly increased to 1.356(3) Å while the C–N–C angle is unchanged at 116.9(3)°. Within the C(9a)–N(10)–C(10a) segment, however, the C–N–C angle [120.5(2)°] and the N–C bond lengths [1.391(3) Å] are significantly enlarged.

In α-**2** the molecules are packed in a chain pattern along the *a*-axis in which the phenyl substituents of adjacent molecules are alternately displaced by 180° [Fig. 1(*b*)]. In β-**2**, on the other hand, the radicals are arranged in pairs along the *c*-axis (Fig. 2). The stacking of the molecules in α-**2** corresponds exactly to the packing arrangement of phenazine.[8] The interplanar distance of 3.29 Å in α-**2**, however, is found to be significantly shorter (phenazine: 3.49 Å). Furthermore, it is notable that only atoms with large spin populations [N(5), C(2), C(4), C(6), C(10a)] are involved in the shortest intermolecular contacts [Fig. 1(*b*)]. This holds also for β-**2** in which the radicals of each pair are related by a centre of inversion (Fig. 2). Within the radical pair the interplanar distance (3.50 Å) is larger than in α-**2** (3.29 Å).

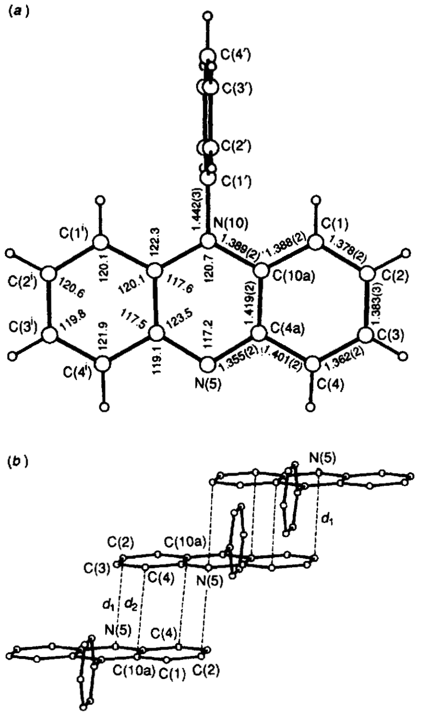


Fig. 1 Molecular structure of α-**2**: (*a*) view onto the 5(10*H*)-phenazinyl plane, showing the atom-labelling scheme, bond distances (Å) and angles (°, standard deviation about 1°). (*b*) Shortest intermolecular contacts between adjacent radicals d_1[C(2)····N(5)] 3.315(2) Å and d_2[C(4)····C(10a)] 3.347(2) Å.

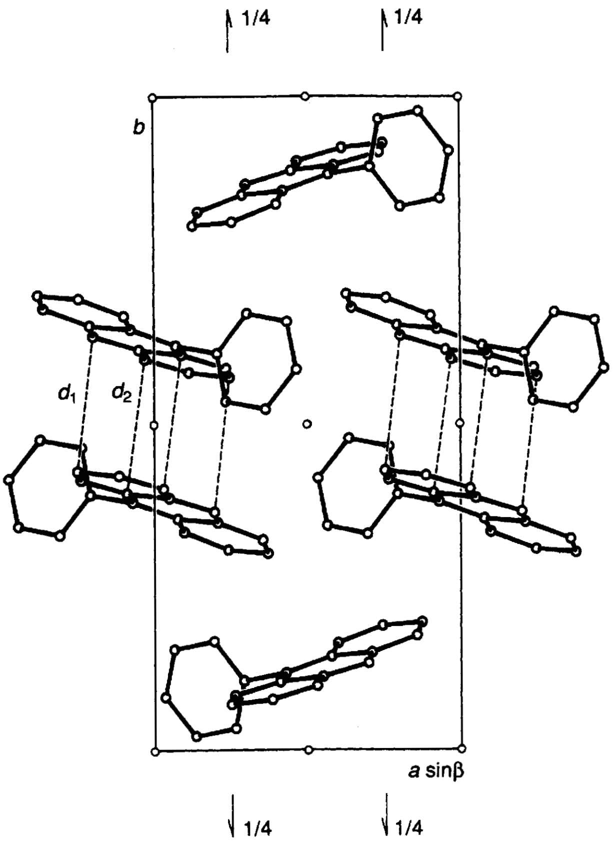


Fig. 2 Packing diagram of β-**2** projected down the *c*-axis showing the radical pairs with shortest intermolecular contacts d_1[C(2)····N(5)] 3.554(3) Å and d_2[C(4)····C(10a)] 3.539(3) Å.

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‡ *Crystal data* for α-**2**, $C_{18}H_{13}N_2$: Black needles from ethyl acetate; dimensions 0.05 × 0.05 × 0.25 mm, M = 257.3, space group *I*2/*a* (No. 15), symmetry of the molecule in crystal: C_2; a = 10.226(2), b = 10.538(2), c = 12.103(2) Å, β = 97.33(2)°, U = 1293.5(9) Å^3, Z = 4, D_c = 1.320 g cm^{-3}, μ(Mo-Kα) = 0.732 cm^{-1}, F(000) = 540 e. The intensity data were collected using an Enraf-Nonius CAD-4 circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å, θ/2θ scanning technique). Total number of unique reflections 1141 (sinθ/λ ⩽ 0.62 Å^{-1}), of which 646 [$I \geqslant 3.0\,\sigma(I)$] were classified to be observed. The structure was solved by direct-methods. In the refinement anisotropic thermal parameters were applied for all non-hydrogen atoms and isotropic thermal parameters for the hydrogens. The final cycle of refinement converged with R = 0.031 and R_w = 0.034; max(Δ/σ) = 0.01, $\Delta\rho_{max}$ = 0.04 e Å^{-3}.

For β-**2**, $C_{18}H_{13}N_2$: Black prisms from ethyl acetate; dimensions 0.08 × 0.01 × 0.15 mm, M = 257.3, space group $P2_1/n$ (No. 14); a = 8.798(1), b = 17.197(3), c = 9.184(1) Å, β = 109.91(1)°, U = 1306.6(7) Å^3, Z = 4, D_c = 1.309 g cm^{-3}, μ(Mo-Kα) = 0.726 cm^{-1}, F(000) = 540 e. Total number of unique reflections 2471 (sinθ/λ ⩽ 0.62 Å^{-1}), of which 1034 [$I \geqslant 3.0\,\sigma(I)$] were classified to be observed. For measurement of the intensity data and solution of structure see α-**2**: R = 0.039 and R_w = 0.028; max (Δ/σ) = 0.01, $\Delta\rho_{max}$ = 0.11 e Å^{-3}.

Atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

For the molecular structures of α- and β-**2** three findings are obvious, the unusual short interplanar distance of the 10-phenyl-5(10*H*)-phenazinyl radicals in the chain of α-**2**, the formation of radical pairs in β-**2**, and the fact that the short intermolecular contacts in α- and β-**2** only occur between atoms bearing large spin populations. These results support the view that the magnetic anomalies of 5(10*H*)-phenazinyl radicals are related to specific intermolecular π-π interactions[9] which may also determine the crystal structures. Phenazine and α-**2**, however, show the same packing arrangement. Therefore further work is necessary to confirm, whether the molecular structures of **2** are an accidental result or typical for 5(10*H*)-phenazinyl radicals.

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