Thermally Unstable 5-(9-Anthrylmethyl)-10-methyl-5,10-dihydrophenazine

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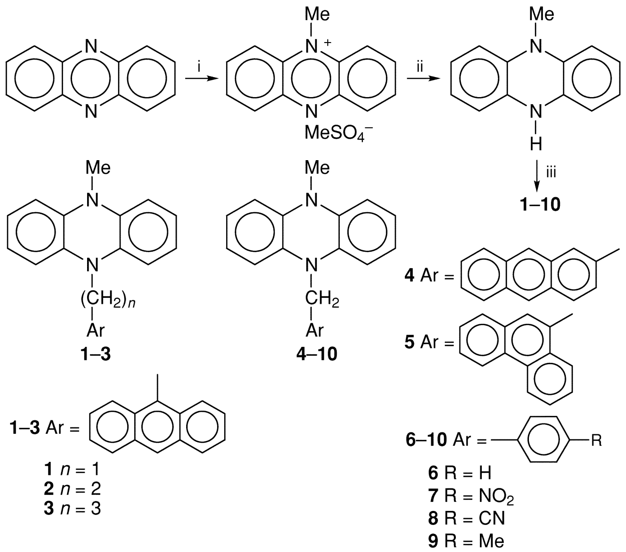
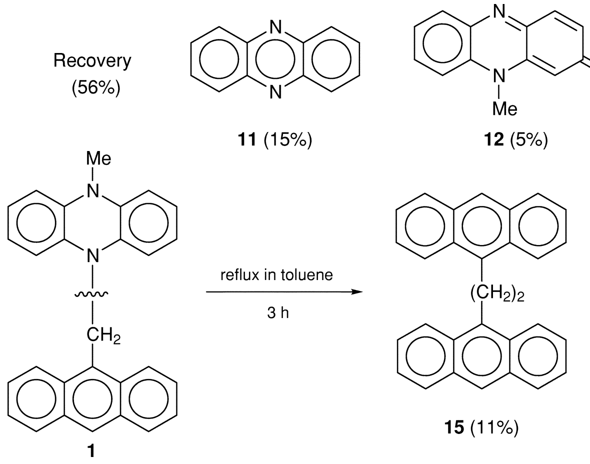
The title compound in refluxing toluene decomposed to 9-anthrylmethyl derivatives and phenazine as major products upon cleavage of the N–CH_2 bond; the orbital interaction of which with π-orbitals of the aromatic ring was suggested by the X-ray crystal structure analysis.

In continuation of our studies on the preparation[2] and properties[3] of *N,N′*-disubstituted 5,10-dihydrophenazines, we report here the synthesis and thermal instability of 5-(9-anthrylmethyl)-10-methyl-5,10-dihydrophenazine (**1**), since we observed the gradual decomposition of **1** even at 70 °C. The thermal stabilities of dihydrophenazines, **1**–**10** shown in Scheme 1, were investigated for comparison. They were prepared by the method reported earlier[2,4] and identified by spectroscopic methods.



Scheme 1 *Reagents*: i, Me_2SO_4, $PhNO_2$; ii, $Na_2S_2O_4$–H_2O; iii, BuLi then $Ar(CH_2)_nX$



Scheme 2

Compound **1** is fairly stable at room temperature, so crystals for X-ray structure analysis were easily grown from a toluene–hexane mixture. However, recrystallization from hot toluene was unsuccessful. Even at 70 °C in C_6D_6, the ^1H NMR spectrum of **1** showed gradual partial decomposition, while other derivatives, **2**–**10**, were perfectly stable under the same conditions. The thermal decomposition products formed by heating in toluene followed by isolation by column chromatography, **11**–**17**, are shown in Scheme 2 with their yields. Although the recovery of phenazine moiety was not good, that of anthracene moiety went up to $(7 + 4 + 11 + 12 + 2)/(100 - 56) = 0.82$. Therefore, these decomposition products demonstrate that the bond cleaved by thermolysis is the N–CH_2 bond. The observations described above suggest that the instability of **1** is due not to the electron donating (compounds **9**, **10**) or accepting (**7**, **8**) abilities of substituents at the N-atom, but to the sterically repulsive interactions between the phenazinyl moiety and the substituent at the N-atom. To obtain further information about the steric repulsion, X-ray crystal structure analyses were performed for **1**, **5**, **7** and **10**. X-Ray structures are shown in Fig. 1.

As can be seen from Fig. 1, the aromatic rings (Ar) are virtually planar for all compounds. The side view of **1** resembles a capital L and the conformational arrangement of phenazinyl and Ar moieties differs from those of the other compounds. The dihydrophenazine moieties are non-planar (folded) and the dihedral angles between the planes of the two benzene rings are 153.0, 156.7, 157.2, and 158.7° for **1**, **5**, **7** and **10**, respectively. For **5**, **7** and **10**, the Ar groups are situated almost in the plane which corresponds to the mirror plane of symmetry for the two benzene rings of the dihydrophenazine moiety. For compound **1**, the anthracene ring is almost perpendicular to this mirror plane and therefore the hydrogen CH_2 atoms and some of the hydrogen atoms in the aromatic ring and in the phenazinyl moiety lie close together and may be one of the factors causing thermal instability. The structures of **1**, **5**, **7** and **10** indicate that the N–CH_2 bonds of **5**, **7** and **10** are almost parallel to the Ar ring, while that of **1** is close to perpendicular to the anthracene ring. Thus while Ar_π–σ^*_{NC} overlap between the π-orbitals of the Ar ring and an antibonding orbital of the N–CH_2 bond for **5**, **7** and **10** is absent, the corresponding interaction of **1** may occur to some extent (Fig. 3). The interaction of the σ^*-orbital with π-orbitals of Ar may facilitate cleavage of the N–CH_2 bond. The anthrylmethyl radical formed by homolytic cleavage is converted into **13** by hydrogen abstraction, **15** and **16** by

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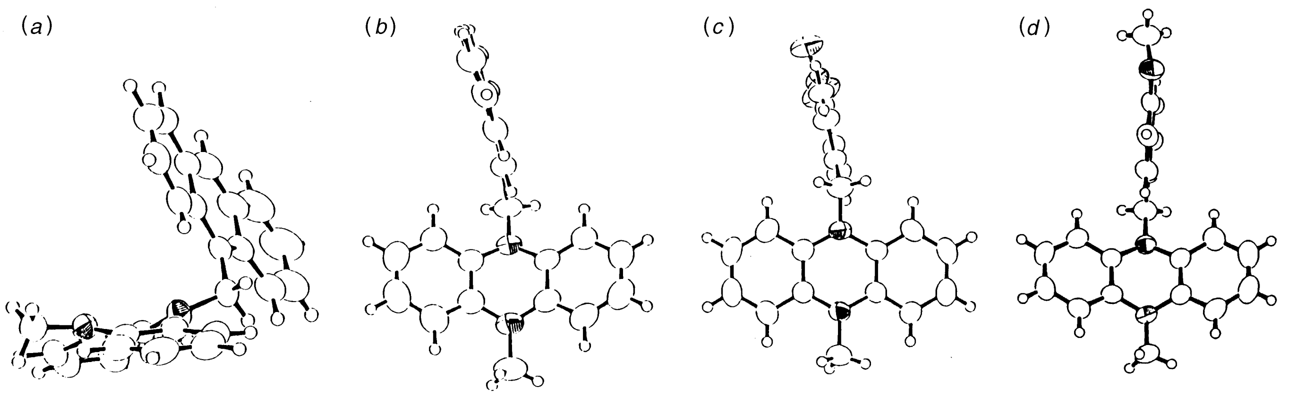
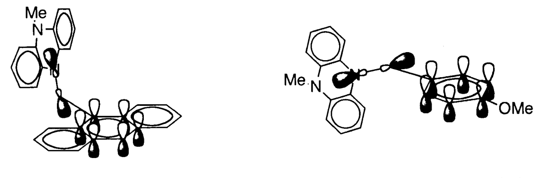


Fig. 1 X-Ray structures of **1**, **5**, **7** and **10**, (a) side view of **1** and (b), (c), and (d) top views of **5**, **7** and **10**, respectively



1 : parallel to π-orbitals

10 : perpendicular to π-orbitals

	Bond angle θ/°	Dihedral angle φ/°
1	113.2	56
5	115.7	8
7	116.6	14
10	116.5	8

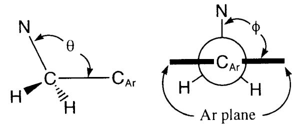


Fig. 3 Interaction between σ^* orbitals of the N–CH_2 bond and π-orbitals of Ar rings

coupling reactions, and **14** by air-oxidation. Similarly, the phenazinyl radical can be oxidized to **11** and **12**.

Experimental

5-(*9-Anthrylmethyl*)-10-*methyl*-5,10-*dihydrophenazine* **1**.—To a solution of 5-methyl-5,10-dihydrophenazine (2.7 g, 13.7 mmol) in DME (59 mL) was added dropwise a solution of *n*-butyllithium in hexane (8.6 mL of 15% solution, 13.7 mmol) and the mixture was stirred for 30 min. To this solution was added a solution of 9-bromomethylanthracene (4.1 g, 15.1 mmol) in DME (80 mL). After being stirred for 1 h, the reaction mixture was treated with an excess of an aqueous solution of sodium dithionite, extracted with toluene, and the organic layer was dried. Hexane was added to this toluene solution and the mixture was cooled in an ice-bath. The solid deposited was collected by filtration to give orange crystals (2.87 g, 54%), mp 162–163.5 °C (decomp.); λ_{max}/nm (cyclohexane) (log ε/dm^3 mol^{-1} cm^{-1}) 250 (5.03), 258 (5.07), 350 (4.08), 370 (4.04), and 390 (3.94); δ_H ($CDCl_3$) 3.02 (3H, s), 5.65 (2H, s), 6.41–6.71 (8H, m), 7.41–7.54 (4H, m), 7.96–7.99 (2H, m), 8.38 (1H, s), and 8.56–8.60 (2H, m) (Found: C, 86.8; H, 5.4; N, 7.05. $C_{28}H_{22}N_2$ requires C, 87.0; H, 5.7; N, 7.25%).

Crystal Data for **1**.—$C_{28}H_{22}N_2$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.128(3)$, $b = 11.501(3)$, $c = 9.696(2)$ Å, $\alpha = 110.83(2)$, $\beta = 95.86(2)$, $\gamma = 61.28(2)°$, $V = 1013.6(5)$ Å^3, $D_c = 1.266$ g cm^{-3}, $Z = 2$, μ(Mo-Kα) = 0.74 cm^{-1}. Final refinement converged to $R(R_w) = 0.068$ (0.070). $S = 1.69$.

Tests of Thermal Stability in Benzene.—Solutions of dihydrophenazines, **1**–**10**, (0.008 M) in C_6D_6 were heated to 70 °C and changes of the ^{1}H NMR signals were followed for 3 h.

Thermolysis of **1**.—A solution of **1** (0.18 g, 0.47 mmol) in toluene (50 mL) was refluxed for 3 h under an argon atmosphere. After cooling, the solution was concentrated almost to dryness under reduced pressure and the residue was separated by flash chromatography with toluene. The products isolated were identified by direct comparison with authentic compounds.

For compound **5**, one crystal cell contains two different conformations whose dimensions differ only slightly. Here only one of the structures is shown and discussed.

Crystal Data for **5**.—$C_{28}H_{22}N_2$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.287(3)$, $b = 13.519(2)$, $c = 12.748(3)$ Å, $\alpha = 91.33(2)$, $\beta = 117.97(1)$. $\gamma = 84.60(1)°$, $V = 2012.8(7)$ Å^3, $D_c = 1.275$ g cm^{-3}, $Z = 4$, μ(Mo-Kα) = 0.74 cm^{-1}. Final refinement converged to $R(R_w) = 0.041$ (0.043). $S = 1.93$.

Crystal Data for 5-*Methyl*-10-(4-*nitrobenzyl*)-5,10-*dihydrophenazine* **7**.[4]—$C_{20}H_{17}N_3O_2$, monoclinic space group $P2_1/a$ (no. 14), $a = 11.357(3)$, $b = 11.849(2)$, $c = 13.020(3)$ Å, $\beta = 111.74(1)°$, $V = 1627.5(5)$ Å^3, $D_c = 1.352$ g cm^{-3}, $Z = 4$, μ(Mo-Kα) = 0.89 cm^{-1}. Final refinement converged to R (R_w) = 0.044 (0.054). $S = 1.74$.

Crystal Data for **10**.—$C_{21}H_{20}N_2O$, monoclinic, space group $P2_1/a$ (no. 14), $a = 11.407(1)$, $b = 11.961(2)$, $c = 13.369(2)$ Å, $\beta = 114.918(8)°$, $V = 1654.4(3)$ Å^3, $D_c = 1.270$ g cm^{-3}, $Z = 4$, μ(Mo-Kα) = 0.79 cm^{-1}. Final refinement converged to R (R_w) = 0.045 (0.049). $S = 1.66$.

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Techniques used: IR, ^{1}H NMR, UV, X-ray crystallography, elemental analysis

References: 11

Schemes: 2

Figures: 3

Appendix: Crystallographic data for compounds **1**, **5**, **7** and **10**

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