

UNEXPECTED SYNTHESIS OF 2-METHYL 1,3-DIAZAPYRENE FROM 1,8-DIAMINO NAPHTHALENE

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Abstract : Treatment of 1,8-diamino naphthalene by glycerol, under Skraup conditions, leads to 2-methyl 1,3-diazapyrene and not to quino[7,8-h]quinoline.

Aromatic polyimines are widely used in coordination chemistry because of the accessibility of their first π^* orbitals, once bound to transition metals¹. Surprisingly, the family of compounds used is mainly restricted to 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), 2,2',6',2''-terpyridine (terpy) and their derivatives. Quino[7,8-h]quinoline (qq) having an unusual chelate ring size (6 atoms) is expected to have low-lying π^* levels as well as interesting complexing properties. Thus we embarked upon its synthesis and study.

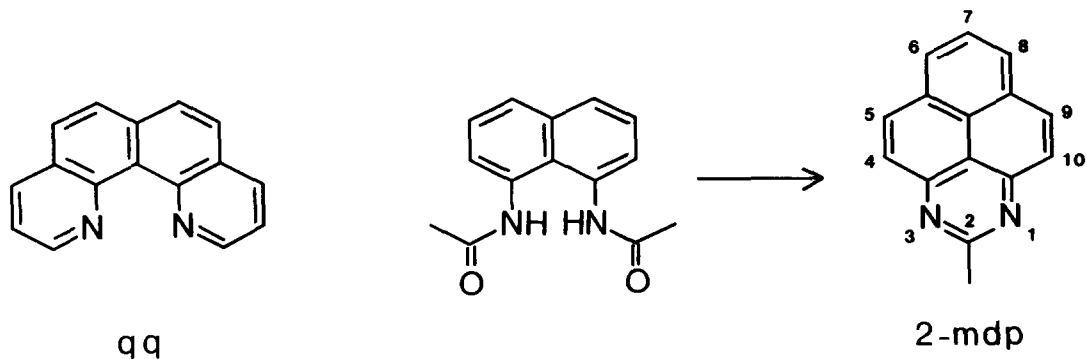


Figure 1

The synthesis of qq has been mentioned twice in the literature. The first report describes a preparation which in fact does not provide the expected compound, as recognized later by the authors themselves². The second paper describes a Skraup type synthesis from 1,8-diamino naphthalene³. Unfortunately, as demonstrated in the present communication, the structure of the product as given by the latter authors was erroneous. Instead of qq, 2-methyl 1,3-diazapyrene (2-mdp) is formed, as shown in figure 1.

Treatment of the diacetamide derivative of 1,8-diamino naphthalene with glycerol, H_2SO_4 and As_2O_5 at 160°C for 30 min. under the Skraup conditions earlier used by Buu-Hoï et al.^{3,4}, followed by work-up, affords a white solid (I) (37%, calc. for $C_{15}H_{10}N_2$). This was recrystallised several times from ethanol/ H_2O (4/1) (v/v). TLC analysis showed the compound to be pure; its melting point (180-180.5°C) was in agreement with that published earlier. This compound is in fact 2-mdp and not qq. Analytical data are collected in Table 1.

	elemental analysis			molecular weight
	C %	H %	N %	
experimental	83.25	4.58	12.74	$m/e = 218$ (mass spectroscopy)
calc. for (I) = qq	83.46	4.38	12.17	$C_{16}H_{10}N_2$: M = 230
calc. for (I) = 2-mdp	82.55	4.62	12.83	$C_{15}H_{10}N_2$: M = 218

Table 1

In order to confirm the structure of (I), a detailed NMR study was undertaken. 1H NMR data for (I) is given in Table 2.

1H NMR spectrum of (I) (200 MHz ; $CDCl_3$; TMS)

assignment ⁴	5.9 and 4.10 (AB)	6.8 and 7 (AB ₂)	CH ₃ (s)
δ (ppm)	8.548 ; 8.183	8.432(d) ; 8.149(m)	3.182
J (Hz)	9.20	7.68	

Table 2

The absence of a signal around $\delta \sim 8.9$ ppm, as found for instance in quinoline, shows that (I) does not contain any protons α to the nitrogen atoms ; in addition, a singlet is observed at 3.182 ppm which is in agreement with (I) being 2-mdp. The ^{13}C NMR spectrum ($CDCl_3$; TMS) shows an intense signal in the benzylic methyl region : $\delta = 27.1$ ppm. The formation of 2-mdp instead of qq under the drastic conditions used is not very surprising : it involves the formation of a 6-membered ring of the perimidine family⁵, followed by Bally's reaction⁶, leading to the addition of the 6, 7 and 8 carbon atoms.

To our knowledge, the synthesis of qq has yet to be realized. Recent work on 1,8-diamino naphthalene⁷ may prove very useful in this regard.

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REFERENCES

1. W.R. McWhinnie and J.D. Miller, *Adv. Inorg. Rad. Chem.*, **12**, 135 (1969) ; V. Balzani, F. Bolleta, M.T. Gandolfi and Maestri, *Topics in Current Chemistry*, **75**, 1 (1978).
2. I. Iwai, S. Hara, *J. Pharm. Soc. Japan*, **70**, 394 (1950) ; I. Iwai, S. Hara, S. Sayegi, *J. Pharm. Soc. Japan*, **71**, 1152 (1951).
3. M. Dufour, N.P. Buu-Hoï, P. Jacquignon, *J. Chem. Soc. (C)*, 1415 (1967).
4. A non ambiguous assignment was obtained by 2D NMR : M. Bourdonneau, C. Brevard, J.P. Kintzinger et P. Maltese, unpublished results.
5. F. Sachs, *Ann. Chem.*, **365**, 53 (1909) ; N.P. Buu-Hoï, P. Jacquignon et M. Marty, *Bull. Soc. Chim. France*, 461 (1960).
6. *Reaktionen der Organischen Chemie*, H. Krauch, W. Kuntz und E. Nonnenmacher, Dr. A. Huthig Verlag, Heidelberg (1976).
7. K. Honda, H. Nakanishi and A. Yabe, *Bull. Chem. Soc. Japan*, **56**, 2338 (1983).

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