



# The structure investigations of dehydroacetic acid and 1,8-diaminonaphthalene condensation product by NMR, MS, and X-ray measurements

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## ABSTRACT

A new unexpected product of condensation reaction of 1,8-diaminonaphthalene (DAN) and carbonyl compound (here: dehydroacetic acid (dha)) was synthesized. Discussion about the molecular structure of possible products of this reaction was done on the base of NMR studies. The structure of the titled product in both DMSO solution and in the solid state was resolved by analysis of its spectral data (X-ray structure analysis, multinuclear NMR in solution and solid state spectra) and MS measurements. The presented studies provided clear evidence that the titled product exists in diluted DMSO solution as the mixture of two kinetic free ionic species whereas in concentrated DMSO solution as well as in the solid state this system forms associated ionic pairs bonded together by hydrogen bonds.

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## 1. Introduction

The reaction between primary amines and carbonyl compounds is known since the end of 19th century [1]. Usually the product of this condensation is Schiff base. However, when 1,8-diaminonaphthalene (DAN) is used as an amine one can obtain perimidine or its derivatives (Scheme 1).

Perimidines (peri-naphtho-fused pyrimidine systems) are heterocycles having two nitrogen atoms in their molecules [2]. They are unusual systems with an excess and deficiency of  $\pi$  electrons simultaneously [3–5]. This feature makes them susceptible to electrophilic [6,7] and nucleophilic attack [7].

Perimidine derivatives are attracting agents due to their broad spectrum of biological activity [8–10]. They have been studied as antiulcer, antimicrobial, antifungal agents [11,12]. Some of them were applied as coupler substances for preparation of oxidation dyestuffs and hair colouring compositions [13,14]. Pyrroloperimidine-containing polymers are studied as colouring materials,

luminescent sensors, organic light emitting diodes and other optoelectronic devices [15].

There is a lot of information about various perimidine derivatives obtained from DAN and aldehydes [13,16,17] or ketones [13,18–20]. If aldehydes or ketones with exocyclic carbonyl groups react with DAN, the structures of reaction products are very similar (Scheme 2).

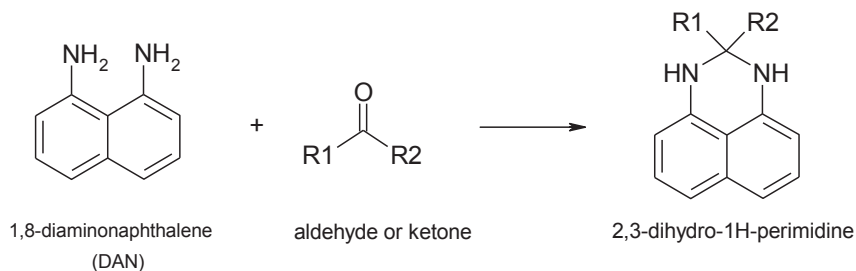
There is some information about products of reaction between DAN and ketones with carbonyl group placed in the ring [13,19,21–23]. Akita and co-workers used ninhydrin as a reagent with carbonyl group located in the ring. They obtained unexpected products having structures dependent on the reaction conditions (different solvents) (Scheme 3) [24].

We were interested in behaviour of ketone having carbonyl groups both outside and inside the ring. Therefore, we selected dehydroacetic acid (3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one) – multi-carbonyl compound having two (potentially efficient in condensation reaction) carbonyl groups in the molecule: one exocyclic and one in the ring (2' or 4' position).

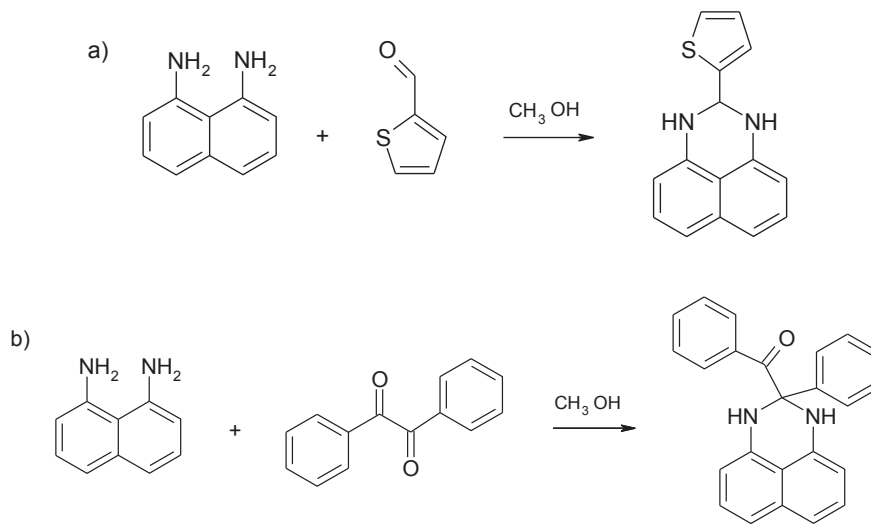
In this paper we present the synthesis of a new product (dha-DAN). The following analytical methods have been applied to define its molecular structure in DMSO solution and in the solid

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**Scheme 1.** The general reaction for obtaining perimidines from 1,8-DAN and carbonyls.



**Scheme 2.** Examples of reaction products of DAN with carbonyl compounds: a) aldehyde [17], b) ketone with exocyclic carbonyl groups [3].

state: <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N NMR in solution, <sup>13</sup>C, <sup>15</sup>N CPMAS NMR, MS, and X-ray single crystal structure analysis.

## 2. Experimental

### 2.1. Synthesis of dhaDAN

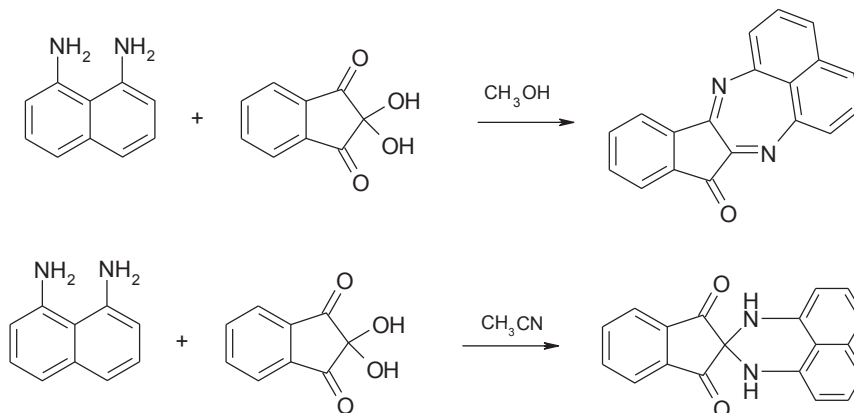
The titled product (dhaDAN) was obtained according to the literature method slightly modified for presented reaction [17].

Dehydroacetic acid (dha) (1 mmol) was added to the methanol

solution of 1,8-diaminonaphthalene (DAN) (1 mmol). The reaction mixture was refluxed and stirring for 2 h. The resulting dark red coloured solution was cooled to the room temperature. After 24 h dark brown coloured solid was filtered, washed by cold methanol, and dried in the air.

Melting point 173 °C.

The solid was dissolved in hot methanol. After two days of slow evaporation of the solvent the crystals suitable for X-ray diffraction investigations precipitated out of the solution.



**Scheme 3.** Two different products of reaction of DAN and ninhydrin in different solvents.

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