Chapter 6
Diazodinitrophenol

6.1 Introduction

The 2-diazo-4,6-dinitrophenol (dinol, diazol, DDNP, DDNPh, or DADNPh) is the first-ever synthesized diazonium compound. Its synthesis is attributed to Griess [1] who prepared it by introducing nitric oxides into an alcoholic solution of 2-amino-4,6-dinitrophenol (picramic acid) [1, 2]. Its explosive character was, however, first reported more than 30 years later in 1892 by Lenze [3].

6.2 Structure

Although DDNP has been known for almost 150 years, its structure is still debated and general consensus does not exist. The most obsolete suggested structures are not mentioned here but may be found in [4].

The properties (chemical, physical, and spectral) of general ortho (structure I, benzo [d][1,2,3]oxadiazole) and para (structure II, 2-oxa-3,4-diazabicyclo[3.2.2] nona-1(7),3,5,8-tetraene) isomers of diazophenols are very similar indicating that the structures should also be similar. Even though the cyclization and formation of two rings does not seem to be unreasonable for the ortho-isomer, it definitely does not look probable for the para-isomer. It is therefore assumed that the structures I and II are rather improbable for diazophenols [5]. This assumption was confirmed when structure I was prepared and shown to be unstable even in a solid argon matrix. The meta-(3-diazo) isomer has not been reported [5, 6].

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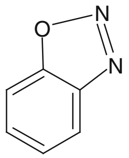
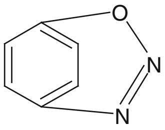
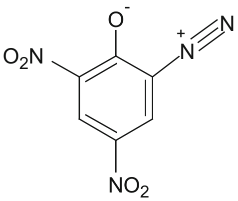


structure I

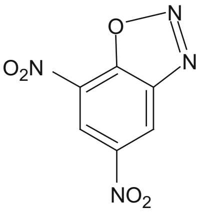


structure II

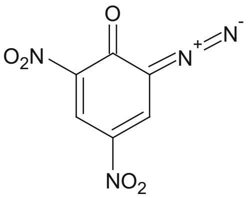
The possible cyclization of the diazo structure III of DDNP and formation of cyclic isomer IV is improbable based on the property-related assumption mentioned above. The theoretical studies employing the AM1 level of theory further support this conclusion [6].



structure III



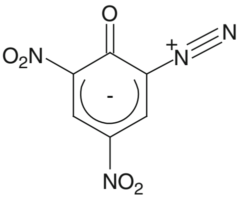
structure IV



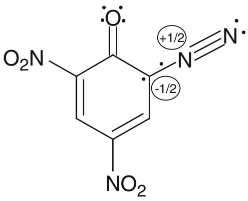
structure V

X-ray diffraction of DDNP was first carried out by Lowe-Ma et al. [5] and later confirmed by Holl et al. [6]. The bonding of DDNP has been discussed on the basis of theoretical calculations and compared to the results of X-ray diffraction, IR, and NMR [5, 6].

According to Lowe-Ma et al. [5], neither the zwitterionic (structure III) nor the quinonoid (structure V) structure provides a satisfactory model for the ortho-diazophenols including DDNP. Some possible tautomeric structure intermediate between these two also does not seem to be probable since DDNP exhibits discrete features of each of them [5]. In later work, these authors incline to structure VI based on the comparison of X-ray crystallography, NMR, and MO calculations. This is closely in agreement with the more recent findings of Holl et al. [6] who proposed diazo structure VII, which is suggested as the best match with single crystal X-ray diffraction and computational studies.



structure VI



structure VII

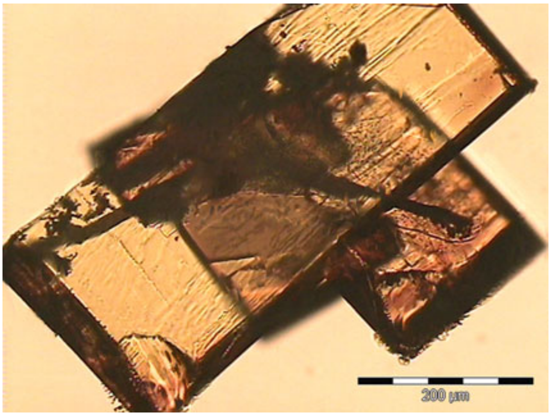


Fig. 6.1 Crystals of DDNP prepared by re-crystallization from acetone

6.3 Physical and Chemical Properties

DDNP crystals are yellow (Fig. 6.1). However, shades of the technical product can range from dark yellow or green to dark brown [4]. The density of DDNP is most often reported as 1.63 g cm^{-3} [7–11]; however, according to Lowe-Ma et al. the density is 1.719 g cm^{-3} (X-ray) [5, 12]. Bagal reports the density of DDNP to be 1.71 g cm^{-3} and states that the value 1.63 g cm^{-3} is for the technical product. The bulk density of DDNP is 0.5–0.9 g cm^{-3} and only 0.27 g cm^{-3} for DDNP in fine powder form [4]. Heat of formation of DDNP is 321 kJ mol^{-1} [13]. It melts at 157–158°C with decomposition; explodes violently at higher temperatures [9, 14, 15].

DDNP is mostly reported as a very slightly hygroscopic compound [11, 16]. Špičák and Šimeček [10] reported 1 % weight gain by storing in 70 % relative humidity (RH) for 40 days; Ficheroulle and Kovache [14] a weight gain of 2.25 % in 100 % RH compared to 1.22 % for LS; TM9-1300-214 reports 0.04 % in 90 % RH at 30 °C [15].

DDNP is slightly soluble in water (0.08 g in 100 ml at 25 °C) [15] but the explosive properties are not affected as the material does not show any signs of reaction at ordinary temperatures. The storage under water does not affect the color or sensitivity of later isolated DDNP [16] and it shows "unimpaired brisance for 24 months at ordinary temperatures or 12 months at 50 °C" when stored under water [15].

The solubility of DDNP in various solvents is shown in Table 6.1. DDNP is readily soluble in acetic acid, hot acetone, and nitrobenzene, less soluble in methanol, ethanol, and ethyl acetate, poorly in other usual organic solvents [4, 7, 16].

It is photosensitive and turns dark when irradiated by light. The samples exposed to sunlight show signs of decomposition after only 40 h of irradiation [13]. However, the photolysed crystal surface becomes a protective layer against further action of the light on the inner portion of the crystal [17]. DDNP is stable in cold mineral acids; it is decomposed by hot concentrated sulfuric acid and by cold diluted hydroxide solution, liberating nitrogen [13, 16]. Reaction with alkalis is

Table 6.1 Solubility of DDNP

	Solubility (g per 100 g of solvent)	
	25°C [15]	50°C [7]
Water	0.08	–
Ethyl acetate	–	2.45
Methanol	0.57	1.25
Ethanol	0.84	2.43
Trichloromethane	–	0.11
Tetrachloromethane	–	Trace
Benzene	0.09	0.23
Toluene	–	0.15
Petrol ether	–	Insol. (at 20°C)
Ethyl ether	0.04	0.08 (at 30°C)
Carbon disulfide	–	Trace (at 30°C)
Acetic acid	1.40	–
Acetone	6.0	–

used for non-explosive disposal of diazidodinitrophenol (0.5 % aqueous solution of sodium hydroxide) [13]. It also reacts with sodium azide forming the sodium salt of 2-azido-4,6-dinitrophenol and liberating nitrogen. This reaction may be used for analysis. The quantity of DDNP in the sample is determined from the volume of nitrogen produced [4].

DDNP is compatible with most usual explosives but is incompatible with LA [8, 14]. Compatibility of wet DDNP with common metals was examined by Ficheroulle and Kovache [14]. They observed that DDNP in a moist atmosphere does not corrode metals, and only attacks them very slightly. The specifications for military type of DDNP are summarized in MIL-D-82885.

Thermal stability of DDNP is higher than stability of MF but significantly lower than that of LA. This is a property which may be limiting its use for some applications [11]. DDNP does not change when stored at 65 °C and it loses 1.25 % of its weight over 96 h at 100 °C [4]. Extensive study of thermal stability of DDNP and kinetics of its decomposition was carried out by Kaiser and Ticmanis. DDNP is stable at moderate temperatures (~60 °C) for a long period; however, it quickly decomposes at temperatures of more than 100 °C [18].

6.4 Explosive Properties

Sensitivity of DDNP to impact is about the same as that for mercury fulminate [4] or slightly less [7, 19] (see Fig. 2.15). Its sensitivity to impact significantly depends on the size of DDNP particles—fine crystals of DDNP are twice as sensitive as the coarse product [3].

Its sensitivity of DDNP to friction is reported lower than that of MF and about the same as that of LA [20]; however, according to our own experiments its

Table 6.2 Detonation velocity of DDNP

Density (g cm^{-3})	Detonation velocity (m s^{-1})	References
0.9	4,400	[8]
1.5	6,600	[9]
1.6	6,900	[8]

sensitivity relatively low – it is between MF and PETN (see Fig. 2.19) [21]. Sensitivity to electric discharge and its comparison with other primary explosives is illustrated in Fig. 2.21. Upon ignition, unconfined and unpressed DDNP burns like nitrocellulose even in quantities of several grams. It does not ignite or detonate under water even when initiated by a blasting cap [4, 16, 22].

Smoleński and Pluciński reported that explosive decomposition of DDNP results mainly in the formation of carbon monoxide, carbon, hydrogen cyanide, and nitrogen. The reaction proceeds according to the following equation [13]:

$$\begin{aligned} 10\ C_6H_2N_4O_5 \longrightarrow\ & 42\ CO + 2.52\ CO_2 + 2.94\ H_2O + 3.15\ H_2 \\ & + 7.67\ C + 7.82\ HCN + 16.1\ N_2 \end{aligned}$$

The dependency of detonation velocity of DDNP on density is summarized in Table 6.2. Its initiating efficiency based on tetryl acceptor charge is better that of MF and LA [12]. The values in TM9-1300-214 [15] confirm superiority of DDNP to MF but the efficiency with respect to LA differs based on the type of acceptor as shown in Table 6.3. It indicates that DDNP is a better initiator for less-sensitive secondary explosives.

Initiating efficiency of DDNP was recently measured by Vala and Valenta. According to their results, it is about the same as of LA when measured using PETN acceptor charge when strong confinement is used (Vala and Valenta private communication).

DDNP belongs to the group of highly brisant explosives being superior to mercury fulminate and also, in some areas, to lead azide. The results of a sand test are summarized in Table 6.3 [7]. Sand-crushing strength of DDNP is not affected by storing under water for 50 days. The power of DDNP measured by a small Trauzl block is significantly superior to LA and MF (Table 6.3).

The ignition temperature is 185 °C [7, 13] or 177 °C [23] (within 5 s); 200 °C for explosion within 1 s [7]. According to our experiments, ignition temperatures of DDNP prepared by Garfield's method [24] are in the range 161–163 °C (heating rate 5 °C min^{-1}, static air atmosphere, sample weight 5 mg). As mentioned previously, sunlight affects the quality of DDNP. The ignition temperature of irradiated DDNP is somewhat lower than for a non-irradiated sample [13].

There has been some disagreement about dead-pressing of DDNP. In older literature, DDNP is reported as a primary explosive, which cannot be dead-pressed

Table 6.3 Initiating efficiency and brisance of LA, MF, and DDNP

	Initiating efficiency [15] (gram of primary explosive)			Brisance[a] [7]	Brisance[b] [7]	Power by small [7]
	Tetryl	TNT	Ammonium picrate	(gram of sand)	(gram of sand)	Trauzl block (cm^3)
DDNP	0.12	0.15	0.28	19.3	90.6	25.0
MF	0.19	0.24	No detonation	6.5	48.4	8.1
LA	0.10	0.26	No detonation	7.2	36.0	7.2

[a] Sand test values are for 0.2 g charge measured in detonator shell and pressed under a reinforcing capsule at 23.4 MPa

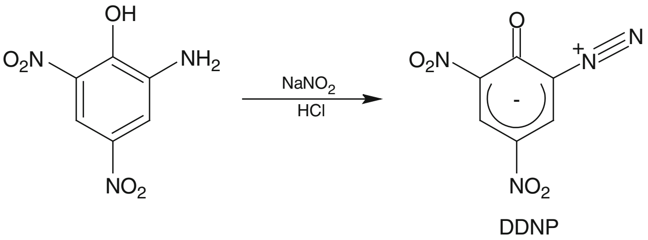
[b] Sand test values are for 1 g charge measured in detonator shell and pressed under a reinforcing capsule at 23.4 MPa

even at high pressures. The attempts to dead-press DDNP reported by Clark indicate that he could not dead-press it when using pressures up to 690 MPa. Two attempts using greater pressures (800 and 900 MPa) both ended by explosion [3, 8, 9, 11]. However, neither the densities obtained at 690 MPa nor other details have been reported. It is therefore difficult to explain why the explosions occurred.

Later experimental works clearly show that it is easily possible to dead-press DDNP. The maximum initiation efficiency is reached at densities from 1.2 to 1.3 g cm^{-3}. At density 1.4 g cm^{-3} it is completely dead-pressed. The density at which DDNP becomes dead-pressed does not depend on the specific surface of the material to be pressed as much as it does in the case of MF [25, 26]. Bagal reported that DDNP becomes dead-pressed by pressure above 19.6 MPa [4].

6.5 Preparation

DDNP is prepared by diazotation of an aqueous solution of 2-amino-4,6-dinitrophenol (picramic acid) or its sodium salt with sodium nitrite and hydrochloric acid [11].



Needle- or leaf-shaped crystalline DDNP is obtained when pure reactants are used at common reaction conditions (Fig. 6.2). The addition of acid to the reaction mixture is the more common way of DDNP preparation [13, 27–29] although addition of nitrite into acidic solution of picraminate acid is also published [7, 24].

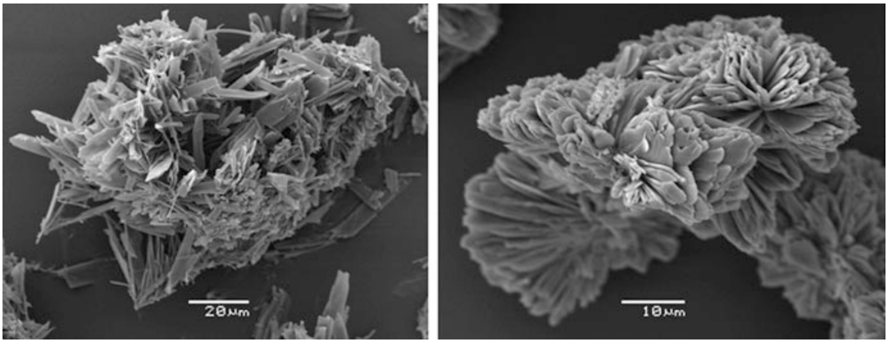


Fig. 6.2 Crystals of DDNP prepared by authors following Alexander's method [27] (*left*) and Garfield and Dreher's method [24] (*right*)—pure reactants were used at both methods; dyes and phenols were not used

The free-flowing product can be obtained by both optimization of the reaction conditions (rate of addition of hydrochloric acid to the mixture) [28] or by use of some crystal shape modifying substances during reaction. Rounded grains of DDNP are reported when pyrogallol, hydroquinone, dinitroresorcinol, and some other substances are added [27] and tabular crystals when adding triphenylmethane dyes to the reaction mixture [24]. Slow mixing of reagents is one of the most important factors for producing free-flowing DDNP according to [28, 29]. Babcock and Kenvil proposed use of an injector or atomizer for acid batching with addition of the acid under the surface of the diazoting mixture. This way acid is added in the form of fine droplets. The process eliminates formation of local high acidity regions and hence prevents the formation of very fine particles of DDNP [29].

Our own experience makes us a bit uncertain about the above-mentioned methodologies for obtaining technologically acceptable product. After numerous unsuccessful trials, we have deviated from the published routes and developed our own which enables us to produce large-size round particles (Fig. 6.3, left). Similar spherical DDNP with a little bit different structure was obtained by Nesveda (Fig. 6.3, right).

Another way of DDNP preparation is oxidation of picramic acid with chromic acid [30]. It is believed by authors that a part of picramic acid is oxidized to complete decomposition forming nitrogen dioxide and subsequently nitrous acid which then diazotizes picramic acid. Strong foaming due to a gas evolution (CO, CO_2, and NO_2) and low yield (32.5 % by weight) support proposed mechanism including partial decomposition of picramic acid.

Re-crystallization may be done from nitrobenzene or from acetone solution by adding the solution to cold ether. DDNP may be purified by dissolving in hot acetone and precipitation by addition of iced water. The purification turns the

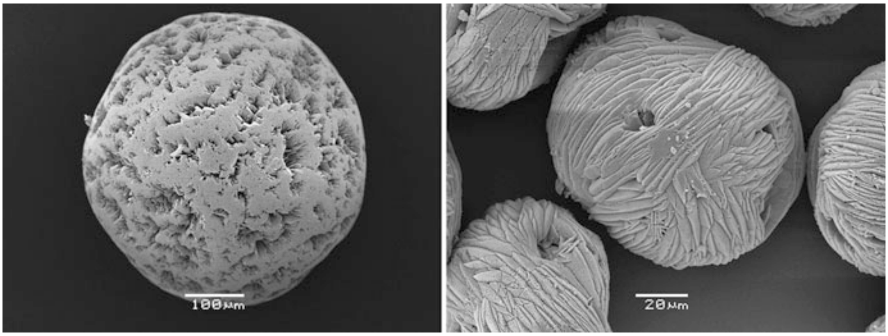


Fig. 6.3 SEM photographs of spherical DDNP prepared by authors (*left*) and the same prepared by Jiří Nesveda, Sellier and Bellot, Vlašim (*right*)

dark brown raw product a brilliant yellow [7, 19]. Several alternative ways of DDNP preparation are summarized in the literature [7].

6.6 Use

Although first prepared in 1858, DDNP was first proposed for use as an explosive in 1892 when Lenze highlighted its valuable explosive properties [13]. Probably the first patent treating DDNP as an explosive was by Dehn in 1922 [16]. DDNP found its application as an initiating explosive in both military and commercial detonators, particularly in USA and Japan [8, 26, 31, 32]. It is also used in stab and percussion primer mixtures and in these applications it has been the subject of many patents including, for example, [31–33]. Due to the absence of heavy metals in the molecule it is widely used in non-toxic types of primer in which it serves as the energizing component (e.g. SINTOX [34]). It is practically the only easily available replacement of LS in today's percussion priming mixtures [35]. A mixture containing DDNP and tetrazene has been proposed as an explosive filler for explosive riveting [36].

Despite its reported use, DDNP exhibits several disadvantages which make it not an ideal primary explosive:

- It causes allergic reactions in some workers
- It can be dead-pressed
- It has low density and therefore it requires a relatively large volume
- It is easily electrified resulting in difficulties during handling and filling [4]
- Problems of waste water treatment
- Relatively low thermal stability for some applications (Vala and Valenta private communication)

The use of DDNP in military applications was further questioned by Fronabarger and Williams pointing out its inability to fulfill shelf-life and reliability requirements [37]. On the other hand, the American technical manual TM 9-1300-214 [15] considers DDNP satisfactory for both commercial and military use.

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