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The Composition of Transformation Products of 2,4,6-trinitrobenzoic Acid in the Aqueous-Phase Hydrogenation over Pd/C Catalysts

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Abstract

Due to a detailed analysis of NMR spectra of the reaction solutions with different composition obtained by the aqueous-phase catalytic (Pd/C) hydrogenation of 2,4,6-trinitrobenzoic acid, the intermediate compounds were identified and a more substantiated mechanism was proposed for the formation of main reaction products – 1,3,5-triaminobenzene and cyclohexane-1,3,5-trione trioxime. Condensation of the 1,3,5-triaminobenzene molecules produced by complete hydrogenation of 2,4,6-trinitrobenzoic acid was shown to result in the formation of a paramagnetic heterocyclic compound.

Keywords

^{1}H and ^{13}C NMR spectroscopy; palladium catalyst; trinitrobenzoic acid; catalytic hydrogenation; aqueous-phase reaction

Introduction

Investigation of catalytic transformations of trinitroaromatic compounds toward the complete hydrogenation yielding triamine derivatives or toward the synthesis of intermediate reduction products is of practical interest for utilization of explosives and production of useful chemical substances [1]. One of the most available and processable trinitrocompounds is the oxidation product of trinitrotoluene, 2,4,6-trinitrobenzoic acid (TNBA), the main technological advantage of which is good water solubility in the composition of alkaline metal salts [2-4]. This allows the reaction to be performed in the medium of this nontoxic and inexpensive solvent. Selective synthesis of the specified products via the multistep hydrogenation of TNBA makes it necessary to develop selective catalysts and obtain a detailed knowledge about individual transformation steps and composition of the intermediates. In this context, a difficult problem is the identification of the reduction products, especially in the intermediate steps of the reaction.

In our earlier studies [5,6], the NMR analysis of the composition of hydrogenation products formed a basis for proposing the scheme of TNBA transformation into 1,3,5-triaminobenzene during its aqua-phase catalytic (Pd/C) hydrogenation. The main intermediate (two isomers of cyclohexane-1,3,5-trione trioxime) and a series of minor components of reaction solutions were identified. Analysis of the additional spectral information obtained by increasing the substrate concentration and varying the catalyst activity made it possible to refine the identification of the intermediates as well as the condensation products of the final 1,3,5-triaminobenzene. As a result, a more reasonable mechanism was proposed for the final stages of TNBA hydrogenation, which is presented in this paper.

Materials and Method

Catalyst Synthesis

The study was carried out using the 5(1)%Pd/C catalysts that were synthesized similar to [5-7], by hydrolytic precipitation of palladium polyhydroxo complexes (PHC) on the surface of carbon material Sibunit (synthesized at the Department of Experimental Technologies, Institute of Hydrocarbons Processing SB RAS, S_{BET} 422 m^2g^{-1}). To this end, an H_2PdCl_4 aqueous solution was supplemented with alkaline precipitant to obtain the required pH. The pH was controlled on a SevenMulti (Mettler Toledo) system using a combined electrode. The obtained PHC solution was mixed with an aqueous suspension of Sibunit. This was

accompanied by a complete absorption of the complexes with decoloration of the solution. The further liquid-phase reduction of palladium on the support surface was carried out with sodium formate in an alkaline medium [8, 9]. After palladium reduction, the samples were washed with water to pH 7, filtered and stored moist (the moisture content of ca. 50%). Before further experiments, no any pretreatments of the synthesized catalyst were performed.

To obtain highly dispersed particles of supported palladium, the synthesis of PHC was performed using $KHCO_3$ alkaline precipitant at pH 4 (catalysts 5(1)%Pd/C(K)). In order to increase the particle size of palladium, $NaHCO_3$ was used as an alkaline precipitant during the synthesis of PHC, and the synthesis of PHC was carried out at pH 5 (catalysts 5%Pd/C(Na)). The TEM data on the particle sizes of the supported palladium for these samples are presented in supplementary materials (Figure 4S).

In addition, to reduce the active surface in samples we employed the partially deactivated catalysts that were obtained by repeated use of the initial catalyst 5%Pd/C(K) after two or three hydrogenation cycles of the substrate (5%Pd/C(K)-D2 and 5%Pd/C(K)-D3, respectively). After removal of the reaction products, a fresh 10% solution of TNBA was added to the used and partially deactivated catalyst; and then the hydrogenation was repeated. Some details of the multi-cycle experiment are presented in supplementary materials (Figure 5S).

Catalytic Tests

The sodium salt of TNBA was obtained by the addition of sodium bicarbonate (2.95 g) to the aqueous suspension of TNBA (10.00 g) until it completely dissolved and CO_2 release ceased. The catalytic hydrogenation of the obtained salt (100 mL of 10 % aqueous solution) was performed at a temperature of 323 K and pressure of 0.5 MPa in the presence of 500 mg (dry) catalyst (the loading was about 400 g of TNBA per 1 g of Pd). The reaction was conducted in a 180 mL steel autoclave equipped with a valve for hydrogen input and an external thermostatted jacket. The reaction mixture was stirred by a magnetic stirrer at 1400 rpm to prevent external diffusion limitations. The progress of the reaction was monitored by measuring the volume of consumed hydrogen with a mass flow meter. The reaction was stopped when the required amount of hydrogen was consumed. After cooling, the sampling was carried out with a syringe.

NMR Spectroscopy

The ^{13}C and ^{1}H NMR spectra of hydrogenation products were recorded on an Avance 400 (Bruker) NMR spectrometer using $DOCD_3$ for deuterium stabilization and as the internal

standard. The pulse programs zg, jmod (APT) with a relaxation delay of 10 s were employed. The lengths of 90° pulses were 3 μs (^{1}H) and 7 μs (^{13}C). The composition of the hydrogenation products was estimated from the integrated intensity of signals from components in the ^{1}H NMR spectra.

EPR Spectroscopy

The EPR spectra were recorded on a BrukerEMXplus (Bruker) spectrometer operating in the X range (9.7 GHz) with an ER 4105 DR resonator at a microwave power 0.2–2.0 mW, at a modulation frequency 100 kHz, amplitude 0.3 G, and temperature 25°C. The spectra were analyzed with Bruker WinEPR Processing software. An accurate determination of *g*-values was made using a Bruker ER 4119HS-2100 marker (g = 1.9800±0.0006). Spectra of aqueous solutions were taken in glass capillaries with the inner diameter of 1 mm. Simulation of the spectra was performed using Bruker WinEPR SimFonia (ver. 1.2) for the rapidly tumbling radicals in solution.

Results and Discussion

The occurrence of consecutive and parallel reactions in the TNBA hydrogenation process makes it difficult to identify the intermediate transformation products and elucidate the reaction mechanism. Earlier we have proposed the reaction scheme based on the NMR analysis of products in the individual steps of TNBA transformation [5]. Based on previously obtained data [5,6] the following mechanism of the final stages of TNBA reduction (Scheme 1) can be represented, according to which 2,4,6-substituted nitrobenzoic acids **1** - **3** are hydrogenated in two directions. The left path in Scheme 1 includes an intramolecular redox reaction followed by decarboxylation, and the right path goes through the reduction of the hydroxyamino group of **1** – **3** with a low probability of decarboxylation. The first of the indicated reaction routes determines its most essential feature and leads to the formation of oximes **14** and **15**, which, depending on the catalyst properties, can either be the main components of the hydrogenation product or occur in minor amounts, as was shown before [6,7]. The following quantitative assessment of the relative content of hydrogenates (wt. %, excluding solvent) was made on the basis of ^{1}H NMR spectra.

It was found [6,7] that at a high dispersion of supported palladium, oximes **14** and **15** virtually completely transform into triaminobenzene **9** due to the reversible step of their formation and further consecutive reactions, according to Scheme 1. The ^{1}H NMR spectrum of transformation products displayed in Figure 1 shows the corresponding signals

characterizing compound **9** (~85%) with insignificant admixtures of compounds **14**, **15** and **8** (1-2%). The other minor components noted in Figure 1 (12 - 15%) are not included in Scheme 1. They are formed by the condensation and hydrolysis of compound **9** and will be considered below. In the case of catalysts containing supported palladium particles of a greater size, the strength of the interaction of oximes **14** and **15** with the metal surface is insufficient for their further transformation into compounds **11, 12, 13** and **9**; the oximes are desorbed from the surface into solution [6,7]. The main components of the hydrogenation products are oximes **14** and **15** (~ 44%), the content of triamine **9** is less than 23% (Figure 2).

The most detailed composition of the intermediate compounds was described in our earlier work [5] using NMR spectra of the reaction solution sampled at the intermediate step of the reaction (Figure 3). Although the hydrogenate giving the spectrum in Figure 3 contains up to 5% of acid **5** formed via the right reaction path, the left path is the main one since the total concentration of intermediate oximes **14** and **15** (24%) is much higher than the concentration of compound **5** and is comparable to the concentration of the final product **9** (38%). However, due to a low concentration of the solution, some compounds were not detected although their formation was implied by the transformation scheme, and identification of several previously described compounds was not quite reliable. To solve these problems, in the present work the concentration of TNBA solution used in the reaction was increased 5-fold (a 10% aqueous solution of TNBA sodium salt). Therewith, the amount of Pd/C catalyst was also increased at a constant ratio of 400 g TNBA per 1 g Pd. To solve the same problem, the reaction was decelerated with the use of partially deactivated catalysts (Experimental Part).

Figure 4 shows the ^{1}H NMR spectrum of the hydrogenate obtained with deactivated catalyst 5%Pd/C(K)-D2. It contains ~ 37% of the final product **9**, up to 20% of each of the acids **5** and **6** but not more than 2% of oximes **14** and **15**. Therefore, in this case, the hydrogenation proceeds mainly along the right path of Scheme 1. Among the intermediates formed via this reaction route, only acid **5** was unambiguously identified in ref. [5]. The identification of four more compounds (**4**, **6, 8, 16**) is described below.

2,6-diamino-4-nitrobenzoic acid 4

In the ^{1}H NMR spectrum in Figure 4, the singlet at 6.40 ppm, whose intensity was high for minor products, was attributed to acid **4**. This characteristic signal was not noted in ref. [5]

because interpretation of the ^{13}C NMR data, which could confirm its attribution to compound **4**, appeared less reliable than in the case of other benzoic acids.

The region of 90–120 ppm, where absorption of C^1, C^3 and C^5 atoms of benzoic acids under consideration is observed, in case of compound **4** is the sole spectral fragment that contains signals suitable for its identification (Figure 5; Table 1). In the indicated spectral region, there are two signals at 102.7 and 111.3 ppm that can be assigned to compound **4** taking into account similar parameters of the spectra for benzoic acids **3**, **5**, **6**, **8** (Figure 5, Table 1). However, the signal at 102.7 ppm from CH carbons of compound **4** is strongly broadened, in contrast to other acids. It is known that broadening and even disappearance of signals in ^{13}C NMR spectra may be caused by chemical exchange [10]. We have not found a convincing mechanism for the chemical exchange; nevertheless, identification of compound **4** only by ^1H NMR spectrum appears to be reasonable because the key intermediate **6** discussed below can be obtained just as the result of reduction of compound **4**.

2,6-diamino-4-hydroxyaminobenzoic acid 6 and 2,4,6-triaminobenzoic acid 8

In our earlier work, the signals in NMR spectra of the main minor component of solutions displayed in Figures 4 and 5 were erroneously assigned to compound **8**, which was not distinguished from a similar symmetric compound **6** because they had close singlet signals at 5.84 ppm (**8**) and 5.85 ppm (**6**) in ^1H NMR spectra. The error was corrected by refining the attribution of signals to compounds **6** and **8** in ^{13}C NMR spectra (Table 1). The asignment of the indicated signals exactly to compound **6** is based primarily on their presence in the spectra of solutions of the reaction products obtained with the use of less active catalysts, along with other intermediate hydrogenation products (acids **4** and **5**). At the same time, compound **6** is absent in the products of exhaustive hydrogenation of TNBA obtained with the use of active fresh catalysts, whereas 2,4,6-triaminobenzoic acid identified now as compound **8** (Table 1) is a constant and noticeable minor component despite the mentioned above preference of the left reaction path in the Scheme 1 with early decarboxylation. We could explain the latter circumstance only by some probability of compound **9** carboxylation with the formation of compound **8**. Although we have not found any examples of the appropriate Kolbe–Schmitt reaction for compound **9**, it is known that the similar substance phloroglucinol is carboxylated by alkali carbonates in water solution at the same pressure and temperature as in our case [11].

~~A high-field shift of a part of signals in ^{13}C NMR spectra of compound **6**, in comparison with the similar signals of compound **8**, agrees with the same shift observed upon substitution of amino group by hydroxylamino one in the case of compounds **9** and **13** (Table 1).~~

2-hydroxyamino-4,6-diaminobenzoic acid 7,2,4-diamino-6-[(3,5-diaminophenyl)-NNO-azoxy]benzoic acid 16

We detected only hardly perceptible signals (not visible in the ^{1}H NMR spectra) that can be attributed to intermediate **7**. Most likely, acid **5** transforms, missing compound **7**, via azoxybenzene **16** as suggested in Scheme 3.

The signals corresponding to compound **16** are observed in the spectra of solutions obtained with the use of low active catalysts (Figures 5 and 6) and have high intensities in the case of some deactivated catalyst (Figure 6). The compound under consideration has two substituted benzene rings. One of them gives a doublet (6.98 ppm, 2H) and a triplet (6.92 ppm, 1H) with the *J* constant of ~2 Hz in the ^{1}H NMR spectrum (Figure 6). These signals correspond to 1,3-diamino-5-X-substituted benzene, where substituent X has the pronounced electron acceptor properties. For example, such effect of the electron acceptor substituent is observed for 1,3-diamino-5-nitrobenzene [12]: the experimental spectrum has doublet and triplet with the chemical shifts of 6.60 and 6.15 ppm, respectively. Two other signals corresponding to compound **16** are represented by the doublet of doublets (6.49 ppm, 1H), which is undistinguishable from the triplet, and the doublet (5.84 ppm, 1H) with the *J* constant ~ 2 Hz. Thus, the second benzene ring in compound **16** with two protons in meta-position has four substituents, one of them causes an additional diastereotopic splitting of the signal from the adjacent proton [13]. This substituent was identified as azoxy group which is characteristic of the typical reduction products of aromatic nitrocompounds – azoxybenzenes [14].
The formation of azoxybenzenes upon reduction of, for example, nitrobenzene is explained by the addition of the aniline amino group to nitroso group of the intermediate nitrosobenzene, which is accompanied by dehydrogenation. Azoxybenzene **16** is formed by a similar mechanism upon interaction of triaminobenzene **9** with acid **5.** The signals in the ^{1}H NMR spectrum (Figure 6) indicated in Scheme 3 were assigned to compound **16**. The assignment agrees with the polarization of the molecule **16** depicted in Scheme 4 which explains unexpectedly wide range (5.84 – 6.98 ppm) of proton chemical shifts and diastereotopic splitting of the signal 6.49 ppm as the result of hindered inversion of stereogenic pyramidal nitrogen –NO^-- in azoxybenzene **16** [13].

As shown by the analysis of the ^{13}C NMR spectrum of a solution of hydrogenation products obtained with the use of deactivated catalyst (Figure 1S), some characteristic signals assignable to compound **16** are detected in the spectrum (Table 1).

The final reduction products of azoxybenzenes are mainly the corresponding hydrazobenzenes. In accordance with this statement, all ^{1}H NMR spectra of the solutions obtained as the result of TNBA exhaustive hydrogenation contain weak but characteristic triplet signals with the chemical shift 5.53 ppm (J ~ 2 Hz). The only reason to make protons of the aminobenzenes involved to absorb in a higher field than 1,3,5 protons in compound **9** is condensation with the formation of dimer **18** discussed below. Protons in position 4 of compound **18** (Scheme 2) absorb at 5.64 ppm (Figure 1). In order to shift this signal to a still higher field, it is necessary to replace –NH- fragment in compound **18** by hydrazine group –NH-NH-. So the signal 5.53 ppm belongs to hydrazobenzene **24** formed by the reduction of compound **16**. Most of the remaining signals of this compound are overlapped partially or completely by the signals of other components, but the second triplet signal 5.93 ppm (J ~ 2 Hz) belongs to it definitely. Taking into account this scarce information and simulated spectra, the following structure of the reduction product of compound **16** was nevertheless suggested (Scheme 5).

As follows from Figure 6, in addition to the product of exhaustive hydrogenation **9** (63%), an intermediate product with a high (~20%) content in solution is compound **16**. The content of oximes **14** and **15** in this case does not exceed 2%. It has not been established under which conditions the main intermediate on the right reaction route (Scheme 1) is compound **6** (Figure 4), and under which conditions it is compound **16** (Figure 6); however, it is obvious that in case of the deactivated catalysts hydrogenation selects predominantly the right path. This experimental information is consistent with the fact that there are two ways of the adsorption of aromatic compounds: either due to the aromatic ring with the formation of π-complex, or due to atoms of functional groups with the orientation of the plane of the aromatic ring normal to the surface [15]. Substrates **1** - **3** are probably adsorbed by the first way on a fresh active catalyst, which induces the intramolecular redox process and decarboxylation (left path); on the deactivated sediment-covered catalyst, they are anchored by oxygen atoms of hydroxylamine or nitro groups so that the plane of the benzene ring is oriented normal with respect to the surface, which reduces the probability of decarboxylation (right path). In ref. [15], such a qualitative change in the adsorption behavior was observed with a change in the surface acidity.

Identification of condensation products of 1,3,5-triaminobenzene 2,8,14-triazatetracyclo[13.3.1.1^{3,7}.1^{9,13}]henicosa-1(19),3(21),4,6,9(20),10,12,15,17-nonaene-5,11,17-triamine 17, N^{1}-(3,5-diaminophenyl)benzene-1,3,5-triamine 18

It is known [16] that, in contrast to aniline, triamine **9** is characterized by a relatively easy polycondensation. Its possible mechanism is displayed in Scheme 6. In our previous paper [5] we failed to identify the condensation products of compound **9** and suggested uncertain polyaniline structures. In fact all noticeable signals of condensation products in the ^{1}H and ^{13}C NMR spectra of hydrogenates are originate from compounds **17** and **18.** Signals that can be attributed to the analogous linear trimer or to the dendrimer type tetramer were detected only at the limit of ^{1}H NMR sensitivity.

Signals from compounds **17** and **18** are most noticeable in the spectra of reaction solutions obtained using the catalyst that is highly active and selective toward the final product **9**; the most pronounced signals marked in Figures 1 and 7 correspond to cyclic trimer **17**. Along with the signals from compounds **17** and **18**, signals assigned to compounds **19** – **22**, which will be discussed below, are marked in the spectra in Figures 1 and 7.

Identification of compounds **17** and **18** is reasonable due to a good agreement of their experimental and simulated ^{13}C NMR spectra displayed in Table 1 and Figures S2 and S3. Despite some differences in chemical shifts for experimental and simulated spectra, it is difficult to find other suitable structures for compounds **17** and **18**.

However, it should be noted that the simulated ^{1}H NMR spectrum of compound **17** (doublet at 6.34 ppm, 6H, and triplet at 6.90 ppm, 3H, J ~ 2 Hz) even qualitatively differs from the experimental spectrum by relative positions of the doublet (6.27 ppm) and triplet (5.90 ppm). The indicated contradiction can be explained and even used as an additional argument in favor of correctness of the identification.

Compound **17** resembles porphyrins and can actually be presented as a macrocyclic aromatic compound using a special variant of prototropic tautomerism, which is typical of porphyrins (Scheme 7). A cyclic translocation of protons and π-electrons results in the formation of the aromatic system including 18 electrons [17]. A pronounced strong-field shift of signals from protons in the porphyrin or other aromatic macrocycles caused by the ring electron current is well known [18]. The ring electron current is the reason why the internal CH protons of

compound **17** have much smaller chemical shifts than the external CH protons, in contrast to the simulated spectra.

The doublet and triplet corresponding to compound **17** in the ^{1}H NMR spectra are always accompanied by a singlet signal with the chemical shift of 7.1 ppm (Figure 1), which is attributed to NH protons involved in the tautomeric transformations displayed in Scheme 7. The ^{1}H NMR spectrum of compound **18** consists only of a 5.64 ppm triplet, attributed to a proton in position 4 (Scheme 2). The doublet signal of protons in positions 2 and 6 of dimer **18** overlaps with the absorption of aminobenzene **9**.

Paramagnetism of cyclic trimer 17

The EPR study of the hydrogenation product whose NMR spectra are shown in Figures 1 and 7 revealed the presence of a stable intense signal with parameters g = 2.0040, $\Delta H_{1/2}$ = 0.20 G, a_N = 2.10 G (2NH), a_N = 0.65 G (NH_2), a_H = 2.20 G ($3H_{Ar}$), a_H = 0.85 G ($2H_{NH2}$), and a_H = 0.75 G (H_{NH}), caused by splitting of a paramagnetic center on magnetic nuclei of hydrogen and nitrogen (Figure 8). This signal appears when the reaction mixture gets in contact with air; it may be related to the oxidation of the reduction product(s) by analogy with derivatives of aniline oligomers [16,18,20]. The EPR spectrum analysis and its simulation indicate the delocalization of the unpaired electron on benzene core and its hyperfine interaction with ^{1}H and ^{14}N nuclei of cyclic trimer **17** fragments. The values of the hyperfine splitting constants (HFSC) are close to similar structural fragments of paramagnetic N-cryptand [21,22].

The mechanism of radical particle formation (Scheme 8) can be proposed via the oxidation [20] of compound **17** to the corresponding radical **17$^{\bullet}$** or via the formation of a radical cation $NH^{+\bullet}$ (**17$^{+\bullet}$**) as a result of single-electron transfer (SET) [23]. The formation of the cation radical **17$^{+\bullet}$** is more likely for such compounds [19], however, it is difficult to determine the charge of a paramagnetic particle using its EPR spectrum [24].

A long-term storage in air of the hydrogenation product whose composition is characterized by the NMR spectra displayed in Figures 1 and 7 led to the formation of a solid product consisting mostly of water-insoluble polycondensation products of aromatic amines [5]. The ^{1}H NMR spectrum of an aqueous extract of this product contains only three signals (Figure 9). The chemical shift of 5.75 ppm singlet corresponds to compound **8**. The second rather intense singlet at 8.45 ppm was earlier assigned to formic acid [5]. The third very weak

doublet at 6.27 ppm corresponds to compound **17**. Since the EPR spectrum of this aqueous extract shows a similar signal as for the initial hydrogenation product, this reliably confirms that the observed EPR signal is due to the presence of compound **17**, taking into account that the samples of analogous extracts whose ^{1}H NMR spectra contain only signals of 5.75 and 8.45 ppm are EPR silent.

It should be noted that the NMR spectra of hydrogenation products (Figures 1, 4, 5 and 7) contain also the signals that are assigned to 2,4,6-triaminobenzamide **20** and weak signals from the products of successive hydrolysis of 1,3,5-triaminobenzene: 3,5-diaminophenol **19** and 5-aminobenzene-1,3-diol **22**, which were considered in our earlier work [5] (Scheme 9). Two not noticed earlier ^{13}C NMR signals of 160.2 and 148.3 ppm (Figure 7) are attributed to carbonate of 1,3,5-triaminobenzene with tentative structure **21**, taking into account that its ammonium and carbonate ions do not participate in fast chemical exchange with free amine **9** and other carbonate ions which are present in the solution.

The identity of compound **19** was completely confirmed when analyzing new ^{13}C NMR spectra. Phenol **22** still remains as the tentative structure suggested only on a basis of the solitary ^{1}HNMR signal. But the identification of phloroglucinol **23** in [5] was wrong. In reality amide **20** yields the relatively intense signal in ^{1}H NMR spectra at 5.89 ppm assigned earlier to compound **23.** Compound **20** was reliably identified on a basis of ^{13}C NMR spectra (Table 1). Its formation by the amidation of acid **8** with ammonia released upon condensation of amine (leading to compounds **17** and **18**) is quite probable.

Conclusion

Reaction mixtures were obtained by catalytic (Pd/C) aqua-phase hydrogenation of 2,4,6-trinitrobenzoic acid using concentrated solutions and catalysts with different activity. A detailed analysis of NMR spectra of these mixtures made it possible to assign all the signals observed in the spectra. Refined identification was used to propose a more substantiated reaction mechanism describing a multicomponent composition of the hydrogenation product.
In the case of exhaustive hydrogenation, the composition of the hydrogenation product is determined in the final step of the reaction upon reduction of 2-amino-6-hydroxyamino-nitrobenzoic acid and its two minor regioisomers. The first route, which is related to intramolecular redox reaction and subsequent decarboxylation, leads to 1,3,5-

triaminobenzene via the formation of intermediate cyclohexane-1,3,5-trione trioximes. The second route, which is caused by reduction of the hydroxyamino group of 2-amino-6-hydroxyamino-nitrobenzoic acid and its isomers in the first step, also leads mainly to 1,3,5-triaminobenzene through a series of intermediate benzoic acids, among which 2,6-diamino-4-hydroxyaminobenzoic acid and 2,4-diamino-6-[(3,5-diaminophenyl)-NNO-azoxy]benzoic acid are likely to be the key ones. The second way is characteristic of the catalysts whose activity is reduced as a result of repeated hydrogenation cycles. The reason for the existence of different routes can be a different orientation of the adsorbed aromatic molecule relative to the catalytic surface.

It was demonstrated for the first time that hydrogenation of 2,4,6-trinitrobenzoic acid is accompanied by condensation of three molecules of the main product of the reaction, 1,3,5-triaminobenzene, with the formation of a paramagnetic aromatic macrocyclic compound.

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Table 1: Assignment of signals in the ^{13}C NMR spectra of TNBA hydrogenation products[a,c].

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-2'	C-4'	C-6'
3	114.9	148.8	104.0	152.0	102.0	150.0	172.0			
4	111.3		102.7		102.7					
5	109.8		101.6		106.7		172.8			
6	106.0	146.3	95.36	147.0	95.36	146.3	160.6			
8	107.7	148.6	95.62	149.6	95.62	148.6	160.0			
9	148.4	96.07	148.4	96.07	148.4	96.07				
13	152.1	94.23	148.2	94.23	148.2	98.53				
16	106.3		100.2		105.2			101.4	108.8	101.4
17[b]	147.8 (147.7)	98.76 (103.8)	142.8 (144.8)	98.76 (103.8)	147.8 (147.7)	98.38 (102.3)				
18[b]	146.4 (148.3)	92.21 (86.4)	146.3 (148.0)	92.21 (86.4)	146.3 (148.0)	94.68 (90.95)				
19	157.8	94.87	148.8	96.71	148.8	94.87				
20	98.9	148.1	95.4	147.3	95.4	148.1	161.4			

[a]Chemical shifts are given in ppm. [b]Values in parentheses were obtained by simulation of the spectra using ACD/Labs 6.00 (Advanced Chemistry Development Inc.) software. [c]The numbering of carbon atoms in the compounds listed in Table 1 is shown in Scheme 2.

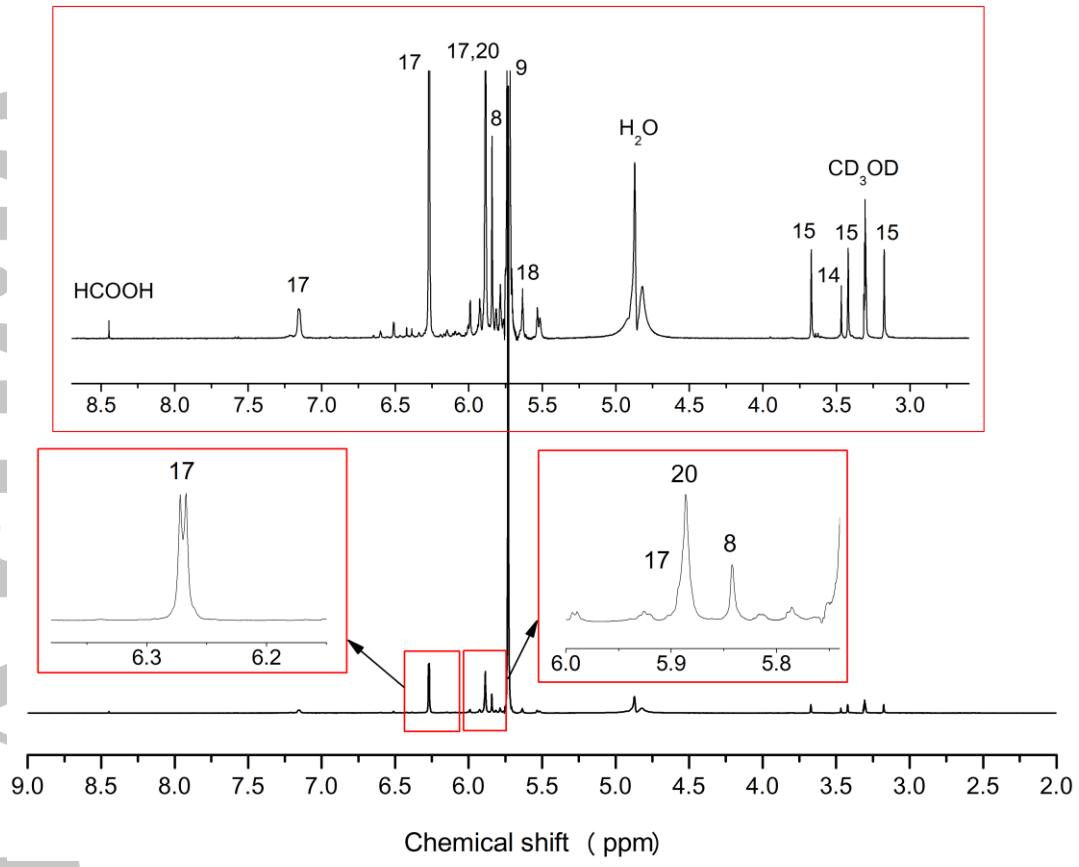


Figure 1: The ^{1}H NMR spectrum of the hydrogenation products of TNBA sodium salt (10% aqueous solution) that were obtained using the highly dispersed 5%Pd/C(K) catalyst.

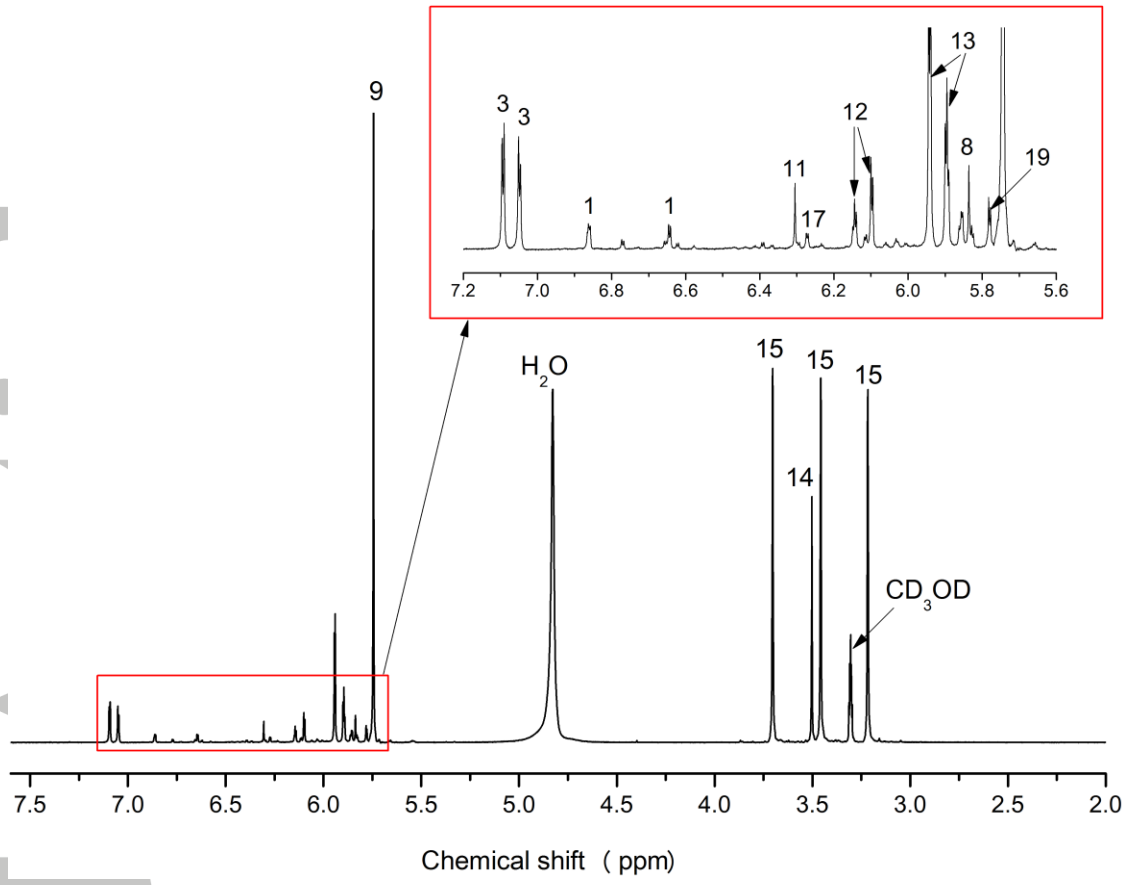


Figure 2: The ^{1}H NMR spectrum of the reaction mixture obtained by hydrogenation of TNBA in aqueous solution (5%Pd/C(Na), concentration of TNBA is 10 wt.%) at a temperature of 343 K and pressure of 0.5 MPa [5].

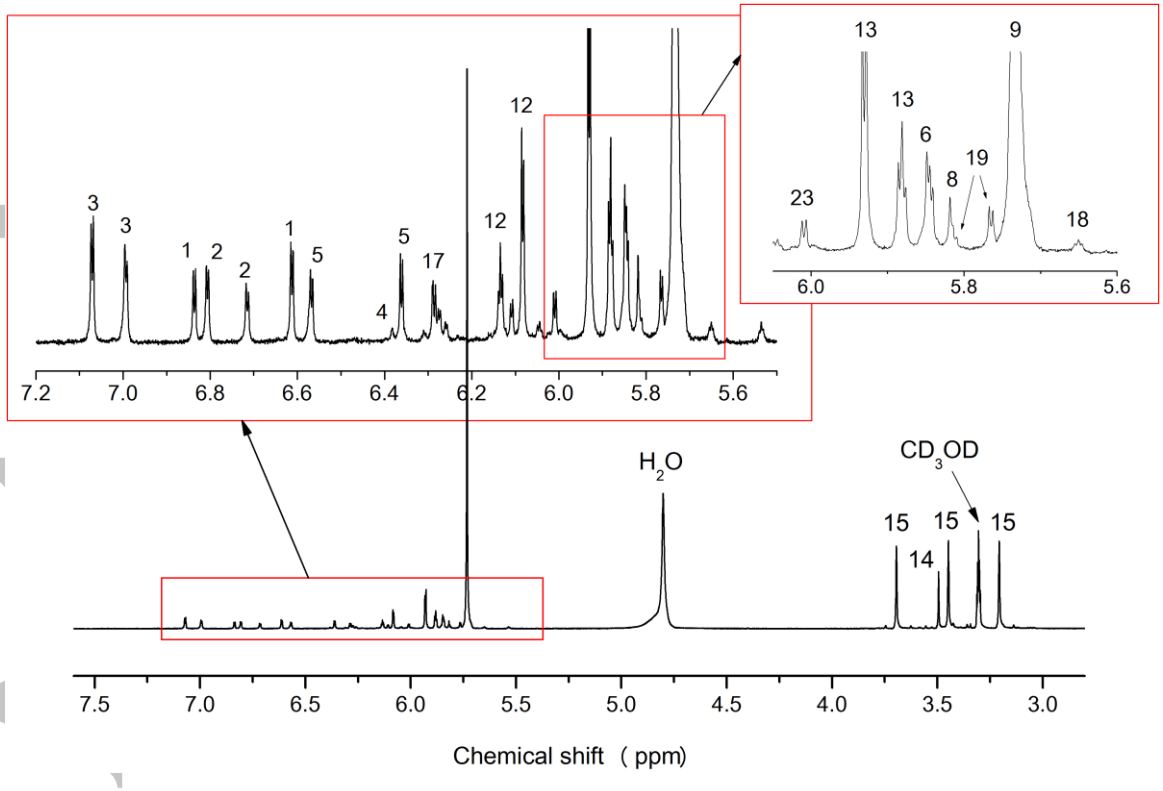


Figure 3: The ^{1}H NMR spectrum of the products formed in the intermediate step of TNBA sodium salt hydrogenation (2% aqueous solution) over 1%Pd/C(K) catalyst [5].

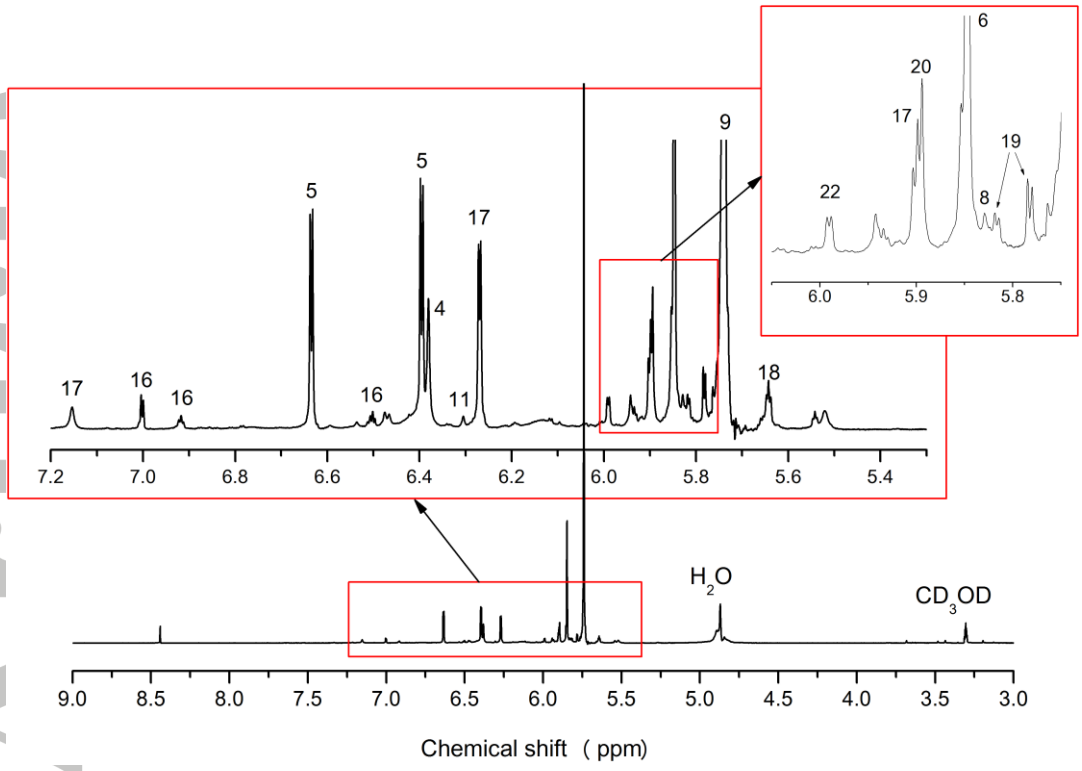


Figure 4: The ^{1}H NMR spectrum of the hydrogenation products of TNBA sodium salt (10% aqueous solution) that were obtained with the use of 5%Pd/C(K)-D2 catalyst (deactivated, second cycle).

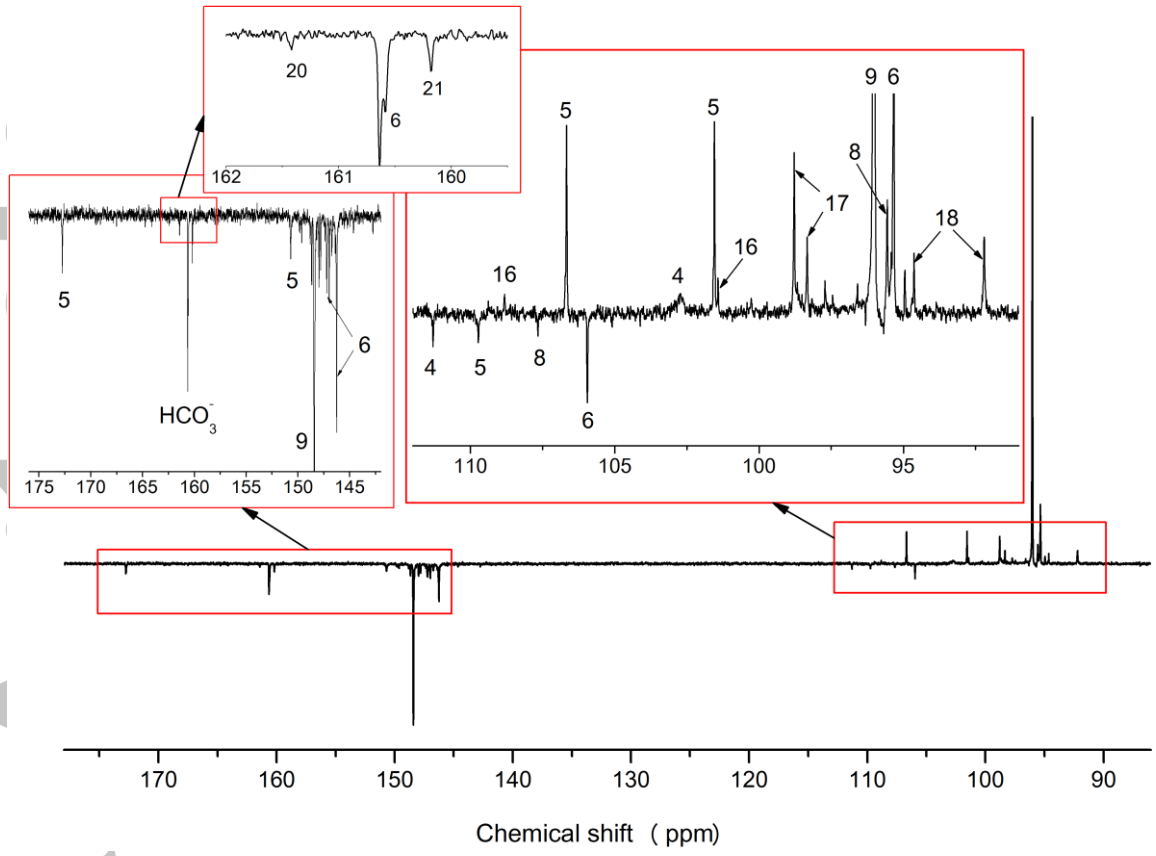


Figure 5: The ^{13}C NMR spectrum of the hydrogenation products of TNBA sodium salt (10% aqueous solution) that were obtained with the use of 5%Pd/C(K)-D2 catalyst (deactivated, second cycle).

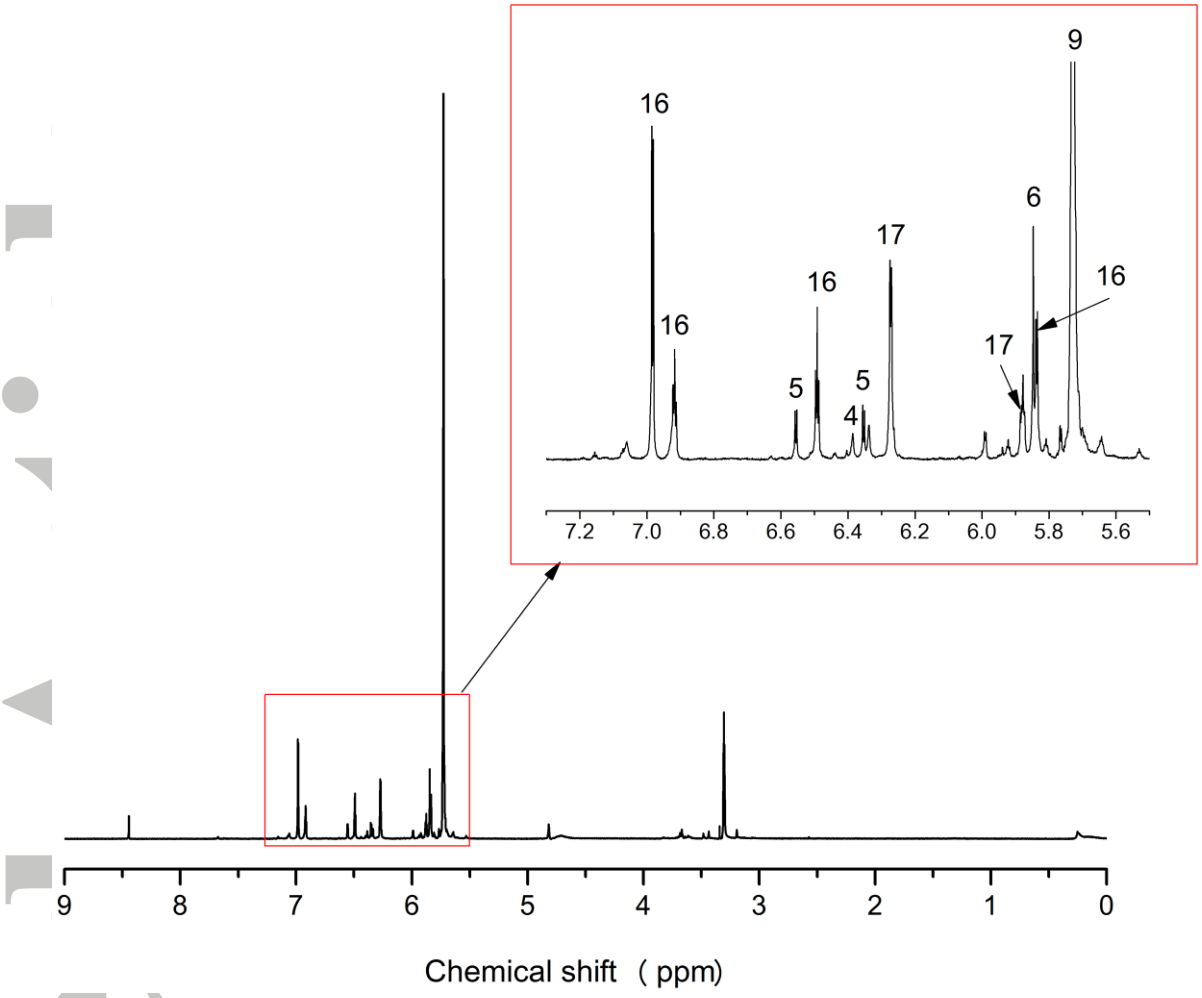


Figure 6: The ^{1}H NMR spectrum of the hydrogenation products of TNBA sodium salt (10% aqueous solution) that were obtained with the use of 5%Pd/C(K)-D3 catalyst (deactivated, third cycle).

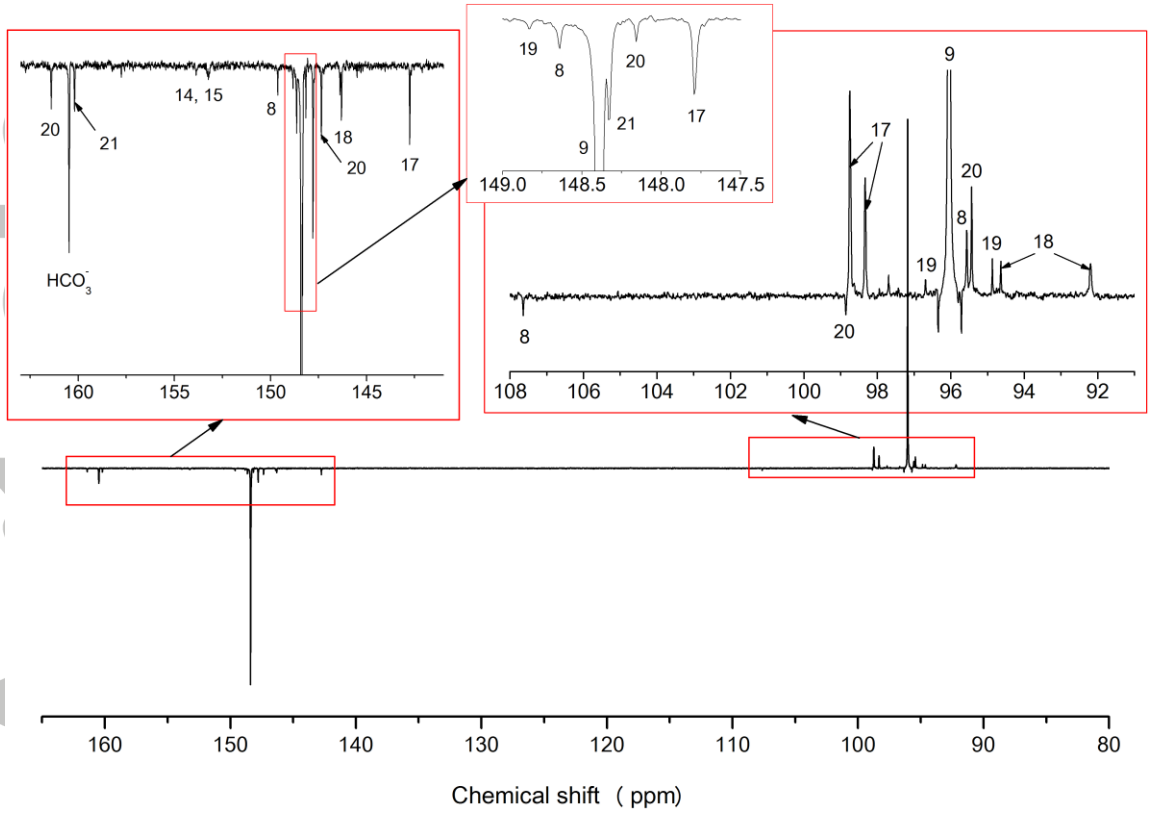


Figure 7: The ^{13}C NMR spectrum of the hydrogenation products of TNBA sodium salt (10% aqueous solution) that were obtained with the use of a highly dispersed 5%Pd/C(K) catalyst.

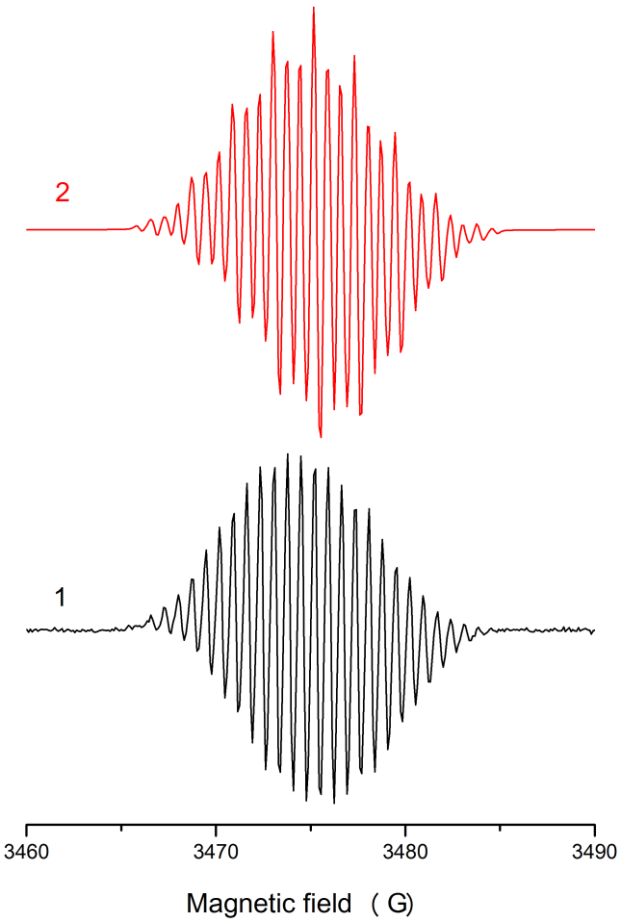


Figure 8: Experimental (1) and simulated (2) EPR spectra of an aqueous solution of TNBA sodium salt hydrogenation products (NMR spectra of this solution are displayed in Figures 1 and 6) stored on air for 1 h.

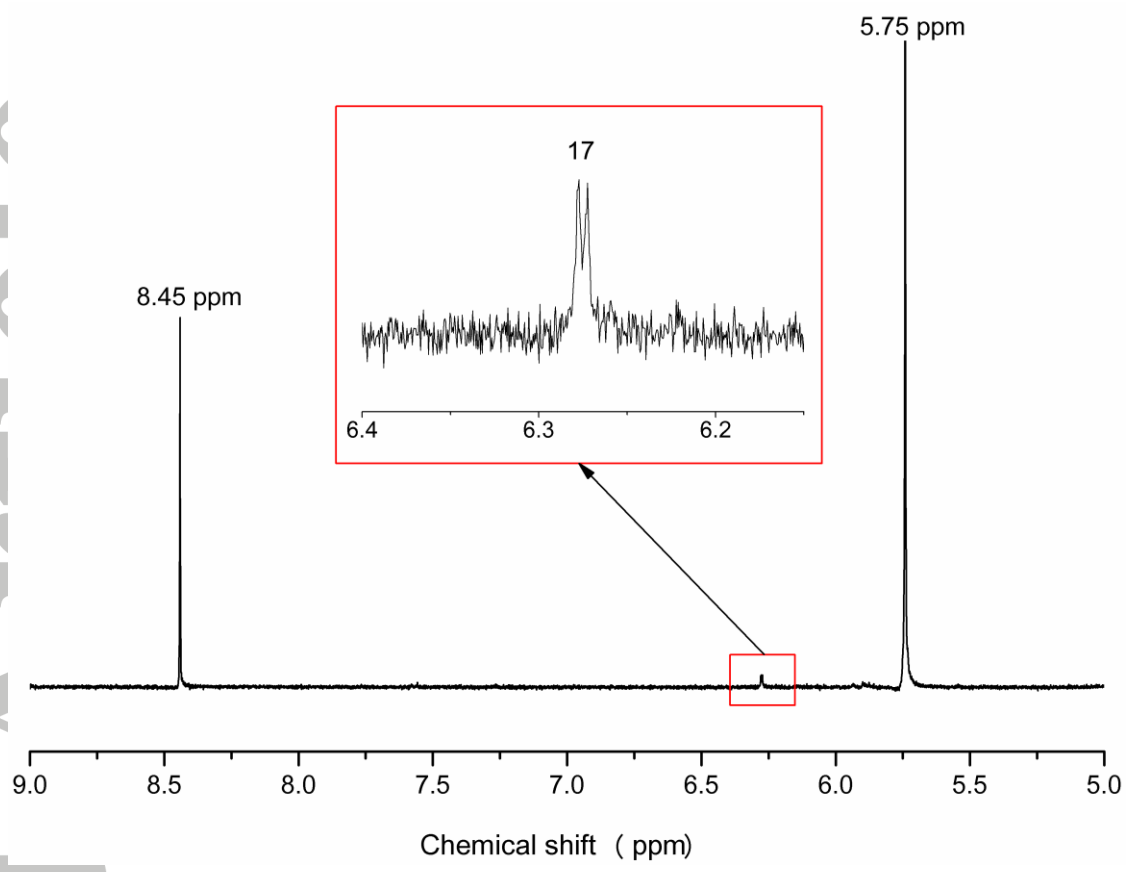
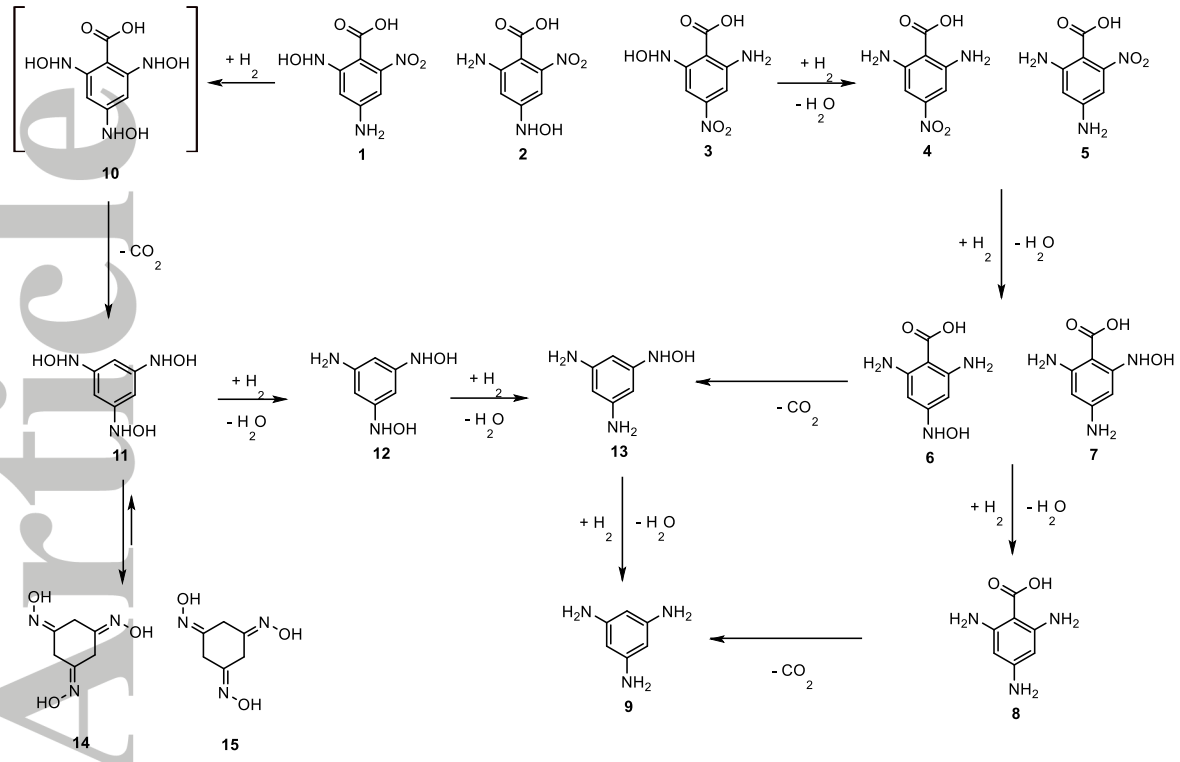
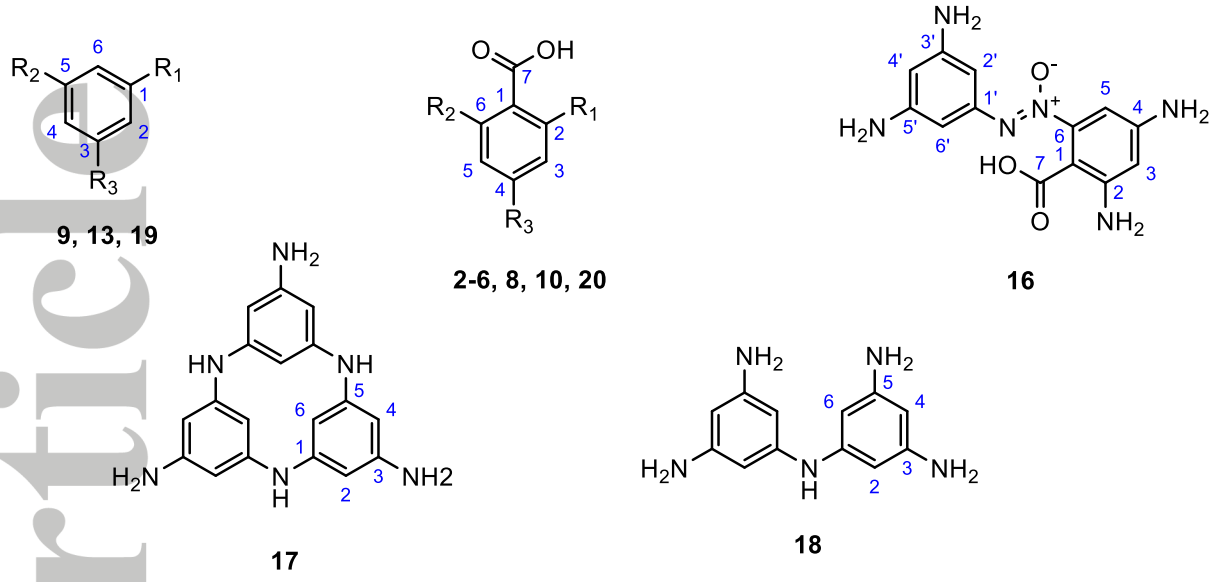


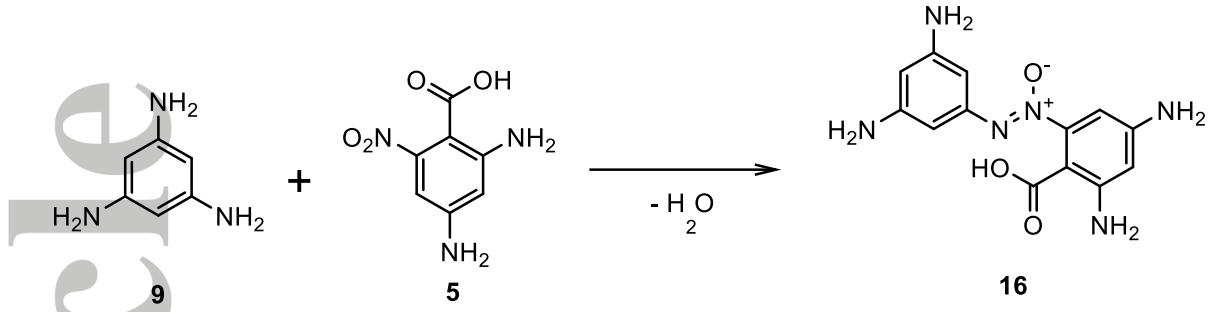
Figure 9: The ^{1}H NMR spectrum of the aqueous solution obtained by water extraction from solid condensation products of the TNBA hydrogenates. An arrow indicates the signal of compound **17**. Two more intense signals may belong to 1,3,5-triaminobenzene carbonate (5.75 ppm) and formate ion (8.45 ppm).



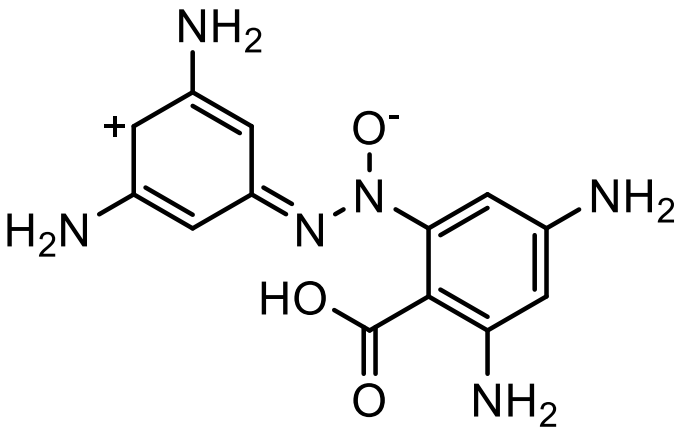
Scheme 1: The mechanisms of TNBA hydrogenation over Pd/Sibunit catalysts according to [5].



Scheme 2: The numbering of carbon atoms in the compounds listed in Table 1.



Scheme 3: The formation of azoxybenzene **16** from compounds **5**, **9** via nitrosoderivative of **5**.



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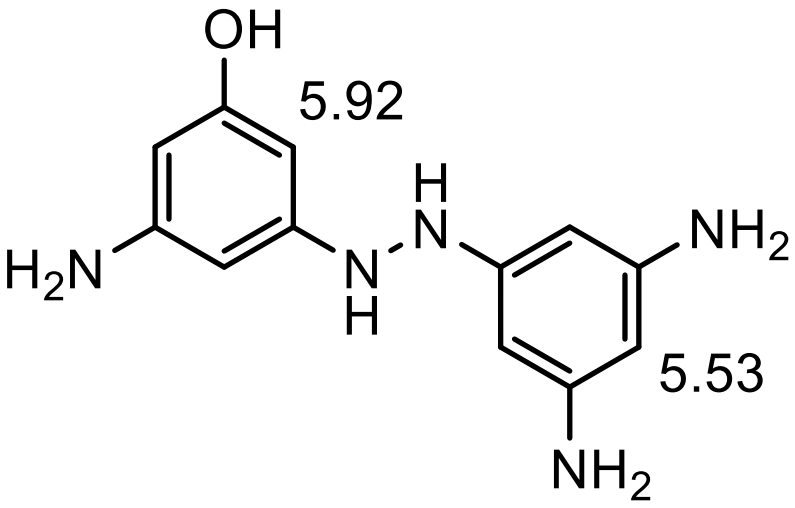
Scheme 4: The displacement of the electrons in the molecule **16**.



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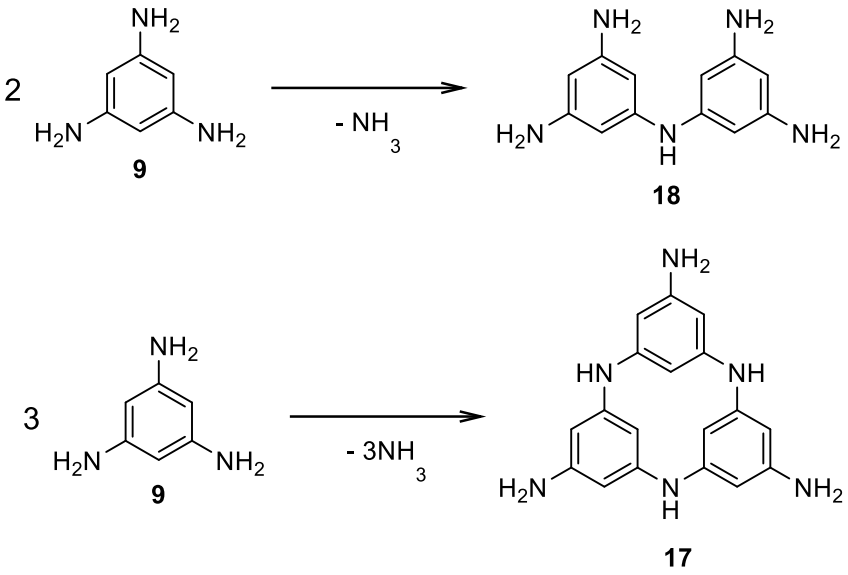
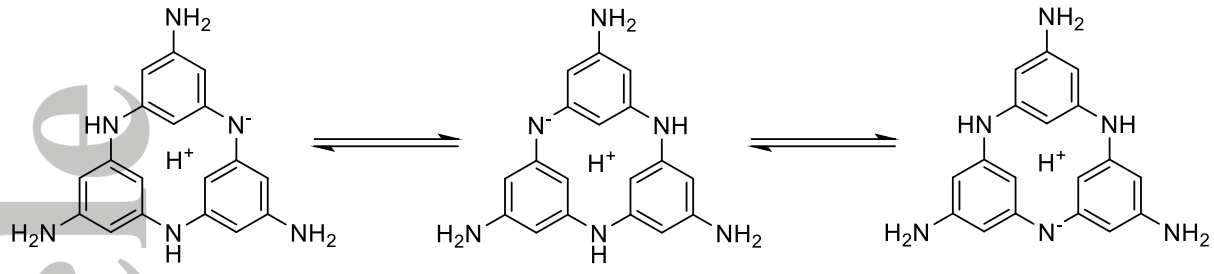
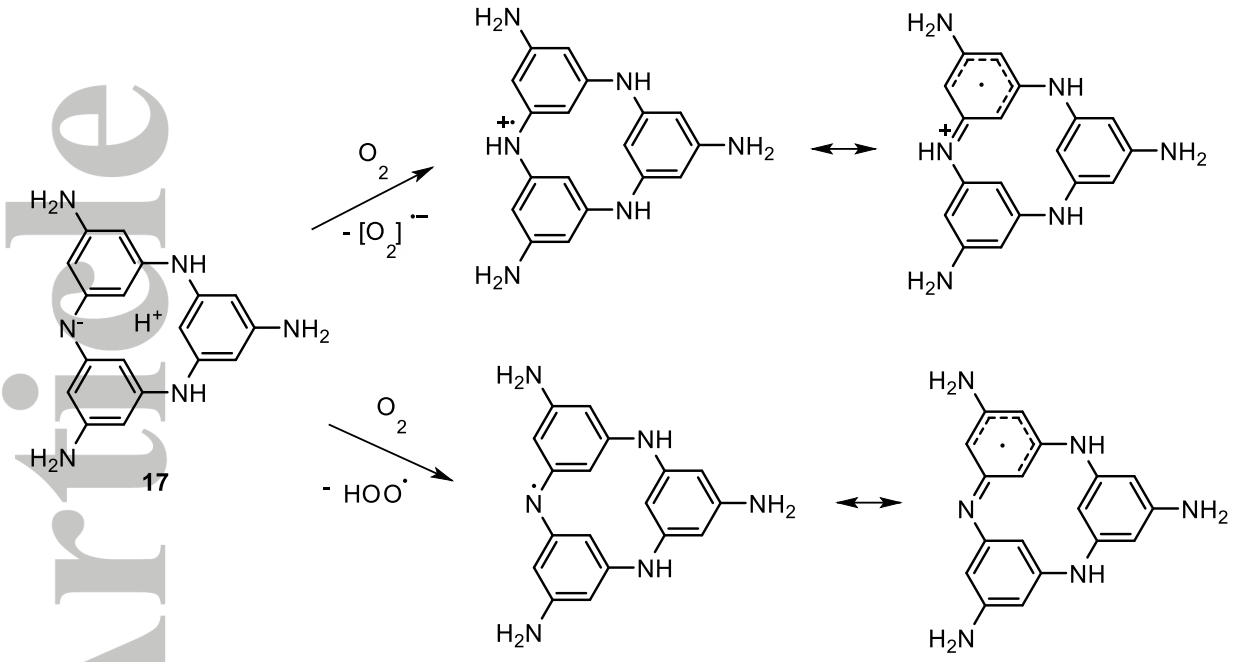
Scheme 5: The structure of the final product of compound **16** reduction.



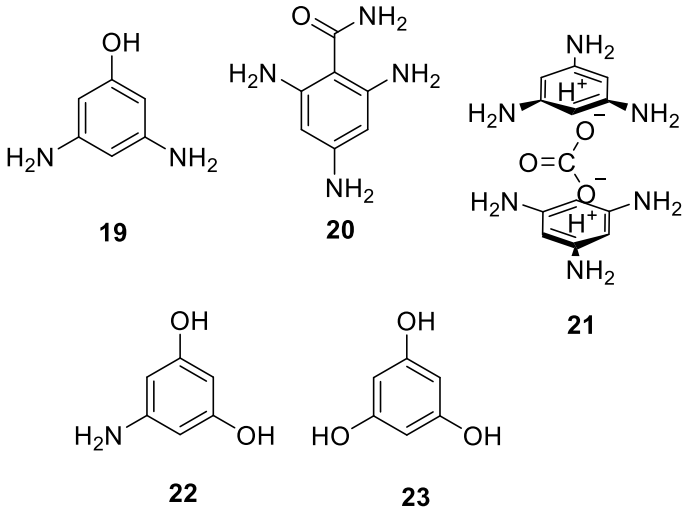
Scheme 6: The possible polycondensation pathway of the compound **9**.



Scheme 7: Tautomeric transformations of the compound **17**.



Scheme 8: The possible routes of **17**$^{\bullet}$ and **17**$^{+\bullet}$ formation.



Scheme 9: The structures of TNBA hydrogenation products **19** – **23**.

Graphical Abstract