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SYNTHESIS OF 2-, AND 3-NITROBENZANTHRONE VIA DIRECT NITRATION OF BENZANTHRONE WITH NITRIC ACID/ACETIC ACID

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Abstract.–Three mono-nitrobenzanthrone isomers (1-, 2-, and 3-nitrobenzanthrone; 1-, 2-, and 3-NBA) were synthesized by reacting benzanthrone (BA) with nitric acid (HNO_3) in acetic anhydride at ice-cold conditions. The major product, 2-nitrobenzanthrone (2-NBA), was confirmed using GC-MS via comparisons with a standard sample. On the basis of the elution profiles and fragmentation patterns two other isomers formed were assigned to 1-, and 3-nitrobenzanthrone (1-, and 3-NBA). The average percent yields of 1-, 2-, and 3-NBA were 0.3 ± 0.1%, 10.5 ± 2.6 %, and 6.4 ± 1.3 %, respectively.

Keywords: benzanthrone, 1-nitrobenzanthrone, 2-nitrobenzanthrone, gas chromatography-mass spectrometry (GC-MS)

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants produced from the incomplete combustion processes in diesel exhaust particles, and air particulate matter. PAHs react with hydroxyl (·OH) and nitrate radicals in atmospheric conditions to form diverse derivatives including hydroxylated-PAHs (OH-PAHs), PAH-quinones (PAHQs), and nitrated-PAHs (NPAHs) (Ramdahl et al. 1986; Arey et al. 1988; Atkinson & Arey 2007; Harrison et al. 2016; Misaki et al. 2007; Niziolek-Kierecka et al. 2012; Fu et al. 2018). NPAH derivatives are known to pose greater deleterious health effects to humans than their parent PAHs. To quantitate NPAHs in the atmosphere requires the availability of authentic standard samples. Due to paucity of analytical reference standards, methods are often sought to synthesize NPAHs to facilitate the analysis of environmental samples.

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Nitrobenzanthrones (NBA) are mutagenic byproducts of incomplete combustion processes in atmospheric reactions with NO_x gases (Enya et al. 1997; Enya et al. 1998b; Takamura-Enya et al. 2006; Arlt et al. 2007; Karavalakis et al. 2010). The synthesis of NPAHs, including nitrobenzanthrones, typically involve the direct nitration with nitric acid (HNO_3), nitration with NO_x gases in the presence and absence of ozone (O_3), and Ullman cross-coupling/Friedel-Crafts cyclization reactions (Enya et al. 1997; Suzuki et al. 1997; Enya et al. 1998b; Arlt 2005; Suzuki et al. 2005; Arlt et al. 2007). Figure 1 shows a schematic for the acidic nitration of BA dissolved in nitrobenzene and solution treated with concentrated HNO_3 (8.9:1 mole ratio, HNO_3:BA). The reaction is normally carried out at 40^{o}C for 30 min and forms a crude product precipitate which is then purified by recrystallization with glacial acetic acid and dichloromethane (DCM). The major product from this reaction is 3-nitrobenzanthrone (3-NBA) with a yield of 83.5% and three other NBA minor products, namely, 1-, 9-, and 11- nitrobenzanthrone (1-, 9-, 11-NBA) with percent yields of 5.8%, 3.0%, and 1.2%, respectively (Enya et al. 1998b; Enya et al. 1997; Takamura-Enya et al. 2006).

The synthesis of NBA has also been carried out using various nitrogen oxide admixtures (NO_2 with N_2O_4, NO_2 with O_3, and N_2O_5) in solvents, including dichloromethane (DCM) and carbon tetrachlo-

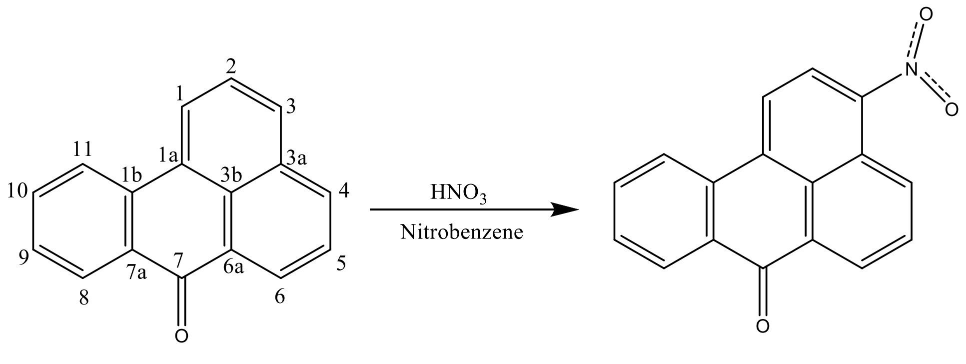


Figure 1. Synthesis of 3-nitrobenzanthrone (3-NBA) by direct nitration of benzanthrone with nitric acid (HNO_3). Other minor products of this reaction include 1-, 9-, and 11-NBA.

ride (CCl_4) (Suzuki et al. 1997; Enya et al. 1998b; Phousongphouang et al. 2000; Phousongphouang & Arey 2003). Reactions using NO_2-N_2O_4 have been performed at ≈ 25° C in DCM. To prevent formation of mixtures of mono-, di-, and tri-nitrated products use of less than stoichiometric amounts of the nitration agent is essential. Enya et al. (1998b) found this reaction to produce five NBA isomers (four mono- and one di-NBA products) in the presence of DCM (Phousongphouang & Arey 2003). From the reaction, the major and minor products are 3-NBA (53.2%), 1-, 2-, 9-NBA, and 1,3-dinitrobenzanthrone (1,3-dNBA) with yields of 7.1%, 2.8%, 13.3%, and 2.1%, respectively (Enya et al. 1998b). The addition of 1 mmol of 2,6-di-*t*-butylpyridine favored 2-NBA as the major product with minor products of 1-, 3-, 9-NBA and 1,3-dNBA. In the presence of CCl_4 as a co-solvent, the reaction was found to produce minimal amounts of NBA (Ramdahl et al. 1986; Asahi et al. 2014). However, 2-NBA was found to be the major product if the reaction was carried in CCl_4 in the presence of O_3 (Enya et al. 1998b). Such differences demonstrate that co-solvents may influence formation of more stable nitrenium ions.

Other methods used for synthesis of nitrobenzanthrones include the addition of NO_2 and O_3 gases in differential ratios into a solution of BA dissolved in DCM over a temperature range of -70 °C to 20 °C. While optimal amounts of 3-NBA (80.0%) are produced within temperature range 0°C to 20°C, minor products 1-, 2-, 9-, and 11-NBA were formed (Enya et al. 1997; 1998b).

The HPLC and GC-MS elution profiles for the various isomers were determined in the order 1-NBA > 3-NBA > 2-NBA > 9-NBA > 11-NBA (Enya et al. 1997; Tang et al. 2004).

Other reported methods for synthesis of NBAs make use of N_2O_5 as the nitration agent in dichloromethane (DCM) (Phousongphouang & Arey 2003). At temperatures between -70°C to 20°C the reaction produces 3-NBA as the major product (67-83%) with an optimal temperature of 20°C. Minor products from this reaction include 1-, 9-, and 11-NBA (Enya et al. 1998b).

In contrast to the above methods, the Ullmann cross-coupling reaction produces high yields of mono-NBAs (Suzuki et al. 1997). In the Ullmann cross-coupling scheme (Fig. 2) iodonitronaphthalene and iodonitrobenzoate are reacted in the presence of copper bronze powder in DMF. The resulting product ester is then refluxed with lithium hydroxide (LiOH) in a methanol (MeOH)/H_2O mixture to produce a carboxylic acid which is then converted to the corresponding acid chloride by reaction with thionyl chloride ($SOCl_2$), followed by ring closure on reaction with aluminum chloride ($AlCl_3$).

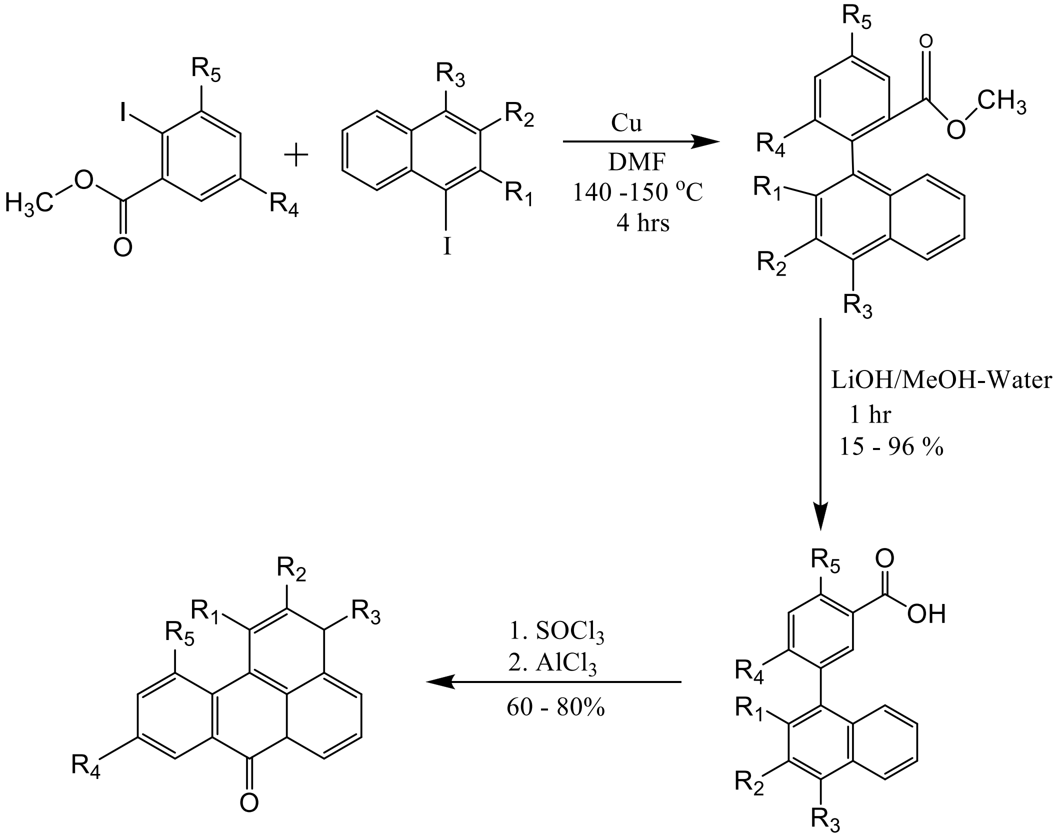


Figure 2. Synthesis of nitrobenzanthrones (NBAs) via the Ullmann cross coupling reaction of iodonitronaphthalene and iodonitrobenzoate followed by a Friedel-Crafts ring closure (from Suzuki et al. 1997).

Although this method biases the formation of certain NBA isomers, it is not free of contamination from other NBA isomers. The Ullman reaction yields 1-NBA (62%), 2-NBA (16%) and 3-NBA (50%). Notably, large percent yields are reported for 9-NBA (96%) and 11-NBA (95%) (Suzuki et al. 1997).

In view of the variety of synthetic methods for NPAHs, we chose to examine the synthesis of NBAs via direct nitration with HNO_3 in acetic anhydride. This method offers flexibility in choosing a co-solvent, and the possibility of producing mono-NBA isomer products. The control of reaction conditions biases the formation of different isomers that can be separated and purified, spectroscopically analyzed, and thence used as standards for quantitation in environmental samples. In this initial study the direct HNO_3 nitration method was investigated without co-solvents. Later reactions will seek to introduce other co-solvents and reaction conditions.

MATERIALS & METHODS

Chemicals and reagents.–Benzanthrone, nitro-benzanthrone derivatives, and dichloromethane are known carcinogens and mutagens. DCM (a mild carcinogenic solvent) was handled with care. Appropriate gloves were worn at all times and reactions performed in a manner appropriate for its known biohazard status. All the reactions were performed in the fume hood. Any waste solvents were collected and disposed of by the Environmental Safety Team.

All chemicals and reagents used were of high analytical purity. Benzanthrone (BA, Alfa Aesar, > 98% purity) and 2-nitro-benzanthrone (2-NBA, Sigma-Aldrich, St. Louis, MO, > 98%) were dissolved in dichloromethane (DCM, Sigma-Aldrich, St. Louis, MO, HPLC grade, ≥ 99.8% purity) and analyzed with gas chromatography-mass spectrometry (GC-MS).

Synthesis of Mono-Nitrated Benzanthrones Via Direct Nitration.– Benzanthrone (≈ 50.0 mg, 2.14 x 10^{-4} mol) was added to a 50 mL round bottom flask. About 6.0 mL of acetic anhydride (Ac_2O, 95% purity, Flinn Scientific Inc.) was then added and the flask submerged in ice. 80.0 µL (1.90 x 10^{-3} mol) of nitric acid (HNO_3, ACS reagent grade, Flinn Scientific Inc.) was then added (HNO_3:BA (mol/mol) = 8.9:1). The reaction was stirred for 4-hours in an enclosed flask kept at ice-cold temperature at all times. Thereafter, 10 mL of DCM was added to the flask to dissolve the precipitate. Aliquots from each flask were analyzed with TLC and GC-MS at intervals. At all times during the reaction, the reaction flask and vials were covered with aluminum foil. A stream of nitrogen was passed into the vial to evaporate the Ac_2O, and reaction products stored in the dark. Three triplicate reaction runs, A, B, and C, were analyzed. The handling of DCM was performed in a manner appropriate for its known biohazard status.

Instrumentation.–Although thin layer chromatography (TLC) was initially tried, it was found inadequate and lacking. Thus, the GC/MS analytical approach was used for the analysis of the reaction products.

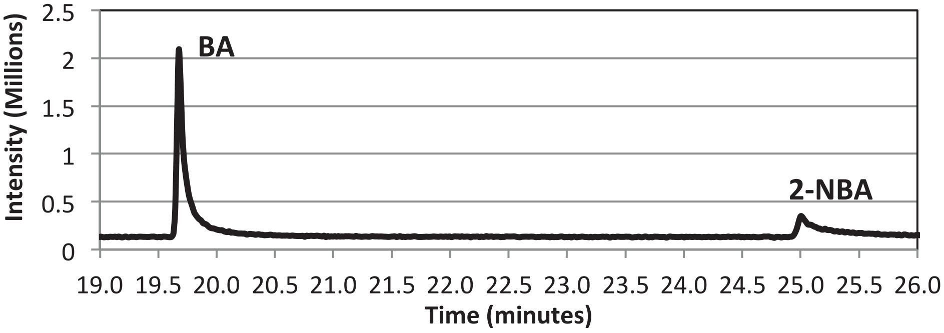
Gas Chromatography-Mass Spectrometry (GC-MS)) Analysis of Mono-Nitrated Benzanthrones.–The reaction products were analyzed with gas chromatography-mass spectrometry (GC-MS, Varian 450-GC) coupled to an ion-trap mass spectrometer (Varian 240-MS). A Phenomenex, Zebron ZB-5 fused silica capillary column (60 m, 0.25 mm i.d., 0.25 µm film thickness) was used for analyte separation. A 1.0 µL sample amounts were injected using a split-splitless method (20% initial split ratio) with an automated sample injector (Varian CP-8400). The injection port, transfer line, and ion-trap temperatures were set at 240°C, 250°C, and 230°C, respectively. A constant flow rate of 1.0 mL/min of helium carrier gas was maintained. The oven temperatures were programmed from 50°C (initial equilibrium time 2.00 min) to 300°C at a ramp rate of 20°C/min (hold time 35.00 min). The retention times and fragmentation patterns of standards (BA and 2-NBA) and reaction products was determined with MS by electron impact ionization. The total ion chromatogram mode (TIC) mode and mass spectral patterns were confirmed with standard MS fragmentation patterns.

RESULTS

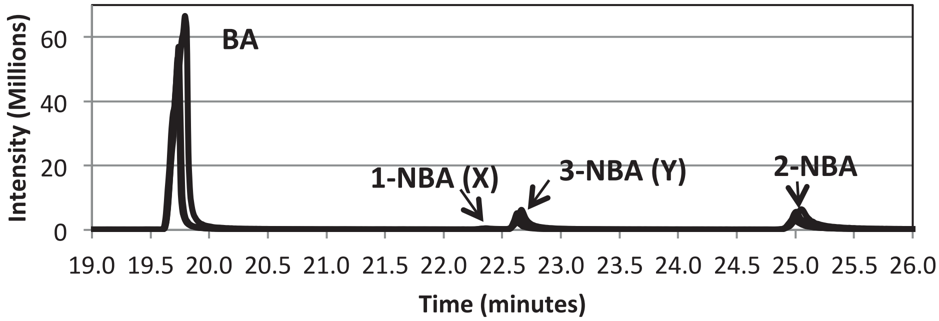
Identification of the Reaction Products via Gas Chromatography-mass Spectrometry.–The identity of compounds and observed bands in TLC were assigned from their mass spectral data and corresponding retention times. The standards BA and 2-NBA eluted at 19.7 and 25.0 min, respectively (Fig. 3). Under the reaction conditions, three mono-NBA isomers (Fig. 3, *b* and *c*), with retention times 22.3, 22.6, and 25.0 min formed. These peaks are assigned to compounds X, Y, and 2-NBA, respectively. 2-NBA was confirmed using an authentic 2-NBA standard. The other NBA isomers X and Y were assigned based on their GC-MS spectral profiles and *m/z* masses. On the basis of reported retention elution profiles, mass fragmentation patterns, X and Y were assigned to 1-NBA and 3-NBA, respectively (Enya et al. 1997; Phousongphouang & Arey 2003; Tang et al. 2004; Onchoke 2011). The integration of the bands (Table 1) indicated that, on average, 18.4% of BA was converted to NBA. The major product during the current reaction was 2-NBA with a yield of 10.5 ± 2.6% (Table 1). On the basis of the relative integrated peak areas isomers 1- and 3-NBA were calculated to have yields of 0.3 ± 0.1% and 6.4 ± 1.3%, respectively.

Mass spectral fragmentation patterns for BA and 2-NBA (Fig. 4, *a* and *b*; Table 2) along with those for 1- and 3-NBA (Fig. 5) confirm that three mono-nitrated isomers were indeed synthesized. As shown in panel *a* of Figure 4, mass spectrum of the molecular ion peak for BA was observed at *m/z* 230.4 $[M]^+$ 100% with mass spectral fragment peaks at *m/z* 200.3 (17.92%), m/z 202.3 $[M - CO]^+$ 59.64%, *m/z* 151.3 $[M\text{–benzene}]^+$ 2.69 %, *m/z* =100.2 (10.10%), 101.2 (16.80%) $[M\text{–naphthalene}]^+$ and *m/z* 51.2 (4.10%) $[M\text{–anthracene}]^+$.

a) Standard Sample of BA and 2-NBA



b) Direct Nitration of Benzanthrone



c) Direct Nitration of Benzanthrone

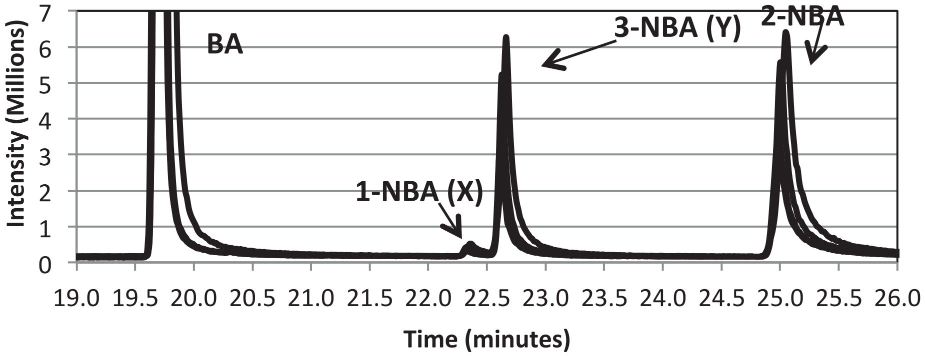


Figure 3. Overlaid gas chromatograms of triplicate reactions acquired in dichloromethane. Three NBA isomers were synthesized assigned as 1-NBA (X), 3-NBA(Y), and 2-NBA, respectively. (a) Gas chromatogram of a standard solution of benzanthrone (BA) and 2-nitrobenzanthrone (2-NBA) in dichloromethane, (b) GC chromatogram of aliquot solutions from direct nitration of benzanthrone, (c) a zoomed-in view of NBA products.

Table 1. Synthetic products from the direct nitration of benzanthrone (BA) using nitric acid (HNO_3). The average values were calculated from four reactions using a mole ratio of 8.9:1.0 (HNO_3: BA, v/v). *SD* = standard deviation; *Avg % Yield for BA is % conversion.

Compound	Avg. product (moles)	*SD*	Avg. product (mg)	*SD*	Avg. % Yield	*SD*
BA	1.77×10^{-4}	8.55×10^{-6}	40.7	2.0	18.4*	-
1-NBA (X)	6.95×10^{-7}	1.88×10^{-7}	0.2	0.1	0.3	0.1
3-NBA (Y)	1.38×10^{-5}	2.62×10^{-6}	3.8	0.7	6.4	1.3
2-NBA	2.28×10^{-5}	5.25×10^{-6}	6.3	1.4	10.5	2.6

The BA spectrum is in agreement with the literature (Taneja et al. 2018) and the Spectral Database for Organic Compounds (SDBS) (AIST:Spectral Database for Organic Compounds 2019)

Despite differences in the base peaks (Figs. 4 & 5), the fragmentation patterns for 1-NBA, 2-NBA and 3-NBA isomers are similar. In all cases the molecular ion peak $[M]^+$ is observed at *m/z* 275.2 $[M]^+$. Each NBA exhibited fragmentation peaks at *m/z* 245.2 $[M - NO]^+$, *m/z* 229.2 $[M\text{-}NO_2]^+$ which indicate that these are mono-nitrated PAHs. Other fragmentation peaks are observed at *m/z* 217.3 $[M\text{- }NO - CO]^+$, *m/z* 200.3 or 201.3 $[M\text{-}NO_2\text{-}CO]^+$, *m/z* 189.4 $[M - NO – CO - 2 \times CH_2]^+$. A comparison between mass spectral data show that 1-, and 3-NBA have a base peak of *m/z* = 189.4 (Fig. 5), vis-à-vis 2-NBA at *m/z* = 275.2 (Fig. 4*, b*). The *m/z* = 275.2 fragment is present in 1- and 3-NBA, but is less abundant vis-à-vis 2-NBA (Phousongphouang & Arey 2003). The mass spectrum of 2-NBA also has a fragment at *m/z* = 189.4, but is less intense than that for 1- and 3-NBA. Thus, for 1- and 3-NBA the fragment peak at *m/z* 189.4 is stabler than that at *m/z* = 275.2. The peaks observed *m/z* = 200.3, 100.2, and 87.2 in each of the NBA isomers, are common fragments for BA. Notably, the HNO_3:BA reaction ratios used in this synthesis was low enough to prevent the synthesis of any di-nitrated NBA isomers with *m/z* = 320.0.

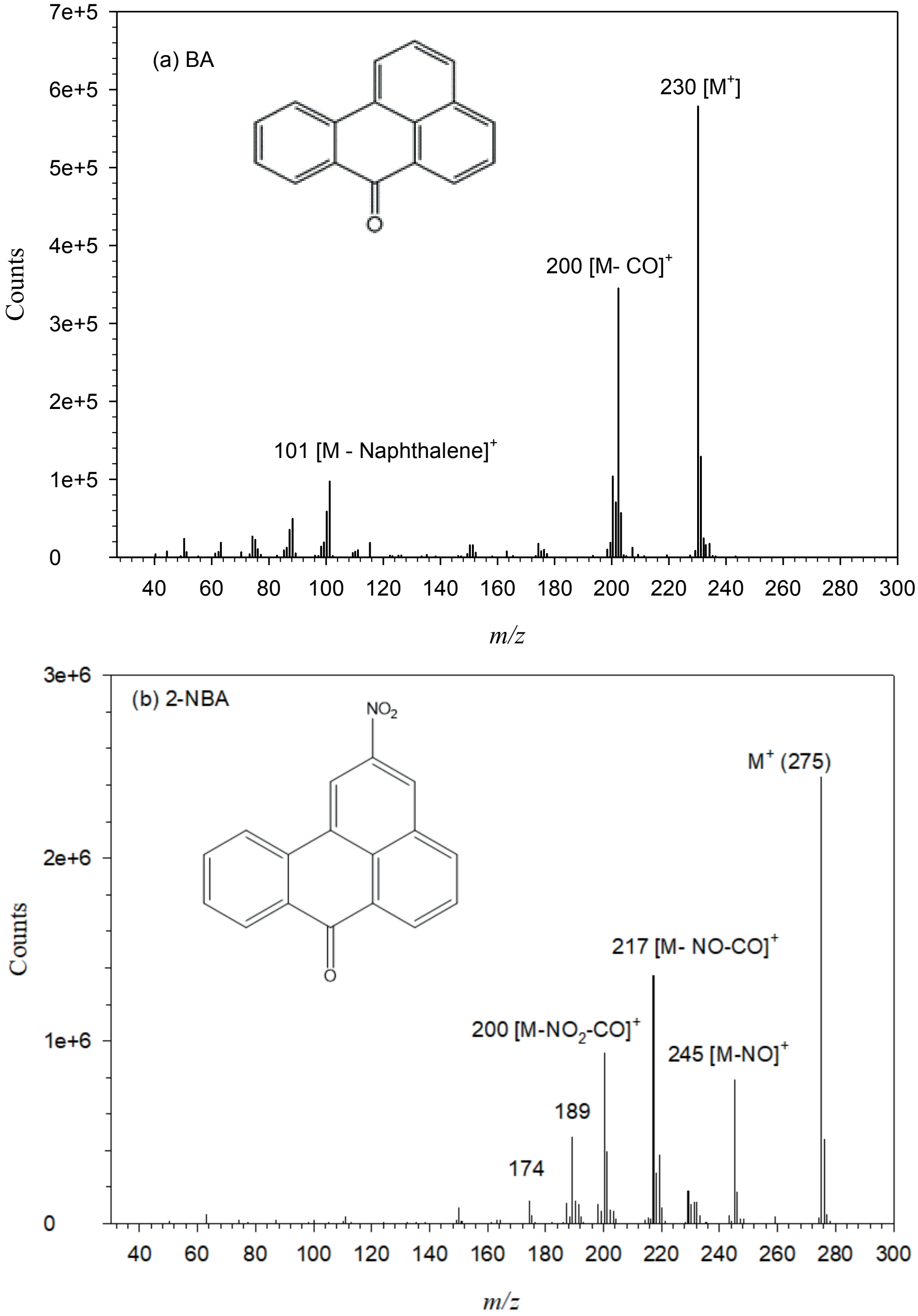


Figure 4. Mass spectra of (a) benzanthrone (BA), and (b) 2-nitrobenzanthrone (2-NBA). The base peak (BP) and molecular ion (M^+) peak is labeled in each mass spectrum.

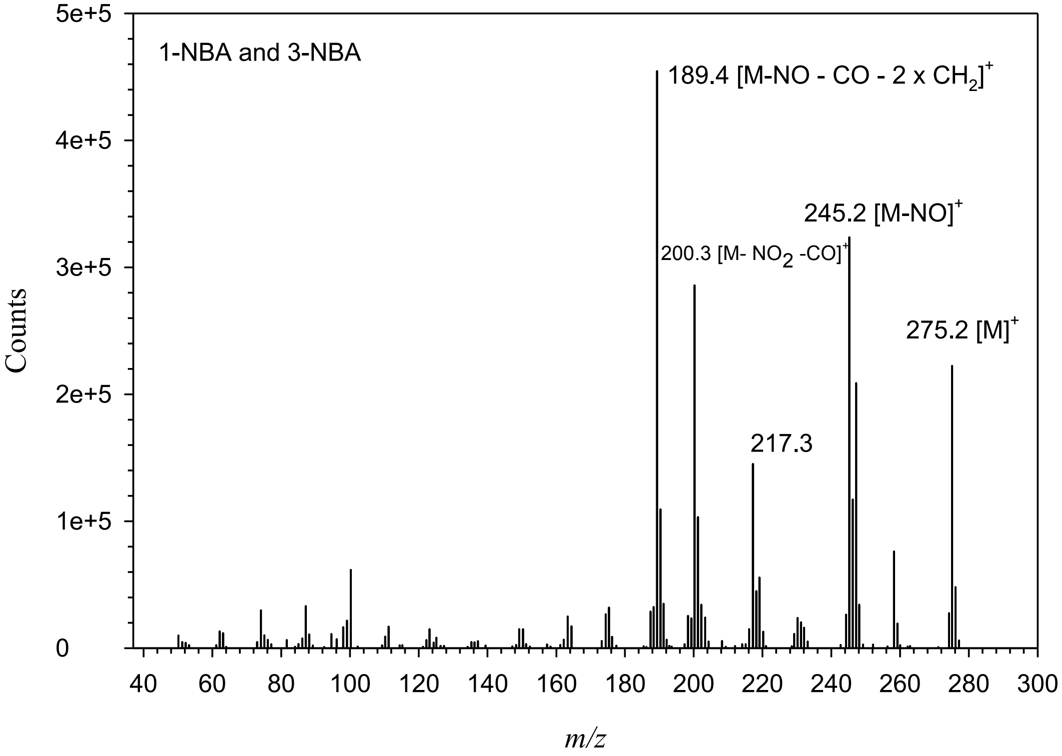


Figure 5. The mass spectrum of synthetic products **X** (1-NBA), and **Y** (3-NBA) were the same. The base peak (BP) and molecular ion (M^+) peak is labeled in the mass spectrum.

It is worth noting the differences in the intensities observed in this investigation vis-à-vis that reported by Phousongphouang & Arey (2003), which may be attributed to the type of mass spectral ionization used; ion trap mass spectrometry in the present study versus time of flight or quadrupole mass spectrometry used, and the type of radical ion formation mechanisms. Murray et al. (2013) noted that "Intensity is a measure of detector response and should not be used to describe the abundance of ions". In addition, the mode of ionization and the solvent used during ionization is important when comparing the peak profiles, which may give rise to these differences in peak intensities, albeit having the same base peaks. It is for the reasons noted that different intensity profile reported by Phousongphouang & Arey (2003) with spectra in Fig. 5 despite having the same fragmentation masses.

Table 2. Fragmentation peaks for the mass spectrum of benzanthrone, 1-, 2-, and 3-nitrobenzanthrone (1-, 2-, and 3-NBA) displayed in Figure 3 and 4. Bolded numbers denote the base peak (BP) for each compound.

Benzanthrone Fragment peaks (*m/z*)	1-NBA (**X**) Fragment peaks (*m/z*)	2-NBA (**Y**) Fragment peaks (*m/z*)	3-NBA Fragment peaks (*m/z*)
-	275.2	**275.2**	275.2
-	245.2	245.2	245.2
230.4	230.4	230.4	230.4
202.3	217.3	217.3	217.3
200.3	200.3	201.3	200.3
-	**189.4**	189.3	**189.3**
-	174.3	174.3	174.3
101.2	100.2	100.2	100.2
88.3	87.2	87.2	87.2

DISCUSSION

In this study, direct nitration of benzanthrone with nitric acid/acetic acid mixture produced three mono-nitrated NBA isomers. The isomer, 2-NBA, with retention time of 25 minutes was the major product (10.54% yield, Table 1). Typically 2-NBA is not a product of this reaction if nitrobenzene is used as the co-solvent at 20 ^{o}C (Enya et al. 1998a; Enya et al. 1998b). However, in the present study ice-cold acetic anhydride was used thereby dramatically changing the reaction outcomes. The major concern in the synthesis when using acetic anhydride with HNO_3 is in the nitration rates. The temperature and longer time-consuming reaction times (in acetic anhydride and HNO_3 mixtures) to mononitrated products affects the amounts of nitronium ion (NO_2^+) formed (Zielinska et al. 1986; Phousongphouang & Arey 2003). Acid-catalyzed hydrolysis of acetic anhydride causes loss of water in HNO_3, forming NO_2^+ in the form of acetyl nitrate (Zielinska et al. 1986). In this reaction, HNO_3 was added to acetic anhydride after the PAH was added. It is envisaged that electrophilic nitration would favor the more reactive carbon (C-3) of benzanthrone (Enya et al. 1997; Onchoke 2011). The formation of 2-NBA as the major product implicates the formation of a radical cation (Enya et al. 1997; Phousongphouang & Arey 2003; Atkinson & Arey 2007;

Zimmermann et al. 2013). Trace amounts of water in acetic anhydride can cause formation of radicals from HNO_3 (Gonzalez & Anglada 2010). The formation of 3-NBA is evidence of NO_2^+ formation.

The assignments of products to 1-NBA and 3-NBA is based on the product nitration yields, NBA dipole moments, and known NBA elution profiles. Notably, 2-NBA did not overlap and 3-NBA eluted at different retention times. This is due to their different dipole moments, 4.00 D and 2.03 D (3-NBA and 2-NBA), respectively) (Onchoke 2011). Typically, 2-NBA and 3-NBA are easier to chromatographically separate vis-à-vis other NBAs. However, the close dipole moments between 1- and 3-NBA (1-NBA (3.27 D) < 3-NBA (4.00 D)) results in their close retention times (Fig. 3, *b* and *c*). In this investigation the resolution of compounds 1-NBA and 3-NBA give further evidence to their synthesis.

Mass spectral data reveals that the fragmentation patterns and masses of mono-NBA isomers are nearly identical. As noted, the base peaks for the mass spectrum of compounds 1-NBA and 3-NBA is *m/z* 189.4 (1-NBA, 3-NBA), and *m/z* 275.2 (2-NBA). It is likely that the base peak for compounds 1- and 3-NBA show a more stable fragment $[M\text{-}NO - CO - 2 \times CH_2]^+$ than the $m/z = 275.2$ $[M]^+$. The calculated percentage intensities relative to the base peak of each of the m/z masses are; 1- and 3-NBA: *m/z* 275.1 = 48.9%, *m/z* 247.2 = 45.95%, m/z 245.2 = 71.23 %, *m/z* 201.20 = 22.73%, *m/z* 200. 2 = 62.90%, *m/z* 89.3 = 100%. For 2-NBA the calculated percentage intensities relative to the base peak of each of the m/z masses are; *m/z* 275.1 (100.%), *m/z* 245.2 (32.05%), *m/z* 229.2 (7.46%), *m/z* 217.2 (55.56%), *m/z* 201.2 (16.26%), *m/z* 200.30 (38.16 %), *m/z* 189.3 (19.37%), *m/z* 174.30 (5.04%). Since the mass spectral data (fragmentation pattern) of these isomers are nearly identical, mass spectrometry alone does not sufficiently distinguish between NBA isomers. Nevertheless, mass spectral data is helpful for confirmation of the presence of different NBA isomers.

CONCLUSIONS

The synthesis of three nitrobenzanthrones (1-NBA, 2-NBA and 3-NBA) via direct nitration with HNO_3 was performed in an ice-cold acetic anhydride solution. Identification of the starting material, benzanthrone (BA) and 2-nitrobenzanthrone (2-NBA) in the reaction product was confirmed using standard samples. Reaction product analyses were performed via thin layer chromatography (TLC) and gas chromatography-mass spectrometry (GC-MS). From the reactions, we conclude the following. Firstly, TLC analysis showed that a hexane:DCM solvent system does not offer complete separation of the NBA isomers. Because of their close polarities, separation of the isomeric products becomes difficult and tedious without other instrumental analytical techniques. This necessitated the use of GC-MS analytical technique for identification. Secondly, 18.5% of benzanthrone was converted to NBA under the reaction conditions. Thirdly, via direct nitration of BA with HNO_3 in acetic anhydride three isomeric NBA isomers were formed and identified using GC-MS with percent yields of 10.5 ± 2.6% (2-NBA), 0.3 ± 0.1% (1-NBA) and 6.4 ± 1.3% (3-NBA), respectively. Assignments of these isomers were based on reported elution profiles of mono-NBA isomers and their fragmentation patterns (Enya et al. 1997; Tang et al. 2004).

More importantly, the synthesis in acetic anhydride limits the exposure to carcinogenic co-solvents traditionally used for the direct nitration synthesis of NBAs, such as nitrobenzene. Although low yields were synthesized, major and minor synthetic products can be biased by altering the mole ratios of HNO_3:BA, changing reaction temperatures and lengthening reaction time.

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Department. Any opinions expressed in this paper are those of the authors, and therefore, no official endorsement should be inferred.

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