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Article

Synthesis, Characterization of Some New Dimer Nitrone Derivatives from Dapsone, Their Use as Initiators for Polymerization

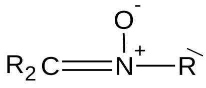
A. A. Ahmed[1], A. A. Turki[2], W. S. Hanoosh[3]

1,2,3. Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq

Abstract: In order to address the demand for effective anionic initiators in polymerization processes, this work investigates the synthesis and characterisation of new dimer nitrone derivatives produced from dapsone. The aim is to close the existing gap in the acrylonitrile polymerization process by using nitrones as initiators. The process entails producing the necessary dimer nitrones by oxidizing with peroxy acid after generating dimer imines through condensation processes. Techniques including FTIR, 1H NMR, and MS were used to conduct the characterization. Evaluating these chemicals' potential as bulk polymerization initiators was the goal. The successful creation of polymers was revealed by the results, indicating that these dimer nitrones are efficient initiators of anionic polymerization, which may improve polymer synthesis techniques.

Keywords: dimer nitrone Derivatives, Dapsone, Polymerization

1. Introduction

In organic chemistry, a nitrone or azomethine oxides contains the functional group of an N-oxide of an imine. The general formula is  $R_2C{=}\overset{O^-}{\overset{|}{N^+}}{-}R$ where R^- is not a hydrogen [1]. It was first discovered by Bekman in 1890 [2]. The name "nitrone" was proposed by Pfeiffer in 1916 from brevation nitrogen-ketones to confirms their similarity to ketones [3]. Nitrones are classified into two main categories. The first category is aldonitrones containing a proton on the alpha-carbon atom, $R_1CH=N(O)R_2$ While the second category is ketonitrones, the alpha- carbon is replaced by alkyl or aryl group $RR_1C=N(O)R$ [4, 5]. Diferents methods have been used for nitrones synthesis including [6]. The condensation reaction between derivatives of N-mono substituted hydroxylamine and carbonyl compounds alkylation of oximes, oxidation of secondary amine or N,N-substituted hydroxylamines and oxidation of imines [7].

Nitrones are interesting intermediates that are used in organic synthesis it was used early in the trapping of free radicals in biological systems and chemical systems [8]. These compounds are also known as 1,3-dipoler cycloaddition reactions to provide numerous heterocyclic systems and it was also used in the radical reaction as spin trap agents [9]. It is the leading applications of nitrones is in polymers manufacturing relying mainly on radical polymerization processes [10]. Copolymer production has begun using the nitrone-mediated radical coupling method (NMRC), which has a high radical-coupling efficiency due to the spin-trap ability of nitrones. A nitrone can react with a free radical to make an intermediate nitroxide, which then captures another radical to produce an alkoxyamine group in the middle of the chain via NMRC. It is possible to produce block copolymers, star polymers, and crosslinked polymers. Nitrones could also be employed as essential repeating units in the manufacture of dendrimers and altemating copolymers, such as step

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growth polymerization [11]. Nitrones chemicals are also used in medicine and the pharmaceutical industry. They demonstrate antifungal, antibacterial, neuroprotective, and antioxidant agents [12]. These chemicals play a vital function in trapping free radicals in the body. Furthermore, some nitrones have been discovered as crucial components in the structure of significant medications [13]. This work produced three novel nitrones based on dapsone.

Experimental

General

Melting points were incorrect. NMR spectra were obtained using a Bruker Ultra Shield (300 MHz). The chemical shifts were compared to tetra methyl silane (TMS) as an internal standard. GC mass spectra were obtained with Shimadzu Qp5050A.

Synthesis of imine-N-oxide compounds

These compounds were prepared as mentioned in the literature from mixed (0.002mole) of dimer-imine compounds in 50 ml conical flask with peracetic acid prepared (from mixture of 0.013 mol (1.2 ml) 36% H_2O_2 and (2.5 ml) from glacial acetic acid were mixed). Were stirred in ice bath to10C^0 for 5 hours. Then cooled to 0C^0 and kept the reaction mixture in this temperature for 24 hours, and the reaction was monitored by TLC (EtAc: Diethylether). The result was filtered and the precipitate was filtered and washed with a mixture of 5ml (acetone, ethanol) and recrystallized using absolute ethanol to give final product.

4,4`-sulphonylbis (N-(1-(4- aminophenyl) ethylidene) aniline oxide)

From 4-amino acetophenone: yield 61%, m.p. (220-222) oC.; Mass spectrum M.wt. (M+ = 514) , the FTIR spectrum using KBr disk, υ(cm-1) 3464 (NH stretching), 3113 (due to C–H stretching of aromatic ring), 2931 (attributed to C–H stretching of aliphatic), 1678 (due to C=N stretching), 1593 (due to C=C stretching of aromatic ring), 1296 (N–O stretching), H NMR spectrum, δH(DMSO) (3.44) ppm (4H,s,5,5/) , (7.68-7.70) ppm (4H,d,1,1/) , (7.49-7.51) ppm (4H,d, 2,2/) , (6.59-6.63) ppm (4H,d, 3,3/,7,7/) , (6.01-6.05) ppm (4H,d, 4,4/,6,6/) , (2.81) ppm (6H, s, 8,8/).

4,4`-sulphonylbis (N-(1-(2,4- dihydroxyphenyl) ethylidene) aniline oxide)

From 2,4-dihydroxy acetophenone: yield 55%, m.p. (272-274) oC. ;Mass spectrum M.wt. (M+ = 548) , the FTIR spectrum using KBr disk, υ(cm-1) 3375 (due to OH stretching), 3101 (was attributed to C–H stretching of aromatic ring), 2920 (attributed to C–H stretching of aliphatic), 1635 (related to C=N stretching), 1597 (due to C=C stretching of aromatic ring), 1292 (N–O stretching), H-NMR spectrum, δH(DMSO) (11.68) ppm(2H,s,5,5/), (12.63) ppm (2H,s,3,3), (7.76-7.80) ppm (4H,d,1,1/) , (7.44-7.48) ppm (4H,d, 2,2/), (6.61-6.63) ppm (4H,d, 7,7/) , (6.27-6.42) ppm (4H,d, 6,6/) , (6.00) ppm (2H,s,4,4/), (2.84) ppm (6H, s, 8,8/).

4,4`-sulphonylbis (N-(4 hydroxybenzylidene) aniline oxide)

From 4-hydroxy benzaldehyde: yield 73%, m.p. (256-258) oC. ;Mass spectrum M.wt. (M+ = 488) , the FTIR spectrum using KBr disk, υ(cm-1) 3375 (due to OH stretching), 3105 (due to C–H stretching of aromatic ring), 1681 (attributed to C=N stretching), 1593 (C=C stretching of aromatic ring), 1149 (due to N–O stretching), H-NMR spectrum, δH(DMSO) (12.5) ppm (2H,s,5,5/), (9.5) ppm (2H,s,8,8/), (8.07-8.10) ppm (4H,d,1,1/), (7.88-7.91) ppm (4H,d, 2,2/), (7.68-7.70) ppm (4H,d, 3,3/,7,7/) , (7.46-7.48) ppm (4H,d, 4,4/,6,6/).

2. Materials and Methods

In this study, the methodology for synthesizing new dimer nitrone derivatives from Dapsone involved a series of precise steps to ensure the accurate preparation and characterization of the compounds. Initially, dimer imine compounds were synthesized through the condensation of carbonyl compounds, such as 4-amino acetophenone, 2,4-dihydroxy acetophenone, and 4-hydroxy benzaldehyde, with 4,4′-diamino diphenyl sulfone (Dapsone). These imines were subsequently oxidized using peroxy acid, which was prepared by mixing hydrogen peroxide and glacial acetic acid, to yield the desired dimer nitrones. The reaction was conducted in an ice bath, maintaining the temperature at 10°C for five hours, followed by a 24-hour period at 0°C to ensure complete reaction. The progress of the reaction was monitored by Thin Layer Chromatography (TLC), and the resulting product was purified through filtration, washing with an acetone-ethanol mixture, and recrystallization in absolute ethanol.

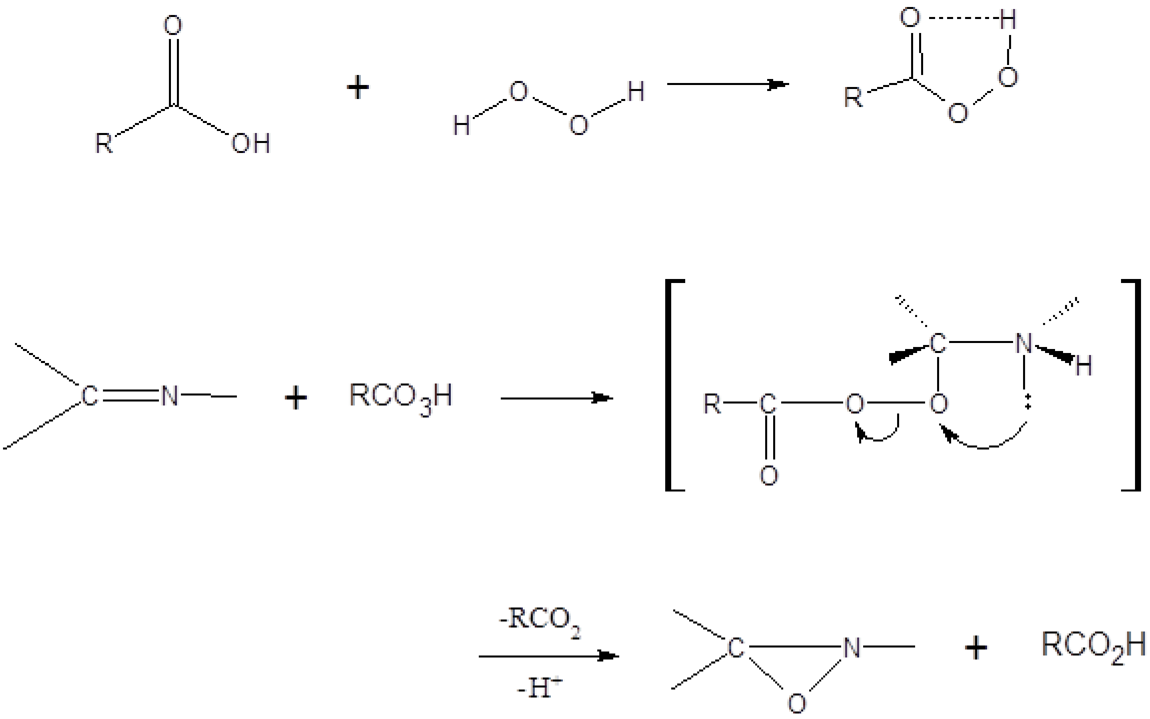
The synthesized dimer nitrones were characterized using Fourier-Transform Infrared Spectroscopy (FTIR), Proton Nuclear Magnetic Resonance (1H NMR), and Mass Spectrometry (MS). FTIR analysis identified key functional groups through their absorption bands, while 1H NMR provided detailed information about the proton environment in the compounds. MS confirmed the molecular weights and fragmentation patterns of the synthesized nitrones.

Subsequently, these dimer nitrone compounds were utilized as initiators for the polymerization of acrylonitrile. The polymerization process involved mixing the monomer and initiator at room temperature and observing the reaction over 72 hours, resulting in the formation of a white solid polymer. This process illustrated the efficacy of the dimer nitrones as initiators for anionic polymerization, opening new avenues for polymer synthesis. The entire methodology underscored the importance of precise reaction conditions and thorough characterization in the synthesis of novel chemical compounds.

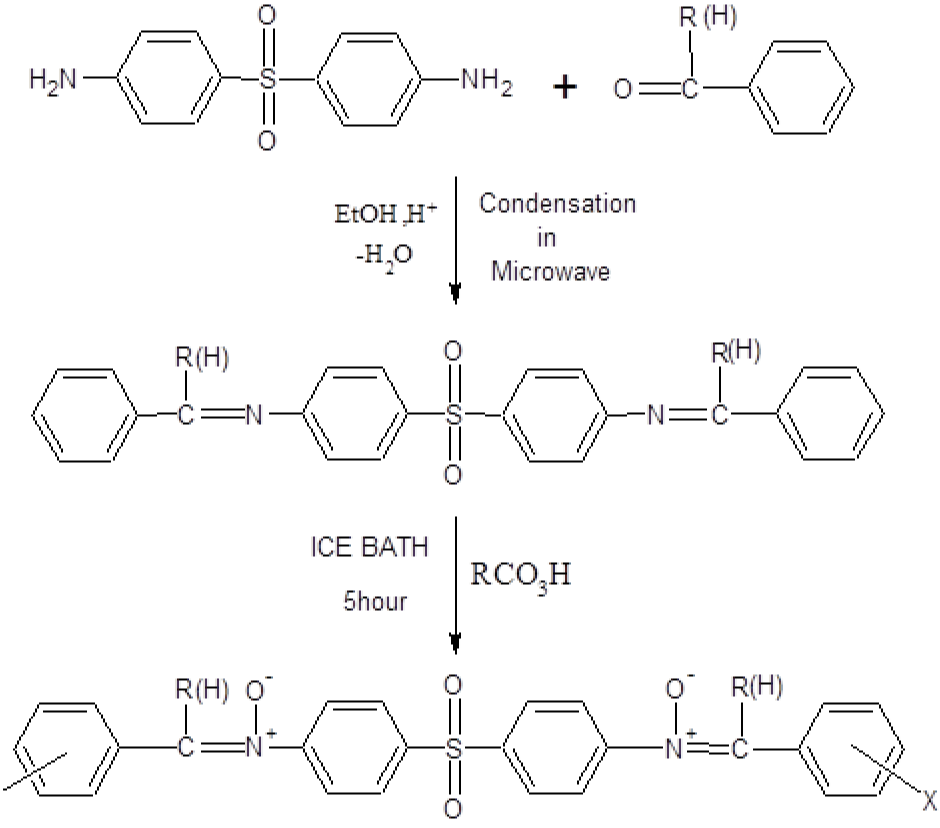
3. Results and Discussion

Reaction Scheme

Dimer nitrones compounds (1,2,3) were prepared through the oxidation of dimer imine compounds prepared from the condensation of carbonyl compounds (4-amino acetophenone, 2,4- di hydroxy acetophenone,4- hydroxy benzaldehyde) with 4,4-diamino diphenyl sulfone (Dapsone) [14]. Under irradiated microwave(332w), Using peroxyacid prepared from (hydrogen peroxide with glacial acetic acid) as shown in (Scheme1) in which nitrone formation through nucleophilic attack of the unshared electron double belonging to the imine group on the oxygen of the acid to form a nitrone [15], While (scheme2) explains the general interaction for the prepared compounds [16]. The chemical structures of the prepared compound were proved from their Mass spectroscopy, FT-IR, and ^{1}H NMR measurements [17, 18].



Scheme 1. The suggested mechanism of nitrone formation



$R=H,CH_3$

$X=4\text{-}NH_2$, 2,4-OH, 4-OH

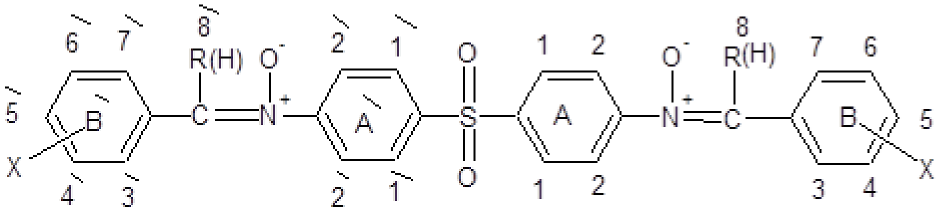
Scheme 2. Rute of the prepared dimer nitrone

Characterization of prepared dimer-nitrone

The FT-IR spectra of dimer nitrone compounds were shown in Figures (1-3) and was identified. The results shown that all the FTIR spectra showed absorption bands distinctive at (1149-1296) cm-1 due to (N+-O-) stretching vibration also absorption bands at (1635-1681) cm-1 was attributed to the stretching vibration of (C=N) group, while the absorption bands at (1593-1597) cm-1 was attributed to the stretching of (C=C) aromatic. The C-H stretching aromatic rings showed absorption bands within the range (3101-3113) cm-1, while the C-H stretching vibration aliphatic absorption bands was appeared within the range (2920-2931) cm-1. The O-H stretching in compounds (1,3) showed absorption bands at (3375) cm-1 while the N-H stretching in compound (1) showed absorption bands within the range (3371-3464).

In the case of 1H NMR measurements, the spectra of the prepared di nitrone compounds which are shown in Figures (4-6), Its spectra were explained according to the following formula (3). The spectra indicate the presence of nitrone group (CH=N+-O-) singlet signal at (9.5) ppm in compound (3). The CH3 proton (8,8/) of compounds (1,2) showed singlet signal at (2.81-2.84) ppm. The OH protons (3,3/and 5,5/) of compounds (2,3) showed singlet signals within the range (11.68-12.63), also the NH2 proton (5,5/) of compound (1) showed singlet signals at (3.44) ppm. The aromatic protons of ring (A) in the positions (1,1/) showed doublet signals within the range (7.68- 8.10) ppm due to interaction with one proton in (2,2\) position, while the other two protons in (2,2\) position showed doublet signals within the range (7.44-7.91) ppm because interaction with protons in (1,1/) position.

The proton of aromatic ring (B) in positions (3,3/ and 7,7/) in compounds (1,3) showed doublet signals within the range (6.59-7.70) ppm due to interaction with protons in (4,4/ and 6,6/), while the other two protons in positions (4,4/ and 6,6/) showed doublet signals within the range (6.01-7.48) ppm due to interaction with protons in (3,3/ and 7,7/). The aromatic protons in compound (2) showed doublet signals in the range (6.61-6.63) ppm due to contact with the proton in position (6,6/), whereas the proton in position (6,6/) showed doublet signals in the range (6.27-6.42) ppm. While the other proton at positions (4, 4/) displayed a singlet signal at (6.00) ppm. Figures (7-9) illustrate the fragmentation products of (1,3) dimer nitrone used in mass spectroscopy.



Scheme 3

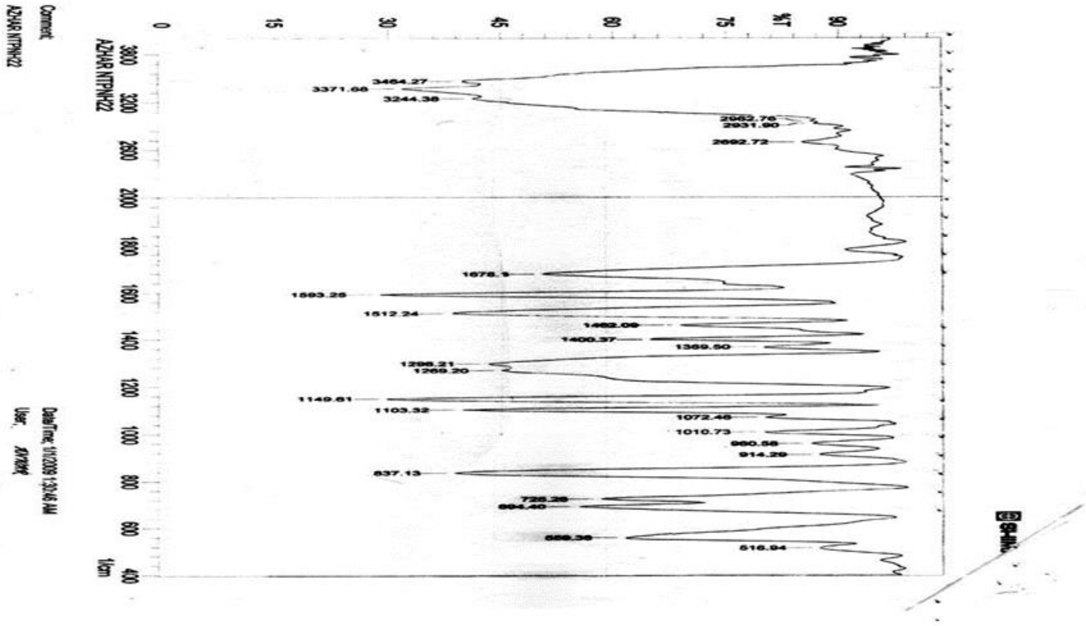


Figure 1. FTIR spectrum of dimer nitrone 1

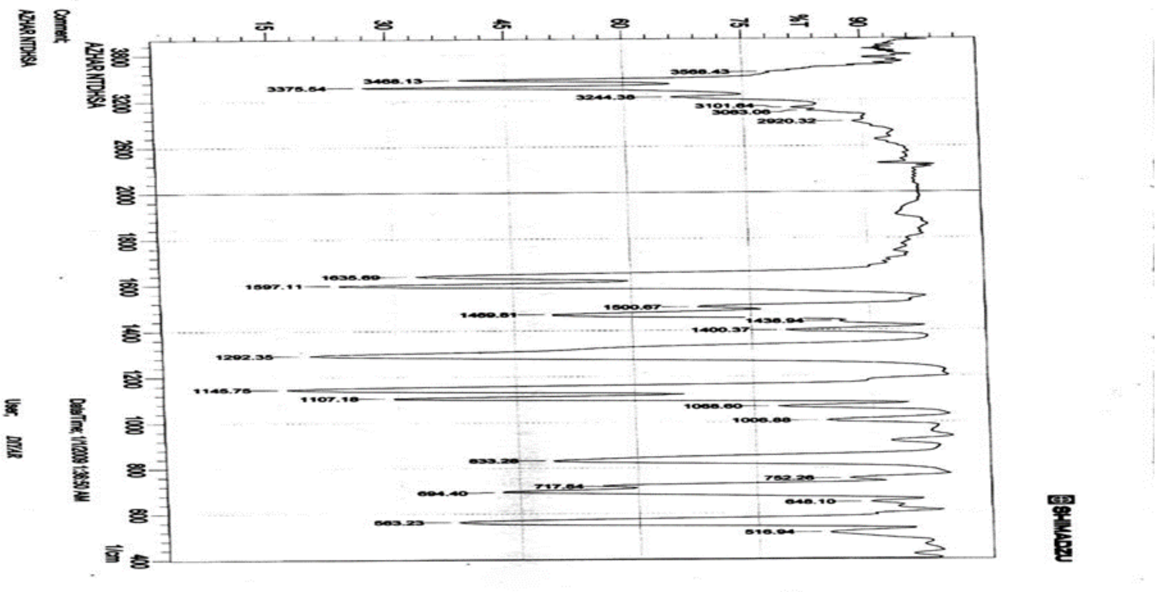


Figure 2. FTIR spectrum of dimer nitrone 2

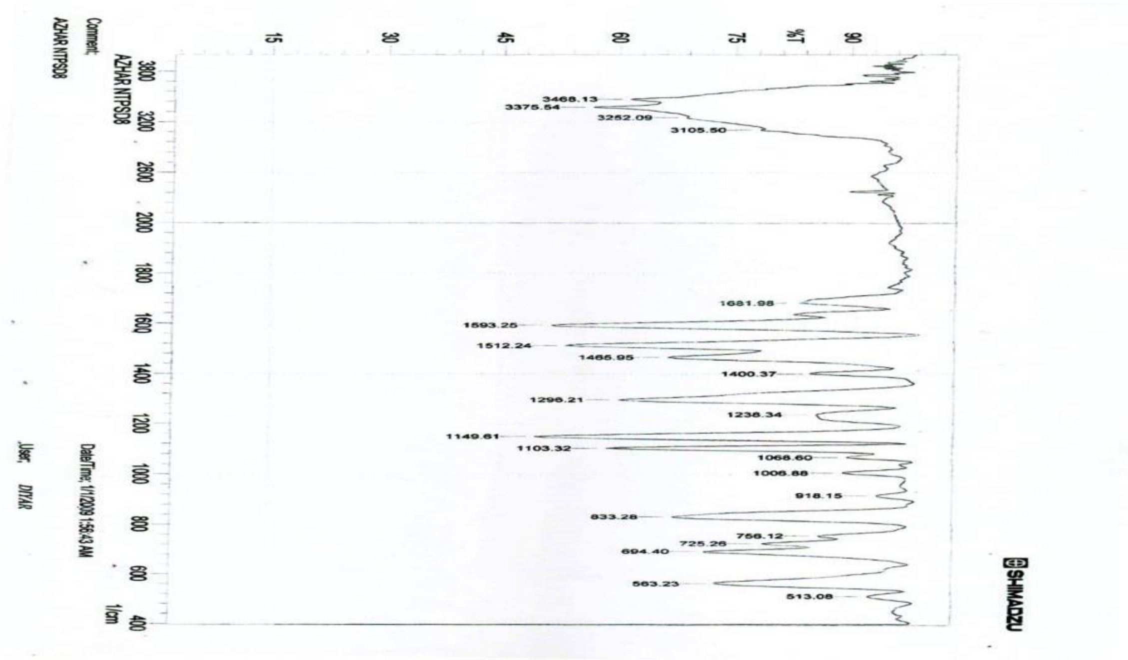
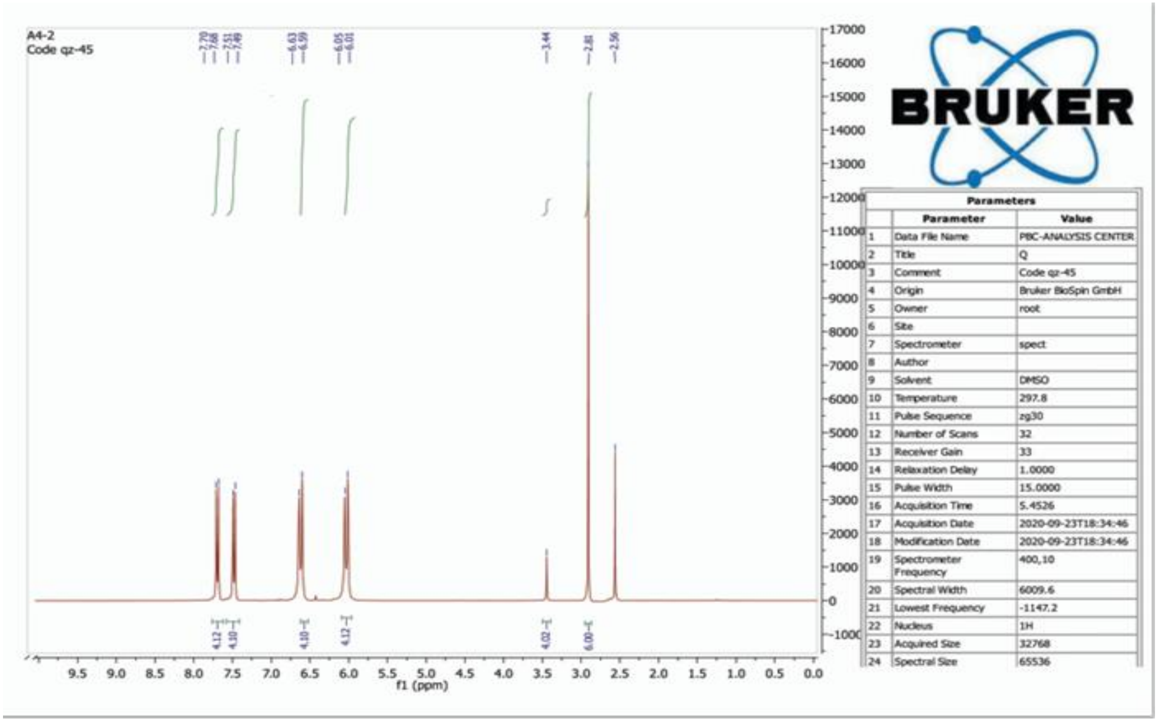


Figure 3. FTIR spectrum of dimer nitrone 3



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14	Relaxation Delay	1.0000
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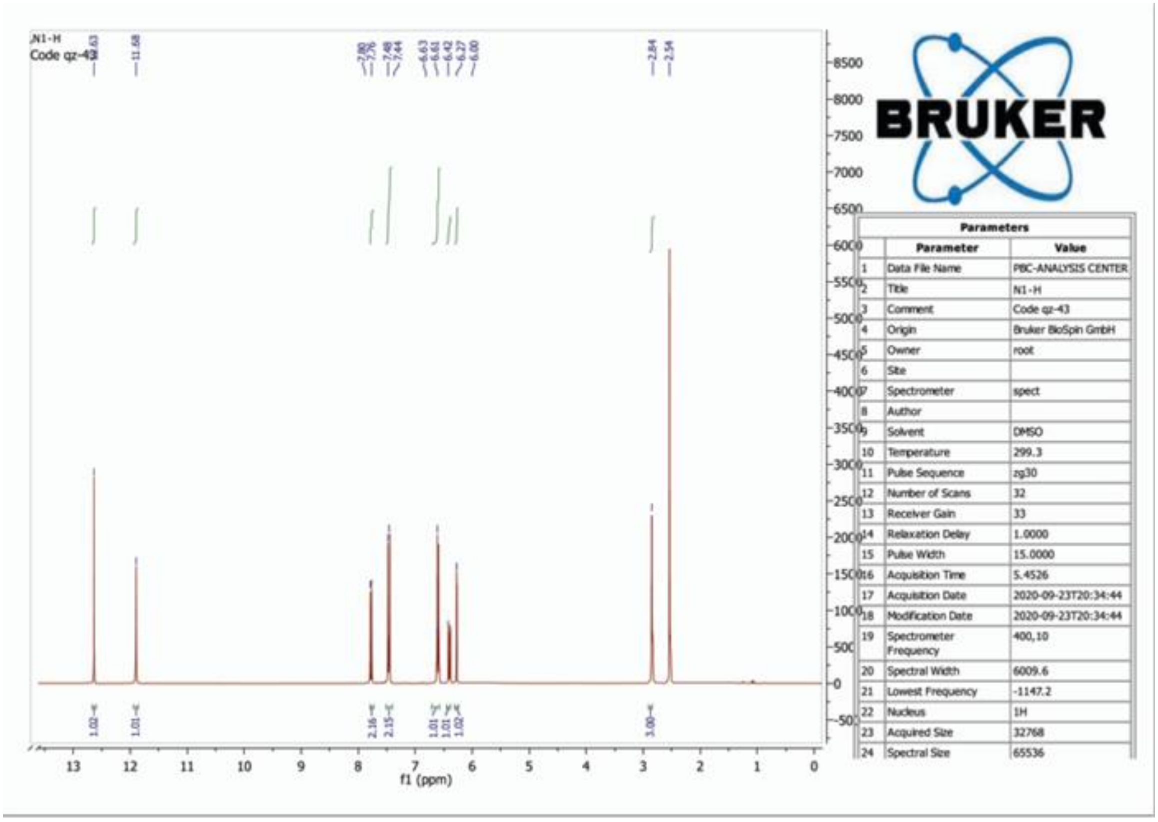
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

Figure 4. H^1NMR spectrum for dimer nitrone 1



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20	Spectral Width	6009.6
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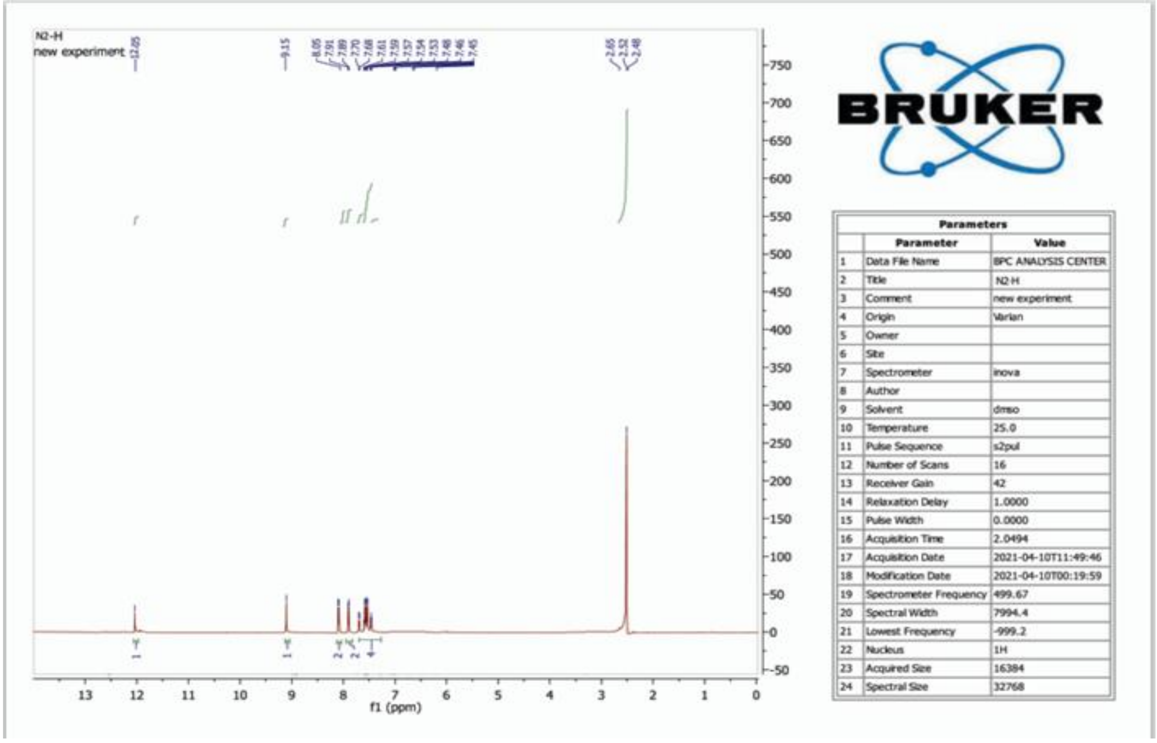
24	Spectral Size	65536

Figure 5. H^{1}NMR spectrum for dimer nitron 2



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22	Nucleus	1H
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24	Spectral Size	32768

Figure 6. H^{1}NMR spectrum for dimer nitrone 3

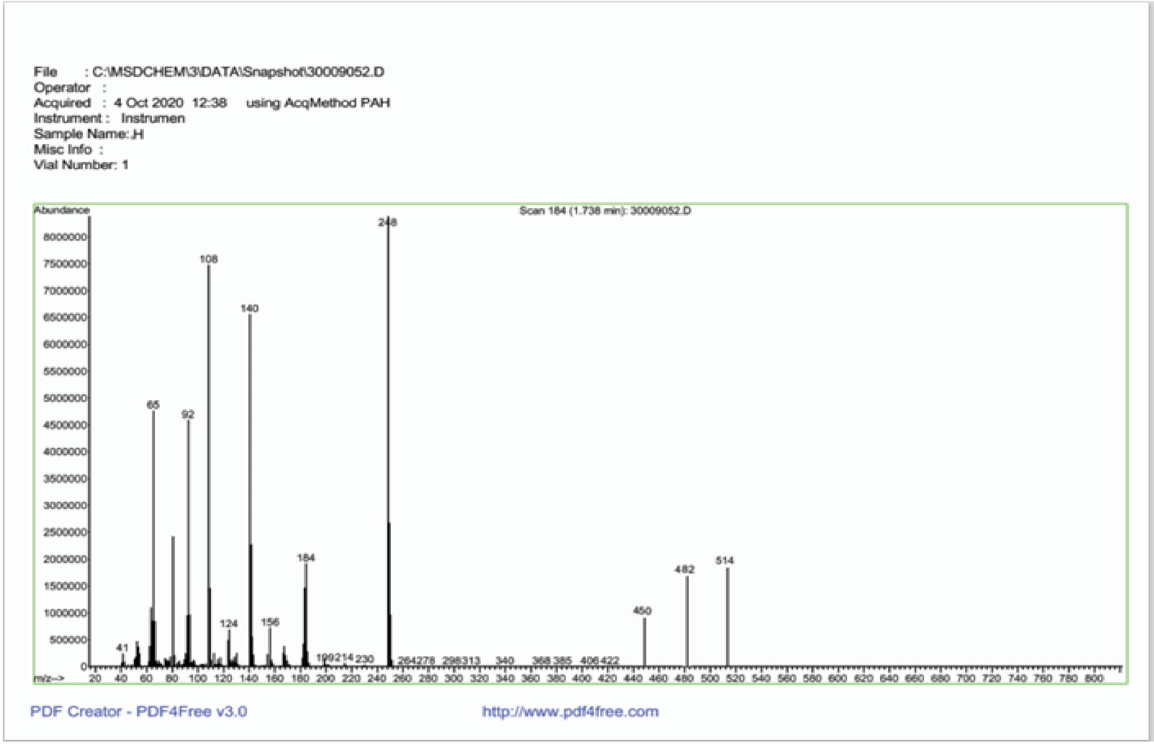

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Figure 7. Mass spectrum of dimer nitrone 1

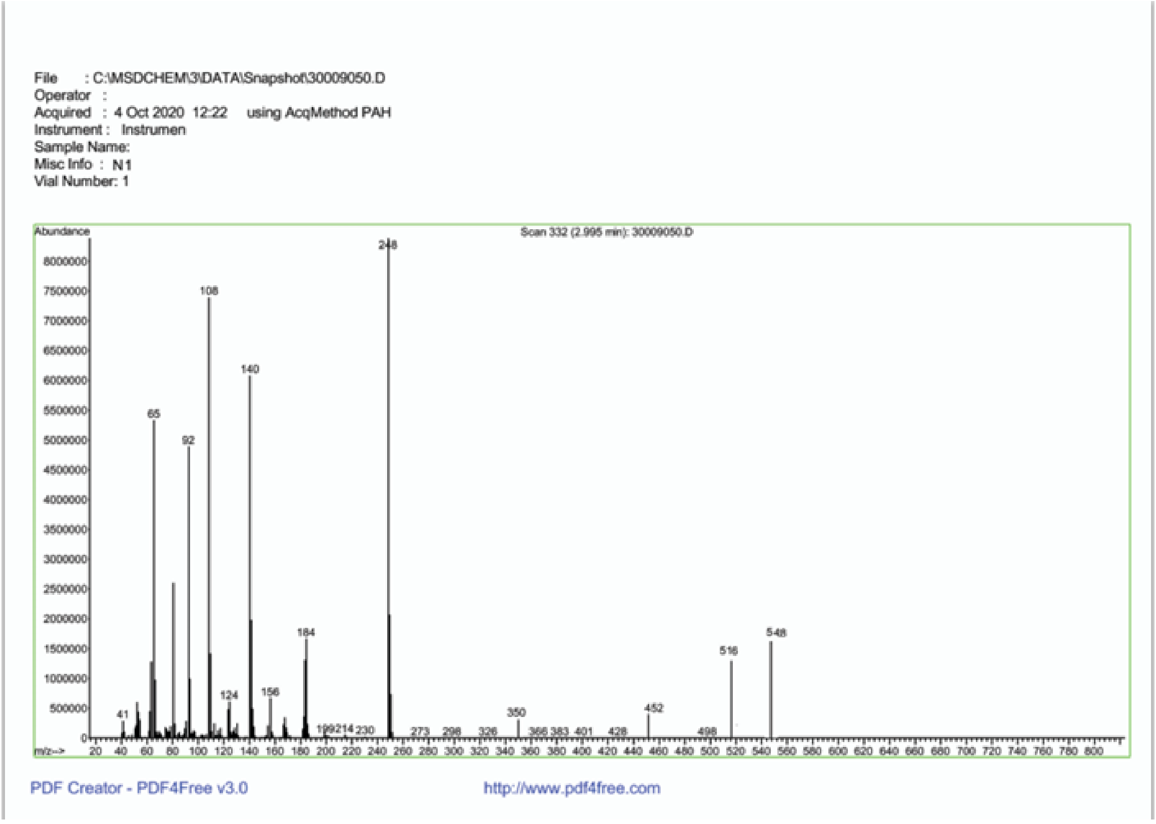

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Figure 8. Mass spectrum of dimer nitrone 2

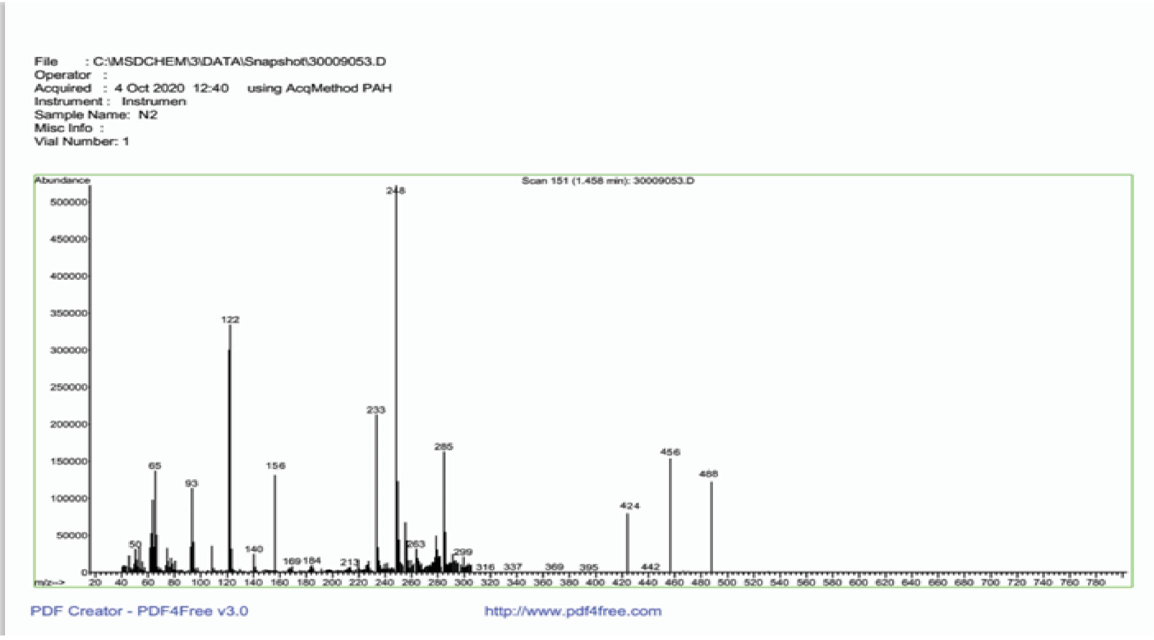

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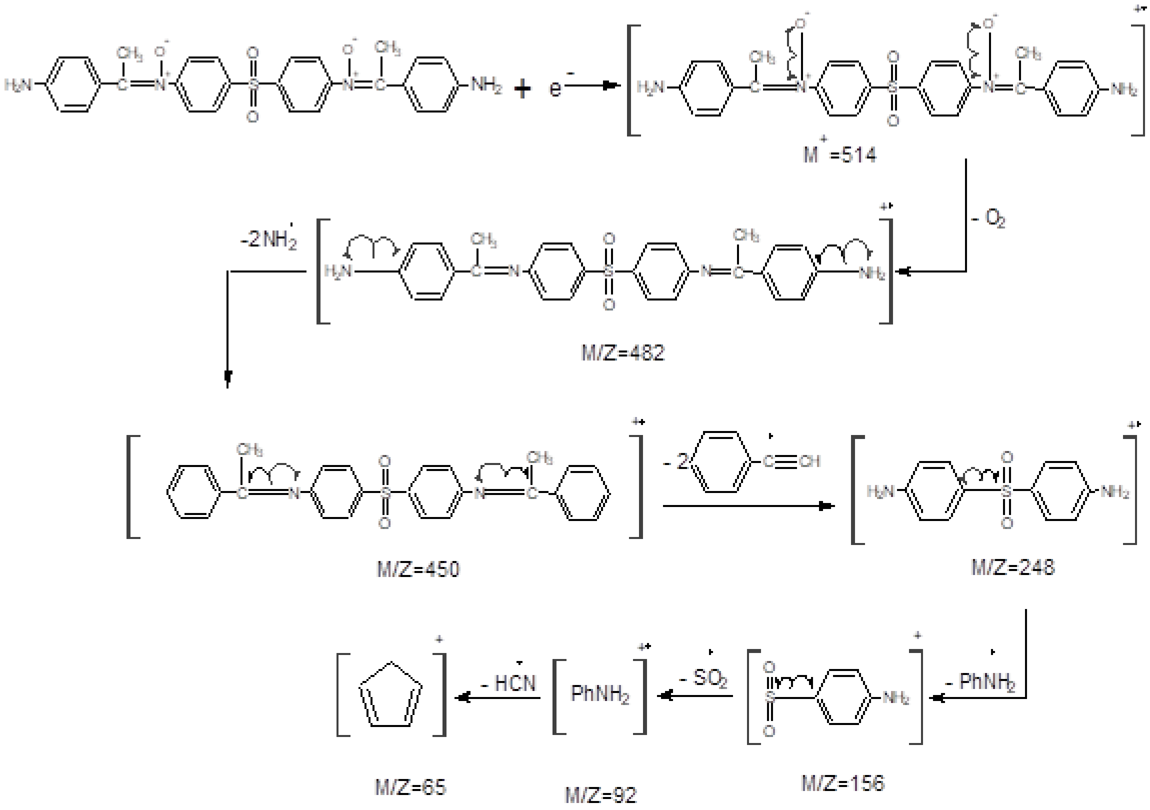
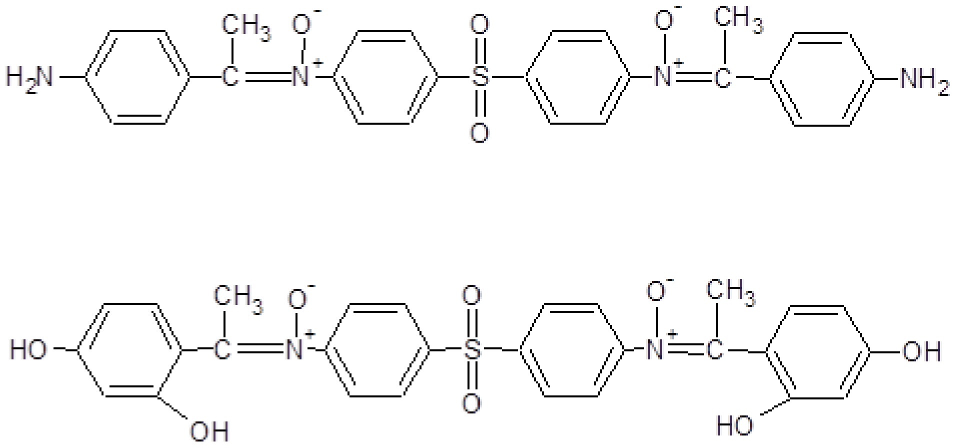
Figure 9. Mass spectrum of dimer nitrone 3



Scheme 4. Mechanism of fragmentation of dimer nitrone 1

Use of dimer nitrone compounds as polymerization initiators

One of the main methods for preparing polymers is the addition polymerization in which the monomers must be contain double bonds and used initiator for this polymerization. In this study use two of the prepared two type of dimer nitrones compounds as initiator for the polymerization of acrylonitrile monomers [19, 20]. The polymerization process was carried out by mixing the monomer and initiator at laboratory temperature (480°C) for a period 24 hour to follow up the course of polymerization it was observed that the monomer didn't polymerizes so it was left at the same temperature for a longer time after 72 hours it was observed that the acrylonitrile monomer polymerized and convent in to a white solid product as shown in the figure (10).

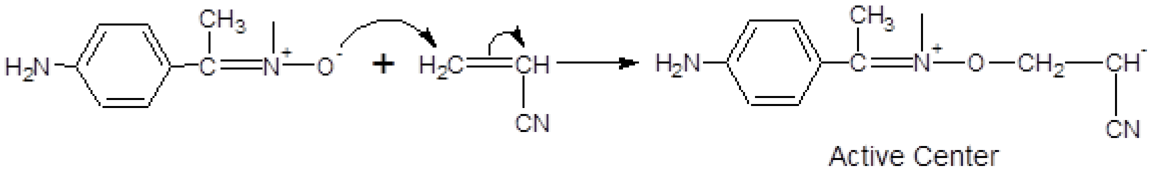


Scheme 5. Chemical structures of dimer-nitrone compounds used as initiators of polymerization

The addition polymerization process of acrylonitrile using one of the dimer nitrone initiator included three steps:

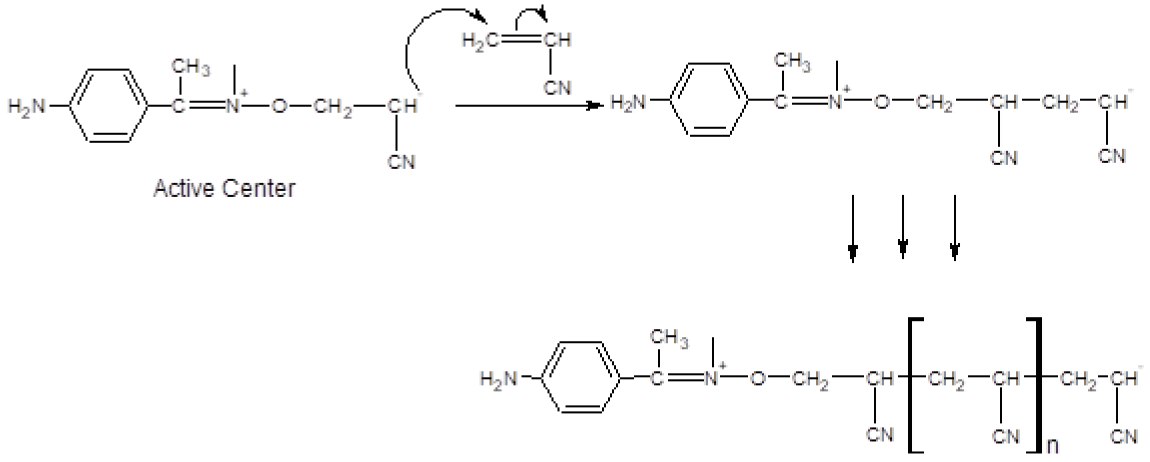
1. Initiation step

Which include the interaction of the initiator with the monomer to form the Active center) as shown in the equation.



2. Propagation step

This step includes adding a new monomer to the active center and an increase in the molecular weight of the product as shown in the equation.



3. Termination step

This is the step where the polymerization process ends and the resulting polymer is obtained. It was noted that the important step in the reaction is the propagation step.

Through which the speed of polymerization is calculated.as we known that the Anionic polymerization called (living polymerization) due to there is no termination steps.

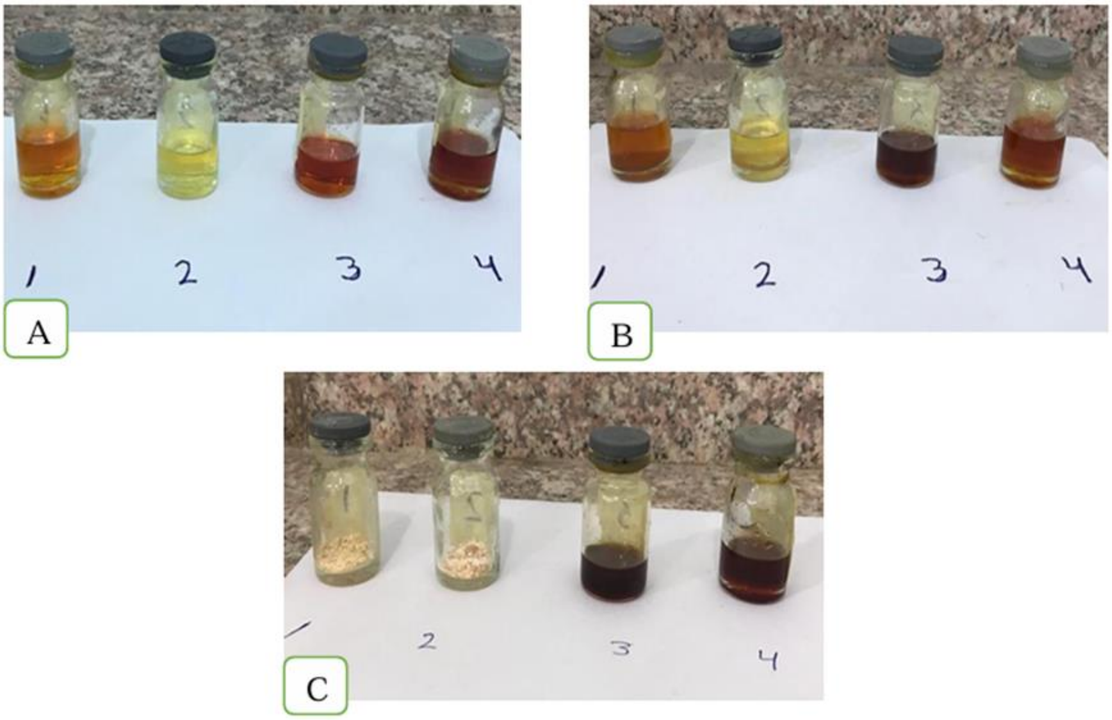


Figure 10. The polymerization process of acrylonitrile in the presence of (1,2) dimer nitrone compounds: (A) It represents the beginning of preparing models for the polymerization process. (B) Forms after 24 hours. (C)Models represent after 72 hours of polymerization process**.**

4. Conclusion

In this study, we successfully synthesized and characterized a series of new dimer nitrone derivatives from Dapsone, demonstrating their effectiveness as initiators for the anionic polymerization of acrylonitrile. Our findings revealed that the synthesized dimer nitrones, when used as initiators, facilitated the formation of a white solid polymer, thus proving their potential utility in polymer chemistry. Characterization techniques such as FTIR, 1H NMR, and mass spectrometry confirmed the structural integrity and composition of these compounds. The implications of these results are significant, suggesting that dimer nitrone derivatives can serve as effective initiators in polymerization processes, potentially leading to novel applications in material science and industrial chemistry. Further research is recommended to explore the full scope of these derivatives' capabilities in various polymerization contexts and to investigate their performance with different monomers and under varied reaction conditions, which could provide deeper insights into their practical applications and enhance their efficacy in industrial applications.

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