

Synthesis, Spectroscopic and Photolysis of Cis Bis (Nitroso benzil)

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Abstract

Cyclic azo dioxide {cis bis (nitroso benzil)} has been prepared by oxidation of the dinitro compound with zinc and ammonium chloride in ethanol / water. This compound studied spectrophotometrically using UV, IR and NMR techniques.

Then photolysis study of this compound by using mercury lamp in solution state to result N-oxide (nitron) compound.

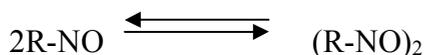
الخلاصة

حضر مركب سز بس (نيتروزو بنزل) من خلال خطوات تفاعل البنزل مع الهيدروكسيل أمين لتكوين الاوكزاييم ومن ثم تكوين الداينيترو باستخدام حامض النتريك الداخن ، وأخيرا تكوين الدايمر باختزال النيترو بواسطة بودر الزنك ووجود كلوريد الامونيوم . وتم تشخيص المركب الأخير باستخدام مطيافية فوق البنفسجية وتحت الحمراء والرنين النووي المغناطيسي للبروتون والكربون 13 . وجد أن المركب سز بس (نيتروزو بنزل) يتحلل ضوئيا باستخدام المصباح الزئبقي في الحالة السائلة إلى النيترون (ن-اوكسايد) ، تم عزله وتشخيصه .

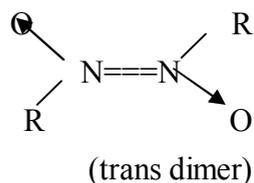
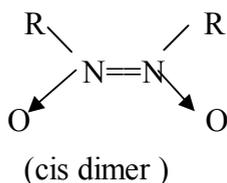
Introduction

Solution of many organic nitroso compounds (R-NO) in organic solvent ,where the NO group is bonded to a carbon atom (C- nitroso compound) , display blue or blue green colours ,due to a weak absorption band in the visible region ($\lambda = 700\text{nm}$)in the crystalline state ,however, most of these compounds are colourless or at most pale yellow . The colour intensity of a solution of c-nitroso compounds depends on the nature of the organic group (R), temperature and concentration [Luttke etal 1994]. The

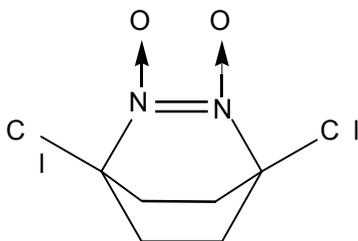
reason of phenomena based on cryoscopic molecular weight measurements .Faintly coloured (R-NO) solution contain significant proportion of dimeric molecules in equilibrium with monomers[Gowenlock 1998].



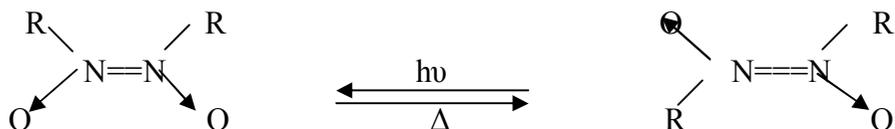
Conclusion that the colourless crystals of c-nitroso compounds were exclusively built from dimeric units .His assumption was verified by two x-ray structure determination and vibrational spectroscopy .The x-ray studies showed that in the dimers the nitrogen atoms of the two R-NO subunits were bonded directly together. The observed NN distance 1.31°A indicates a certain degree of double bond character, when compared to the NN distance in hydrazine (1.447°A) and in azo methane (1.247°A) respectively. The dimers may therefore be characterized as azodioxy compounds or more correctly as diazene 1, 2 dioxides, such compound should in principle exist in two stereoisomeric forms [Gowenlock 1997]:-



Some dimers are exist in cyclic configuration especially the cis dimer as of 1,4-dichloro-1,4-dinitroso which are limited for stieric reason to internal dimerization of the nitroso groups in the cis configuration [Gowenlock etal1998].



In general trans dimers are converted to cis dimer by ultra violet irradiation while heat isomerizes the cis dimer converted to trans dimers [Gowenlock et al 1997].



Although internal nitroso group have been a little spectroscopies [Smith et al 1981] information compare to the external nitroso group { monomer and dimer (cis , trans) }, In this paper, we have prepare and study (UV, IR , NMR) and photolysis cis bis (nitroso benzil) .

The generally favored preparative cis bis (nitroso benzil) involving the condensation with hydroxyl amine to give oxime following by converted to the dinitro , reduction the final in ammonium chloride with zinc , resulting pale white crystalline obtained 36% yielded for this reaction ($R_f=0.24$) .There is no evidence for any occurrence of monomerization and oxime in this reaction .

Recent spectral evidence on some substituted aromatic c-nitroso compound has yielded information on the effect of substitution dimmer [Fletcher et al 1997] .The ground and excited electronic states for both monomer and dimer were identified from absorption spectra. It is of interest to determine were especially the nature of the bonding forces in the dimer and to gain further insight into the rate of monomer formation.

The photolysis of c-nitroso compound overlaps extensively with those of nitro compound since they are intermediates in photo reduction as will as photo rearrangement process. C-nitroso compound are also intermediate in certain photo reaction of nitriles, nitrosoamine, and nitrosoamide.

Photolysis of cis bis (nitroso benzil) in 400 watt as a source irradiating, the resulting expected was N-oxide details by TLC and identification it by UV and IR.

Experimental

1- Spectrophotometric measurement :-

^1H NMR spectra were recorded on a Varian VXR spectrometer; 300 MHz for proton and 75 MHz for carbon, in CDCl_3 in University of Exeter (UK) , infrared spectra were recorded on Shimadzu FT.IR model 8400, Ultraviolet spectra were recorded on a pye unicam SP8-100S spectrometer , CHN analysis were carried out on Shimadzu 8011 (Syria).

2- Preparation of Cis Bis (nitroso benzil) :-

i) Preparation of dioxime compound:-

Dissolve (0.7gm 0.02 mole) of hydroxylamine hydrochloride and 4gm of crystallized sodium acetate in 10ml of water in a small flask, warm the solution to about 40°C and added (2.1gm,0.01 mole) of benzil. Stopper the vessel securely with a cork and shake vigorously for a few minutes: the dioxime soon separates as a crystalline solid, cool in ice, and filtration and wash with a little cold water .Recrystallise from light petroleum mp 236 deco. (lit [Brady 1967] 238 d^o).

ii) Preparation of dinitro compound :-

Fuming nitric acid (30 ml) was added cautiously during (10 min) to a stirred solution of (2.4gm,0.01mole)in ethanol ,the temperature was then allowed to rise slowly for (30 min) and maintained at 15°C for a further (30 min) . Stirring being contained throughout. The mixture was dilute with water, extracted with ethanol and then dried, the resulting crystalline yellow needles mp 210-212 $^\circ\text{C}$. UV absorption in ethanol λ_{max} 240; Infrared of CH) 3007, (C=C) 1442, (N-O) 1141 cm^{-1} .

iii) Preparation of Cis Bis (nitroso benzil)

Dinitro benzil (2.6gm ,0.01mole) and ammonium chloride (1.3gm ,0.02mole) were added to 100ml of ethanol and 10ml of water , while the mixture was stirred , freshly activated zinc dust (10.2gm) was added over 5min (the temperature rose to 40°C) .After 25min the solution was filtered to give cis azodioxide as tan crystals (mp 116-118 $^\circ\text{C}$) CHN analyzer Calc. for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$; C,70.123 H , 5.102 N , 11.670 found C, 69.320 H ,4.822 N , 11.221 ; Ultraviolet absorption in CH_3Cl λ_{max} 285 and 248

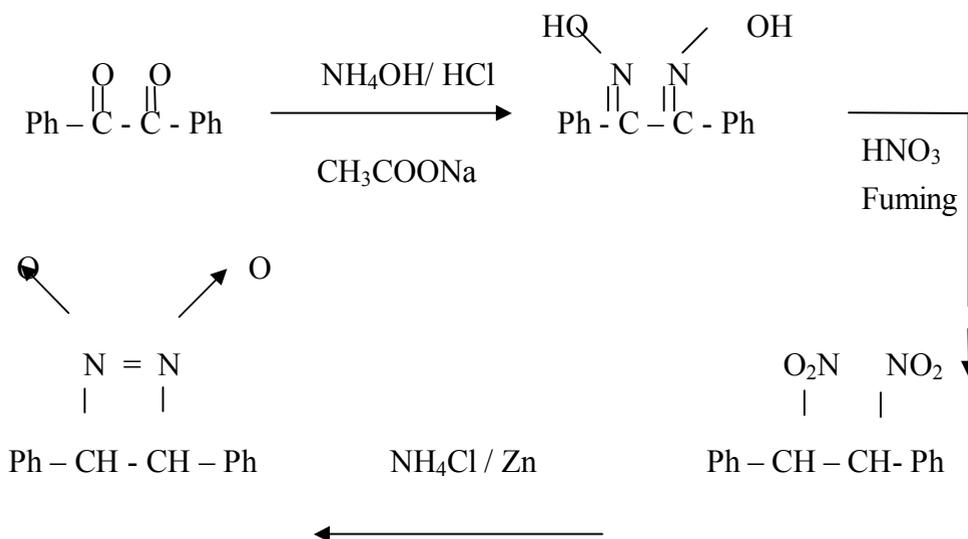
nm ; Infrared absorption 3013 (CH) ,1573(C=C) ,1345(N=O) , 1097(C-N),(N-N)1010 . ¹HNMR in CDCl₃ δ_H 2.1m (1H), 7.9s (5H). ¹³CNMR in CDCl₃ δ_C(ppm) 138C₁, 127 C₂ , 129C₃ , 128 C₄ , 85 C₅ .

Photolysis of Cis Bis (nitroso benzil)

Irradiate 2gm of crystalline nitroso compound in chloroform at room temperature for 6 hour, in pyrex tube with 400 W mercury lump located within and immersion thimble within in appropriate reaction vessel. Irradiation gave oily compound washed with light petroleum ether and filtered to gave (mp 60-62), UV absorption of this compound (in CH₃Cl λ_{max} 240nm) , IR absorption (CH)3043,(C=C)1446,(C=N) 1620 , (N-O) 1313,(C-N)1137cm⁻¹ .

Result and Discussion

Synthesis of cis bis (nitroso benzil) was shown in scheme (1):-



Scheme (1)

The method of preparation oxime has been known from years ago [Brady 1967] [Vogel 1974], it was developed after obtaining poor yields with sodium acetate sequence in the diketone it was interest to compare the one group of ketone. The over all yields of which from the oxime were 86% by using this method.

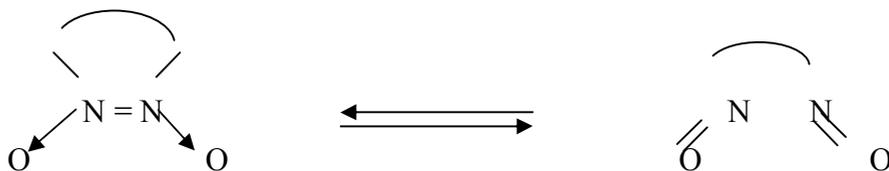
The nitration of oxime was carry out from by slow addition with stirring of purified fuming nitric acid to a solution of the dioxime .The product was dinitro compound ,in yield 45% .When using nitrous acid (HNO_2) during the nitration of oxime would lead to regeneration of the diketone.

There is no evidence of occurrences of substituted on aromatic ring in literatures [Cheronis, 1990] [Chow, 1996] [Al-Shamkhani, 2000], because this compound very sensitive of light in solid state or solution and conversation to hydroxylamine derivatives.

To avoid formation any side product during preparing azodioxide, the addition of active zinc powder to the reaction of mixture drop wise to complete reduction. When addition it directly, the chloride of hydroxylamine was formed as a salt which was dissolved in water.

This compound is not isomersied neither by aqueous 1N sodium hydroxide nor 1N hydrochloric acid although acidic and basic media are reported to accelerate the isomerism secondary nitroso compounds, to oximes. Insolubility of the dimer in aqueous media may partly account for the solubility.

This dimer are a white crystalline solids dissolve in ethanol ,chloroform ,methylene chloride solvents to give nearly colourless solution developed green-blue colour, the solution losses its colour when cooling , indicating that these solids are dimers in solution dissociated to there monomer from by heating .



The existence of compound in solid or solution was proved by the studying it by electronic and infra red spectra. The electronic absorption were recorded in chloroform at room temperature (25⁰C) show that these compound exhibits two (π - π^*) bands. The transition bands ascribable to the dimer grouping (N₂O₄), and the other transition ascribable to the double bond of the aryl residual. There is no trace of monomeric (n - π^*) band. The analyses of the (π - π^*) transition relieved that a comparison between the electronic configuration of the monomers and that of dimers suggest that dimerization process required organization of electron distribution in the R-NO subunit. An experimental evidence , indicating that this indeed happens .The colour of monomers in solution might due to a weak (n - π^*) transition which involve electron lone pair predominating localized on the nitrogen atom , this (n - π^*) transition disappears when the nitrogen lone pair in the monomer was used to form the (N-N) bond on dimerization considering the nitroso monomer has two electron , and then the dimer accommodates six electrons ,it is obvious that during the dimerization to a (N-N) σ bond and to occupancy in the π electron system of the dimer .

Infrared spectra recorded at room temperature, many workers [Al-Shamkhani, 2000][Al-Shamkhani, 2002] were assigned (N-O) stretching frequency in trans and cis nitroso dimers compound, the range of (1380-1420cm⁻¹) exist in cis form has a strong double bond, but the trans and a same have (N-O) stretching frequencies corresponding to a strong infrared absorption in the region, the assignment of IR spectra are based on CNONOC grouping of this dimer dependable on a group theory.

The spectra indicate the strong bands above 900 cm⁻¹ in these have been sorted into five bands which are believed to be corresponded to five vibrations characteristic of the skeleton, though it is possible that some features of the aryl group have been included. The basic skeleton has C_{2v} symmetry; the A₁ class included the (N-O) and(C-N) starching modes and the (N-N) stretching mode, the stretching frequencies for this band at 1345, 1097, 1010 cm⁻¹ respectively shown that in KBr disk. Also the B₁ class with the symmetric (N-O) and(C-N) stretching contain infrared active

vibration .The trans dimmer skeleton has essentially C_{2h} symmetry and two B_2 class skeleton frequencies are existed to lie 900 cm^{-1} and absorb strongly in the infra red region, they may be considered as essentially antisymmetric (N-O) and(C-N) stretching vibration, the (N-O) bands which may have partial double bond character and are strongly polar.

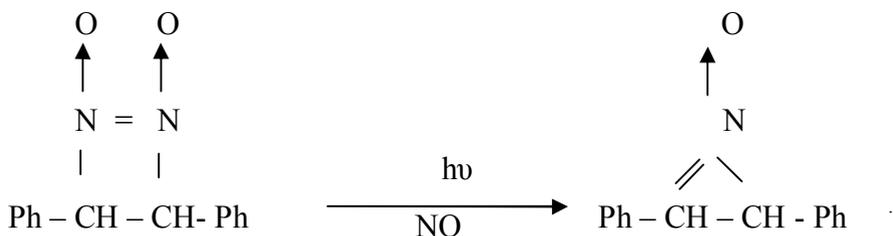
Proton resonance signals , spin-spin coupling constant are used to determine the nitroso groups conformation , in particular those attach to the near atoms , the nitroso groups adopts cis arrangement due to small spin-spin coupling which is reaches 5.3 Hz .

The ^1H NMR in CDCl_3 solvent appear spectra two resonance signals in addition to resonance signal of CDCl_3 solvent which using in technique , the signals of aromatic ring were interaction owing the proton which were analogues in chemical environmental.

^{13}C NMR spectra of the cis compound, five lines were shown in Fig (5), these lines were cause by the four carbon atoms of the aromatic ring in addition of one line for carbon atom attach with nitroso group in addition to three lines for CDCl_3 using in this technique.

This spectroscopy has yielded interesting structural information of c-nitroso compound , the large difference between the resonance for C-NO and C-N₂O₄-C clearly permits an estimate to be made for any participation of monomeric NO end groups in the solid[Fletcher etal 1995][Anderson etal 1994] .

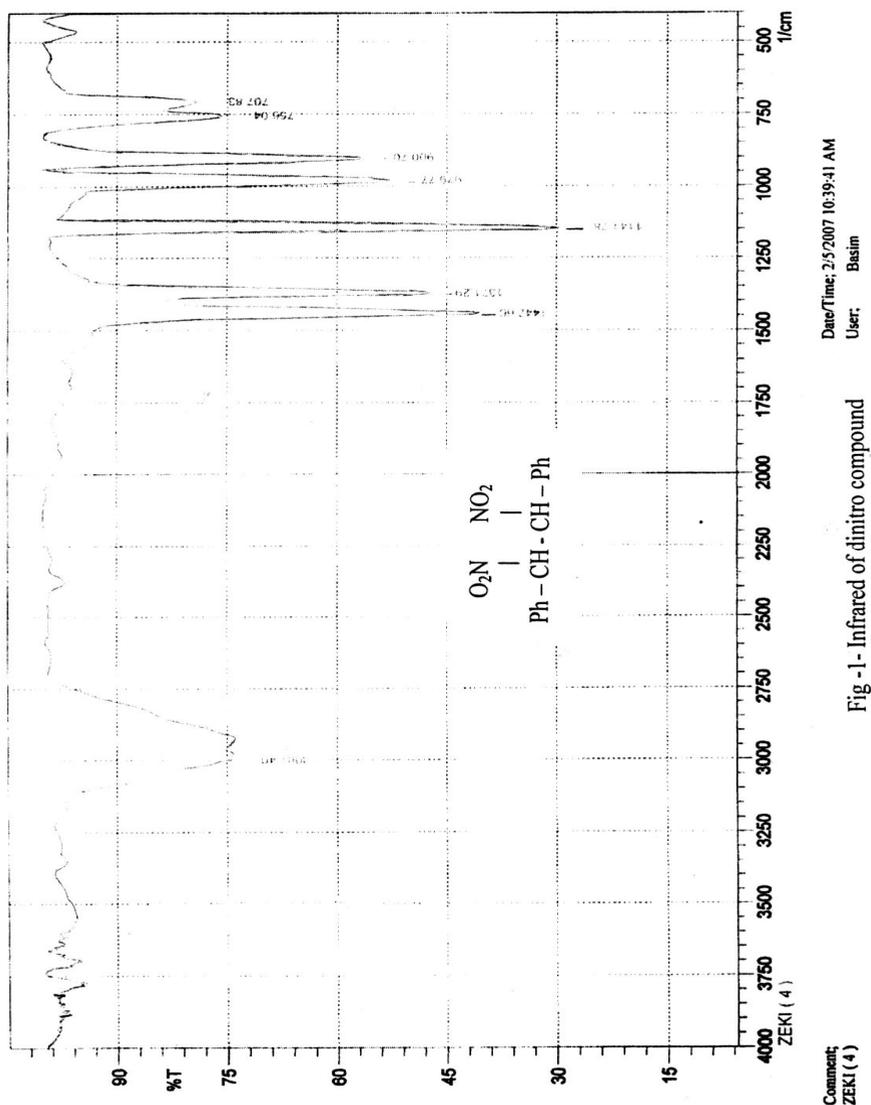
Photo addition mechanism suggests that cleavage of (N-N) bond formation the N-oxide and NO radical as shown in scheme (2):-

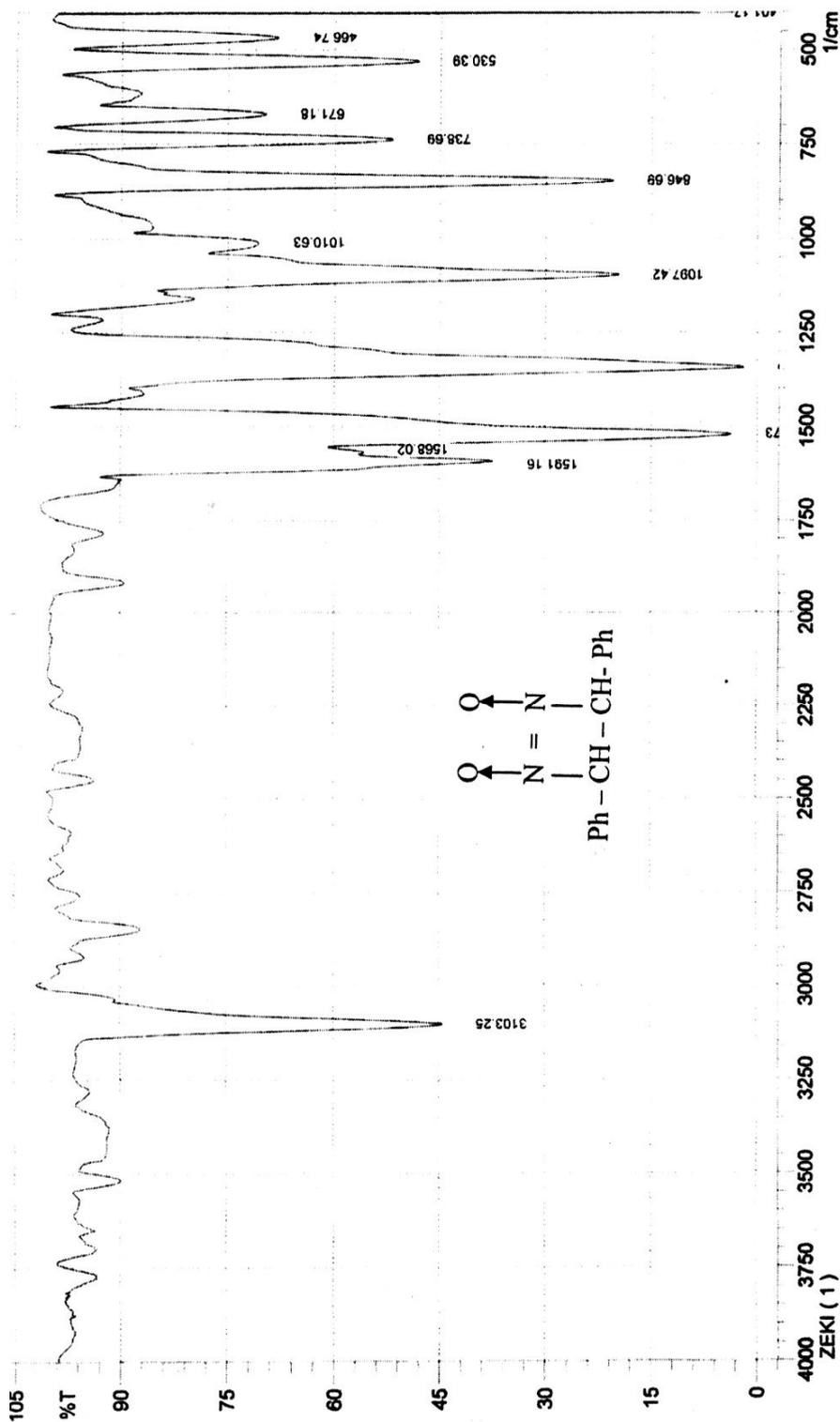


Scheme (2)

N-oxide compound was isolated as oily, it was very stable, purified by using ethanol. The radiation gave yield 65% .The other resulting (NO radical) is unstable and disappear thought the irradiation because the half life very small, approximately $(0.1 \times 10^{-5} \text{ sec})$.

The most important reaction for the nitroso was their ability to donate electrons, since the nitroso groups generally have low oxidation potentials; the donor ability was further enhanced by photoexcitation, the chemical consequence of this single electron transfer nitroso radical.





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Fig -2- Infrared of cis dimer compound

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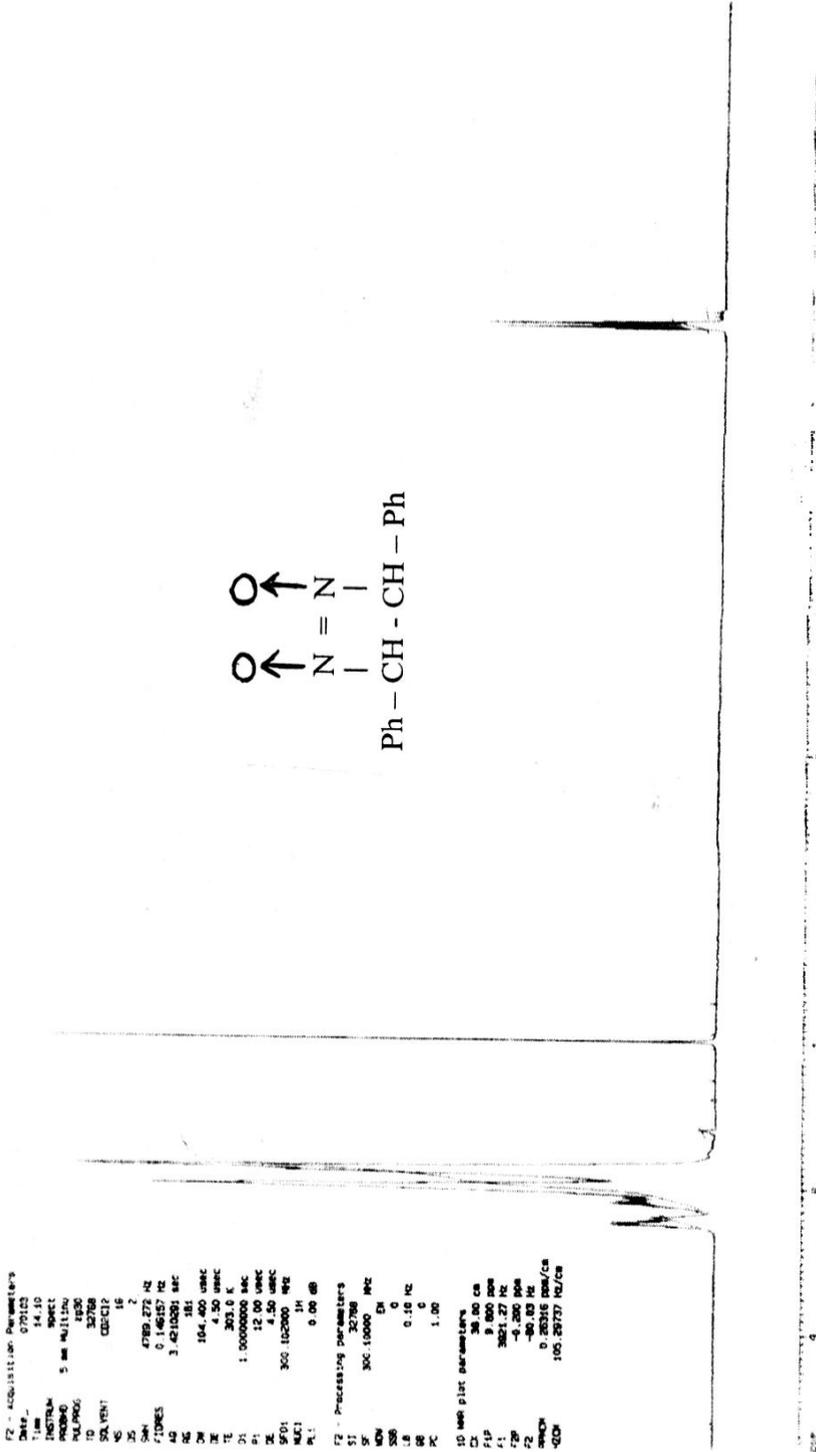


Fig -3- ¹H NMR of cis dimer compound

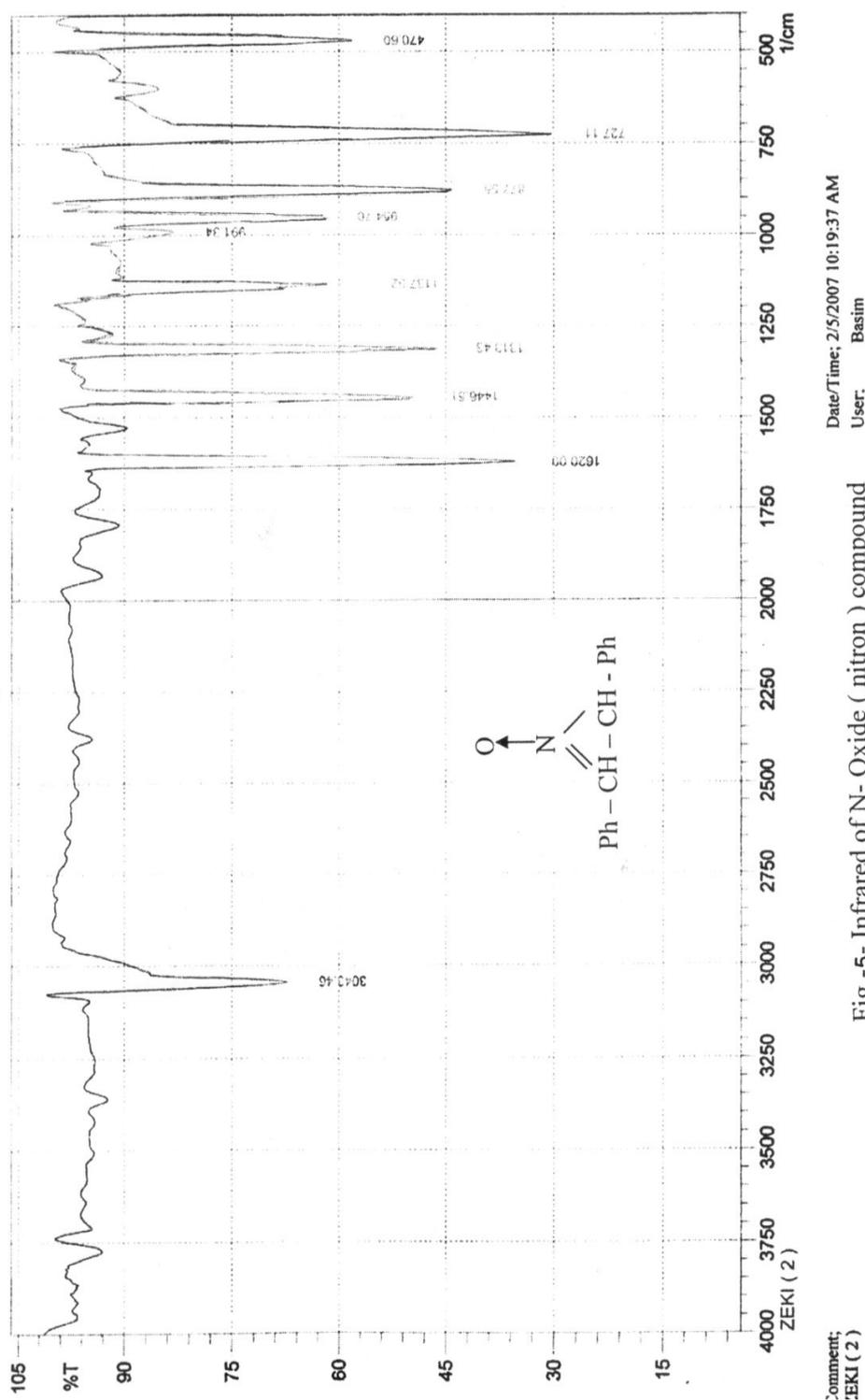


Fig -5- Infrared of N-Oxide (nitron) compound

References

- Al-Shamkhani, Z.A.N.,(2000) {Synthesis, Conformation, and Configuration of Norbona-5-ene Nitrosite}. *Basrah, J. Researches*, **38**, 81.
- Al-Shamkhani, Z. A. N., Mejeed N. N. and Al-Mowali A. H.,(2000) {An ESR Study of The Aminoxyl Radicals Generated by U.V. Irradiation of Some Dimeric Nitrosite }. *Basrah ,J. Science*, **18**,19 .
- Al-Shamkhani, Z.A.N., M.Sc. Thesis, University of Basrah, (2000). {Synthesis, Conformation, Configuration and Photolysis of Some Nitroso Compounds}
- Anderson, L., Boyed A.S., Cameron M., Gowenlock B.G., Higginson C.M., McEwen I.J. and Smith J.P.,(1994) { Properties and Spectroscopic Studies of Substituted 1,4-Dinitroso Benzenes}. *J Chem. Research(S)*, 245.
- Brady, J. D. and Muers S. F. ;(1967) {Study and Preparation of Benzil Glyoxime}. *J. Chem., Soc.*, 220.
- Cheronis, N. D. and Enttrikin J. B.(1990) "Identification of Organic Compound", New York 4th ed. 146.
- Chow, Y. L. and Ho T. I., (1996) "The Chemistry of Amino Nitroso, Nitro and related groups", Ed. By S. Patia, New York 2, 747.
- Fletcher, D. A. , Gowenlock B. G. and Orell K. G.,(1997){ Structural Investigation of C-Nitroso Benzenes}. *J. Chem. Soc. Perkin Trans 2*, 2201.
- Fletcher, D., Gowenlock B.G., Orrell K. G., and Sik V., (1995) {Dynamic NMR Study of the Factor Governing Nitroso Group Rotation in P-Nitroso Anilines in the Solution and Solid State}. *Mag.Reso.Chem.*, **35**, 569.
- Gowenlock, B.G. and Batt L.;(1998) {the Isomerisation of Nitroso Methane to Formaldoxime}. *J of Molecular Structure (Theo Chem.)* **454**,103.
- Gowenlock, B. G. and Mc Cullough K. J.;(1997) {The Crystal Structure of (e)-1,2-Bis (1,1-Dimethyl-2-Oxopropyl Diaz-1-ene-1,2 Dilum-1,2-Diolate}. *J. Chem. Res. (M)*; 220 .

- Gowenlock, B. G. and Mc Cullough K. J.:(1997) {The Crystal Structure of (e)-1,2-Bis (1,1-Dimethyl-2-Oxopropyl Diaz-1-ene-1,2 Dilum-1,2-Diolate }.J.Chem.Res.(S),1801 .
- Gowenlock, B. G., B . King, Pfab J. and Wittnowsk M. i;(1998) {Kinetic Studies of the Reaction of Some Nitroso Alkane with Nitrogen Dioxide}. J. Chem. Soc. Perkin Trans 2, 483.
- Gowenlock, B. G., Pfab J. and Young V. M.:(1997) {the Photolysis of Some N-Nitroso and N-Nitroso Anilines in Solution}. J. Chem. Soc. Perkin Trans 2, 915.
- Luttke, W. Skancke P. N. and Teretteberg M. ;(1994) {On the Dimerization Process of Nitroso Compound}. Theo Chemica Acta **87**,321.
- Smith, M.A., Weinstein B. and Green F. D.:(1981) {Synthesis and Properties of Bis O-Nitroso Benzyl}. J.Org. Chem. **45**, 4597.
- Vogel's "Text book of Practical Organic Chemistry" 3rd ed. Longman Inc. New York 1974, 45.

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