



ISSN: 0067-2904

Synthesis and Characterization of New Azo Compounds Linked to 1, 8-Naphthalimide and Studying Their Ability as Acid-Base Indicators

Suaad M.H. Al-Majidi, Mohammed G.A Al-Khuzai*

Department of Chemistry, College of Science, Baghdad University, Baghdad, Iraq

Received: 14 /5/ 2019 Accepted: 18/ 6/2019

Abstract

New Azo compounds containing an 1,8-naphthalimide moiety were synthesized from 1, 8-naphthalic anhydride by a reaction with *p*-phenylenediamine or benzidine to produce 1,8-naphthalimide derivatives (1 or 2), which were converted to diazonium salt derivatives by using sodium nitrite and acetic acid at 0-5 °C. The diazonium salt was subjected to a coupling reaction with different substituted phenol in alkaline media at 0-5 °C to produce azo compound derivatives (3-14).

The New Azo compound derivatives (3-14) were identified by ¹H-NMR, ¹³C-NMR, and FTIR and by measuring characteristic physical properties and specific reactions. Also, the ability of the prepared azo compounds to work as acid-base indicator was investigated, since azo dyes have different and sharp colors in acidic or basic solutions.

Keywords: 1, 8-naphthalic anhydride, Azo compound, Acid-base indicators.

تحضير و تشخيص مركبات أزو جديدة مرتبطة بـ 1,8-نفثال إيميد و دراسة قابليتها كدلائل حامض-قاعدة

سعاد محمد حسين الماجدي، محمد غانم عباس الخزاعي*

قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

تم تحضير مركبات أزو جديدة تحتوي على وحدة 1,8-نفثال إيميد. من تفاعل 1,8-نفثالك انهدريد مع بارافينيلين داي امين او بنزدين لتعطي مشتقات نفثال إيميد (1 او 2) التي تم تحويلها الى مشتقات ملح الديازونيوم بواسطة معاملتها مع حامض الخليك و نترتيت الصوديوم. بعد ذلك، خضعت املاح الديازونيوم الى تفاعل ازدواج مع فينولات مختلفة في وسط قاعدي و بدرجة حرارة (0-5)°C لتنتج مشتقات مركبات الأزو (3-14).

تم تشخيص مركبات الأزو (3-14) الجديدة بواسطة [FTIR، ¹HNMR و ¹³CNMR] و قياس بعض خواصها الفيزيائية المميزة و التفاعلات الخاصة. كذلك تمت دراسة قابلية مركبات الأزو المحضرة للعمل كدلائل حامض-قاعدة لامتلاكها اللون واضحة و مختلفة في الاوساط الحامضية و القاعدية.

Introduction

pH indicators or acid-base indicators are halo chromic weak acids or bases which change their structures upon the pH change in solution. Such indicators should be stable and not interfere with the solution components, sensitive, preferably selective and occasionally specific, and undergo some marked and sharp visual changes such as color, fluorescence, luminescence or turbidity at the lowest

*Email: mgabbas89@gmail.com

concentration as possible. When used as a dilute solution, a pH indicator does not have a significant impact on the acidity or alkalinity of a chemical solution [1, 2]. Many of indicators occur naturally. For example, the anthocyanins found in flowers and vegetables are pH indicators. Litmus is a natural pH indicator derived from a mixture of lichens [3]. Some of the azo compounds have two tautomeric forms such as methyl orange and methyl red, each one has a different color and can be transformed from one form to another depending on the pH level of the environment, hence, they are used as pH-indicator. For example, Methyl red is red at pH below 4.4, yellow at pH over 6.2, and orange in between [1]. This property is very useful to detect the pH-level and was used extensively by researchers in various fields; it is employed in biological research to determine the acidity of the living media [4] and in analytical chemistry to detect the end point in acid-base titration.[5] Furthermore, azo compounds were studied extensively because of their excellent thermal and optical properties in applications such as optical recording medium, inkjet printing [6], oil-soluble light fast dyes [7], organic photoconductors[8] and molecular memory storage [9].

In addition, 1,8-Naphthalimide derivatives have unique properties such as excellent absorptions, large absorption coefficient, high fluorescence quantum yield, large Stoke's shift, sensitivity to solvent polarities, high stability, and being easy to modify structures [10]. 1,8-Naphthalimide derivatives are widely used as fluorescent pH-sensors, metal cations (Hg^{2+} , Zn^{2+} , Cu^{2+} , Ag^+ , Cd^{2+} , Pd^{2+} , Cr^{3+} , Al^{3+} , Fe^{3+}) sensors, photo-emitting organic materials, fluorescent dyes, cell imaging probes and bioactive molecules [11-14].

Experimental Instruments and Chemicals

All chemicals used were supplied from BDH, Merck, Fluka and Sigma Aldrich. Melting points were measured using SMP3 melting point apparatus and left uncorrected. FTIR spectra were studied on SHIMADZU FTIR-8400 spectrophotometer by using KBr disc in the 4000-600 cm^{-1} spectrum range. ^1H NMR and ^{13}C NMR spectra were recorded on ECA 500 MHz by using TMS as a reference and DMSO- d_6 as a solvent. TLC was performed for all prepared compounds.

Synthesis of N-[4-amino (phenyl) or((1,1'-biphenyl)-4-yl)]-1,8-naphthalimide 1 & 2 [15]

(5g, 0.025mol) of 1,8-Naphthalic anhydride dissolved in (20ml) DMSO with heating. Then, p-phenylenediamine or benzidine (0.025mol) were added to the reaction mixture and refluxed for 18-22 hrs. The final mixture was poured onto iced water and the solid precipitate was filtered and recrystallized from acetic acid. The physical properties of compounds 1-2 are listed in Table- 1.

Synthesis of N-(4-(sub-Aryldiazenyl)(phenyl or 1,1'biphenyl-4-yl))-1,8-naphthalimide 3-14 [16]

Either compound (**1** or **2**) (0.007 mol) was dissolved in 15 mL of concentrated AcOH and 15 mL of distilled water. The mixture was cooled in an ice bath until reaching 0-5 °C. Then, NaNO_2 solution (0.47g, 0.007mol) was dissolved in 5mL of distilled water (added drop-by-drop to the reaction mixture) and stirred for 10 min. Finally, the mixture was added carefully and very slowly to the solution of different substituted phenols (0.007 mol) dissolved in 60 mL of 10% NaOH at 0-5 °C and stirred for 30 min. The colored product was filtered, washed with cooled distilled water, and dried by hot steam. The physical properties of compounds **3-14** are listed in Table-1.

pH-Indicator test [17]

• **Preparation of Indicator Solution**

In a test tube, 0.004-0.005 gm of compounds **3-14** was dissolved in 10 mL of DMSO. The indicator solution was shaken well until the entire compound was dissolved completely.

• **Titrations**

The following titrations were performed in the presence of 0.5 mL of the indicator solution at room temperature:

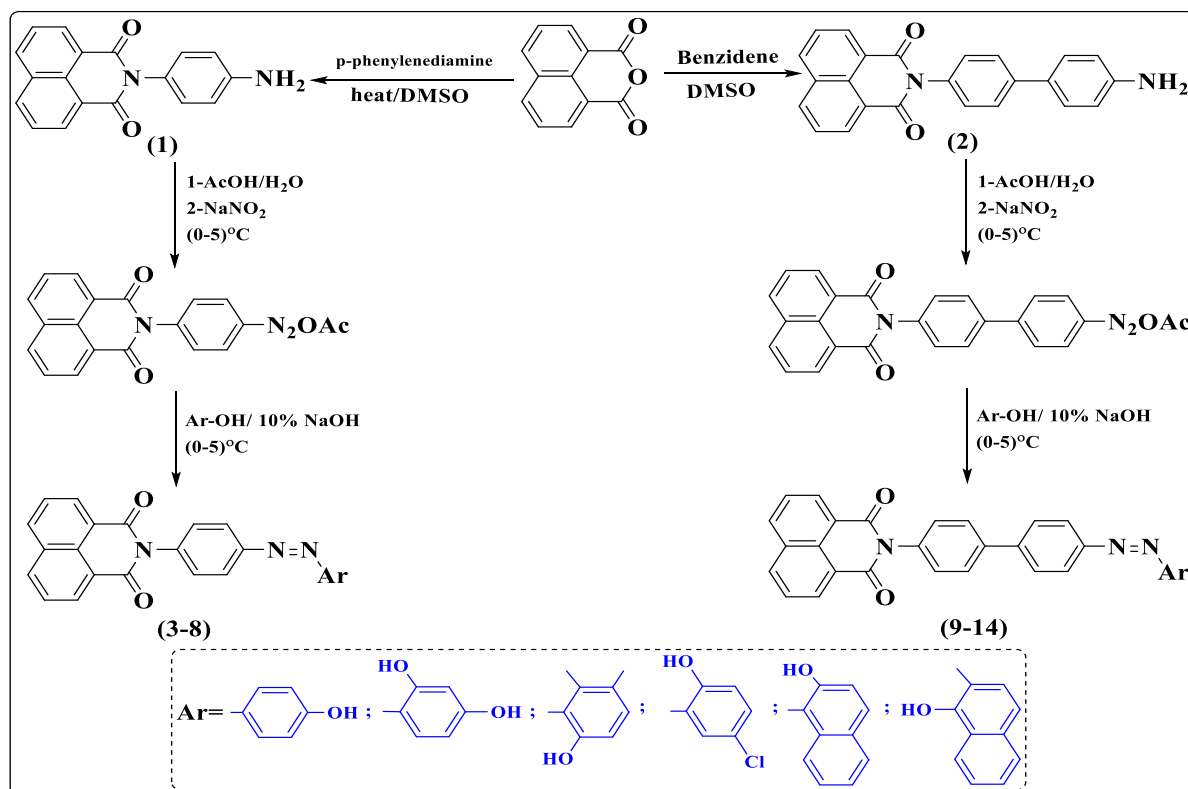
1. 5 mL of 0.1 M of HCl versus 0.1 M of NaOH.
2. 5 mL of 0.1 M of AcOH versus 0.5 M of NaHCO_3 .
3. 5 mL of 0.1 M of HCl versus 0.1 M of NaHCO_3 .
4. 5 mL of 0.1 M of AcOH versus 0.5 M of NaOH.

Table 1-Physical properties and FTIR spectral data of compounds 1-14

No	Compound Structure	Physical properties			Major FTIR Absorptions Cm ⁻¹					
		m.p °C	Color	Yield %	v(O-H)	v(O-H)	v(C-H) Arom.	v(C=O) Imide	v(N=N)	Other bands
1		240-242	Green	76	-	-	3064	1706 1658	-	v(NH ₂) asym. 3433 sym. 3355
2		231-233	Dark brown	72	-	-	3064	1706 1662	-	v(NH ₂) asym. 3413 sym. 3363
3		188-189	Greenish -yellow	86	3396	3242	3064	1703 1656	1465	-
4		180-182	Dark red	91	3384	3355	3064	1706 1660	1471	-
5		173-174	Yellow	96	3417	3326	3070	1708 1668	1463	v(C-H) alph 2958 2920
6		180-181	Green	79	3421	3174	3070	1706 1668	1483	v(C-Cl) 1024
7		131-133	Red	94	3415	3274	3056	1703 1656	1481	-
8		120-122	Red	92	3365	3213	3053	1703 1662	1461	-
9		166-167	Yellow	88	3357	3178	3043	1706 1662	1463	-
10		110-112	Dark red	93	3379	3267	3066	1704 1668	1496	-
11		133-134	Red	97	3379	3278	3060	1706 1666	1461	v(C-H) alph. 2956 2925
12		122-123	Brown	76	3434	3280	3072	1706 1668	1494	v(C-Cl) 1190
13		115-117	Violet	95	3423	3269	3055	1706 1658	1448	-
14		108-110	Dark red	90	3415	3261	3062	1704 1664	1458	-

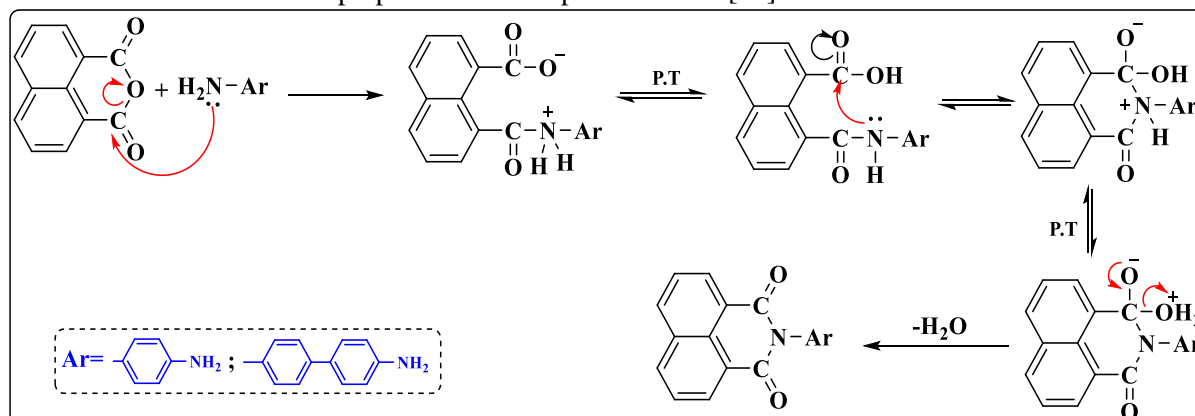
Results and Discussions

The synthetic sequences for the preparation of the new derivatives of 1,8-naphthalimide moieties are as in scheme 1.



Scheme 1

Compounds 1 & 2 were prepared via cyclic condensation reaction of 1,8-Naphthalic anhydride with *p*-Phenylenediamine or benzidine in DMSO as a solvent. Scheme 2 represents the cyclic condensation mechanism of preparation of compounds 1 & 2 [18].



Scheme 2

The FTIR spectrum confirmed the formation of compounds 1 & 2 by the presence of $\nu(\text{N-H}_2)$ bands at 3438 cm^{-1} asym., 3355 cm^{-1} sym. and the occurrence of a red shift on the $\nu(\text{C=O})$ absorption bands to asym. 1706 cm^{-1} , sym., 1658 cm^{-1} , while other absorption bands appeared at 3064 cm^{-1} and 1602 , 1585 cm^{-1} due to $\nu(\text{C-H})$ aromatic and $\nu(\text{C=C})$ aromatic, respectively. [19]. All details of FTIR spectral data of compounds 1 & 2 are listed in Table-1.

$^1\text{H-NMR}$ spectrum of compound 1 showed a singlet signal of ($-\text{NH}_2$) protons at $\delta = 5.28\text{ ppm}$ and multi signals aromatic protons at $\delta = 6.95\text{--}8.56\text{ ppm}$, as shown in Table-2 and Figure-1. The $^{13}\text{C-NMR}$ spectrum data of compound 1 are demonstrated in Table-3 and Figure-2.

The $^1\text{H-NMR}$ spectrum of compound 2 showed a singlet signal of ($-\text{NH}_2$) protons at $\delta= 5.31$ ppm and multiple signals of aromatic protons at $\delta= 6.58-8.51$ ppm (Table-2, Figure-3). The $^{13}\text{C-NMR}$ spectrum data of compound 2 are shown in Table- 3 and Figure-4.

Table 2- $^1\text{H-NMR}$ spectral data of compounds 1 & 2

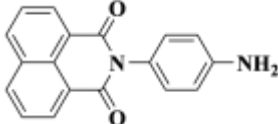
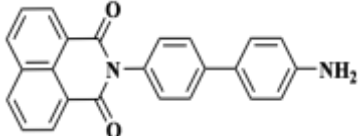
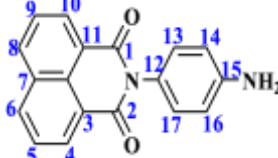
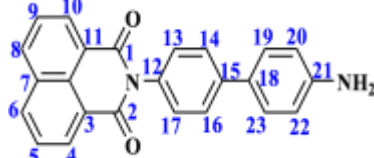
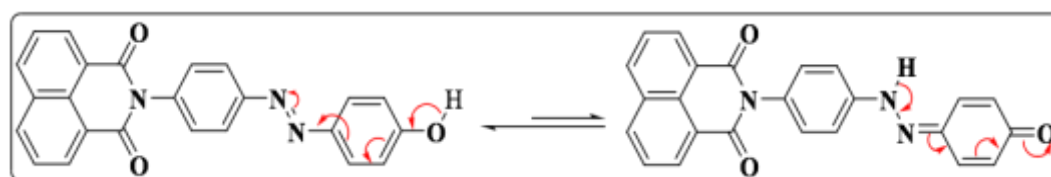
No.	Structure	$^1\text{H-NMR}$ Spectral data($^{\circ}\text{ppm}$)
1		5.28 (S,2H, NH_2); 6.95-8.49 (m,10H,Ar-H)
2		5.31 (S,2H, NH_2); 6.58-8.51 (m,14H, Ar-H)

Table 3- $^{13}\text{C-NMR}$ spectral data of compounds 1 & 2

No.	Structure	$^{13}\text{C-NMR}$ spectral data($^{\circ}\text{ppm}$)
1		114.15-148.99 ($\text{C}_3\text{-C}_{17}$); 164.20 (C_1, C_2)
2		114.15-148.99 ($\text{C}_3\text{-C}_{23}$); 164.16 (C_1, C_2)

Azo dyes 3-14 were prepared by coupling reactions of diazonium salts of compounds 1 & 2 with different substituted phenols. FTIR spectral data confirmed the formation of azo dyes 3-10 by the appearance of $\nu(\text{OH})$ stretching bands at $\nu(3421-3365)$ cm^{-1} and $\nu(\text{NH})$ stretching bands at $(3355-3174)$ cm^{-1} due to the occurring of a tautomerization process between OH and $\text{N}=\text{N}$ groups, as explained in equation 1 [20]. Also, FTIR spectral data showed the appearance of $\nu(\text{N}=\text{N})$ stretching bands at $1483-1461$ cm^{-1} , while $\nu(\text{NH}_2)$ stretching bands disappeared from the spectrum. In addition, FTIR spectral data included the appearance of $\nu(\text{CH})$ aromatic bands at $3070-3053$ cm^{-1} , $\nu(\text{C}=\text{O})$ absorption bands of imide group at asym.1708-1703, sym.1668-1656 cm^{-1} and $\nu(\text{C}=\text{C})$ aromatic bands at $(1595-1585)$ cm^{-1} . All details of FTIR spectral data of compounds 3-14 are listed in Table-1.



Equation 1

The $^1\text{H-NMR}$ spectrum of compound 4 showed multiple signals of aromatic protons at $\delta= 6.39-8.56$ ppm, a singlet signal of ($-\text{OH}$) protons at $\delta= 10.13$ and 10.63 ppm, and a singlet signal of ($-\text{NH}$)

protons at $\delta = 12.30$ ppm (Table- 2). The chemical shift of the (NH) proton went to the down field due to the effect of the tautomerization process and the intramolecular H-bonding that occur between O atom in ortho position and N atom of azo group to form six membered rings [21]. The ^{13}C -NMR spectrum data of compound 4 are listed in Table-5.

The ^1H -NMR spectrum of compound 7 showed multiple signals of aromatic protons at $\delta = 7.05$ -8.53 ppm, a singlet signal of (-OH) protons at $\delta = 8.95$ ppm, and a singlet signal of (-NH) protons at $\delta = 11.24$ ppm (Table-4). The ^{13}C -NMR spectrum data of compound 7 are listed in Table- 3.

The ^1H -NMR spectrum of compound 11 showed a singlet signal of (-CH₃) protons at $\delta = 3.43$ ppm, multiple signals of aromatic protons at $\delta = 6.71$ -8.46 ppm, a singlet signal of (-OH) protons at $\delta = 10.10$ ppm, and a singlet signal of (-NH) protons at $\delta = 11.39$ ppm (Table-2, Figure-5). The ^{13}C -NMR spectrum data of compound 11 are shown in Table-5 and Figure-6.

Table 4- ^1H -NMR spectral data of compounds 4, 7 & 11

No.	Structure	^1H -NMR Spectral data($^\circ\text{ppm}$)
4		6.39-8.56 (m,13H, Ar-H); 10.13, 10.63 (S,1H, OH); 12.30 (S,1H, NH)
7		7.05-8.53 (m,16, Ar-H); 8.95 (S,1H, OH); 11.24 (S,1H, NH)
11		3.43 (S,3H, CH₃); 6.71-8.46 (m,16H, Ar-H); 10.10 (S,1H, OH); 11.39 (S,1H, NH)

Table 5- ^{13}C -NMR spectral data of compounds 4, 7 & 11

No.	Structure	^{13}C -NMR Spectral data($^\circ\text{ppm}$)
4		123.02-131.89 (C₃-C₂₃); 164.13 (C₁, C₂)
7		123.00-134.92 (C₃-C₂₇); 164.15 (C₁, C₂)
11		20.11 (C₃₀, C₃₁); 122.89-134.86 (C₃-C₂₃); 164.11 (C₁, C₂)

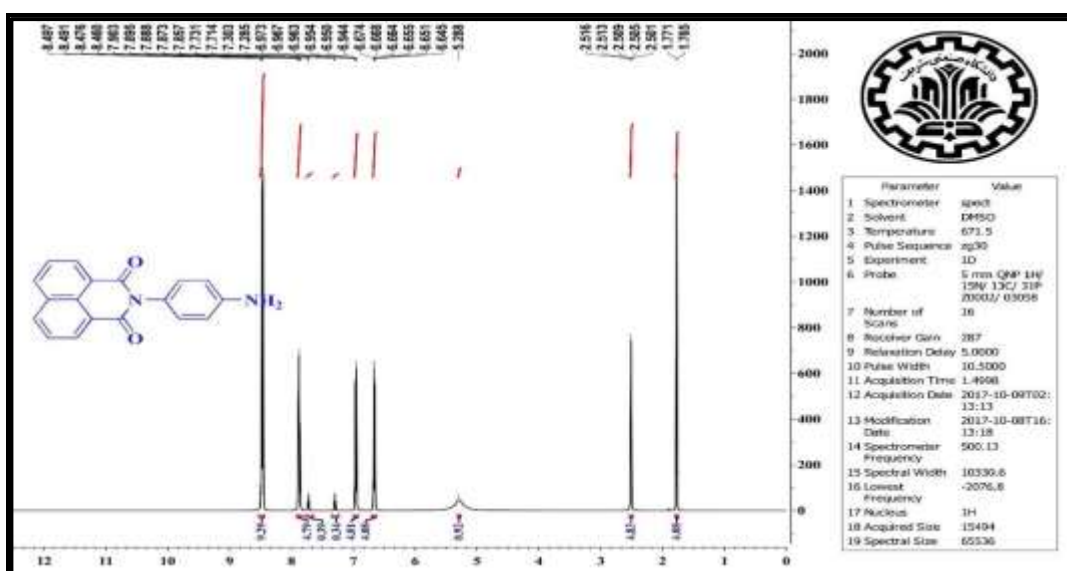


Figure 1-¹H-NMR spectrum of compound 1.

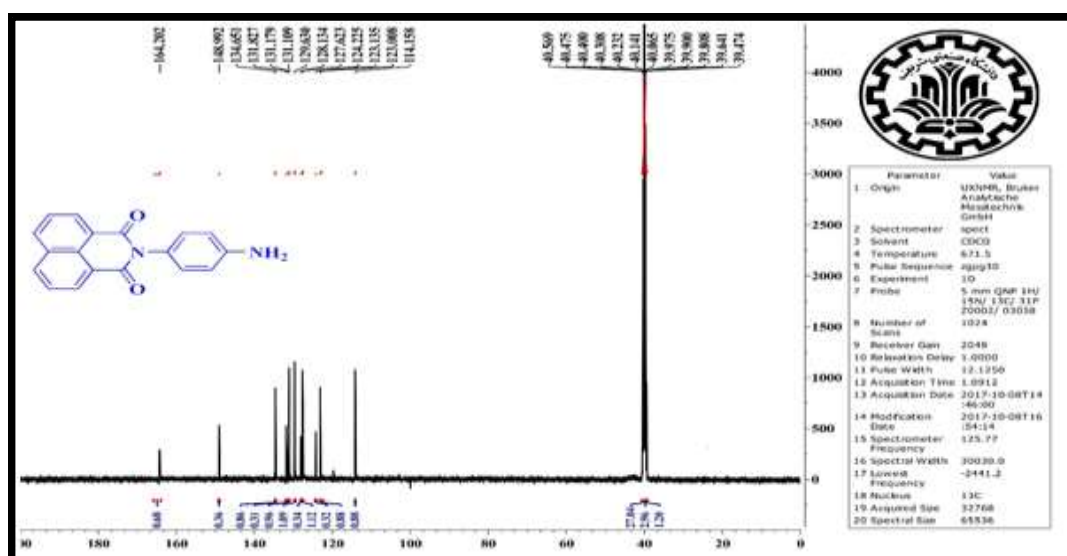


Figure 2-¹³C-NMR spectrum of compound 1.

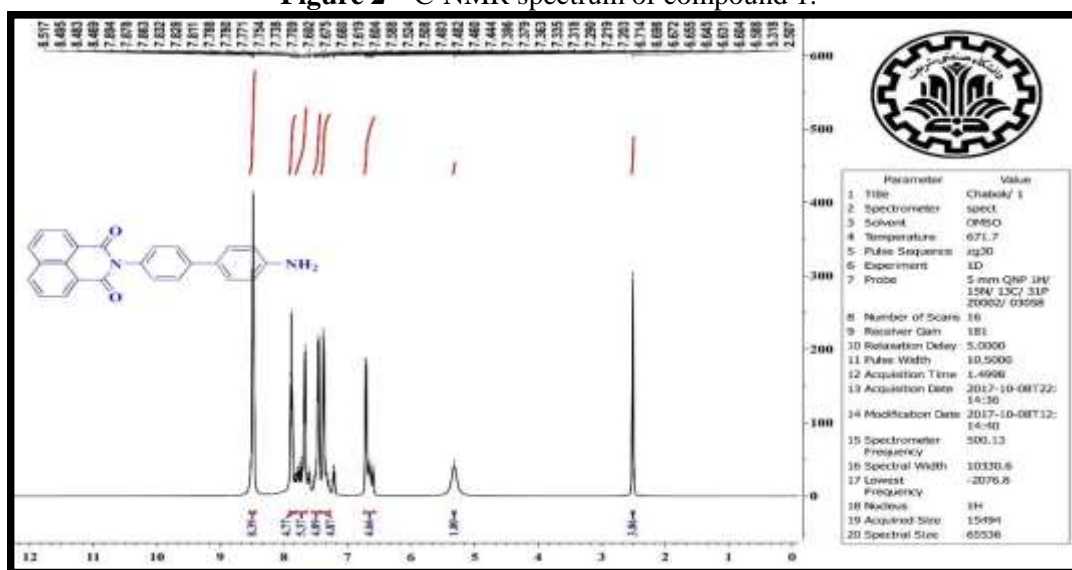
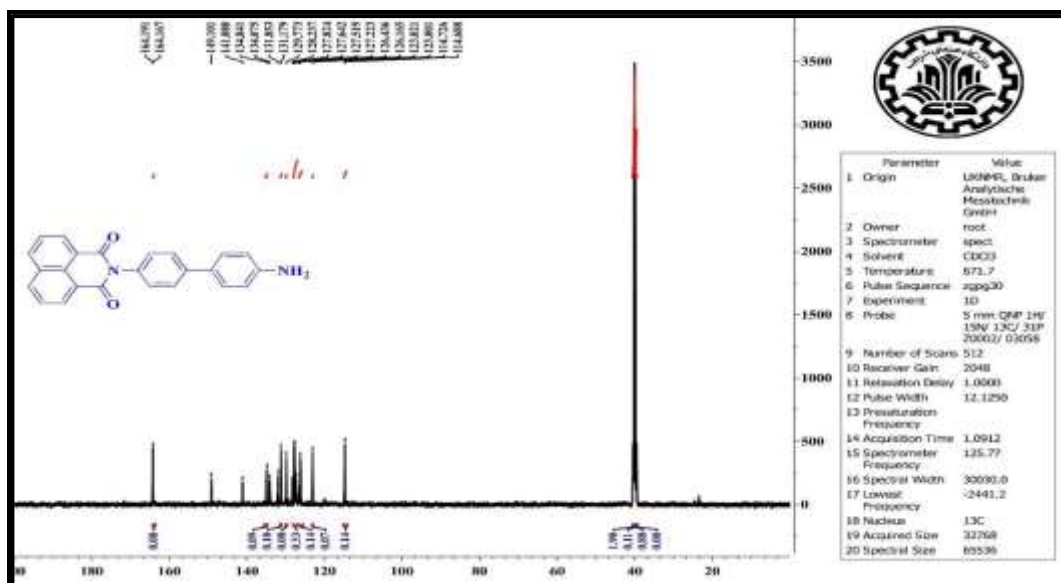
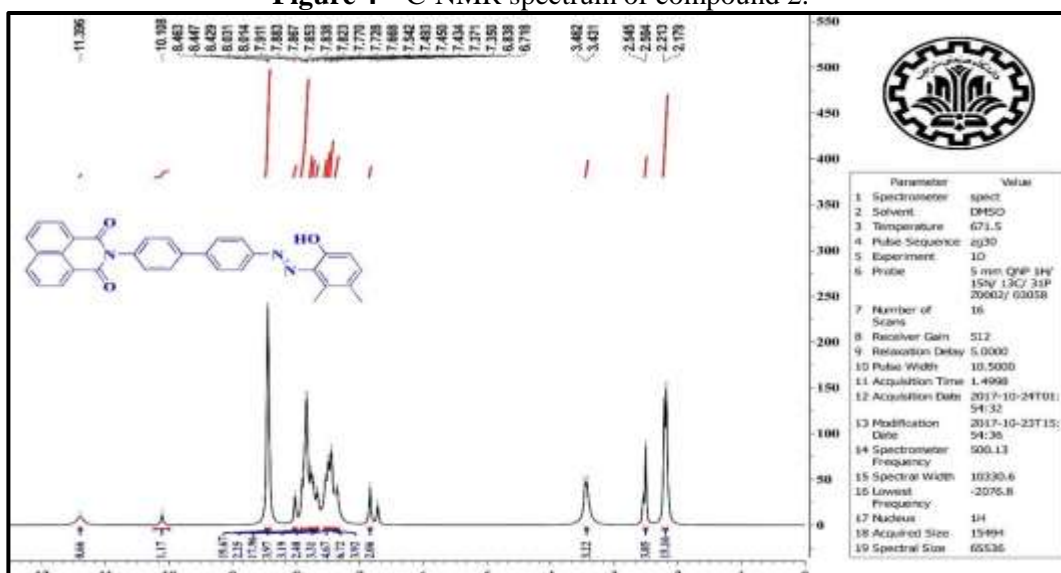
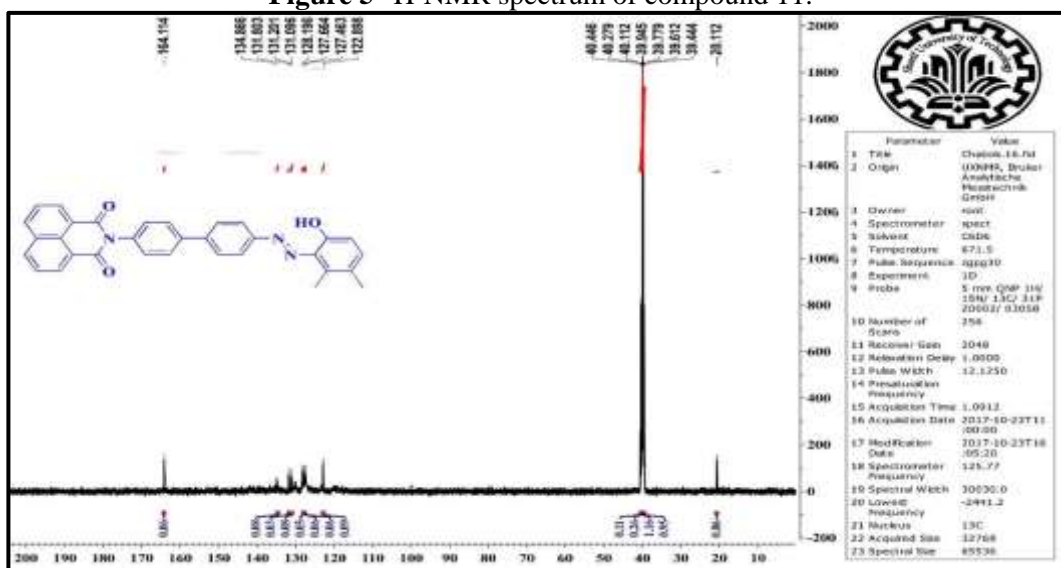


Figure 3-¹H-NMR spectrum of compound 2.

Figure 4- ^{13}C -NMR spectrum of compound 2.Figure 5- ^1H -NMR spectrum of compound 11.Figure 6- ^{13}C -NMR spectrum of compound 11.

Azo dyes (3-14) as acid-base indicators

Acid–base indicators are organic dyes possessing different colors in solutions with varying pH. They are popularly employed to determine the equivalence point in acid-base titrations. They give sharp color change with the change in pH. Azo dyes are the most popular organic compounds that are used as acid-base indicators for their ability to change color as a function of pH [17, 22]. For this reason, this property was investigated in all synthesized Azo dyes (3-14) by using acid-base titrations. All synthesized azo dyes, except compounds 7, 8, 13 & 14, had a stable color in acid and base solutions and showed reversible and sharp color changes when moving from acidic condition to the basic condition or vice versa. All azo compounds determined the end point with a high precision, except compounds 7, 8, 13 & 14, which showed no color change. Tables- 6-9 include titrations data of acid-base reactions that are used to evaluate the indicator property of azo dyes. Figure-7 shows the colors of azo dyes solutions in acid and base conditions.

Table 6-Titration of HCl (0.1M) against NaOH (0.1M)

No	Volume of HCl (ml)	Mean volume of NaOH (ml)	Color in acid	Color in base
3	5	4.8	Light yellow	Bright Yellow
4	5	4.9	Light red	Yellow
5	5	5.2	Yellow	Orange
6	5	4.9	Yellow	Light red
7	5	-	Red	Red
8	5	-	Bright Orange	Bright Orange
9	5	4.9	Light yellow	Orange
10	5	4.8	Red	Orange
11	5	5.1	Yellow	Orange
12	5	4.8	Yellow	Orange
13	5	-	Red	Red
14	5	-	Red	Red

Table 7-Titration of acetic acid (0.1M) against NaOH (0.1M)

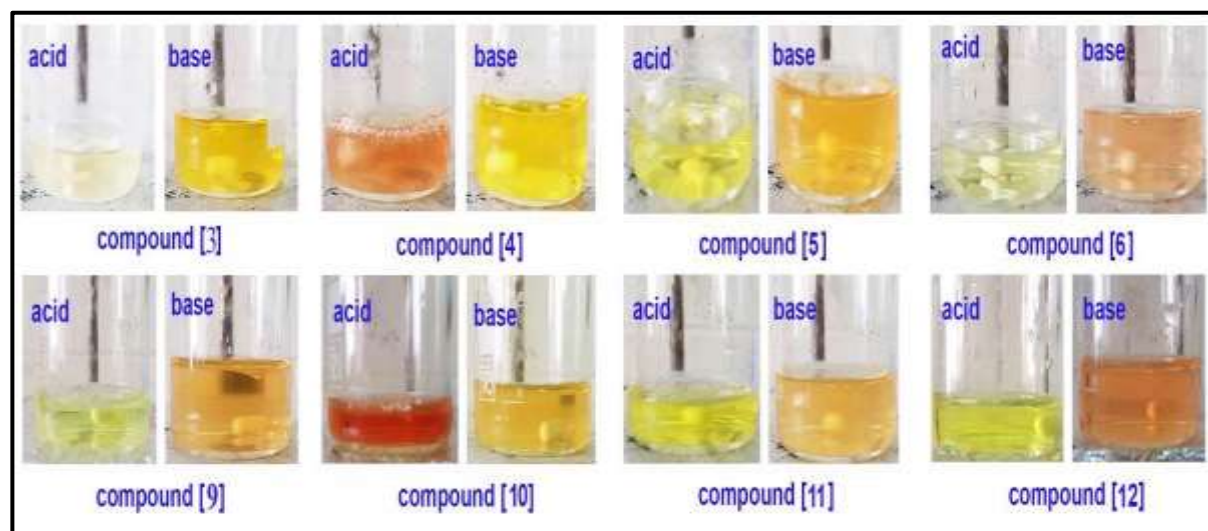
No	Volume of Acetic acid (ml)	Mean volume of NaOH (ml)	Color in acid	Color in base
3	5	4.9	Light yellow	Bright Yellow
4	5	4.9	Light red	Yellow
5	5	5.1	Yellow	Orange
6	5	4.9	Yellow	Light red
7	5	-	Red	Red
8	5	-	Bright Orange	Bright Orange
9	5	4.9	Light yellow	Orange
10	5	4.9	Red	Orange
11	5	5.1	Yellow	Orange
12	5	5.2	Yellow	Orange
13	5	-	Red	Red
14	5	-	Red	Red

Table 8-Titration of HCl (0.1M) against NaHCO₃ (0.1M)

No	Volume of HCl (ml)	Mean volume of NaHCO ₃ (ml)	Color in acid	Color in base
3	5	4.9	Light yellow	Bright Yellow
4	5	4.8	Light red	Yellow
5	5	4.8	Yellow	Orange
6	5	4.9	Yellow	Light red
7	5	-	Red	Red
8	5	-	Bright Orange	Bright Orange
9	5	4.9	Light yellow	Orange
10	5	4.8	Red	Orange
11	5	4.9	Yellow	Orange
12	5	4.8	Yellow	Orange
13	5	-	Red	Red
14	5	-	Red	Red

Table 9-Titration of acetic acid (0.1M) against NaHCO₃ (0.1M)

No	Volume of Acetic acid (ml)	Mean volume of NaHCO ₃ (ml)	Color in acid	Color in base
3	5	4.9	Light yellow	Bright Yellow
4	5	4.8	Light red	Yellow
5	5	4.9	Yellow	Orange
6	5	4.8	Yellow	Light red
7	5	-	Red	Red
8	5	-	Bright Orange	Bright Orange
9	5	4.9	Light yellow	Orange
10	5	4.8	Red	Orange
11	5	4.8	Yellow	Orange
12	5	4.9	Yellow	Orange
13	5	-	Red	Red
14	5	-	Red	Red

**Figure 7**-Color of Azo dyes in acid and base solutions.

The reason of color change is the tautomerization process that occurred in all prepared azo dyes 3-14 which are composed of an azo group as a chromophore and different auxochromes, as was shown in equation 1. This process makes each dye possess two isomers, each of which carrying a different chromophore group and absorbs light in a different region of the spectrum. Except for compounds 7, 8, 13 & 14, the chromophores of these isomers absorb light in the same region because of the strong effect of naphthalene rings that act as auxochrome groups and shift the apparent color to the red region. While, the other azo dyes have different auxochromes with different shifting powers and, hence, their isomers show different colors.

Conclusions

New azo compounds 3-14 containing an 1,8-naphthalimide moiety were synthesized from 1, 8-naphthalic anhydride. The ability of the prepared azo compounds 3-14 to work as acid-base indicators was investigated by different acid-base titrations. All azo compounds determined the end point with a high precision compared with the phenolphthalein indicator, except compounds 7, 8, 13 & 14, which showed no color change because of the strong effect of naphthalene rings that act as auxochrome groups and shift the apparent color to the red region.

References

1. Bishop, E. **2013**. *Indicators: International series of monographs in analytical chemistry*. 1st ed. Vol. 51. Elsevier.
2. Vogel, A.I. **2013**. *A text-book of quantitative inorganic analysis-theory and practice*. 2nd ed.: Longmans, Green And Co. London; New York; Toronto.
3. Houghton, J. and G.A.F. Hendry **2012**. *Natural food colorants*. 2nd ed.: Springer Science & Business Media. new york, USA.
4. Khan, P.M.A. and M. Farooqui **2011**. Analytical applications of plant extract as natural pH indicator: A review. *J. Adv. Sci. Res.* **2**(4): 20-27.
5. Kahlert, H., Meyer, G. and A. Albrecht **2016**. Colour maps of acid–base titrations with colour indicators: How to choose the appropriate indicator and how to estimate the systematic titration errors. *ChemTexts.* **2**(2): 7-35.
6. Otutu, J. **2013**. Synthesis and application of azo dyes derived from 2-amino-1, 3, 4-thiadiazole-2-thiol on polyester fibre. *Int. j. recent res. appl. stud.* **15**(2): 292-296.
7. Yang, Y., Zhang, J., Yin, J. and Yang, Y. **2019**. Fast simultaneous determination of eight sudan dyes in chili oil by ultra-high-performance supercritical fluid chromatography. *J Anal Methods Chem.* 2019: 1-8.
8. Mousavi, S.S., B. Sajad, B. Efafi, H. Alaibakhsh, K.E. Jahromi, M.H. Majlesara, and B. Ghafary **2018**. Practical optimization of highly sensitive azo photoconductor with circular electrode scheme. *J. Light. Technol.* **36**(24): 5800-5806.
9. Ma, Y., H.-X. Chen, F. Zhou, H. Li, H. Dong, Y.-Y. Li, Z.-J. Hu, Q.-F. Xu, and J.-M. Lu **2015**. Metal complex modified azo polymers for multilevel organic memories. *Nanoscale.* **7**(17): 7659-7664.
10. Saito, G., Velluto, D. and Resmini, M. **2018**. Synthesis of 1,8-naphthalimide-based probes with fluorescent switch triggered by flufenamic acid. *R. Soc. open sci.* **5**(6): 172137-172149.
11. Zeng, W., H.-Y. Lai, W.-K. Lee, M. Jiao, Y.-J. Shiu, C. Zhong, S. Gong, T. Zhou, G. Xie, M. Sarma, K.-T. Wong, C.-C. Wu, and Yang, C. **2018**. Organic light-emitting diodes: Achieving nearly 30% external quantum efficiency for orange–red organic light emitting diodes by employing thermally activated delayed fluorescence emitters composed of 1,8-naphthalimide-acridine hybrids *Adv. Mater.* **30**(5): 1870033.
12. Liu, C., Xu, J., Yang, F., Zhou, W., Li, Z., Wei, L. and Yu, M. **2015**. Nanomolar Cu²⁺ and F⁻ naked-eye detection with a 1,8-naphthalimide-based colorimetric probe. *Sensor Actuat B Chem.* **212**: 364-370.
13. Rad, J.A., A. Jarrahpour, C. Latour, V. Sinou, J.M. Brunel, H. Zgou, Y. Mabkhot, T.B. Hadda, and E. Turos **2017**. Synthesis and antimicrobial/antimalarial activities of novel naphthalimido trans-β-lactam derivatives. *Medicinal Chemistry Research.* **26**(10): 2235-2242.
14. Okonkwo, A., J. Mitra, G.S. Johnson, L. Li, W.M. Dashwood, M.L. Hegde, C. Yue, R.H. Dashwood, and Rajendran, P. **2018**. Heterocyclic analogs of sulforaphane trigger DNA damage

- and impede DNA repair in colon cancer cells: Interplay of hats and hdacs. *Mol. Nutr. Food Res.* **62**(18): 1800228-1800267.
15. Suaad M.H.Al-Majidi, Mohammed R. A. and Ayad Kareem Khan **2013**.Synthesis and characterization of novel 1, 8-naphthalimide derivatives containing 1, 3-oxazoles, 1, 3-thiazoles, 1, 2, 4-triazoles as antimicrobial agents. *Jour. Al-Nahrain Univ.-Sci.* **16**(4): 55-66.
 16. Vogel, A.I. **2013**. *A text-book of practical organic chemistry including qualitative organic analysis*. 4th ed. Vol. 6. Longmans Green And Co; London; New York; Toronto. London; UK.
 17. Purwono, B., C. Anwar, and A.J.I.J.o.C. Hanapi **2013**.Syntheses of azo-imine derivatives from vanillin as an acid base indicator. *Indones. J. Chem.* **13**(1): 1-6.
 18. Ayad Kareem K. **2014**. Synthesis and characterization of novel heterocyclic derivatives from 1,8-naphthalic anhydride and studying the possibility of their application as antimicrobial agents,photophysics or dyestuffs.Ph. D, department of chemistry, University of Baghdad, Baghdad, Iraq.
 19. Silverstein, R.M., Webster, F.X., Kiemle, D.J. and Bryce, D.L. **2014**.*Spectrometric identification of organic compounds*. John wiley & sons.
 20. Georgiev, A., A. Stoilova, D. Dimov, D. Yordanov, I. Zhivkov, and M. Weiter **2019**.Synthesis and photochromic properties of some n-phthalimide azo-azomethine dyes. A dft quantum mechanical calculations on imine-enamine tautomerism and trans-cis photoisomerization. *Spectrochim Acta A Mol Biomol Spectrosc.* **210**: 230-244.
 21. Claramunt, R.M.,
 22. López, C., Santa María, M.D., Sanz, D. and Elguero, J. **2006**.The use of nmr spectroscopy to study tautomerism. *Prog. Nucl. Magn. Reson. Spectrosc.* **49**(3-4): 169-206.