

## Synthesis of Mono- and Bis-Triazoles via 1,3-Dipolar Cycloaddition Reactions of Azide Derivatives with Naphtho- and Benzoquinone†

Sultan T. Abu-Orabi\*<sup>a</sup>, Maysaa Saleh<sup>b</sup>, Lo'ay Al-Momani<sup>a</sup>, Ibrahim Jibril<sup>a</sup>, Yaser Yousef<sup>b</sup>

a) Department of Chemistry, Tafila Technical University, Tafila, Jordan

b) Department of Chemistry, Yarmouk University, Irbid, Jordan

Received on Jul. 27, 2006

Accepted on Oct. 19, 2006

### Abstract

In this publication we report some of our work in which bis-triazoles **3a-u** and mono-triazoles **5a-u** and **7a-c** were prepared via 1,3-dipolar cycloaddition reaction of azide derivatives **1a-u** and **6a-c** with benzoquinone **2** and naphthoquinone **4**. Products were characterized by <sup>1</sup>H-NMR, IR and mass spectroscopy, as well as elemental analysis.

**Keywords:** Triazoles; 1,3-Dipolar cycloaddition; Azide; Quinine.

### Introduction

Azides are very important precursors for the preparation and synthesis of heterocyclic aromatic compounds. They are considered to be important for both industrial and biological applications. Azide derivatives have been used in rubber, polymers, dyes and plastics technology, as well as in pharmaceuticals, pesticides and herbicides developments.<sup>[1]</sup> Some azides have shown mutagenic activities.<sup>[2-4]</sup> They also have an important position in the organic synthesis map.<sup>[5-8]</sup> Azides are used in the synthesis of 1,2,3-triazoles via 1,3-dipolar cycloaddition reactions.<sup>[9-13]</sup> Triazoles and their derivatives have attracted the attention of many chemists, and they were tested in several directions. They are studied as fungicides, herbicides, anti-corrosive agents as well as in some medical and biological aspects. Some of them showed antimicrobial and anti-inflammatory activities.<sup>[14-18]</sup> Our interest in this respect is the synthesis and the methodology development of triazole derivatives to supply the industry with new substances which could hopefully show important pharmaceutical and industrial significance.

### Experimental part

#### *Analysis Methods*

Melting points were measured on electrothermal melting point apparatus without any further corrections. The infrared data were measured on a Pye-Unicam Sp300 spectrophotometer as potassium bromide disk. <sup>1</sup>H-NMR spectra were recorded on a Bruker 80 SY spectrometer. Tetramethylsilane (TMS) as an internal reference, the chemical shifts ( $\delta$ ) were recorded in ppm. The elemental analyses were measured at

\* Corresponding author, e-mail: [President@TTU.edu.jo](mailto:President@TTU.edu.jo).

† Based in part on the M.Sc. thesis of Maysaa Saleh, Yarmouk University, Irbid, Jordan.

M-H-W laboratories, Phoenix, Arizona, USA. The internal energy of geometrical isomers; noncentrosymmetric and centrosymmetric, were calculated and drawn by Chem-X program, which is an advanced 3D modeling software for all types of molecular structures, small molecules, polymers, biopolymers, and other materials. It is a powerful technique for understanding the properties of molecules and to calculate the internal energies.

#### *Chemicals and materials*

The commercially available chemicals and reagents were purchased from Aldrich, and were used without further purification. Benzyl azide **1a**, substituted benzyl azides **1b-u** and bis-azidomethyl benzenes **6a-c** derivatives were prepared from the precursor halides.<sup>[19-21]</sup> 1,4-benzoquinone **2** was prepared from the commercially available 1,4-hydroquinone. 1,4-naphthoquinone **4** was recrystallized from petroleum ether 80-100 °C before using.<sup>[19]</sup>

*Preparation of substituted benzyl azides 1a-u and bis-azidomethylbenzenes 6a-c* Benzyl azide derivatives **1a-u** and the bis-azidomethyl benzenes **6a-c** were prepared according to procedure reported in literature.<sup>[19-21]</sup>

#### *Conversion of 1,4-hydroquinone to 1,4-benzoquinone 2*

1,4-hydroquinone 5.0 g (45.5 mmol) was dissolved in of 300 mL of 2/1 mixture of diethyl ether and distilled water. A solution of 15 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 150 mL distilled water was cooled and added dropwise to the stirred mixture then left for extra 10 min. The ether layer was separated, and washed twice with distilled water. The organic layer was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure to obtain 4.4 g (40.7 mmol, 90 %) of 1,4-benzoquinone **2** as yellow crystals of m.p. of 115-117 °C. The crude product was used without further purification.

#### *General procedure of the reaction of substituted benzyl azide derivatives 1a-u with 1,4-benzoquinone 2*

To a solution of substituted benzyl azide derivative (20.0 mmol) in 50 mL of absolute ethanol, 1,4-benzoquinone 1.1 g (10.0 mmol) was added. The reaction mixture was heated under reflux for 24 h. The mixture was allowed to cool to room temperature. The solid product that formed was filtered, washed with ethanol then acetone and collected. The produced triazolo derivatives **3a-u** were found to be sufficiently pure for characterization, they needed no further purification. Analytical and spectral data for compounds **3a-u** were summarized in Tables 1 and 2.

#### *General procedure of the reaction of substituted benzyl azide derivatives 1a-u with 1,4-naphthoquinone 4*

To a solution of substituted benzyl azide derivative (20.0 mmol) in 50 mL of absolute ethanol, 3.2 g (20.0 mmol) 1,4-naphthoquinone **4** was added. The reaction mixture was heated under reflux for 24 h. The mixture was allowed to cool to room temperature. The solid product that formed was filtered, washed with ethanol then acetone and collected. The produced triazolo derivatives **5a-u** were recrystallized from

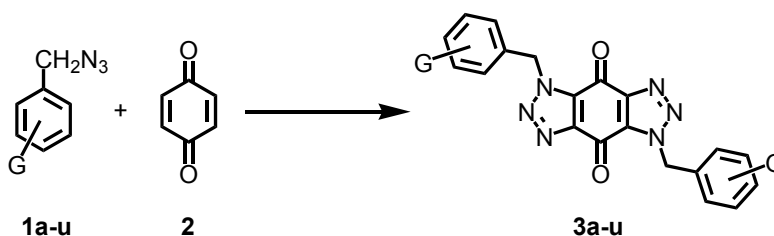
THF. Compounds **5a** and **5q** were synthesized and published previously by Tedder *et al.*<sup>[22]</sup>. Analytical and spectral data for compounds **5a-u** were summarized in Tables 4 and 5.

*General procedure of the reaction of bis-azidomethylbenzenes 6a-c with 1,4-naphthoquinone 4*

3.2 g (20.0 mmol) of 1,4-naphthoquinone **4** was added to 50 mL of an ethanolic solution of (10.0 mmol) bis-azidomethylbenzenes **6a-c**. The mixture was left to stir under reflux for 24 h. The resulting mixture was cooled to room temperature. The precipitated solid was filtered, washed with ethanol followed by acetone. The solid products were recrystallized from THF. Analytical and spectral data for compounds **7a-c** were summarized in Tables 6 and 7.

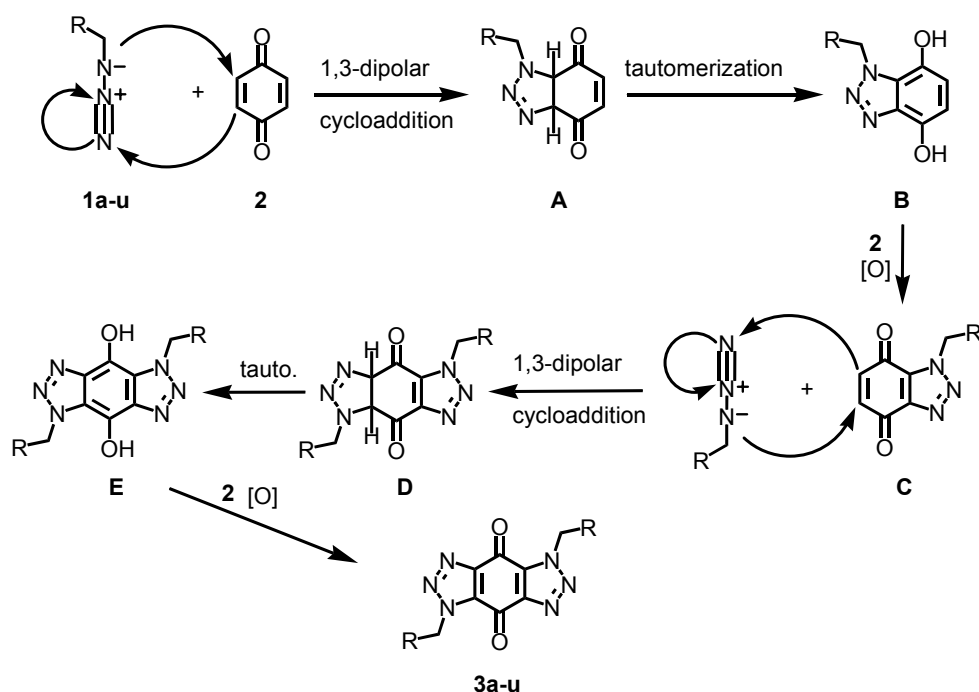
### Results and Discussion

The 1,3-dipolar cycloaddition reactions of substituted benzyl azides with olefinic and acetylenic compounds have been studied by many research groups world wide.<sup>[5, 22-30]</sup> Some work has been reported on the reaction with 1,4-benzoquinone **2** and with 1,4-naphthoquinone **4** as dipolarophile.<sup>[22, 31, 32]</sup> The reaction of azides **1a-u** with 1,4-benzoquinone **2** in the ratio 2:1 under reflux conditions in ethanol yielded the bis-triazole derivatives **3a-u** as solid products. These products have low solubility in most known organic solvents. They were purified by washing the solids with ethanol and acetone successively to remove the excess of reactants. The products were obtained in yields of 40-70%. IR spectroscopy shows the characteristic stretching frequencies of C=O between 1700-1690 cm<sup>-1</sup>, the aromatic C=C 1610-1580 cm<sup>-1</sup>, and N=N 1440-1430 cm<sup>-1</sup>. Spectroscopic and analytical data were summarized in tables 1 and 2.

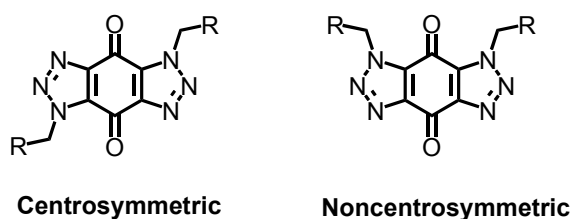


G: a=H, b=2-NO<sub>2</sub>, e=2-Br, h=2-Cl, k=2,4-Di-Cl, n=3-F, q=4-OMe, t=4-Me  
 c=3-NO<sub>2</sub>, f=3-Br, i=3-Cl, l=2,6-Di-Cl, o=4-F, r=2-Me, u=2,4,6-Tri-Me  
 d=4-NO<sub>2</sub>, g=4-Br, j=4-Cl, m=2-F, p=3-OMe, s=3-Me

A rational mechanism was proposed (Scheme 1) for the formation of bis-triazoles **3a-u**. The first step is the 1,3-dipolar cycloaddition reaction of azides **1a-u** with the activated C=C of the 1,4-benzoquinone **2** to produce the mono-triazoline **A** intermediate which is tautomerized and oxidized to form the mono-triazole **C** derivative. A second 1,3-dipolar cycloaddition takes place to produce the centrosymmetric bis-adducts **3a-u** as the most stable regioisomer.

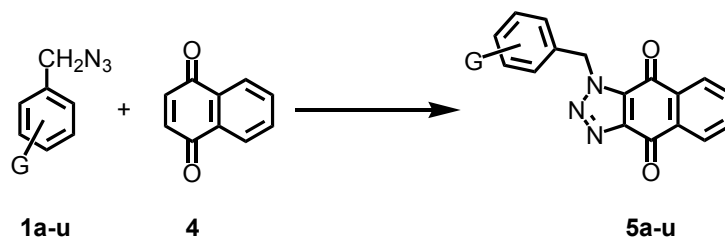


The calculated internal energies of both centrosymmetric and noncentrosymmetric isomers are summarized in table 3. For the centrosymmetric isomers, the internal energies are found to be less than those of the noncentrosymmetric.



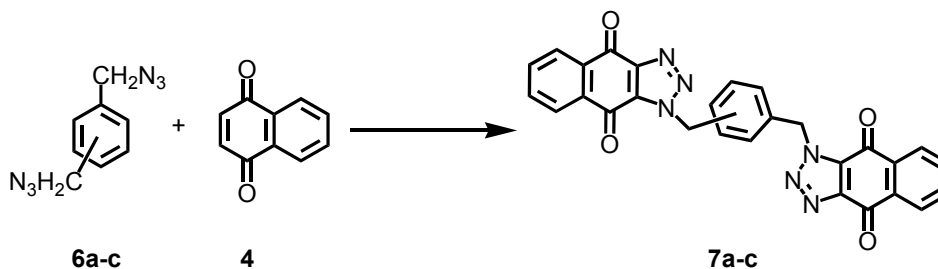
This means that the regioisomer in which the two R groups are far away from each other (the centrosymmetric isomer) is the most stable one. To illustrate this result, one should consider the steric factor and the size of the R group. It seems that the reaction favours the formation of centrosymmetric isomer to decrease the steric effect of the R groups.

The reaction of azide derivatives **1a-u** with 1,4-naphthoquinone **4** was also carried out in the same manner to that with the 1,4-benzoquinone **2**. The dipolarophile **4** which has only one activated C=C could be attacked by 1,3-dipole (azides) to produce the corresponding triazole derivatives **5a-u** as solid products.



G: a=H, b=2-NO<sub>2</sub>, e=2-Br, h=2-Cl, k=2,4-Di-Cl, n=3-F,            q=4-OMe, t=4-Me  
 c=3-NO<sub>2</sub>, f=3-Br, i=3-Cl, l=2,6-Di-Cl, o=4-F,            r=2-Me, u=2,4,6-Tri-Me  
 d=4-NO<sub>2</sub>, g=4-Br, j=4-Cl, m=2-F,            p=3-OMe, s=3-Me

The produced solids were found to be insoluble in most organic solvents. The purification was achieved through washing the solids with ethanol and acetone, successively followed by recrystallization from THF. The products were obtained in yields of 50-80%. The reaction occurs via the same mechanism proposed for 1,4-benzoquinone **2** (Scheme 1). IR spectroscopy shows the characteristic stretching frequencies of C=O between 1700-1690 cm<sup>-1</sup>, aromatic C=C 1610-1580 cm<sup>-1</sup>, and N=N 1440-1430 cm<sup>-1</sup>. The spectral and analytical data are given in tables 4 and 5. Since the reaction of the azides **1a-u** with 1,4-benzoquinone **2** and with 1,4-naphthoquinone **4** took place smoothly, it was extended using the bis-azidomethylbenzene **6a-c** with 1,4-naphthoquinone **4** to obtain the bis-triazole derivatives **7a-c**. The bis-triazole derivatives were produced in a yield of 50-55% as solid products.



*a=ortho, b=meta, c=para*

The products were found to be insoluble in most organic solvents. The derivative **7a** was recrystallized from THF, while substances **7b** and **7c** were purified by washing with ethanol and acetone, successively. The IR spectroscopy shows the characteristic stretching bands; C=O 1690-1675 cm<sup>-1</sup>, the aromatic C=C 1590-1575 cm<sup>-1</sup>, and N=N 1450-1440 cm<sup>-1</sup>. The spectral and analytical data are given in tables 6 and 7.

**Table (1):** Analytical data for bis-triazoles 3a-u

Product	G	Molecular Formula	Molecular mass (g/mol)	Yield %	M. P. (°C)	Elemental Analysis Found (Calculated)		
						% C	% H	%N
3a	H	C <sub>20</sub> H <sub>14</sub> O <sub>2</sub> N <sub>6</sub>	370	40.5	230-233	64.77 (64.87)	3.78 (3.78)	22.69 (22.70)
3b	2-NO <sub>2</sub>	C <sub>20</sub> H <sub>12</sub> O <sub>6</sub> N <sub>8</sub>	460	65.2	257-260	52.36 (52.17)	2.49 (2.61)	24.17 (24.35)
3c	3-NO <sub>2</sub>	C <sub>20</sub> H <sub>12</sub> O <sub>6</sub> N <sub>8</sub>	460	65.2	225-227	52.36 (52.17)	2.49 (2.61)	24.12 (24.35)
3d	4-NO <sub>2</sub>	C <sub>20</sub> H <sub>12</sub> O <sub>6</sub> N <sub>8</sub>	460	65.2	240-242	52.36 (52.17)	2.63 (2.61)	23.97 (24.35)
3e	2-Br	C <sub>20</sub> H <sub>12</sub> O <sub>2</sub> N <sub>6</sub> Br <sub>2</sub>	528	54.0	251-253	45.44 (45.45)	2.44 (2.27)	15.85 (15.91)
3f	3-Br	C <sub>20</sub> H <sub>12</sub> O <sub>2</sub> N <sub>6</sub> Br <sub>2</sub>	528	56.8	228-231	45.32 (45.45)	2.41 (2.27)	15.89 (15.91)
3g	4-Br	C <sub>20</sub> H <sub>12</sub> O <sub>2</sub> N <sub>6</sub> Br <sub>2</sub>	528	56.8	268-269	45.22 (45.45)	2.12 (2.27)	15.76 (15.91)
3h	2-Cl	C <sub>20</sub> H <sub>12</sub> O <sub>2</sub> N <sub>6</sub> Cl <sub>2</sub>	439	68.3	252-254	54.70 (54.67)	2.61 (2.27)	18.81 (19.13)
3i	3-Cl	C <sub>20</sub> H <sub>12</sub> O <sub>2</sub> N <sub>6</sub> Cl <sub>2</sub>	439	58.1	213-215	54.94 (54.67)	2.56 (2.73)	18.83 (19.13)
3j	4-Cl	C <sub>20</sub> H <sub>12</sub> O <sub>2</sub> N <sub>6</sub> Cl <sub>2</sub>	439	67.6	256-258	54.75 (54.67)	2.60 (2.73)	18.89 (19.13)
3k	2,4-Dichloro	C <sub>20</sub> H <sub>10</sub> O <sub>2</sub> N <sub>6</sub> Cl <sub>4</sub>	508	58.5	260-262	47.40 (47.24)	2.01 (1.97)	16.42 (16.53)
3l	2,6-Dichloro	C <sub>20</sub> H <sub>10</sub> O <sub>2</sub> N <sub>6</sub> Cl <sub>4</sub>	508	65.0	257-260	47.18 (47.24)	2.03 (1.97)	16.34 (16.53)
3m	2-F	C <sub>20</sub> H <sub>12</sub> O <sub>2</sub> N <sub>6</sub> F <sub>2</sub>	406	62.8	227-228	59.50 (59.11)	3.01 (2.96)	20.71 (20.69)
3n	3-F	C <sub>20</sub> H <sub>12</sub> O <sub>2</sub> N <sub>6</sub> F <sub>2</sub>	406	59.1	223-227	60.17 (59.11)	3.13 (2.96)	19.30 (20.69)
3o	4-F	C <sub>20</sub> H <sub>12</sub> O <sub>2</sub> N <sub>6</sub> F <sub>2</sub>	406	62.8	268-269	58.97 (59.11)	2.74 (2.96)	20.80 (20.69)
3p	3-OCH <sub>3</sub>	C <sub>22</sub> H <sub>18</sub> O <sub>4</sub> N <sub>6</sub>	430	66.3	187-190	61.60 (61.39)	4.30 (4.19)	19.54 (19.53)
3q	4-OCH <sub>3</sub>	C <sub>22</sub> H <sub>18</sub> O <sub>4</sub> N <sub>6</sub>	430	69.8	217-220	61.45 (61.39)	4.22 (4.19)	19.34 (19.53)
3r	2-CH <sub>3</sub>	C <sub>22</sub> H <sub>18</sub> O <sub>2</sub> N <sub>6</sub>	398	67.8	244-246	66.57 (66.33)	4.69 (4.52)	20.96 (21.11)
3s	3-CH <sub>3</sub>	C <sub>22</sub> H <sub>18</sub> O <sub>2</sub> N <sub>6</sub>	398	56.5	213-215	66.16 (66.33)	4.29 (4.52)	21.18 (21.11)
3t	4-CH <sub>3</sub>	C <sub>22</sub> H <sub>18</sub> O <sub>2</sub> N <sub>6</sub>	398	67.8	252-254	66.45 (66.33)	4.73 (4.52)	20.18 (21.11)
3u	2,4,6-Trimethyl	C <sub>26</sub> H <sub>26</sub> O <sub>2</sub> N <sub>6</sub>	454	52.9	300-303	68.94 (68.72)	5.84 (5.73)	18.36 (18.50)

**Table (2):** Spectral data for bis-triazoles 3a-u

Product	G	IR (KBr, $\nu$ ; $\text{cm}^{-1}$ )	Mass Spectra (m/z)	$^1\text{H-NMR}$ $\delta$ in (ppm) DMSO
<b>3a</b>	H	1700, 1580, 1450	237, 223, 104, 91	7.37 (s, 10H), 6.00 (bs, 4H)
<b>3b</b>	2-NO <sub>2</sub>	1700, 1580, 1540, 1440	-	7.14-8.34 (m, 8H), 6.38(s, 4H)
<b>3c</b>	3-NO <sub>2</sub>	1690, 1580, 1530, 1440	-	7.57-8.34(m, 8H), 6.18 (s, 4H)
<b>3d</b>	4-NO <sub>2</sub>	1690, 1603, 1521, 1430	429, 399, 371, 324	8.24 (d, $J=8.6$ Hz), 7.63 (d, $J=8.6$ Hz, 4H), 6.18 (s, 4H)
<b>3e</b>	2-Br	1690, 1600, 1435, 610	-	7.06-7.88 (m, 8H), 6.09(s, 4H)
<b>3f</b>	3-Br	1697, 1580, 1430, 588	-	7.32-7.75 (m, 8H), 6.03 (s, 4H)
<b>3g</b>	4-Br	1690, 1580, 1430, 620	169, 160, 132, 104	7.95 (d, $J=8.6$ Hz, 4H), 7.33(d, $J=8.4$ Hz, 4H), 5.98 (s, 4H)
<b>3h</b>	2-Cl	1690, 1593, 1438, 700	403, 382, 327, 125, 111	7.14-7.72 (m, 8H), 6.12 (bs, 4H)
<b>3i</b>	3-Cl	1695, 1600, 1430, 750	-	7.40 (s, 8H), 6.00 (bs, 4H)
<b>3j</b>	4-Cl	1695, 1580, 1430, 680	-	7.42 (s, 8H), 5.97 (bs, 4H)
<b>3k</b>	2,4-Dichloro	1695, 1580, 1430, 670	452, 436, 417, 293, 159	7.28-7.68 (m, 6H), 6.10 (bs, 4H)
<b>3l</b>	2,6-Dichloro	1700, 1600, 1430, 700	-	7.57 (s, 6H), 6.2 (bs, 4H)
<b>3m</b>	2-F	1697, 1600, 1434	-	7.07-7.69 (m, 8H), 6.06 (bs, 4H)
<b>3n</b>	3-F	1700, 1600, 1460	-	7.09-7.57 (m, 8H), 6.06 (bs, 4H)
<b>3o</b>	4-F	1695, 1605, 1450	377, 330, 311, 297, 109	7.06-7.62 (m, 8H), 5.97 (bs, 4H)
<b>3p</b>	3-OCH <sub>3</sub>	2951, 1700, 1580, 1450	-	6.82-7.59 (m, 8H), 5.97 (s, 4H), 3.74 (s, 6H)
<b>3q</b>	4-OCH <sub>3</sub>	1695, 1608, 1448	266, 253, 208, 121	7.37 (d, $J=6.7$ Hz, 4H), 6.93 (d, $J=6.7$ Hz, 4H), 5.92 (bs, 4H), 3.73 (s, 6H)
<b>3r</b>	2-CH <sub>3</sub>	2912, 1685, 1600, 1470	-	7.03-7.37 (m, 8H), 6.01 (s, 4H), 2.43 (s, 6H)
<b>3s</b>	3-CH <sub>3</sub>	2922, 1695, 1590, 1430	369, 340, 237, 105, 91	7.19 (s, 8H), 5.95 (s, 4H), 2.27 (s, 6H)
<b>3t</b>	4-CH <sub>3</sub>	2950, 1690, 1608, 1430	-	7.0-7.4 (m, 8H), 5.92 (b, 4H), 2.26 (s, 6H)
<b>3u</b>	2,4,6-Trimethyl	2900, 1685, 1600, 1460	383, 320, 133, 199	6.94 (s, 4H), 5.93 (bs, 4H), 2.3 (s, 12H), 2.24 (s, 6H)

**Table (3):** Computed data energies of bis-triazoles 3a-u

Product	G	Internal Energy Values (kJ)	
		Noncentrosymmetric Isomer	Centrosymmetric Isomer
3a	H	11.100	10.647
3b	2-NO <sub>2</sub>	100.807	89.246
3c	3-NO <sub>2</sub>	70.120	65.086
3d	4-NO <sub>2</sub>	72.494	70.875
3e	2-Br	12.614	11.274
3f	3-Br	9.925	9.019
3g	4-Br	9.881	9.397
3h	2-Cl	12.806	12.190
3i	3-Cl	9.88	8.838
3j	4-Cl	9.658	9.489
3k	2,4-Dichloro	7.606	7.541
3l	2,6-Dichloro	11.670	11.290
3m	2-F	9.515	9.065
3n	3-F	7.379	6.472
3o	4-F	9.902	8.932
3p	3-OCH <sub>3</sub>	16.192	16.128
3q	4-OCH <sub>3</sub>	20.209	19.741
3r	2-CH <sub>3</sub>	14.355	13.785
3s	3-CH <sub>3</sub>	11.757	10.038
3t	4-CH <sub>3</sub>	10.687	2.829
3u	2,4,6-Trimethyl	17.56	17.045

**Table (4)** :Analytical data for triazoles 5a-u

Product	G	Molecular formula	Molecular mass (g/mol)	Yield %	M.P. (°C)	Elemental analysis found (calculated)		
						%C	%H	%N
5a	H	C <sub>17</sub> H <sub>11</sub> O <sub>2</sub> N <sub>3</sub>	289	59.0	193-195	70.67 (70.59)	3.77 (3.81)	14.71 (14.53)
5b	2-NO <sub>2</sub>	C <sub>17</sub> H <sub>10</sub> O <sub>4</sub> N <sub>4</sub>	334	51.0	189-191	60.96 (61.08)	3.01 (2.99)	17.00 (16.77)
5c	3-NO <sub>2</sub>	C <sub>17</sub> H <sub>10</sub> O <sub>4</sub> N <sub>4</sub>	334	66.0	185-189	60.93 (61.08)	3.00 (2.99)	16.87 (16.77)
5d	4-NO <sub>2</sub>	C <sub>17</sub> H <sub>10</sub> O <sub>4</sub> N <sub>4</sub>	334	57.0	225-227	60.89 (61.08)	3.05 (2.99)	16.94 (16.77)
5e	2-Br	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> N <sub>3</sub> Br	368	65.0	197-200	55.60 (55.43)	2.74 (2.71)	11.60 (11.41)
5f	3-Br	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> N <sub>3</sub> Br	368	63.0	164-166	55.30 (55.43)	2.70 (2.71)	11.60 (11.41)
5g	4-Br	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> N <sub>3</sub> Br	368	73.0	216-219	55.52 (55.43)	2.57 (2.71)	11.60 (11.41)
5h	2-C1	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> N <sub>3</sub> C1	323.5	62.0	208-211	63.09 (63.06)	3.12 (3.09)	12.94 (12.98)
5i	3-C1	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> N <sub>3</sub> C1	323.5	56.0	173-175	63.09 (63.06)	3.09 (3.09)	13.19 (12.98)
5j	4-C1	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> N <sub>3</sub> C1	323.5	49.0	218-220	63.00 (63.06)	3.04 (3.09)	13.03 (12.98)
5k	2,4-Dichloro	C <sub>17</sub> H <sub>9</sub> O <sub>2</sub> N <sub>3</sub> C1 <sub>2</sub>	358	70.0	185-188	57.04 (56.98)	2.42 (2.51)	12.00 (11.73)
5l	2,6-Dichloro	C <sub>17</sub> H <sub>9</sub> O <sub>2</sub> N <sub>3</sub> C1 <sub>2</sub>	358	75.0	226-229	57.09 (56.98)	2.35 (2.51)	11.86 (11.73)
5m	2-F	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> N <sub>3</sub> F	307	72.0	302-205	66.33 (66.45)	3.33 (3.26)	13.75 (13.68)
5n	3-F	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> N <sub>3</sub> F	307	65.0	201-204	66.52 (66.45)	3.13 (3.26)	13.89 (13.68)
5o	4-F	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> N <sub>3</sub> F	307	72.0	195-197	66.26 (66.45)	3.18 (3.26)	13.86 (13.68)
5p	3-OCH <sub>3</sub>	C <sub>18</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub>	319	66.0	147-149	67.63 (67.71)	4.15 (4.08)	13.26 (13.17)
5q	4-OCH <sub>3</sub>	C <sub>18</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub>	319	66.0	180-182	67.54 (67.71)	4.22 (4.08)	13.35 (13.17)
5r	2-CH <sub>3</sub>	C <sub>18</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub>	303	69.0	171-174	71.31 (71.29)	4.26 (4.29)	14.00 (13.86)
5s	3-CH <sub>3</sub>	C <sub>18</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub>	303	79.0	183-186	71.25 (71.29)	4.17 (4.29)	13.92 (13.86)
5t	4-CH <sub>3</sub>	C <sub>18</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub>	303	63.0	193-195	71.44 (71.29)	4.01 (4.29)	14.11 (13.86)
5u	2,4,6-Trimethyl	C <sub>20</sub> H <sub>17</sub> O <sub>2</sub> N <sub>3</sub>	331	39.0	216-218	72.47 (72.51)	5.11 (5.14)	12.52 (12.69)

**Table (5):** Spectral data for triazoles 5a-u

Product	G	IR (KBr, $\nu$ ; $\text{cm}^{-1}$ )	Mass spectra (m/z)	$^1\text{H-NMR}$ $\delta$ in (ppm) DMSO
5a	H	1680, 1580, 1450	260, 232, 204, 91	7.80–8.63 (m, 4H), 7.39 (s, 5H), 6.05 (s, 2H)
5b	2-NO <sub>2</sub>	1675, 1600, 1520, 1450	-	7.12-8.42 (m, 8H), 6.42 (s, 2H)
5c	3-NO <sub>2</sub>	1685, 1580, 1540, 1445	-	7.50-8.63 (m, 8H), 6.21(s, 2H)
5d	4-NO <sub>2</sub>	1685, 1600, 1528, 1430	306, 277, 259, 232	7.81-8.44 (m, 6H), 8.1 (d, $J=8.5$ Hz, 2H), 7.65(d, $J=8.5$ Hz, 2H), 6.21 (s, 2H)
5e	2-Br	1675, 1600, 1435, 580	-	6.93-8.5 (m, 8H) , 6.12 ( s, 2H)
5f	3-Br	1690, 1594, 1429, 595	-	7.85-8.34 (m, 4H) , 7.31-7.73 (m, 4H), 6.05 (s, 2H)
5g	4-Br	1685, 1584, 1429, 620	339, 282, 260, 204, 171	7.85-8.37 (m, 4H), 7.60 (d, $J=8.4$ Hz, 2H), 7.37 (d, $J=8.2$ , 2H ), 6.03 (s, 2H)
5h	2-C1	1680, 1579, 1443, 700	295, 288, 260, 127, 125	7.86-8.36 (m, 4H ), 7.07-7.64 (m, 4H), 6.15 (s, 2H)
5i	3-C1	1685, 1580, 1435, 670	-	7.78-8.34 (m, 4H) , 7.56 (m, 4H) , 6.06 (s, 2H)
5j	4-C1	1680, 1580, 1430, 685	-	7.85-8.56 (m, 4H) , 7.44 (s, 4H), 6.04 (s, 2H)
5k	2,4-Dichloro	1680, 1600, 1430, 710	329, 294, 238, 159	7.14-8.43 (m, 6H) , 6.14 (s, 2H)
5l	2,6-Dichloro	1685, 1600, 1449, 740	-	7.81-8.50 (m.4H),7.59 (s,7H), 6.25 (s,2H)
5m	2-F	1685, 1584, 1448	-	7.86-8.36 (m, 4H), 7.04-7.54 (m, 4H), 6.1 (s, 2H)
5n	3-F	1680, 1580, 1455	-	7.89-8.36 (m, 4H), 7.00-7.54 (m, 4H), 6.12 (s, 2H)
5o	4-F	1695, 1600, 1430	274, 250, 222, 109	7.86-8.32 (m, 4H), 7. 10-7.64 (m, 4H), 6.03 (s, 2H)
5p	3-OCH <sub>3</sub>	2951, 1680, 1579, 1438	-	7.79-8.38 (m, 4H) , 6. 82-7.45 (m, 4H), 6.97 (s, 2H), 3.73 (s, 3H)
5q	4-OCH <sub>3</sub>	2951, 1680, 1579, 1453	319, 291, 276, 121	7.86-8.32 (m, 4H) . 7. 39 (d, $J=8.7$ Hz, 2H), 6.92 (d, $J=8.7$ Hz, 2H). 5.95 (s, 2H), 3.72 (s, 3H)
5r	2-CH <sub>3</sub>	2980, 1685, 1580, 1430	-	7.83-8.52 (m, 4H) , 6. 93-7.37 (m, 4H), 6.04 (s, 2H), 2.44 (s, 3H)
5s	3-CH <sub>3</sub>	2950, 1685, 1580, 1430	-	7.86-8.32 (m, 4H) , 7. 09-7.45 (m, 4H). 5.98 (s, 2H), 2.26 (s, 3H)
5t	4-CH <sub>3</sub>	2968, 1260, 1580, 1430	275, 260, 218, 204, 105	7.83-8.62 (m, 4H), 7.03-7.48 (m, 4H), 5.97 (s, 2H), 2.24 (s, 3H)
5u	2,4,6-Tri-methyl	2961, 1680, 1600, 1460	303, 288, 260, 133	7.86-7.43 (m, 4H), 6. 94 (s, 2H), 5.98 (s, 2H), 2.30 (s, 6H) ,2.25 (s, 3H)

**Table (6):** Analytical data of bis-triazoles 7a-c

Product	G	Molecular formula	Mass spectra (m/z)	Yield (%)	M.P (°C)
7a	Ortho-	C <sub>28</sub> H <sub>16</sub> O <sub>4</sub> N <sub>6</sub>	500	52	250-252
7b	Meta-	C <sub>28</sub> H <sub>16</sub> O <sub>4</sub> N <sub>6</sub>	500	56	203-205
7c	Para-	C <sub>28</sub> H <sub>16</sub> O <sub>4</sub> N <sub>6</sub>	500	54	293-295

**Table (7):** Spectral data of bis-triazoles 7a-c

Product	G	IR (KBr, ν; cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ in (ppm) DMSO
7a	Ortho-	1680, 1579, 1453	7.83-8.26 (m, 8H), 7.33 (s, 4H), 6.31 (s, 4H)
7b	Meta -	1675, 1584, 1443	7.76-8.3 (m, 8H), 7.38 (s, 4H), 6.02 (s, 4H)
7c	Para-	1690, 1588, 1429	7.83-8.31 (m, 8H), 7.41 (s, 4H), 6.04 (s, 4H), 6.02 (s, 2H)

### Acknowledgement

We would like to thank Mrs. Reema Al-Zorqan for typing this manuscript.

### References

- [1] Scriven, E. F. V., "Azides and Nitrenes: Reactivity and Utility", Orlando, Fla., 1984.
- [2] Nilan, R.A.; Sideris, E.G.; Kleinhofs, A., *Mut. Res.*, 1973, 17, 142.
- [3] Owais,W.; Rosichan, J.L.; Roland, R.C.; Kleinhofs, A.; Nilan, R.A., *Mut. Res.*, 1983, 118, 299.
- [4] Sander, D.; Muelbour, F. *J. Enviromental Exp. Bot.*, 1977, 17, 43.
- [5] Abu-Orabi, S.T., *Molecules*, 2002, 7, 302.
- [6] Scriven, E.F.V.; Turnbull, N., *Chem. Rev.*, 1983, 88, 35.
- [7] Patai, S., "The Chemistry of the Azide Group", Interscience Publisher, New York, 1971.
- [8] Ridois, N.A., *J. Heterocycl. Chem.*, 1984, 21, 1169.
- [9] Gilchrist, T.L.; Gymer, G.E.; Katrizky, A.R.; Boulton, J.A., *Adv. Heterocycl. Chem.*, 1974, 16, 33.
- [10] Finely, K. T.; Weissberge, A.; Taylor, E. C., "The Chemistry of Heterocyclic Compounds", John Wiley, New York, 1984.
- [11] Purvisis, P.; Smalley, R.K.; Saschitsky, M.A.; Alkhader, M.A., *J. Chem. Soc. Perkin 1*, 1984, 249.
- [12] Patei, D.I.; Smalley, R.K., *J. Chem. Soc. Perkin 1*, 1984, 2587.
- [13] Loubinoux, B.; Colm, J.; Tabbache, S., *J. Heterocycl. Chem.*, 1984, 21, 1669.
- [14] Abdallah, M.M.; Abu-Orabi, S.T., *Korrosion*, 1991, 22, 520.
- [15] Abdulhadi, A.J., Thesis, King Fahd of Petroleum and Minerals (Saudi Arabia), 1995.
- [16] Fox, P.G.; Lewis, G.; Boden, P., *Corrosion Science*, 1979, 4, 425.
- [17] Abdennabi, A.M.S.; Abdulhadi, A.J.; Abu-Orabi, S.T., *Anti Corrosion Methods and Materials*, 1998, 45, 103.
- [18] Abdennabi, A.M.S.; Abdulhadi, A.J.; Abu-Orabi, S.T.; Saricimen, H., *Corrosion Science*, 1996, 38, 1791.
- [19] Ali, A.A.-S., Thesis, Yarmouk University (Jordan), 1990.
- [20] Henkel, H.; Weygand, F., *Chem. Ber.*, 1943, 76, 812.
- [21] Abu-Orabi, S.T.; Harmon, R.E., *J. Chem. Eng. Data*, 1986, 31, 379.
- [22] Buckle D.R.; Smith H.; Spicer B.A.; Tedder J.M., *J. Med. Chem.*, 1983, 26, 714; Tedder, J.M., *Eur. Pat. Appl.*, 1981, pp13, CODEN: EPXXDW EP 33214 19810805. Application: EP 81-300250 19810121. CAN 95:203966 AN 1981:603966. Buckle, D.R.; Tedder, J.M, *Eur. Pat. Appl.*, 1981, pp9, CODEN: EPXXDW EP 33215 19810805. Application: EP 81-300251 19810121. CAN 95:203967 AN 1981:603967.
- [23] Abu-Orabi, S.T.; Atfah, M.A.; Jibril, I.; Marii, F.M.; Ali,A.A.-S., *J. Heterocycl. Chem.*, 1989, 26, 1461.
- [24] Abu-Orabi, S.T.; Atfah, M.A.; Jibril, I.; Marii, F.M.; Ali, A.A.-S., *Gazzetta Chimica Italiana*, 1991, 121, 397.

- [25] Abu-Orabi, S.T.; Atfah, M.A.; Jibril, I.; Ali, A.A.-S.; Marii, F.M., *Gazzetta Chimica Italiana*, 1992, 122, 29.
- [26] Abu-Orabi, S.T.; Al-Hamadany, R.; Atfah, M.A.; Ali, A.A.-S.; Abu-Shandi, K., *Asian J. Chem.*, 1999, 11, 774.
- [27] Reynolds, G.A., *J. Org. Chem.*, 1964, 29, 3733.
- [28] Regiz, M.; Himbert, G., *Tetrahedron Lett.*, 1970, 2823.
- [29] Schkeryantz, J.M.; Pearson, W.H., *Tetrahedron*, 1996, 52, 107.
- [30] Houk, K.N., *J. Am. Chem. Soc.*, 1972, 94, 8953.
- [31] Moore, H.; Wikholm, R., "Chemistry of Quinonoid Compounds", Ed. S. Patai, Interscience, New York, 1974.
- [32] Wolff, L., *Ann.*, 1931, 299, 274.