SHORT PAPER

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Utility of cyanothioformamides in synthesis of some bis(imidazole, oxazole, thiazole, oxadiazole, triazole, benzoxazinethione and quinazoline) derivatives

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Interaction of 1,4-bis(cyanothioformamido)benzene **2** with various electrophilic and nucleophilic reagents furnished the corresponding bis(imidazole, oxazole, thiazole, oxadiazole, triazole, benzoxazinethione and quinazoline) derivatives.

Keywords: cyanothioformamides, bis(imidazole, oxazole, thiazole, oxadiazole, triazole, benzoxazinethrone, quinazoline)

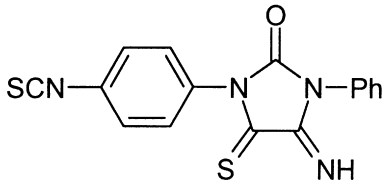
A variety of heterocyclic ring closure reactions with cyanothioformamide,[1-3] give rise to imidazoles,[4] oxazoles,[5] thiazoles[6,7] and other heterocycles.[8-11] Our interest in this type of reaction,[12] activated nitriles[13] and the chemistry of cyanothioformamides[14-18] led us to synthesise some fused heterocyclic system such as pyrrolothiazole, pyrrolopyrrole,[19] imidazothiophene, imidazothiopyrane,[20] and benzothiazoloquinazolinones, imidazoquino-xalines.[21] Also, comparative studies between (cyanothioformamides and oxazolidineimino-thiones)[22] and (oxazolidineiminothiones and imidazolidineiminothiones)[23] derived from cyanothioformamides) were carried out. Cyanothioformamides were also reacted as nucleophiles either by nitrogen to give imidazoles or by sulfur to give thiazoles.[6,7] El-Sharief *et al*[21,24] reacted different types of cyanothioformamides and *o*-chlorocyanothioformanilide with various electrophilic, nucleophilic and *o*-substituted nucleophilic reagents.

In the present investigation some bis imidazoles, oxazoles, thiazoles, oxadiazoles, triazoles, benzoxazinethiones and quinazolines derived from 1,4-bis(cyanothioformamido)benzene have been synthesized. The key intermediate 1,4-bis(cyanothioformamido)benzene **2** was prepared from the reaction of 1,4-bis(isothiocyanato)benzene **1**[25] with potassium cyanide at room temperature[3].

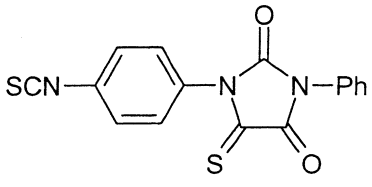
The structure of **2** was established on the basis of elemental and spectral analyses.IR measurements of **2** showed bands characteristic of (NH, CN and CS–N<); its ^{1}H NMR spectrum exhibited an AB quartet and variable hydrogen NH which disappeared on addition of D_2O. The mass spectrum of **2** revealed *m/z* 219 (27%) (M–HCN) and the base peak at *m/z* 192 (100%), from 1,4-bis(isothiocyanato)benzene. ^{13}C NMR showed four types of carbon: 2CS, 2Ar–C (b), 4Ar–C (a) and 2C≡N. 1,4-bis(cyanothioformamido)benzene **2** was allowed to react with some electrophiles (acetonitrile, phenyl isocyanate, phenyl isothiocyanate and acetaldehyde) and with some binucleophiles (*o*-phenylenediamine, *o*-aminophenol and *o*-aminothiophenol), also with other reagents (acetylhydrazine, benzoylhydrazine, salicylic acid and methyl salicylate).

Thus, when compound **2** was reacted with two moles of acetonitrile in tetrahydrofuran containing triethylamine at room temperature cyclisation occurred to afford a product, which analysed for $C_{14}H_{12}N_6S_2$. The structure of this product has been supported by spectral data (IR, ^{1}H NMR and mass spectra) and was formulated as 3,3′-(1,4-phenylene) bis(5-imino-2-methyl-3,5-dihydroimidazole-4-thione) **3**, Scheme 1. ^{1}H NMR data of **3** exhibited δ at 2.49 (s, 6H, $2CH_3$) and δ 7.3–7.9 ppm (q, 4H, AB system). The variable hydrogens 2NH appeared underneath the aromatic protons and disappeared on addition of D_2O. The mass spectrum of **3** revealed the molecular ion peak M^+ at *m/z* 328 (8%) and another significant peak at *m/z* 126 (21%) corresponding to the 5-imino-2-methyl-4-thioxoimidazoline ring while the base peak appeared at *m/z* 91.

Compound **2** also, underwent cyclisation upon its reaction with phenyl iso (thio)cyanate in tetrahydrofuran containing a catalytic amount of triethylamine giving products with analytical and spectral data in good agreement with the proposed structures **4a,b**, respectively. The mass spectrum of **4a** showed a molecular ion peak M^+ at *m/z* 484 (27.7%) with a base peak at *m/z* 192 (100%) corresponding to 1,4-bis(isothiocyanato) benzene and other significant peaks were at: *m/z* 485 (M + 1; 40%), 486 (M + 2; 13.6%), 487 (M + 3; 4.5%) & 338 (49%) due to



A chemical characterisation of 1,1`-(1,4-phenylene)bis (4-imino-3-phenyl-5-thioxoimidazolidin-2-one) **4a** was afforded through its reaction with DMF/HCl and with phenyl hydrazine to give the corresponding bis-imidazolidinedione derivatives **5** and 1,1`-(1,4-phenylene)bis(4-imino-3-phenyl-5-phenylhydrazono-imidazolidin-2-one) **6** respectively. The structures of compounds **5**,**6** were confirmed on the basis of their spectral and analytical data.IR measurements of **5** exhibited the absence of ν_{NH} and the presence of ν_{CO} around 1700 and CS-N< at 1509 and 1211 cm^{-1} (amide II and I). The mass spectrum of **5** revealed a molecular ion peak M^+ at *m/z* 486 (32.6%) with a base peak at *m/z* 192 (100%): from 1,4-bis(isothiocyanato)benzene and other significant peaks were at *m/z* 487 (M+1; 28.9), 488 (M+2; 9.2%), 489 (M+3; 3.7%), 490 (M+4; 1.5%) and 339 (28.9) due to



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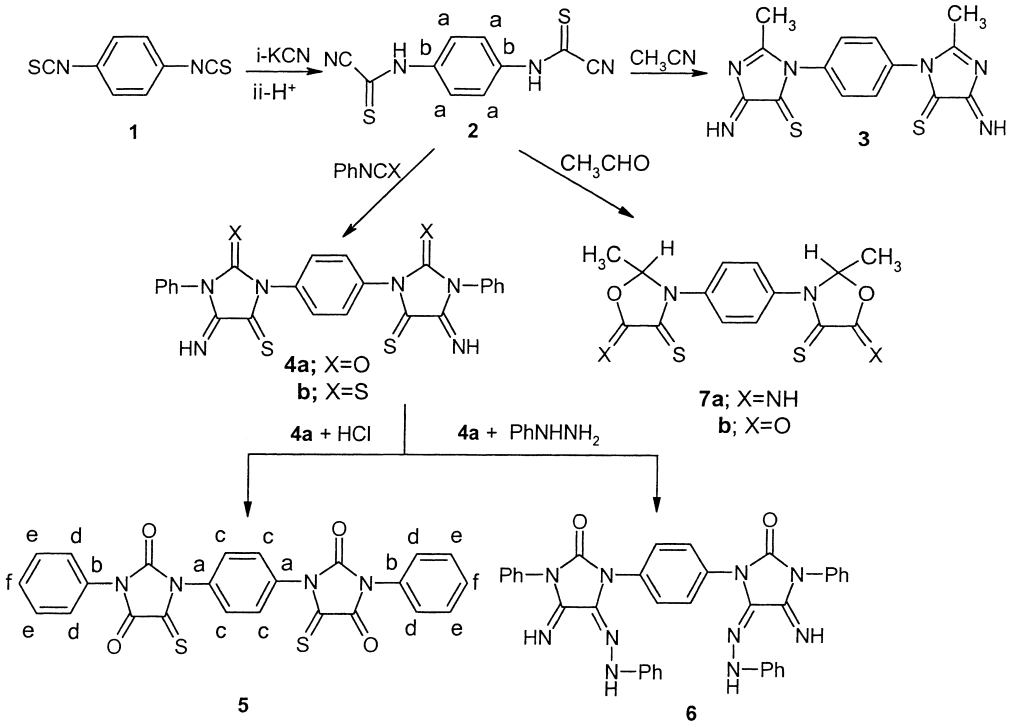
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 1

Similarly, interaction of **2** with aldehydes as electrophile was investigated. Thus when compound **2** was treated with two moles of acetaldehyde in THF/TEA a product was formed which was formulated as 3,3`-(1,4-phenylene)bis(5-imino-2-methyl-oxazolidine-4-thione) **7a** (Scheme 1). Hydrolysis of **7a** by DMF/HCl furnished 3,3`-(1,4-phenylene)-bis (2-methyl-4-thioxo-oxazolidin-5-one) **7b** (Scheme 1). Both **7a** and **7b** were confirmed by IR, 1H NMR, mass spectra and elemental analyses. A point of interest is that mass spectra of compounds **2**, **4a**, **5** and **7a** have the same base peak at *m/z* 192 from: 1,4-bis(isothiocyanato)benzene.

This study was extended to investigate the behavior of compound **2** towards some binucleophiles. Thus interaction of **2** with *o*-phenylenediamine in refluxing DMF containing TEA produced a sulfur free product of composition $C_{20}H_{16}N_6$ (*m/z* 340). Its IR and elemental analysis were compatible with the assigned structure, which was formulated as *N*,*N*`-bis-(1*H*-benzimidazol-2-yl)benzene-1,4-diamine **8** (Scheme 2). The reaction was proceeding via nucloeophilic attack with elimination of HCN followed by cyclocondensation with $H_2S$ elimination. Similarly, *N*,*N*`-Bis-(benzoxazol-2-yl)-benzene-1, 4-diamine **9** and *N*,*N*`-Bis-(benzothiazol-2-yl)-benzene-1,4-diamine **10** were obtained when compound **2** was refluxed in DMF with *o*-aminophenol and *o*-aminothiophenol in presence of TEA. The assumed structures **9** and **10** were elucidated by analytical and spectral data.

Similarly, interaction of **2** with acetylhydrazine was also investigated. Thus two equivalents of acetylhydrazine were allowed to react with **2** where evolution of H_2S could be easily detected during the reaction period. This indicated that the product must be sulfur free and hence only one isomeric structure could be given. Elemental and spectral data of the obtained product were in complete agreement with structure **11** (Scheme 2) as: *N*,*N*`-Bis-(5-methyl-[1,3,4]oxadiazol-2-yl)-benzene-1,4-diamine.

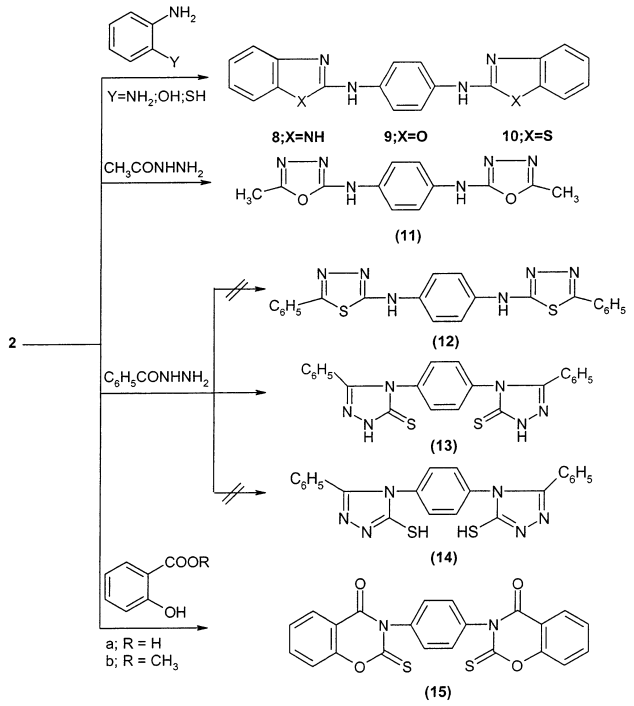
On the other hand, when two moles of benzoylhydrazine were reacted with **2** under the same conditions, H_2S was not liberated and could not observed during the experiment which indicated that the resultant must be an organo-sulfur compound. Both elemental and spectral data were compatible with the three possible isomeric structures (**12**, **13** and **14**; Scheme 2).

IR spectrum (KBr disks) of the product obtained from this reaction exhibited the presence of thioamide group (–CS–N<) at 1512.1 cm^{-1} (amide II), 1218.9 cm^{-1} (amide I) and ν_{NH} stretching at 3201.6 cm^{-1} and the absence of any absorption bands around 2600–2550 cm^{-1} characteristic of the thiol group (S–H stretching). Also, these IR measurements showed no absorption bands around 750 cm^{-1} indicative of the thioether group[26] (C–S–C) which favoured structure **13** over the possible isomers **12** and **14**.

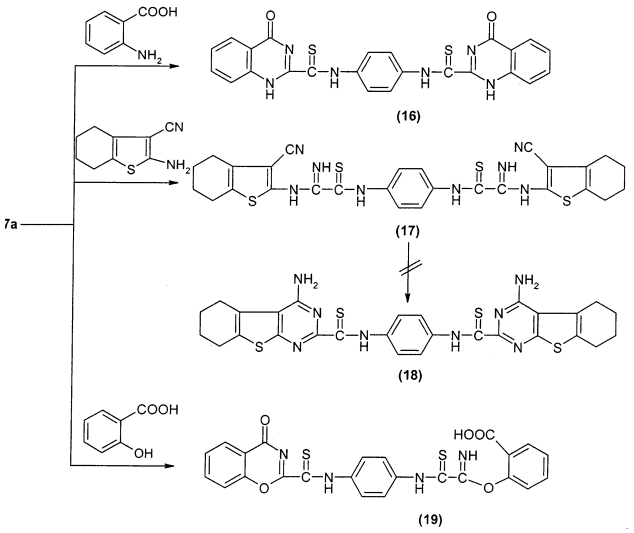
Molecular mechanics calculations (MM5) were performed using the computer program PC MODEL 486 version 5 available from Serena software. This study proved that 4,4'(1,4-phenylene)bis(5-phenyl-3-thioxo-2,4-dihydro[1,2,4]triazole) **13** (Scheme 2) has less energy *E* (kcal/mol) = 34.86 than the other isomeric structures **12** (*E* = 60.49) or **14** (*E* = 50.06). This indicated that the molecular minimization energy (*E*) favours the formation of **13** rather than **12** or **14** (Fig.1). These findings are in complete agreement with those recently obtained[27].

A variety of these compounds: 3-thioxo-2,4-dihydro-[1,2,4]triazoles were synthesised by the authors[28-31] which demonstrated that these products may exist in thione-thiol tautomeric forms and that the thione structures dominate in the solid state. These results are in complete agreement with our previous work[26] on thioamide compounds for which both IR and PMR were carried out by Sadtler Research Laboratories, Division of Bio-Rad Laboratories, INC., Philadelphia USA.

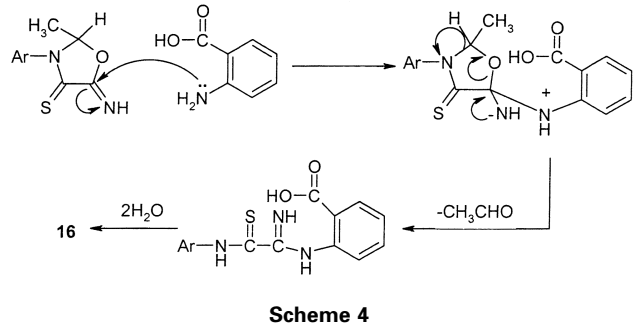
They postulated thione–thiol tautomerism for these products and presumed that in solid state they exist in the thione form but in the liquid state they undergo tautomerisation to the thiol form. The mechanism of formation of **11 or** 13 could be achieved through nucleophilic attack with elimination of



Scheme 2



Scheme 3



Scheme 4

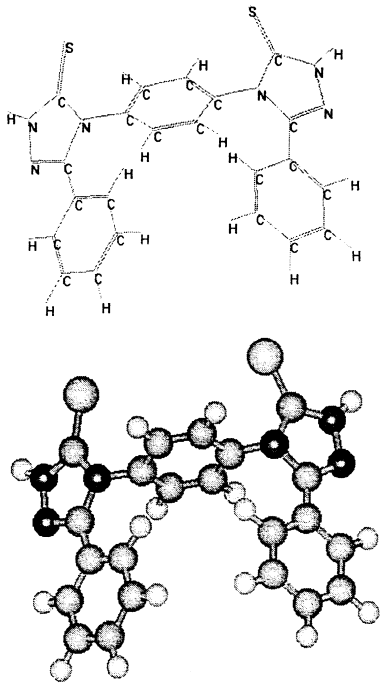


Fig. 1

2HCN molecules then cyclisation either by evolution of H_2S or elimination of $2H_2O$ molecules to give **11** or **13** respectively which are in complete agreement with our recent results[22].

Furthermore, on refluxing compound **2** with two moles of salicylic acid or methyl salicylate in DMF containing a catalytic amount of TEA, 3,3`-(1,4-phenylene)bis(2-thioxo-2,3-dihydro-benzo[e][1,3]oxazine-4-one) **15** was obtained. Formation of compound **15** is assumed to proceed via elimination of two moles of each of HCN and H_2O or CH_3OH, (Scheme 2). The structure of **15** was proved on the basis of its IR mesurements 1677 (C=O) and its mass spectrum which revealed a molecular ion peak at *m/z* 432 (M+, 28.26) with a base peak at *m/z* 86.

We moved to study the behaviour of bis-oxazolidine-iminothione **7a** towards *o*-substituted nucleophiles (anthranilic acid and 2-amino-4,5,6,7-tetrahydrobenzothiophene-3-carbonitrile) as well as salicylic acid. Thus, refluxing of **7a** with anthranilic acid in DMF containing a catalytic amount of triethylamine furnished a product which is formulated as 1,4-bis-[4-oxo-1,4-dihydroquinazoline-2-(thiocarbonyl) amino]benzene **16**, (Scheme 3). The structure of **16** was established by microanalytical and spectral data. IR spectrum exhibited characteristic bands for NH, C=O and CS groups, ^{1}H NMR spectrum of **16** (DMSO-d6) Showed signals at δ 12.3 assigned to four variable hydrogens and a multiplet at δ 7.6–8.26 assigned to 12 aromatic protons. Also, the mass spectrum of **16** showed a molecular ion peak at *m/z* 484, which is in agreement with the proposed formula $C_{24}H_{16}N_6O_2S_2$. The mechanism of formation of **16** can be rationalised as described in Scheme 4 through nucleophilic attack of the amino group of anthranilic acid on the imino group of **7a** with loss of an acetaldehyde molecule followed by cyclisation with elimination of water. These findings are in complete agreement with those obtained by El-Sharief *et al.*[22,23] In a similar manner, Compound **7a** was reacted with 2-amino-4,5,6,7-tetrahydrbenzothiophene-3-carbonitrile to give bis-thioamide derivative **17**. The other possible structure **18** for this product was excluded on the basis of spectral data (IR exhibited the presence of νCN at 2200 cm^{-1}).

Table 1 Characterisation Data for prepared compounds

Compd. no.	M.p./°C	Yield/%	Mol.formula (mol.wt.)	Elemental analyses Calcd./Found (%) C	H	N	S
2	166-70	90	$C_{10}H_6N_4S_2$ (246)	48.78 48.60	2.44 2.40	22.76 22.60	26.02 25.90
3	>300	65	$C_{14}H_{12}N_6S_2$ (328)	51.22 51.10	3.66 3.50	25.61 25.40	19.51 19.60
4a	260	85	$C_{24}H_{16}N_6O_2S_2$ (484)	59.50 59.30	3.31 3.20	17.36 17.20	13.22 13.10
4b	>300	43	$C_{24}H_{16}N_6S_4$ (516)	55.81 55.60	3.10 3.00	16.28 16.10	24.81 24.80
5	290	76	$C_{24}H_{14}N_4O_4S_2$ (486)	59.26 58.80	2.89 2.90	11.52 11.40	13.17 13.20
6	>300	78	$C_{36}H_{28}N_{10}O_2$ (632)	68.35 68.20	4.43 4.30	22.15 22.00	- -
7a	>300	55	$C_{14}H_{14}N_4O_2S_2$ (334)	50.30 50.10	4.19 4.10	16.77 16.30	19.16 19.10
7b	295	84	$C_{14}H_{12}N_2O_4S_2$ (336)	50.00 49.50	3.57 3.40	8.33 8.10	19.05 19.10
8	>300	56	$C_{20}H_{16}N_6$ (340)	70.59 70.50	4.71 4.60	24.71 24.50	- -
9	>300	42	$C_{20}H_{14}N_4O_2$ (342)	70.18 70.00	4.09 3.90	16.37 16.20	- -
10	>300	37	$C_{20}H_{14}N_4S_2$ (374)	64.17 63.90	3.74 3.50	14.97 14.70	17.11 17.00
11	200	68	$C_{12}H_{12}N_6O_2$ (272)	52.94 52.80	4.41 4.40	30.88 30.90	- -
13	>300	55	$C_{22}H_{16}N_6S_2$ (428)	61.68 61.60	3.74 3.70	19.63 19.50	14.95 14.90
15	>300	77	$C_{22}H_{12}N_2O_4S_2$ (432)	61.11 61.00	2.78 2.60	6.48 6.30	14.82 14.70
16	>300	84	$C_{24}H_{16}N_6O_2S_2$ (484)	59.50 59.40	3.31 3.20	17.36 17.10	13.22 13.20
17	152	43	$C_{28}H_{26}N_8S_4$ (602)	55.81 55.70	4.32 4.20	18.61 18.40	21.26 21.20
19	>300	66	$C_{24}H_{16}N_4O_5S_2$ (460)	57.14 57.10	3.18 3.10	11.11 11.40	12.70 12.80

Finally interaction of bis-oxazolidineiminothione **7a** with salicylic acid, afforded a product with analytical and spectral data which indicated that two moles of salicylic acid were consumed with elimination of one mole of both acetaldehyde and water. This product was formulated as 2-{4-[(4-oxo-4*H*-benzo[e][1,3]oxazine-2-carbothioyl)-amino]-phenylthioic arbamoanecarboximidoyloxy}-benzoic acid (thiocarbonyl) amino]benzene **19** (Scheme 3). The mechanism of this reaction was profused to be a similar manner to that in the case of anthranilic acid.

Experimental

All melting points are uncorrected. IR spectra (KBr) were measured on a Shimadzu 440 spectrometer, ^{1}H NMR spectra were obtained in DMSO on a Varian Gemini 200 MHz spectrometer using TMS as internal standard; chemical shifts are reported as δ (ppm). Mass spectra were obtained on GC MS\QP 1000 Ex mass spectrometer at 70 eV. Elemental analyses were carried out at the Microanalytical Centre of Cairo University.

The starting compound 1,4-bis(cyanothioformamido)benzene **2** was prepared according to the reported method[3]; recrystallisation from THF gave yellow crystals (Table 1): IR spectrum exhibited the following bands: 3261(NH), 2217(-CN), 3030(CH-arom.) and 1425 and 1100 cm^{-1} (CS–N).^{1}H NMR spectrum exhibited the following signals: δ 7.6 (s, 2H, 2NH; exchangeable with D_2O), 7.3-7.6(q, 4H,AB system), ^{13}C NMR [$(CD_3)_2$ CO] at δ =163.7(2CS), 137.9[2Ar-C (*b*)], 125.0:[4Ar-C (*a*)], 114.9(2CN) and mass spectrum (%) 219(M-HCN; 27), 192(100), 160(19), 134(38), and 75(19).

3,3`-(1,4-phenylene)bis(5-imino-2-methyl-3,5-dihydroimidazole-4-thi-one) **(3)**: A mixture of **2** (0.01 mole) in THF (20 ml), acetonitrile (0.022 mole), and triethylamine (0.5 ml) was stirred at room temperature for 30 min. The obtained solid was recrystallised from ethanol to give **3** (Table 1). IR spectrum exhibited bands around: 3240(NH), 2900(CH-aliph.) and 1512 and 1160 cm^{-1} (CS–N). ^{1}H NMR spectrum of **3** showed signals at δ 2.49 (s, 6H, $2CH_3$),and 7.3–7.9 ppm. (m, 6H, Ar-H+2NH, exchangeable with D_2O), MS (%): 328(M^+; 8), 329(M+1; 8), 330(M+2; 8), 312(10),281(9), 234(9.6), 198(15), 155(28), 126(21), 118(20), and 91(100).

1,1`-(1,4-phenylene)bis(4-imino-3-phenyl-5-thioxoimidazolidin-2-one)* **(4a)**, *and 1,1`-(1,4-phenylene)bis(4-imino-3-phenylimidazolidin-2,5-dithione) (**4b)**: A mixture of **2** (0.01 mole), phenyl isocyanate or isothiocyanate (0.02 mole) in THF (20 ml), and triethylamine (0.5 ml) was stirred at room temperature for 30 min. The obtained solid was recrystallised from dioxane to give **(4a,b)** (Table 1). IR spectra of **4a** exhibited bands at: 3210(NH), 1680(C=O), 1590(C=N), 1450 and 1120 cm^{-1} (CS-N). **4b**: 3200(NH), 1610(C=N), 1470 and 1130 cm^{-1} (CS-N). ^{1}H NMR spectrum of **4a** exhibited signals: δ 7.45–7.49 (m, 14H,Ar-H), 9.73 (s, 2H, 2NH;exchangeable with D_2O), ^{1}H NMR of **4b**: 7.27–8.08 (m, 14H, Ar-H), and 9.89 ppm (s, 2H, 2NH;exchangeable with D_2O). MS (%) of **4a**: 484(M^+; 27.7), 485(M+1; 40), 486(M+2; 13.6), 487(M+3; 4.5), 365(6), 338(49), and 192(100).

Hydrolysis of **4a** *to give* **(5)**: To a solution of **4a** (0.01 mole) in boiling DMF (20 ml) Conc. HCl (5 ml) was added. The solution was refluxed for 1 h to give **5** which was recrystallised from dioxane (Table 1). IR spectrum of **5** showed the absence of ν_{NH}. ^{1}H NMR spectrum of **5** showed the following signals: 7.3–7.8(m, 14H,Ar-H). ^{13}C NMR [$(CD_3)_2CO$] of **5**: δ 185.9(4CO), δ 154.8(2CS), and six types of Ar-C at δ= 135.2(2C; (a), 132.7(2C; (b), 130.1(4C; (c),

130.0(4C; (d), 129.5(4C; (e) and 127.9(2C; (f). MS (%) of 5: 486(M^+; 32.6), 487(M+1; 28.9), 488(M+2; 9.2) 489(M+3; 3.7), 490(M+4; 1.5), 367(0.5), 340(21.3), 339(28.9), and 192(100).

Formation of bis-hydrazone **(6)***:* A solution of **4a** (0.01 mole) in DMF (30 ml) was treated with phenyl hydrazine (0.02 mole), and the reaction mixture was refluxed for 6h. The solid that obtained was recrystallised from dioxane to give **6** (Table 1). IR spectrum showed 3289(NH), 1749(C=O) and 1600 cm^{-1} (C=N). MS (%) spectrum of **6** showed peaks: 632(M^+; 24.49), 513(20), 460(24.49), 370(45), 354(39), 296(43), 145(24.49), 135(49), and 58(100).

3,3`-(1,4-phenylene)bis(5-imino-2-methyloxazolidine-4-thione) **(7a)***:* A mixture of **2** (0.01 mole), acetaldehyde (0.02 mole) in THF (20 ml), and triethylamine (0.5 ml) was stirred at room temperature for 30 min. The obtained solid was recrystallised from dioxane to give **7a** (Table 1). IR spectrum of **7a** exhibited the following bands: 3220 (NH), 2900(CH-aliph.), and 1540 and 1100 cm^{-1} (CS–N). ^{1}H NMR: at δ=1.7(6H,d,2CH_3), 6.1(2H,q,2CH), 7.2–7.7(4H,q,AB system) and 10.3(2H,hump,2NH disappeared by D_2O). MS (%): 334(M^+; 5), 335(M+1; 3), 265(4), 263(18), 219(9), 192(100), 160(20), 134(37), 90(32), and 76(13).

Hydrolysis of **(7a)** *to give* **(7b)***:* To a solution of **7a** (0.01 mole) in boiling DMF (20 ml), conc. HCl (5 ml) was added. The product was recrystallised from dioxane to give **7b** (Table 1). IR spectrum of **7b** showed the absence of ν_{NH}.

N,N`-Bis-(1H-benzimidazole-2-yl)-benzene-1,4-diamine **(8)**: A mixture of **2** (0.01 mole), *o*-phenylenediamine (0.02 mole) and triethylamine (0.5 ml) in DMF (30 ml) was refluxed for 12h, then allowed to cool and poured into cold water (50 ml). Acidification with HCl yielded a solid product, which was recrystallised from dioxane to give **8** (Table 1). IR spectrum of **8** showed the following bands: 3250(NH), 3030(CH-arom.) and 1595(C=N). MS (%): 340(M^+; 15), 341 (M+1; 33), 342(M+2; 16), 284(40), 279(41), 250(37), 234(31.6), 196(21), 178(30), and 136(100).

N,N`-Bis-(benzoxazol-2-yl)-benzene-1,4-diamine **(9)**: A mixture of **2** (0.01 mole),*o*-aminophenol (0.02 mole) and triethylamine (0.5 ml)in DMF (30 ml)was reacted and treated as above to give **9** (Table 1). IR spectrum of **9** exhibited the following bands: 3270(NH), 3050(CH-arom.) and 1610(C=N). MS (%): – 342(M^+; 41), 289(66), 252(55), 227(12), 170(52), 158(50), 157(82), 141(42), 114(64), 103(100), and 87(65).

N,N`-Bis-(benzothiazol-2-yl)-benzene-1,4-diamine **(10)**: A mixture of **2** (0.01 mole), *o*-aminothiophenol (0.02 mole) and triethylamine (0.5 ml) in DMF (30 ml) was reacted and treated similarly to give **10** (Table 1). IR spectrum of **10** showed the following bands: 3230(NH), 3070(CH-arom.) and 1600(C=N). ^{1}H NMR spectrum of **10** exhibited the signals: 7.36-8.20 (m, 12H, Ar-H), 10.58(2s, 2H, 2NH, exchangeable with D_2O). MS (%): 374(M^+; 19), 375(M+1; 22), 358(35), 338(47), 337(100), 307(41), 296 (72), 239(47) and 158(59).

N,N`-Bis-(5-methyl-[1,3,4]oxadiazol-2-yl)-benzene-1,4-diamine **(11)**: A mixture of **2** (0.01 mole), acetylhydrazine (0.02 mole) and triethylamine (0.5 ml) in DMF (30 ml) was refluxed for 24 h and treated as above to give **11** (Table 1). IR spectrum of **11**: 3217(NH), 2839(CH-aliph.) and 1612(C=N). MS (%): 272(M^+; 0.57), 140(100), 112(31), 98(5), 85(80), 71(18).

4,4`-(1,4-phenylene)bis(5-phenyl-3-thioxo-2,4-dihydro-[1,2,4]-triazole) **(13)**: A mixture of **2** (0.01 mole), benzoylhydrazine (0.02 mole) and triethylamine (0.5 ml) in DMF (30 ml) was refluxed for 24 h and treated as above to give **13** (Table 1). IR spectrum of **13** exhibited the following bands: 3250(NH), 1512 and 1118 cm^{-1} (CS-N) and absence of $\nu_{C=O}$. MS (%) of **13**: 446(M+H_2O; 10%), 382(10), 208(12), 134(28), 105(28), 75(30), 63(74), and 52(100).

3,3`-(1,4-phenylene)bis(2-thioxo-2,3-dihydro-benzo[e][1,3]-oxazine-4-one) **(15)**: A mixture of **2** (0.01 mole), salicylic acid or methyl salicylate (0.02 mole) and triethylamine (0.5 ml) in DMF (30 ml) was refluxed for 24 h The obtained solid was recrystallised from dioxane to give **15** (Table 1). IR spectrum of **15** exhibited bands at: 1677 (C=O) and 1515 and 1124 cm^{-1} (CS-N). MS (%) of **15**: 432(M^+; 28), 398(44), 369(44), 339(54), 223(46), 199(54), 164(48), 130(50), 126(70), and 86(100).

1,4-Bis[4-oxo-1,4-dihydroquinazoline-2-(thiocarbonyl) amino] benzene **(16)**: A mixture of (**7a**; 0.01 mole), anthranilic acid (0.02 mole) and triethylamine (0.5 ml) in DMF (30 ml) was refluxed for 12h. The solid that obtained was recrystallised from dioxane to give **16** (Table 1). IR spectrum of **16** exhi-bited the following bands: 3246 (NH), 1682 (C=O), and 1514 and 1184 cm^{-1} (CS-N). MS (%) of **16**: 484(M^+; 14), 412(17), 340(30), 338(100), 318(19), 296(64), 295(46), 246(11), 219(12), 191(25), 78(32). ^{1}H NMR spectrum of **16** exhibited the following signals: at δ 7.64–8.22(m; 12H;Ar-H), 12.3(s; 4H; 4NH exchangeable with D_2O).

2-(3-Cyano-4,5,6,7-tetrahydro-benzo[b]thiophen-2-ylamino)-N-(4-{[N-(3-cya-no-4,5,6,7-tetrahydro-benzo[b]thiophen-2-yl)-carbamimidoane-carbothioyl]-amino}-phenyl)-2-imino-thioacetamide **(17)**: A mixture of (**7a**; 0.01mole), 2-amino-4,5,6,7-tetrahydro-benzo[b]thiophen-3-carbonitrile (0.02 mole) and triethylamine (0.5 ml) in dioxane (30 ml) was refluxed for 10 h. The solid that obtained was recrystallised from dioxane to give **17** (Table 1). IR spectrum exhibited bands at 3209 (NH), 2934 (CH-aliph.), 2196 (CN) and 1512 and 1182 cm^{-1} (CS-N). MS (%) of **17**: 603(M+1; 50), 527(42), 441(50), 350(46), 240(58), 192(46), 164(62), 121(58), 75(100).

2-{4-[(4-Oxo-4H-benzo[e][1,3]oxazine-2-carbothioyl)-amino]-phenyl-thioic arbamoanecarboximidoyloxy}-benzoic acid (thiocarbonyl)-amino]-benzene **(19)**: A mixture of (**7a**; X=NH; 0.01 mole), salicylic acid (0.02 mole) and triethylamine were refluxed for 24 h. The solid that obtained was recrystallised from dioxane to give **19** (Table 1). Its IR spectrum exhibited bands at 3360 (NH), 1741 (C=O), 1512 and 1127 cm^{-1} (CS–N). MS (%) of **19**: 460(M-CO_2), 398(41), 293(44), 227(55), 190(58), 172(41), 157(68), 138(55), 121(75), 72(100).

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