Azopyrazolobenzylidene Derivatives of 4-Amino-1,2,4-triazol-3-ones. Synthesis of 4-{[4-(3,5-Dimethyl-1*H*-pyrazol-4-yl)diazenyl]-benzylidene}amino-2-aryl-5-methyl-3*H*-[1,2,4]-triazol-3-ones.

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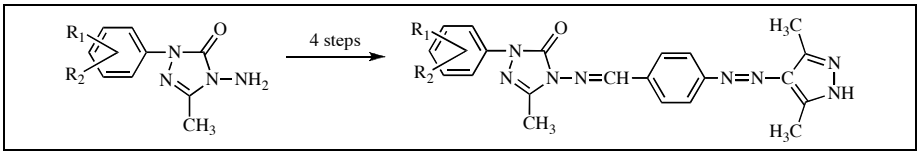

The Schiff bases **3a-h** obtained from 4-amino-1,2,4-triazol-3-ones **1a-h** when subjected to Japp-Klingemann reaction yielded the corresponding 3-{2-[(2-aryl-5-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-pentane-2,4-diones **4 a-h**. These diones on cyclisation with N_2H_4 yielded the title compounds **5a-h**. The energetics of the Keto-enol tautomers of the diones was calculated by semiemperical calculations using AM1 and PM3 methods. All these compounds were screened for their antimicrobial activity against few microbes and most of them exhibited fungal inhibition more than the reference drugs used.

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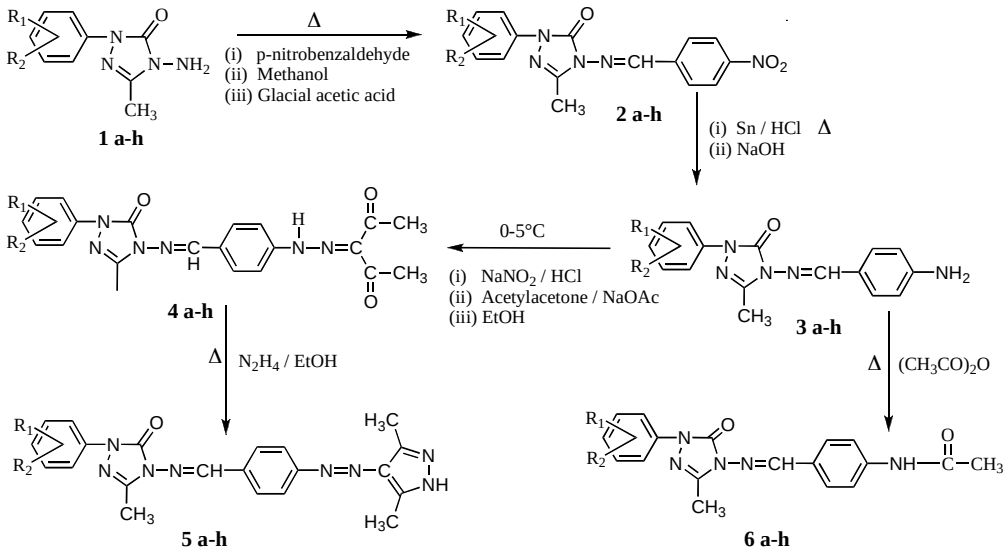
INTRODUCTION

The facile synthesis of 4-amino-2-aryl-5-methyl-3*H*-[1,2,4]-triazol-3-ones **1a-h** from 3-arylsydnones by two facile successive one-pot ring conversions has been recently reported from our laboratory [1]. These new triazolinone derivatives, reported for the first time, have not been investigated for their reactions. Hence, we thought of exploiting the synthetic utility of the potential amino group in these compounds. In this paper we report the synthetic utility of compounds **1a-h** for the synthesis of the title compounds **5a-h**. The amino group was unreactive towards reagents like alpha-halogen esters, KCNS, nitrous acid *etc*. indicating its weak nucleophilic character, which is due to the strong electron-withdrawing triazolinone ring. However, some Schiff bases of compounds **1a-h** have been prepared in our laboratory [2] by reaction with aromatic aldehydes on prolonged heating. One of these Schiff bases **2a-h** (the *p*-nitro derivatives) were found to be useful as they could be converted to amino compounds **3a-h** by reduction of the nitro group. This amino group was reactive enough to undergo Japp-Klingemann reaction resulting in the formation of the 2,4-

Scheme



(a) R_1& R_2=H; (b) R_1=H& R_2=4-Br; (c) R_1=H & R_2=3-Me; (d) R_1=H & R_2=4-Me; (e) R_1=H & R_2=3-Cl; (f) R_1=H & R_2=4-Cl; (g) R_1=H & R_2=4-OCH_3; (h) R_1=3-Cl & R_2=4-CH_3;

diones **4a-h**. These diones were used as building blocks for the preparation of the title compounds - 4-{[4-(3,5-dimethyl-1*H*-pyrazol-4-yl)diazenyl]benzylidene}amino-2-aryl-5-methyl-3*H*-[1,2,4]-triazol-3-ones **5a-h** (Scheme).

The azopyrazoles are known to possess good biological activity [3-6]. Heterocyclic azo dyes containing pyrazole rings have also been used as pigments for dyeing of paper and textiles and also as optical recording medium for worm (write once read many) discs [7-8a]. Hence, compounds **5a-h** containing two heterocycles coupled through the imine and the azo functions would be expected to possess biological activity and would also be suitable molecules for further structural modifications. The experiments for exploring the application of these azo compounds as dyes are under progress.

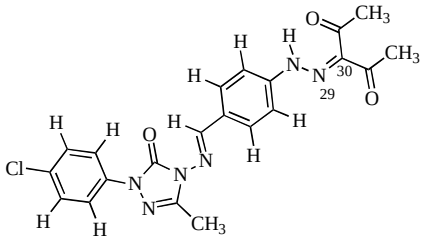
Spectral Characterisation. The IR spectra of the amino compounds **3a-h** showed bands for the asymmetric and symmetric stretching vibrations of NH_2 at 3401 cm^{-1} and 3326 cm^{-1}. The $\gamma_{C=O}$ band of the triazolinone ring appeared as a sharp band at 1703 cm^{-1}. The ^{1}H-NMR spectra of these compounds showed a singlet at δ 4.48 ppm (D_2O exchanged) for the NH_2 protons. The singlets at δ 2.48 ppm (triazolinone CH_3 protons) and δ 9.70 ppm (the imine proton) and the signals at δ 7.43 - 7.94 ppm for the aromatic protons did not show significant changes in the rest of the compounds.

The IR spectra of the diones **4a-h** showed a broad band at 3438 cm^{-1} due to γ_{N-H} vibrations. The $\gamma_{C=O}$ for the 2,4-dione moiety appeared at 1678 cm^{-1}, while the $\gamma_{C=O}$ of the triazolinone ring appeared at 1709 cm^{-1}. The ^{1}H-NMR spectra of compounds **4a-h** showed two singlets at δ 2.42 and 2.44 ppm for the two $-OCH_3$ groups of the 2,4-dione and the imine –CH appeared at δ 9.71ppm. The NH proton observed at δ 14.03 ppm was D_2O exchanged.

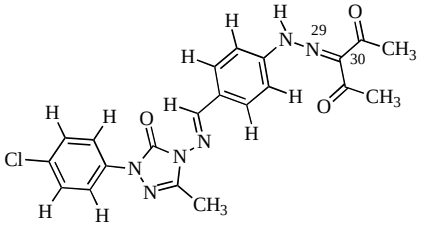
The IR spectra of the pyrazole derivatives **5a-h** showed a broad band at 3215 cm^{-1} due to γ_{N-H} vibrations and only one $\gamma_{C=O}$ band of the triazolinone ring at 1709 cm^{-1}. The absence of the $\gamma_{C=O}$ at 1678 cm^{-1} evidences the formation of the pyrazole ring.The ^{1}H-NMR spectra of these compounds showed the two $-CH_3$ protons of the pyrazole ring as two singlets at δ 2.40 and 2.47 ppm. The spectrum showed the presence of an -NH proton at δ 12.90 ppm (D_2O exchanged).

The N-acetyl derivatives **6a-h** in their IR spectra showed a band at 3320 cm^{-1} due to γ_{N-H} vibrations. The $\gamma_{C=O}$ band of the triazolinone ring appeared at 1709 cm^{-1} and the amide $\gamma_{C=O}$ appeared at 1678 cm^{-1}. The ^{1}H-NMR spectra showed the amide $-CH_3$ protons at δ 2.10 ppm while the amide –NH resonated at δ 10.03 ppm (D_2O exchanged).

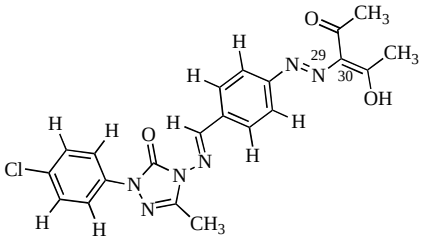
Semiemperical Calculations. The diones **4a-h** would possibly exist in keto-enol forms **TA1 & TA3** and **TA2 & TA4** (**N29-C30 –Syn form**) (Figure 1). The spectral data alone did not reveal which of the tautomeric or the isomeric form is more preferred. Hence, we thought of studying the energetics of these tautomeric and isomeric forms (stereochemistry of the imine group) by molecular orbital methods - semiemperical calculations using AM1 and PM3 methods. We have evidenced the geometry of the Schiff bases (imine double bond attached to the triazolinone ring) by the X-ray crystal studies of a similar type of the compound [9].



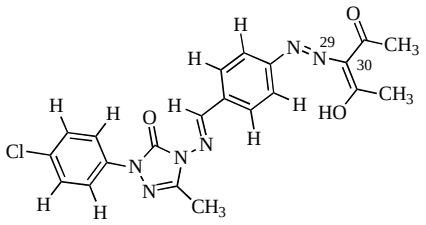
TA1



TA2



TA3



TA4

1

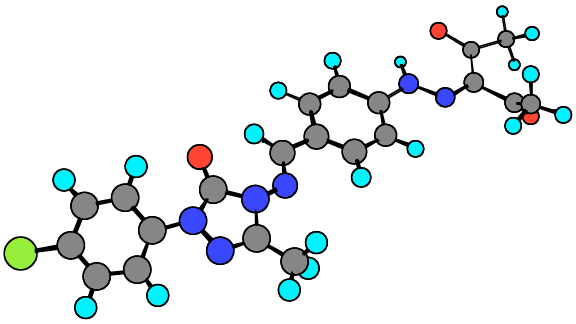
Computational Details. The size of the system studied prevents the use of *ab initio* molecular quantum mechanical methods to perform optimization. Therefore, full geometry optimization was carried out using the MOPAC quantum chemical program [10]. The calculations were carried out with the Restricted Hartree–Fock formalization (RHF) using AM1 [11] and PM3 [12]

semiemperical methods. All the calculations were carried out using PC version of GAMESS.

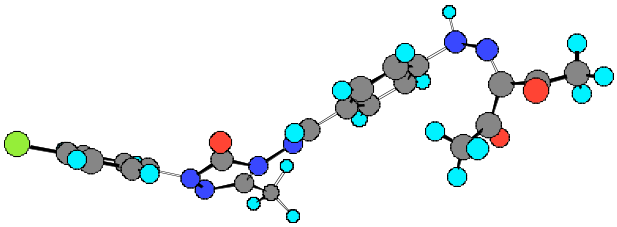
RESULTS AND DISCUSSION

It can be inferred from the energy of heat of formation (**Table**), that the keto form (**TA1**) in which the substituted triazolinone ring and the 2,4-dione group are *trans* with respect to NH-N- bond is more stable than the corresponding *cis* isomer (**TA2**). Similarly, the enol form (**TA3**) in which the substituted triazolinone ring and the 2,4-dione group are *trans* with respect to N=N bond is more stable than the corresponding *cis* isomer (**TA4**). The energy of heat of formation also indicates that the keto form is more stable than the enol form.

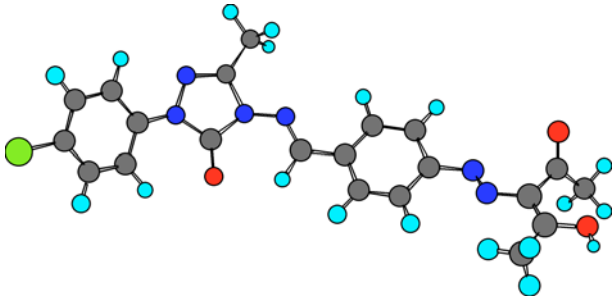
Structure	Heat of formation (ΔH_f) (Kcal/mol)	
	PM3	AM1
TA1	41.159	96.642
TA2	43.881	102.327
TA3	46.315	102.906
TA4	49.585	107.050



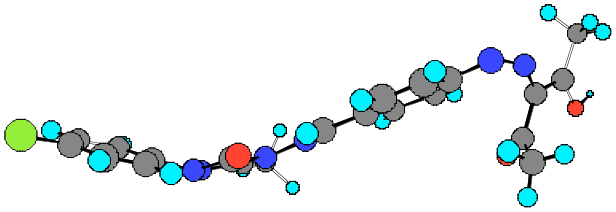
TA1



TA2



TA3



TA4

Figure 2. The energy optimized structures.

Antimicrobial Activity. The preliminary antimicrobial activity of all these compounds was assayed by using cup-plate agar diffusion method, against two bacterial strains- *Bacillus cirroflagellosus* (Gram-positive) and *Escherichia coli* (Gram-negative) and *Asperigillus niger* and *Penicillium notatum* as the fungal strains. Norfloxacin and Griseofulvin were used as reference drugs respectively. The compounds and the reference drugs were screened under identical conditions at a dose of 100 μg/1 ml with DMF as the control solvent. The inhibition measured in mm is used only for qualitative comparative studies. (Norfloxacin 15mm against *E. coli* and 22 mm against *B. cirroflagellosus* and Griseofulvin 18 mm against *P. notatum* and 12 mm against *A. niger*). All the halogenated compounds were found to be more active against the fungi. Fungal inhibition was observed for compounds **3a** (20mm), **3d & 3f** (both 21mm) against *P. notatum* while all these, in particular the halogenated derivatives, exhibited growth inhibition of *A. niger* (14-16 mm), greater than Griseofulvin. Compounds **5a**, **5d**, **5e** and **5h** were also selectively active against *P. notatum* while the 4-chloro (**5e**) exhibited inhibition only against *A. niger* (18mm), considerably greater than Griseofulvin. Bacterial inhibition against *E.coli* was exhibited by compounds **6d**,**6f & 6g** (17mm) while only the chloro compounds **6e & 6f** were active selectively against *A. niger*. It may be noted here that all these microbial inhibitions are found to be more than that of the reference drugs. This observation initiated us to prepare some more structurally modified compounds in the hope of obtaining a potentially active drug and this work will be submitted shortly.

EXPERIMENTAL

The IR spectra were recorded on a NICOLET-IMPACT-410 FT-IR spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AC-300 F, 300 MHz spectrometer in $CDCl_3$/DMSO-d_6 with TMS as internal standard. The mass spectra were recorded on MIver 14 UIC 002002 spectrometer. Elemental analysis was obtained on Heraus C, H, N rapid analyser.

General Procedures. 4-[(4-Aminobenzylidene)-amino]-5-methyl-2-aryl-2,4-dihydro-[1,2,4]-triazol-3-ones **3 a-h**. To (0.5 g, 0.001 mol) of compound **2a-h** and (0.250 g, 0.0015 mol) of tin, 3 ml of concentrated hydrochloric acid was added drop-wise and refluxed on a water bath till the solution was clear (30 min). The reaction mixture was then cooled and made alkaline by addition of NaOH solution and the amino derivatives were extracted with THF. The amorphous pale yellow compounds obtained after the evaporation of the solvent were purified by crystallisation from ethanol.

4-[(4-Aminobenzylidene)-amino]-5-methyl-2-phenyl-3*H*-[1,2,4]-triazol-3-one (3a). Yield 73%; mp. 164-166 °C; ir 3326-3401 (γ_{NH}), 1709 ($\gamma_{C=O}$); ^{1}H-NMR: δ 2.50(s, 3H, CH_3), 4.45 (s, 2H, NH_2), 7.20-7.95 (m, 8H, ArH), 9.55 (s, 1H, =CH). Mass calcd for $C_{16}H_{15}N_5O$: 293.15. Found: 293. *Anal.* Calcd. for $C_{16}H_{15}N_5O$(293.15): C, 65.55; H, 5.11; N, 23.87 %; Found: C, 65.12; H, 4.90; N, 23.51.

4-[(4-Amino-benzylidene)-amino]-5-methyl-2-(4-bromo)-phenyl-3*H*-[1,2,4]-triazol-3-one (3b). Yield 85%; mp.140-142°C; ir 3320-3380 (γ_{NH}), 1709 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.42(s, 3H, CH_3), 4.46(s, 2H, NH_2), 7.30-7.86(m, 8H, ArH), 9.48(s, 1H, =CH). Mass calcd for $C_{16}H_{14}BrN_5O$: 372.22 & 374.22. Found: 372 & 374. *Anal.* Calcd. for $C_{16}H_{14}BrN_5O$(372.22): C, 51.62; H, 3.76; N, 18.80; Found: C, 51.20; H, 3.28; N, 18.40.

4-[(4-Amino-benzylidene)-amino]-5-methyl-2-(3-methyl)-phenyl-3*H*-[1,2,4]-triazol-3-one (3c). Yield 78%; mp.160-162°C; ir 3315-3368 (γ_{NH}), 1709 ($\gamma_{C=O}$); ^{1}H-NMR δ 1.87(s, 3H, CH_3), 2.45(s, 3H, CH_3), 4.40(s, 2H, NH_2), 7.20-7.95(m, 8H, ArH), 9.45(s, 1H, =CH). *Anal*. Calcd. for $C_{17}H_{17}N_5O$ (307.31): C, 66.43; H, 5.53; N, 22.77; Found: C, 66.01; H, 5.18; N, 22.48.

4-[(4-Amino-benzylidene)-amino]-5-methyl-2-(4-methyl)-phenyl-3*H*-[1,2,4]-triazol-3-one (3d). Yield 75%; mp.170-172°C; ir 3320-3381 (γ_{NH}), 1709 ($\gamma_{C=O}$); ^{1}H-NMR δ1.95(s, 3H, CH_3), 2.48(s, 3H, CH_3), 4.42(s, 2H, NH_2), 7.20-7.95(m, 8H, ArH), 9.48(s, 1H, =CH). *Anal*. Calcd. for $C_{17}H_{17}N_5O$ (307.31): C, 66.43; H, 5.53; N, 22.77; Found: C, 66.04; H, 5.28; N, 22.42.

4-[(4-Amino-benzylidene)-amino]-5-methyl-2-(3-chloro)-phenyl-3*H*-[1,2,4]-triazol-3-one (3e). Yield 80%; mp.152-154 °C; ir 3326-3388 (γ_{NH}), 1709 ($\gamma_{=O}$); ^{1}H-NMR δ 2.50(s, 3H, CH_3), 4.50(s, 2H, NH_2), 7.28-7.86(m, 8H, ArH), 9.48(s, 1H, =CH). *Anal.* Calcd. for $C_{16}H_{14}ClN_5O$ (327.77): C, 58.62; H, 4.27 N, 21.35; Found: C, 58.23; H, 3.98; N, 21.01.

4-[(4-Amino-benzylidene)-amino]-5-methyl-2-(4-chloro)-phenyl-3*H*-[1,2,4]-triazol-3-one (3f). Yield 85%; mp.120-122°C; ir 3320-3375 (γ_{NH}), 1709 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.45(s, 3H, CH_3), 3.27(s, 3H, OCH_3), 4.48(s, 2H, NH_2), 7.25-7.98(m, 8H, ArH), 9.50(s, 1H, =CH). Mass calcd for $C_{16}H_{14}ClN_5O$: 327.77 & 329.77. Found: 327&329. *Anal.* Calcd. for $C_{16}H_{14}ClN_5O$(327.77): C, 58.62; H, 4.27; N, 21.35; Found: C, 58.28; H, 3.99; N, 20.95.

4-[(4-Amino-benzylidene)-amino]-5-methyl-2-(4-methoxy)-phenyl-3*H*-[1,2,4]-triazol-3-one (3g). Yield 70%; mp. 120-122°C; ir 3320-3375 (γ_{NH}), 1709 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.45(s, 3H, CH_3), 3.27(s, 3H, OCH_3) 4.48(s, 2H, NH_2), 7.25-7.98(m, 8H, ArH), 9.50(s, 1H, =CH). Mass calcd for $C_{17}H_{17}N_5O$: 323.45. Found: 323. *Anal.* Calcd. for $C_{17}H_{17}N_5O$(323.45): C, 63.12; H, 5.25; N, 21.64; Found: C, 62.81; H, 5.01; N, 21.24.

4-[(4-Amino-benzylidene)-amino]-5-methyl-2-(3-chloro-4-methyl)phenyl-3*H*-[1,2,4]-triazol-3-one (3h). Yield 78%; mp. 120-122°C; ir 3315-3370 (γ_{NH}), 1709 ($\gamma_{C=O}$); ^{1}H-NMR δ 1.77(s, 3H, CH_3), 2.38(s, 3H, CH_3), 4.52(s, 2H, NH_2), 7.20-7.76(m, 8H, ArH), 9.40(s, 1H, =CH). *Anal*. Calcd For $C_{17}H_{16}ClN_5O$ (341.77): C, 59.73; H, 4.68; N, 20.48; Found: C, 59.34; H, 4.32; N, 20.12.

General Procedure for Preparation of 3-{2-[(2-Aryl-5-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-pentane-2,4-diones (4 a-h). The amino compounds (**3 a-h**) (0.4 g, 0.001 mol) were diazotised in 0.4 ml HCl with a cold solution of sodium nitrite (0.2 g, 0.001 mol in 2 ml of water) during a period of 10 minutes. The reaction mixture was stirred for 30 minutes at 0-5°C. This diazotised solution was treated with acetylacetone (0.001 mol) and sodium acetate (0.005 mol) in 10 ml of ethanol, during 15 minutes and stirred for one hour. The reaction mixture was and stirred for one hour, then poured into water and the solid obtained was collected by filtration and crystallised from ethanol to get the 2,4-diones **4a**: Yield 75%; mp. 142-144°C; ir 3485 (γ_{NH}), 1709 (ring $\gamma_{C=O}$), 1675 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.40-2.45(2s, 6H, ($COCH_3$), 2.50(s, 3H, ring CH_3), 7.40-7.90(m, 8H, ArH), 9.71(s, 1H, =CH), 14.03(s, 1H, NH). Mass calcd for $C_{21}H_{20}N_6O_3$: 404.18. Found: 404. *Anal.* Calcd. for $C_{21}H_{20}N_6O_3$(404.18): C, 62.407; H, 4.94; N, 20.78; Found: C, 62.03; H, 4.68; N, 20.48.

3-{2-[(2-(4-Bromo)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-pentane-2,4-dione (4b). Yield 85%; mp. 135-137°C; ir 3438 (γ_{NH}), 1709 (ring $\gamma_{C=O}$), 1672 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.42-2.44(2s, 6H, $COCH_3$), 2.55(2s, 3H, ring CH_3), 2.48(s, 3H, ring CH_3), 7.43-7.90(m, 8H, ArH), 9.75(s, 1H, =CH), 13.90(s, 1H, NH). Mass calcd for $C_{21}H_{19}BrN_6O_3$: 483.32 & 485.32. Found: 483&485. *Anal.* Calcd. for $C_{21}H_{19}BrN_6O_3$ (483.32): C, 52.18; H, 3.93; N, 17.37; Found: C, 51.81; H, 5.60; N, 17.08.

3-{2-[(2-(3-Methyl)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-pentane-2,4-dione (4c). Yield 78%; mp. 152-154°C; ir 3436 (γ_{NH}), 1709 (ring $\gamma_{C=O}$), 1676 ($\gamma_{C=O}$); ^{1}H-NMR δ 1.88 (s, 3H,CH_3), 2.36-2.40(2s, 6H, $COCH_3$), 2.45(2s, 3H, ring CH_3), 7.40-7.90(m, 8H, ArH), 9.60(s, 1H, =CH), 13.90(s, 1H, NH). Mass calcd for $C_{22}H_{22}N_6O_3$: 418.81. Found: 418. *Anal.* Calcd. for $C_{22}H_{22}N_6O_3$(418.81): C, 63.08; H, 5.25; N, 20.05; Found: C, 62.85; H, 4.88; N, 19.78.

3-{2-[(2-(4-Methyl)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-pentane-2,4-dione (4d). Yield 78%; mp.164-166°C; ir 3434 (γ_{NH}), 1709 (ring $\gamma_{C=O}$), 1674 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.00(s, 3H, CH_3), 2.38-2.42(2s, 6H, $COCH_3$), 2.48(s, 3H, ring CH_3), 7.50-8.00(m, 8H, ArH), 9.68(s, 1H, =CH), 14.00(s, 1H, NH). *Anal.* Calcd. for $C_{22}H_{22}N_6O_3$ (418.81): C, 63.08; H, 5.25; N, 20.05; Found: C, 62.77; H, 4.90; N, 19.88.

3-{2-[(2-(3-Chloro)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-pentane-2,4-dione (4e). Yield 78%; mp. 205-207°C; ir 3436 (γ_{NH}), 1709 (ring $\gamma_{C=O}$), 1678 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.38-2.40(2s, 6H, $COCH_3$), 2.50(s, 3H, ring CH_3), 7.40-8.00(m, 8H, ArH), 9.65(s, 1H, =CH), 14.00(s, 1H, NH). *Anal.* Calcd. for $C_{21}H_{19}ClN_6O_3$ (438.32): C, 57.54; H, 4.33; N, 19.16; Found: C, 57.05; H, 4.09; N, 18.84.

3-{2-[(2-(4-Chloro)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-pentane-2,4-dione (4f). Yield 80%; mp.260-262°C; ir 3438 (γ_{NH}), 1709 (ring $\gamma_{C=O}$), 1678 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.40-2.42(2s, 6H, $COCH_3$), 2.55(s, 3H, ring CH_3), 7.50-8.00(m, 8H, ArH), 9.70(s, 1H, =CH), 14.00(s, 1H, NH). Mass calcd for $C_{21}H_{19}ClN_6O_3$: 438.32 & 440.32 Found: 438&440. *Anal.* Calcd. for $C_{21}H_{19}ClN_6O_3$(438.32): C, 57.54; H, 4.33; N, 19.16; Found: C, 57.08; H, 4.05; N, 18.75.

3-{2-[(2-(4-Methoxy)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-pentane-2,4-dione (4g). Yield 70%; mp. 244-246°C; ir 3440 ($\gamma\nu_{NH}$), 1709 (ring $\gamma_{C=O}$), 1674($\gamma_{C=O}$); ^{1}H-

NMR δ 2.42-2.44(2s, 6H $COCH_3$), 2.50(s, 3H, ring CH_3), 3.40(S,3H,OCH_3), 7.43-7.94(m, 8H, ArH), 9.75(s, 1H, =CH), 13.90(s, 1H, NH). Mass calcd for $C_{22}H_{22}N_6O_4$: 439.81. Found: 434. *Anal.* Calcd. for $C_{22}H_{22}N_6O_4$(439.81): C, 60.76; H, 5.05; N, 19.31; Found: C, 60.47; H, 4.76; N, 19.06.

3-{2-[(2-(3-Chloro-4-methyl)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-pentane-2,4-dione (**4h**). Yield 78%; mp.190-192°C; ir 3430 (γ_H), 1709 (ring $\gamma_{C=O}$), 1670 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.44-2.48(2s, 6H $COCH_3$), 2.48(s, 3H, ring CH_3), 7.40-8.10(m, 8H, ArH), 9.85(s, 1H, =CH), 14.00(s, 1H, NH). *Anal.* Calcd. for $C_{22}H_{21}ClN_6O_3$ (453.26): C, 58.29; H, 4.63; N, 18.53; Found: C, 58.01; H, 4.26; N, 18.19.

General Procedure for Preparation of 4-{[4-(3,5-Dimethyl-1*H*-pyrazol-4-yl)diazenyl]benzylidene}amino-2-aryl-5-methyl-3*H*-[1,2,4]-triazol-3-ones (**5 a-h**). Diones (**4a-h**) (0.438 g, 0.001 mol) and hydrazine hydrate 99% (0.2 ml, 0.004 mol) in ethanol (15 ml) were refluxed on a water- bath for 8 hours. The solid obtained after cooling was filtered and washed with hot ethanol to get (**5a**); Yield 70%; mp. 150-152°C; ir 3210 (γ_{NH}), 1709 (ring $\gamma_{C=O}$); ^{1}H-NMR δ 2.44-2.48(2s, 6H, CH_3), 2.55(s, 3H, ring CH_3), 7.55-8.04(m, 8H, ArH), 9.76(s, 1H, =CH), 13.00(s, 1H, NH). Mass calcd for $C_{21}H_{20}N_8O$: 400.67. Found: 400. *Anal.* Calcd. for $C_{21}H_{20}N_8O$(400.67): C, 62.94; H, 4.99; N, 27.95; Found: C, 62.69; H, 4.72; N, 27.68.

4-{[4-(3,5-Dimethyl-1*H*-pyrazol-4-yl)diazenyl]benzylidene}-amino-2-(4-bromo)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one (**5b**). Yield 80%; mp.186-188°C; ir 3218 (γ_{NH}), 1709 (ring $\gamma_{C=O}$); ^{1}H-NMR δ 2.40-2.46(2s, 6H, CH_3), 2.53(s, 3H, ring CH_3), 7.55-8.00(m, 8H, ArH), 9.80(s, 1H, =CH), 13.00(s, 1H, NH). Mass calcd for $C_{21}H_{19}BrN_8O$: 479.10 & 481.10. Found: 479&481. *Anal.* Calcd. for $C_{21}H_{19}BrN_8O$ (479.10): C, 52.64; H, 3.96; N, 23.37; Found: C, 52.35; H, 3.59; N, 23.04.

4-{[4-(3,5-Dimethyl-1*H*-pyrazol-4-yl)diazenyl] benzylidene}-amino-2-(3-methyl)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-ones (**5c**). Yield 70%; mp.160-162°C; ir 3208 (γ_{NH}), 1709 (ring $\gamma_{C=O}$); ^{1}H-NMR δ 2.00(s, 3H, CH_3), 2.38-2.44(2s, 6H, CH_3), 2.45(s, 3H, ring CH_3), 7.40-7.90(m, 8H, ArH), 9.70(s, 1H, =CH), 12.90(s, 1H, NH). *Anal.* Calcd. for $C_{22}H_{22}N_8O$(414.21): C, 63.78; H, 5.31; N, 27.03; Found: C, 63.45; H, 5.05; N, 26.74.

4-{[4-(3,5-Dimethyl-1*H*-pyrazol-4-yl)diazenyl] benzylidene}-amino-2-(4-methyl)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one (**5d**). Yield 78%; mp. 140-142°C; ir 3215 (γ_{NH}), 1709 (ring $\gamma_{C=O}$); ^{1}H-NMR δ 2.03(s, 3H, CH_3), 2.40-2.46(2s, 6H, CH_3), 2.50(s, 3H, ring CH_3), 7.45-8.00(m, 8H, ArH), 9.74(s, 1H, =CH), 12.94(s, 1H, NH). Mass calcd for $C_{22}H_{22}N_8O$: 414.21. Found: 414. *Anal.* Calcd. for $C_{22}H_{22}N_8O$: (414.21):C, 63.78; H, 5.31; N, 27.03; Found: C, 63.38; H, 5.08; N, 26.67.

4-{[4-(3,5-Dimethyl-1*H*-pyrazol-4-yl)diazenyl] benzylidene}-amino-2-(3-chloro)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one (**5e**). Yield 75%; mp.144-146°C; ir 3210 (γ_{NH}), 1709 (ring $\gamma_{C=O}$); ^{1}H-NMR δ 2.35-2.40(2s, 6H, CH_3), 2.50(s, 3H, ring CH_3), 7.55-8.00(m, 8H, ArH), 9.70(s, 1H, =CH), 12.86(s, 1H, NH). *Anal.* Calcd. for $C_{21}H_{19}ClN_8O$(434.5): C, 58.04; H, 4.37; N, 25.77; Found: C, 57.74; H, 4.15; N, 25.53.

4-{[4-(3,5-Dimethyl-1*H*-pyrazol-4-yl)diazenyl] benzylidene}-amino-2-(4-chloro)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one (**5f**). Yield 78%; mp.22°-222°C; ir 3215 (γ_{NH}), 1709 (ring $\gamma_{C=O}$); ^{1}H-NMR δ 2.40-2.47(2s, 6H, CH_3), 2.55(s, 3H, ring CH_3), 7.55-8.00(m, 8H, ArH), 9.75(s, 1H, =CH), 12.90(s, 1H, NH). Mass calcd for $C_{21}H_{19}ClN_8O$: 435&437. Found: 434.5 & 436.5. *Anal.* Calcd. for $C_{21}H_{19}ClN_8O$(434.5): C, 58.04; H, 4.37; N, 25.77; Found: C, 57.55; H, 4.01; N, 25.51.

4-{[4-(3,5-Dimethyl-1*H*-pyrazol-4-yl)diazenyl] benzylidene}-amino-2-(4-methoxy)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one (**5g**). Yield 75%; mp. 138-140°C; ir 3212(γ_{NH}), 1709 (ring $\gamma_{C=O}$); ^{1}H-NMR δ 2.45-2.50(2s, 6H, CH_3), 2.48(s, 3H, ring CH_3), 3.25(s, 3H,CH_3), 7.55-8.00(m, 8H, ArH), 9.75(s, 1H, =CH), 12.98(s, 1H, NH). Mass calcd for $C_{22}H_{22}N_8O_2$: 430.84. Found: 430. *Anal.* Calcd. for $C_{22}H_{22}N_8O_2$(430.84): C, 61.32; H, 5.10; N, 25.99; Found: C, 58.01; H, 4.82; N, 25.77.

4-{[4-(3,5-Dimethyl-1*H*-pyrazol-4-yl)diazenyl] benzylidene}-amino-2-(3-chloro-4-methyl)phenyl-5-methyl-3*H*-[1,2,4]-triazol-3-one (**5h**). Yield 78%; mp.160-162°C; ir 3210(γ_{NH}), 1709 (ring $\gamma_{C=O}$); ^{1}H-NMR δ 1.88(s, 3H, CH_3), 2.35-2.42(2s, 6H, CH_3), 2.45(s, 3H, ring CH_3), 7.48-8.00(m, 8H, ArH), 9.70(s, 1H, =CH), 12.88(s, 1H, NH). *Anal.* Calcd. for $C_{22}H_{21}ClN_8O$ (449.37): C, 58.79; H, 4.67; N, 24.92; Found: C, 58.48; H, 4.32; N, 24.66.

General Procedure for Preparation of *N*-{[4-(2-Aryl-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-acetamides (**6a-h**). Amino compounds (**3a-h**) (0.438 g, 0.001 mol) in excess of acetic anhydride were heated on a water- bath for 3 hours and then poured into ice cold water. The resulting N-acetyl derivative was filtered and washed with water and crystallised from ethanol; yield 75%; mp.124-126°C; ir 3320 (γ_{NH}), 1709 (ring $\gamma_{C=O}$), 1678 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.10(s, 3H, $COCH_3$), 2.40(s, 3H, ring CH_3), 7.46-7.85(m, 8H, ArH), 9.60(s, 1H, =CH), 10.03(s, 1H, NH). Mass calcd for $C_{18}H_{17}N_5O_2$: 335.16. Found: 335. *Anal.* Calcd. for $C_{18}H_{17}N_5O_2$(335.16): C, 64.50; H, 5.07; N, 20.88; Found: C, 64.12; H, 4.81; N, 20.58.

***N*-{[4-(2-(4-Bromo)phenyl-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-acetamide** (**6b**). Yield 80%; mp. 182-184°C; ir 3318 (γ_{NH}), 1709 (ring $\gamma\nu_{C=O}$), 1676 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.10(s, 3H, $COCH_3$), 2.53(s, 3H, ring CH_3), 7.45-7.90(m, 8H, ArH), 9.64(s, 1H, =CH), 10.05(s, 1H, NH). Mass calcd for $C_{18}H_{16}BrN_5O_2$: 414.16 & 416.16. Found: 414&416. *Anal.* Calcd. for $C_{18}H_{16}BrN_5O_2$(414.16):C, 52.19; H, 3.86; N, 16.90; Found: C, 51.82; H, 3.56; N, 16.74.

***N*-{[4-(2-(3-Methyl)phenyl-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-acetamide** (**6c**). Yield 75%; mp. 170-172°C; ir 3308 (γ_{NH}), 1709 (ring$\gamma_{C=O}$;), 1676 ($\gamma_{C=O}$); ^{1}H-NMR δ 1.82(s, 3H, CH_3), 2.05(s, 3H, $COCH_3$), 2.40(s, 3H, ring CH_3), 7.40-7.88(m, 8H, ArH), 9.50(s, 1H, =CH), 9.80 (s, 1H, NH). *Anal.* Calcd. for $C_{19}H_{19}N_5O_2$(349.17): C, 65.35; H, 5.44; N, 20.04; Found: C, 65.02; H, 5.16; N, 19.74.

***N*-{[4-(2-(4-Methyl)phenyl-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-acetamide** (**6d**). Yield 78%; mp. 154-156°C; ir 3310 (γ_{NH}), 1709 (ring$\gamma_{C=O}$;), 1678 ($\gamma_{C=O}$); ^{1}H-NMR δ 1.85(s, 3H, CH_3), 2.07(s, 3H, $COCH_3$), 2.43(s, 3H, ring CH_3), 7.50-7.85(m, 8H, ArH), 9.57(s, 1H, =CH), 9.85(s, 1H, NH). Mass calcd for $C_{19}H_{19}N_5O_2$: 349.17. Found: 349. *Anal.* Calcd. for $C_{19}H_{19}N_5O_2$(349.17): C, 65.35; H, 5.44; N, 20.04; Found: C, 59.81; H, 5.05; N, 19.79.

***N*-{[4-(2-(3-Chloro)phenyl-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-acetamide** (**6e**). Yield 80%; mp. 184-186°C; ir 3315 (γ_{NH}), 1709 (ring$\gamma_{C=O}$;), 1672 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.07(s, 3H, $COCH_3$), 2.48(s, 3H, ring CH_3), 7.45-7.90(m, 8H, ArH), 9.60(s, 1H, =CH), 10.03(s, 1H, NH). *Anal.* Calcd. for $C_{18}H_{16}ClN_5O_2$ (369.61): C, 58.48; H, 4.32; N, 18.93; Found: C, 58.06; H, 4.06; N, 18.64.

***N*-{[4-(2-(4-Chloro)phenyl-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-acetamide** (**6f**). Yield 85%; mp. 190-192°C; ir 3320 (γ_{NH}), 1709 (ring$\gamma_{C=O}$;), 1670 ($\gamma_{C=O}$); ^{1}H-NMR δ

2.15(s, 3H, $COCH_3$), 2.50(s, 3H, ring CH_3), 7.45-7.90(m, 8H, ArH), 9.65(s, 1H, =CH), 10.10(s, 1H, NH). Mass calcd for $C_{18}H_{16}ClN_5O_2$: 369.61 & 371.61 Found: 369&371. *Anal*. Calcd. for $C_{18}H_{16}ClN_5O_2$(369.61): C, 58.48; H, 4.32; N, 18.93; Found: C, 58.10; H, 3.95; N, 18.58.

***N*-{[4-(2-(4-Methoxy)phenyl-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-acetamide** (**6g**). Yield 75%; mp. 142-144°C; ir 3312 (γ_{NH}), 1709 (ring $\gamma_{C=O}$), 1676 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.10(s, 3H, $COCH_3$), 2.40(s, 3H, ring CH_3), 3.52(s, 3H, OCH_3), 7.50-7.90(m, 8H, ArH), 9.58(s, 1H, =CH), 9.90(s, 1H, NH). Mass calcd for $C_{19}H_{19}N_5O_3$: 365.16. Found: 365. *Anal*. Calcd. for $C_{19}H_{19}N_5O_3$ (365.16): C, 62.49; H, 5.20; N, 19.16; Found: C, 62.14; H, 4.85; N, 18.88.

***N*-{[4-(2-(3-Chloro-4-methyl)phenyl-methyl-3*H*-[1,2,4]-triazol-3-one-4-yl)]-iminophenyl}-acetamide** (**6h**). Yield 80%; mp. 182-184°C; ir 3318 (γ_{NH}), 1709 (ring $\gamma_{C=O}$), 1676 ($\gamma_{C=O}$); ^{1}H-NMR δ 2.10(s, 3H, $COCH_3$), 2.53(s, 3H, ring CH_3), 7.45-7.90(m, 8H, ArH), 9.64(s, 1H, =CH), 10.05(s, 1H, NH). Mass calcd for $C_{19}H_{18}ClN_5O_2$: 383.62 &385.62. Found: 383&385. *Anal*. Calcd. for $C_{19}H_{18}ClN_5O_2$(383.62): C, 59.48; H, 4.69; N, 18.24; Found: C, 59.14; H, 4.45; N, 17.88.

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