

Preparation, Characterization, and Potentiometric Titrations of Some New Di-[3-(3-alkyl/aryl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate/terephthalate Derivatives

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3-Alkyl(Aryl)-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-ones (**2**) reacted with di-(3-formylphenyl) isophthalate (**3**) and di-(3-formylphenyl) terephthalate (**6**) to afford the corresponding 6 novel di-[3-(3-alkyl/aryl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalates (**4**) and 6 novel di-[3-(3-alkyl/aryl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalates (**7**), respectively. The acetylation reactions of compounds **4** and **7** were investigated, and **5** and **8** type compounds were obtained, respectively. The new compounds synthesized were characterized by using IR, ¹H-NMR, ¹³C-NMR, and UV spectral data together with elemental analysis. In addition, to investigate the effects of solvents and molecular structure upon acidity, compounds **4** and **7** were titrated potentiometrically with tetrabutylammonium hydroxide in 5 non-aqueous solvents (isopropyl alcohol, *tert*-butyl alcohol, *N,N*-dimethylformamide, acetone, and dimethyl sulfoxide). The half-neutralization potential values and the corresponding p*K*_a values were determined for all cases.

Key Words: 4,5-Dihydro-1*H*-1,2,4-triazol-5-one, Schiff base, acidity, potentiometric titration, acetylation.

Introduction

1,2,4-Triazole and 4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives are reported to possess a broad spectrum of biological activities such as antifungal, antimicrobial, hypoglycemic, antihypertensive, analgesic, antiparasitic, hypocholesteremic, antiviral, anti-inflammatory, antitumor, and anti-HIV properties.^{1–12} In addition, several articles reporting the synthesis of some *N*-arylidenamino-4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives have been published.^{12–16} The acetylation of 4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives has also

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been reported.^{11,15–17} On the other hand, it is known that 1,2,4-triazole and 4,5-dihydro-1*H*-1,2,4-triazol-5-one rings have weak acidic properties, and so some 1,2,4-triazole and 4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives were titrated potentiometrically with tetrabutylammonium hydroxide in non-aqueous solvents, and the corresponding pK_a values of the compounds were determined.^{15,16,18–22} These reports prompted us to synthesize some new potential biological active 4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives.

In this paper, we present the synthesis of a series of di-[3-(3-alkyl/aryl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalates (**4a-f**) and di-[3-(3-alkyl/aryl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalates (**7a-f**). The starting compounds 3-alkyl/aryl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-ones (**2a-f**) were prepared from the reactions of the corresponding ester ethoxycarbonylhydrazones (**1a-f**) with an aqueous solution of hydrazine hydrate as described in the literature.^{17,24} Compounds **4** and **7** were obtained from the reactions of compounds **2** with di-(3-formylphenyl) isophthalate (**3**) and di-(3-formylphenyl) terephthalate (**6**), which were synthesized by the reactions of 3-hydroxybenzaldehyde with isophthaloyl chloride and terephthaloyl chloride by using triethylamine, respectively. Moreover, the reactions of compounds **4** and **7** with acetic anhydride were investigated and compounds **5** and **8** were prepared, respectively (**Figure 1**).

In addition, we also examined the potentiometric titrations of the synthesized compounds **4a-f** and **7a-f** with tetrabutylammonium hydroxide (TBAH) in 5 non-aqueous solvents (isopropyl alcohol, *tert*-butyl alcohol, *N,N*-dimethylformamide, acetone, and dimethyl sulfoxide) to determine the half-neutralization potentials (HNPs) and the corresponding pK_a values. The data obtained from the potentiometric titrations were interpreted and the effects of molecular structure and solvents were studied.^{15,16,18–23}

Experimental

Melting points were recorded on an Electrothermal 9100 digital melting point apparatus and are uncorrected. IR spectra were registered on a Perkin-Elmer Instruments Spectrum One FT-IR spectrometer. ¹H-NMR and ¹³C-NMR spectra were recorded in deuterated dimethyl sulfoxide with TMS as internal standard on a Varian Mercury spectrometer at 200 MHz and 50 MHz, respectively. UV absorption spectra were measured in 10 mm quartz cells between 200 and 400 nm using a Shimadzu UV-1201 spectrophotometer. Combustion analyses were performed on an ECS 4010 Costech Elemental Analyzer. In this study, a Jenway 3040 ion analyzer pH meter equipped with an Ingold pH electrode was used for potentiometric titrations. For each compound titrated, a 0.001 M solution was separately prepared in each non-aqueous solvent. A 0.05 M solution of TBAH in isopropyl alcohol, which is widely used in the titration of acids, was used as titrant. The mV values obtained on the pH meter were recorded. Finally, the half-neutralization potential (HNP) values were determined by plotting the volume (mL) (TBAH)-mV graph.

General method for the synthesis of di-[3-(3-alkyl/aryl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (4a-f**):** 3-Hydroxybenzaldehyde (0.02 mol) dissolved in ethyl acetate (30 mL) was treated with isophthaloyl chloride (0.01 mol), and to this solution was added triethylamine (0.02 mol) in 10 mL of ethyl acetate slowly with stirring at 0–5 °C. Stirring was continued for 2 h; then the mixture was refluxed for 4 h and filtered. The filtrate was evaporated in vacuo and the crude product was washed with water and recrystallized from ethanol to afford compound **3**. mp 115 °C; IR (KBr) (ν , cm^{-1}): 2844, 2731 (CHO), 1729, 1702 (C=O), 1207 (C-O), 788 and 719 (1,3-disubstituted benzenoid ring). The corresponding compound **2** (0.02 mol) was dissolved in acetic acid (15 mL) and treated with di-(3-formylphenyl) isophthalate (**3**) (0.01 mol). The mixture was refluxed for 1.5 h and then evaporated

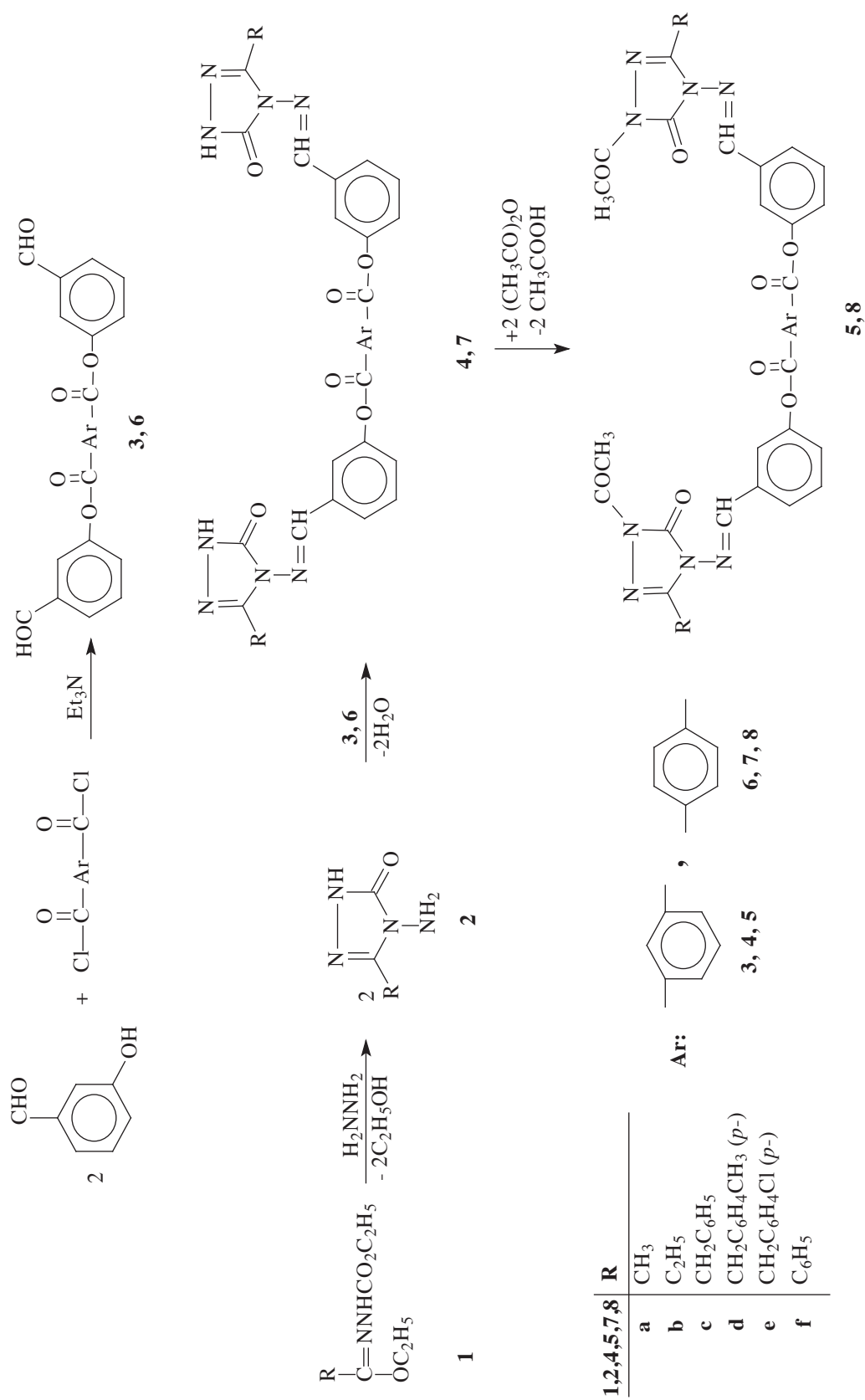


Figure 1

at 50-55 °C in vacuo. Several recrystallizations of the residue from AcOH-H₂O (1:3) gave pure compounds **4a-f** as colorless crystals.

Di-[3-(3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (4a): This compound was obtained as white needles (yield: 2.83 g, 50%); mp 305 °C; IR (KBr) (ν , cm⁻¹): 3188 (NH), 1736, 1715 (C=O), 1613, 1577 (C=N), 1227 (C-O), 799 and 714 (1,3-disubstituted benzenoid ring); ¹H-NMR (DMSO-d₆, δ ppm): 2.28 (s, 6H, 2CH₃), 7.52 (d, 2H, arH, $J=8.1$ Hz), 7.63 (t, 2H, arH, $J=7.8$ Hz), 7.79 (d, 2H, arH, $J=7.7$ Hz), 7.85-7.91 (m, 3H, arH), 8.50 (d, 2H, arH, $J=7.8$ Hz), 8.83 (s, 1H, arH), 9.79 (s, 2H, 2N=CH), 11.86 (s, 2H, 2NH); ¹³C-NMR (DMSO-d₆, δ ppm): 11.58 (2CH₃), ar-C: [120.7 (2C), 122.7, 125.4 (2C), 126.6, 128.6, 130.1 (2C), 130.5, 130.8 (2C), 131.3, 135.5, 135.8 (2C), 144.8 (2C)], 151.4 (2triazole-C₃), 151.7 (2N=CH), 152.9 (2triazole-C₅), 164.2 (2C=O); UV λ_{max} (ϵ): 292 (8250), 215 (26179) nm. *Anal.* Calcd. (%) for C₂₈H₂₂N₈O₆: C, 59.36; H, 3.91; N, 19.78. Found; C, 59.38; H, 3.94; N, 19.77.

Di-[3-(3-ethyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (4b): This compound was obtained as white needles (yield: 2.91 g, 49%); mp 236 °C; IR (KBr) (ν , cm⁻¹): 3183 (NH), 1743, 1705 (C=O), 1610, 1593 (C=N), 1222 (C-O), 784 and 686 (1,3-disubstituted benzenoid ring); ¹H-NMR (DMSO-d₆, δ ppm): 1.20 (t, 6H, 2CH₃, $J=7.5$ Hz), 2.69 (q, 4H, 2CH₂, $J=7.5$ Hz), 7.52 (d, 2H, arH, $J=8.1$ Hz), 7.63 (t, 2H, arH, $J=7.8$ Hz), 7.78 (d, 2H, arH, $J=7.8$ Hz), 7.83-7.90 (m, 3H, arH), 8.50 (d, 2H, arH, $J=7.8$ Hz), 8.82 (s, 1H, arH), 9.78 (s, 2H, 2N=CH), 11.74 (s, 2H, 2NH); ¹³C-NMR (DMSO-d₆, δ ppm): 10.4 (2CH₃), 18.9 (2CH₂), ar-C: [120.7 (2C), 122.7, 125.4, 126.5, 128.1, 128.6, 130.1, 130.5, 130.8, 131.1, 131.3, 135.5, 135.8 (2C), 138.1, 148.5 (2C)], 151.4 (2triazole-C₃), 151.8 (2N=CH), 152.9 (2triazole-C₅), 164.2 (2C=O); UV λ_{max} (ϵ): 292 (31185), 215 (101481) nm. *Anal.* Calcd. (%) for C₃₀H₂₆N₈O₆: C, 60.60; H, 4.41; N, 18.85. Found; C, 60.61; H, 4.44; N, 18.85.

Di-[3-(3-benzyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (4c): This compound was obtained as white needles (yield: 3.37 g, 47%); mp 268 °C; IR (KBr) (ν , cm⁻¹): 3194 (NH), 1741, 1716 (C=O), 1589, 1577 (C=N), 1209 (C-O), 783 and 719 (1,3-disubstituted benzenoid ring), 760 and 685 (monosubstituted benzenoid ring); ¹H-NMR (DMSO-d₆, δ ppm): 4.04 (s, 4H, 2CH₂), 7.17 (t, 2H, arH, $J=7.2$ Hz), 7.24-7.32 (m, 7H, arH), 7.47 (d, 2H, arH, $J=7.9$ Hz), 7.57 (t, 2H, arH, $J=7.8$ Hz), 7.69-7.73 (m, 4H, arH), 7.82-7.87 (m, 2H, arH), 8.46 (d, 2H, arH, $J=7.8$ Hz), 8.84 (s, 1H, arH), 9.72 (s, 2H, 2N=CH), 11.96 (s, 2H, 2NH); ¹³C-NMR (DMSO-d₆, δ ppm): 31.6 (2CH₂), ar-C: [120.8 (2C), 122.6, 125.2, 126.4, 127.1 (2C), 128.0, 128.5, 128.8 (3C), 129.3 (3C), 130.0, 130.1, 130.4, 130.7, 131.0, 131.2, 131.3, 135.4, 135.8 (2C), 136.2 (2C), 138.1, 146.7 (2C)], 151.3 (2triazole-C₃), 151.7 (2N=CH), 152.4 (2triazole-C₅), 164.1 (2C=O); UV λ_{max} (ϵ): 292 (5481), 214 (27500) nm. *Anal.* Calcd. (%) for C₄₀H₃₀N₈O₆: C, 66.85; H, 4.21; N, 15.59. Found; C, 66.89; H, 4.21; N, 15.55.

Di-[3-(3-*p*-methylbenzyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethin-phenyl] isophthalate (4d): This compound was obtained as white needles (yield: 3.65 g, 49%); mp 243 °C; IR (KBr) (ν , cm⁻¹): 3179 (NH); 1747, 1715 (C=O), 1607, 1588 (C=N), 1223 (C-O), 831 (1,4-disubstituted benzenoid ring), 779 and 685 (1,3-disubstituted benzenoid ring); ¹H-NMR (DMSO-d₆, δ ppm): 2.18 (s, 6H, 2CH₃), 3.99 (s, 4H, 2CH₂), 7.05 (d, 4H, arH, $J=7.9$ Hz), 7.18 (d, 4H, arH, $J=7.9$ Hz), 7.44-7.52 (m, 2H, arH), 7.61 (t, 2H, arH, $J=8.2$ Hz), 7.73-7.75 (m, 4H, arH), 7.90-7.94 (m, 1H, arH), 8.51-8.55 (m, 2H, arH), 8.87 (s, 1H, arH), 9.72 (s, 2H, 2N=CH), 12.01 (s, 2H, 2NH); ¹³C-NMR (DMSO-d₆, δ ppm): 21.0 (2CH₃), 31.2 (2CH₂), ar-C: [120.7 (2C), 122.7, 125.3, 126.7, 128.6, 129.2 (4C), 129.4 (4C), 130.1 (2C), 130.6, 130.8 (2C), 131.1, 131.3, 133.1, 135.6, 135.9 (2C), 136.2 (2C), 138.1, 146.7 (2C)], 151.3 (2triazole-C₃), 151.6 (2N=CH), 152.4 (2triazole-C₅), 164.2 (2C=O); UV λ_{max} (ϵ): 293 (11175), 215 (37108) nm. *Anal.* Calcd.

(%) for $C_{42}H_{34}N_8O_6$: C, 67.55; H, 4.59; N, 15.00. Found; C, 66.62; H, 4.55; N, 15.02.

Di-[3-(3-*p*-chlorobenzyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (4e): This compound was obtained as white needles (yield: 3.70 g, 47%); mp 272 °C; IR (KBr) (ν , cm^{-1}): 3174 (NH), 1745, 1720, 1705 (C=O), 1604, 1573 (C=N), 1222 (C-O), 844, 830 (1,4-disubstituted benzenoid ring), 779 and 685 (1,3-disubstituted benzenoid ring); 1H -NMR (DMSO- d_6 , δ ppm): 4.04 (s, 4H, 2CH₂), 7.30 (s, 8H, arH), 7.46-7.87 (m, 10H, arH), 8.49 (d, 2H, arH, $J=7.7$ Hz), 9.71 (s, 2H, 2N=CH), 12.01 (s, 2H, 2NH); UV λ_{max} (ϵ): 291 (9461), 216 (39019) nm.

Di-[3-(3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (4f): This compound was obtained as white needles (yield: 3.38 g, 49%); mp 288 °C; IR (KBr) (ν , cm^{-1}): 3165 (NH), 1746, 1713 (C=O), 1606, 1576 (C=N), 1224 (C-O), 802 and 716 (1,3-disubstituted benzenoid ring), 762 and 681 (monosubstituted benzenoid ring); 1H -NMR (DMSO- d_6 , δ ppm): 7.46-7.89 (m, 20H, arH), 8.44 (d, 2H, arH, $J=7.7$ Hz), 9.69 (s, 2H, 2N=CH), 12.41 (s, 2H, 2NH); UV λ_{max} (ϵ): 215 (24276) nm.

General method for the synthesis of compounds di-[3-(1-acetyl-3-alkyl/aryl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (5a-f): The corresponding compound 4 (0.01 mol) was refluxed with acetic anhydride (20 mL) for 0.5 h. After the addition of absolute ethanol (100 mL), the mixture was refluxed for 1 h more. Evaporation of the resulting solution at 40-45 °C in vacuo and several recrystallizations of the residue from EtOH gave pure compounds 5a-f as colorless needles.

Di-[3-(1-acetyl-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethin-phenyl] isophthalate (5a): This compound was obtained as white needles (yield: 6.31 g, 97%); mp 305 °C; IR (KBr) (ν , cm^{-1}): 1745, 1733 (C=O), 1622, 1575 (C=N), 1215 (C-O), 792 and 685 (1,3-disubstituted benzenoid ring); 1H -NMR (DMSO- d_6 , δ ppm): 2.33 (s, 6H, 2CH₃), 2.46 (s, 6H, 2COCH₃), 7.50-7.89 (m, 10H, arH), 8.46 (d, 2H, arH, $J=7.7$ Hz), 9.62 (s, 2H, 2N=CH); UV λ_{max} (ϵ): 292 (8390), 241 (14032), 215 (23869) nm.

Di-[3-(1-acetyl-3-ethyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (5b): This compound was obtained as white needles (yield: 6.57 g, 97%); mp 236 °C; IR (KBr) (ν , cm^{-1}): 1777, 1737 (C=O), 1614, 1575 (C=N), 1212 (C-O), 767 and 684 (1,3-disubstituted benzenoid ring); 1H -NMR (DMSO- d_6 , δ ppm): 1.21 (t, 6H, 2CH₃, $J=7.4$ Hz), 2.49 (s, 6H, 2COCH₃), 2.74 (q, 4H, 2CH₂, $J=7.4$ Hz), 7.52-7.91 (m, 10H, arH), 8.48 (d, 2H, arH, $J=7.7$ Hz), 9.63 (s, 2H, 2N=CH); UV λ_{max} (ϵ): 291 (27322), 243 (44387), 216 (74419) nm.

Di-[3-(1-acetyl-3-benzyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethin-phenyl] isophthalate (5c): This compound was obtained as white needles (yield: 5.77 g, 72%); mp 268 °C; IR (KBr) (ν , cm^{-1}): 1782, 1765, 1746, 1704 (C=O), 1609, 1575 (C=N), 1215 (C-O), 784 and 711 (1,3-disubstituted benzenoid ring), 761 and 689 (monosubstituted benzenoid ring); 1H -NMR (DMSO- d_6 , δ ppm): 2.58 (s, 6H, 2COCH₃), 4.15 (s, 4H, 2CH₂), 7.21 (t, 2H, arH, $J=7.3$ Hz), 7.29 (t, 4H, arH, $J=7.7$ Hz), 7.36 (d, 4H, arH, $J=7.3$ Hz), 7.53-7.56 (m, 2H, arH), 7.63 (t, 2H, arH, $J=8.2$ Hz), 7.77-7.79 (m, 4H, arH), 7.92 (t, 1H, arH), 8.53 (d, 2H, arH, $J=7.8$ Hz), 8.86 (s, 1H, arH), 9.62 (s, 2H, 2N=CH); ^{13}C -NMR (DMSO- d_6 , δ ppm): 24.0 (2COCH₃), 31.5 (2CH₂), ar-C: [121.1 (2C), 122.2, 125.9 (2C), 126.9, 127.4 (2C), 128.9 (4C), 129.5 (4C), 130.1 (2C), 130.6, 130.9 (2C), 131.3, 133.9, 135.1 (2C), 135.2 (2C), 135.6, 148.5, 148.8], 151.4 (2triazole-C₃), 152.1 (2N=CH), 154.4 (2triazole-C₅), 164.1 (2C=O), 166.5 (2COCH₃); UV λ_{max} (ϵ): 292 (14777), 213 (52857) nm. *Anal.* Calcd. (%) for $C_{44}H_{34}N_8O_8$: C, 65.83; H, 4.27 N, 13.96. Found; C, 65.84; H, 4.27 N, 13.96.

Di-[3-(1-acetyl-3-*p*-methylbenzyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (5d): This compound was obtained as white needles (yield: 8.05 g, 97%); mp 244 °C;

IR (KBr) (ν , cm^{-1}): 1771, 1737, 1720 (C=O), 1610, 1576 (C=N), 1215 (C-O), 810, 795 (1,4-disubstituted benzenoid ring), 778 and 686 (1,3-disubstituted benzenoid ring); $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 2.17 (s, 6H, 2CH₃), 2.47 (s, 6H, 2COCH₃), 4.06 (s, 4H, 2CH₂), 7.05 (d, 4H, arH, $J=7.7$ Hz), 7.21 (d, 4H, arH, $J=8.1$ Hz), 7.50-7.94 (m, 10H, arH), 8.51 (d, 2H, arH, $J=7.7$ Hz), 9.59 (s, 2H, 2N=CH); UV λ_{max} (ϵ): 293 (15922), 216 (56567) nm.

Di-[3-(1-acetyl-3-*p*-chlorobenzyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (5e): This compound was obtained as white needles (yield: 8.53 g, 98%); mp 272 °C; IR (KBr) (ν , cm^{-1}): 1795, 1765, 1745, 1715 (C=O), 1609, 1575 (C=N), 1218 (C-O), 844, 800 (1,4-disubstituted benzenoid ring), 783 and 684 (1,3-disubstituted benzenoid ring); $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 2.56 (s, 6H, 2COCH₃), 4.16 (s, 4H, 2CH₂), 7.33-7.91 (m, 17H, arH), 8.52 (m, 2H, arH), 8.87 (s, 1H, arH), 9.62 (s, 2H, 2N=CH); $^{13}\text{C-NMR}$ (DMSO- d_6 , δ ppm): 24.0 (2COCH₃), 30.9 (2CH₂), ar-C: [121.0 (2C), 125.9 (2C), 127.0 (2C), 128.8 (4C), 130.1 (2C), 130.6 (2C), 130.9 (2C), 131.3 (2C), 131.5 (4C), 132.1 (2C), 134.1 (2C), 135.2 (2C), 135.6 (2C)], 148.5 (2triazole-C₃), 151.4 (2N=CH), 154.4 (2triazole-C₅), 164.2 (2C=O), 166.4 (2COCH₃); UV λ_{max} (ϵ): 292 (9478), 216 (36565) nm. *Anal.* Calcd. (%) for C₄₄H₃₂Cl₂N₈O₈: C, 60.63; H, 3.70 N, 12.85. Found; C, 60.63; H, 3.71 N, 12.85.

Di-[3-(1-acetyl-3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethin-phenyl] isophthalate (5f): This compound was obtained as white needles (yield: 7.50 g, 97%); mp 288 °C; IR (KBr) (ν , cm^{-1}): 1777, 1740 (C=O), 1606, 1574 (C=N), 1215 (C-O), 793 and 717 (1,3-disubstituted benzenoid ring), 768 and 683 (monosubstituted benzenoid ring); $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 2.58 (s, 6H, 2COCH₃), 7.51-7.61 (m, 8H, arH), 7.68 (t, 2H, arH, $J=8.3$ Hz), 7.81-7.97 (m, 9H, arH), 8.51 (d, 2H, arH, $J=7.8$ Hz), 8.83 (s, 1H, arH), 9.60 (s, 2H, 2N=CH); $^{13}\text{C-NMR}$ (DMSO- d_6 , δ ppm): 24.0 (2COCH₃), ar-C: [121.8 (2C), 125.7 (2C), 126.1, 126.5, 128.4 (2C), 129.0 (2C), 129.2 (6C), 130.1 (2C), 130.5, 131.0 (2C), 131.3, 131.8 (2C), 135.0 (2C), 135.5 (2C), 146.5 (2C)], 148.6 (2triazole-C₃), 151.4 (2N=CH), 158.2 (2triazole-C₅), 164.1 (2C=O), 166.7 (2COCH₃); UV λ_{max} (ϵ): 215 (30274) nm. *Anal.* Calcd. (%) for C₄₄H₃₀N₈O₈: C, 65.11; H, 3.90 N, 14.46. Found; C, 65.11; H, 3.54 N, 14.45.

General method for the synthesis of compounds di-[3-(3-alkyl/aryl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalate (7a-f): 3-Hydroxybenzaldehyde (0.02 mol) dissolved in ethyl acetate (30 mL) was treated with terephthaloyl chloride (0.01 mol), and to this solution was added triethylamine (0.02 mol) in 10 mL of ethyl acetate slowly with stirring at 0-5 °C. Stirring was continued for 2 h; then the mixture was refluxed for 4 h and filtered. The filtrate was evaporated in vacuo and the crude product was washed with water and recrystallized from ethanol to afford compound **6**. mp 278 °C; IR (KBr) (ν , cm^{-1}): 2840, 2759 (CHO), 1731, 1687 (C=O), 1271 (C-O), 782 and 711 (1,3-disubstituted benzenoid ring), 765 and 711 (monosubstituted benzenoid ring). The corresponding compound **2** (0.02 mol) was dissolved in acetic acid (15 mL) and treated with di-(3-formylphenyl) terephthalate (**6**) (0.01 mol). The mixture was refluxed for 1.5 h and then evaporated at 50-55 °C in vacuo. Several recrystallizations of the residue from AcOH-H₂O (1:3) gave pure compounds **7a-f** as colorless crystals.

Di-[3-(3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalate (7a): This compound was obtained as white needles (yield: 2.99 g, 53%); mp 287 °C; IR (KBr) (ν , cm^{-1}): 3184 (NH), 1732, 1711 (C=O), 1614, 1595, 1576 (C=N), 1239 (C-O), 824 (1,4-disubstituted benzenoid ring), 800 and 686 (1,3-disubstituted benzenoid ring); $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 2.29 (s, 6H, 2CH₃), 7.54-7.91 (m, 8H, arH), 8.37 (s, 4H, arH), 9.80 (s, 2H, 2N=CH), 11.87 (s, 2H, 2NH); $^{13}\text{C-NMR}$ (DMSO- d_6 , δ ppm): 11.7 (2CH₃), ar-C: [121.4 (2C), 126.2 (2C), 127.4 (2C), 131.6 (6C), 134.7 (2C), 136.6 (2C), 145.7 (2C)], 152.2 (2triazole-C₃), 152.6 (2N=CH), 153.9 (2triazole-C₅), 165.3 (2C=O); UV λ_{max} (ϵ): 291 (10448), 248

(23514), 210 (21368) nm. *Anal.* Calcd. (%) for $C_{28}H_{22}N_8O_6$: C, 59.36; H, 3.91; N, 19.78. Found; C, 59.39; H, 3.91; N, 19.76.

Di-[3-(3-ethyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalate

(7b): This compound was obtained as white needles (yield: 2.85 g, 48%); mp 281 °C; IR (KBr) (ν , cm^{-1}): 3170 (NH), 1743, 1711 (C=O), 1605, 1591, 1572 (C=N), 1238 (C-O), 803 (1,4-disubstituted benzenoid ring), 782 and 715 (1,3-disubstituted benzenoid ring); 1H -NMR (DMSO- d_6 , δ ppm): 1.19 (t, 6H, 2CH₃, $J=7.3$ Hz), 3.08 (q, 4H, 2CH₂, $J=7.3$ Hz), 7.65-7.92 (m, 8H, arH), 8.04-8.38 (m, 4H, arH), 9.79 (s, 2H, 2N=CH), 11.90 (s, 2H, 2NH); ^{13}C -NMR (DMSO- d_6 , δ ppm): 10.5 (2CH₃), 18.9 (2CH₂), ar-C: [120.8, 122.7, 125.4, 128.6, 129.9 (2C), 130.2 (2C), 130.6 (2C), 130.9 (2C), 131.1, 133.9, 135.8, 138.1, 148.6 (2C)], 149.2 (2triazole-C₃), 151.8 (2N=CH), 153.2 (2triazole-C₅), 164.3 (2C=O); UV λ_{max} (ϵ): 250 (8284), 209 (9208) nm. *Anal.* Calcd. (%) for $C_{30}H_{26}N_8O_6$: C, 60.60; H, 4.41; N, 18.85. Found; C, 60.59; H, 4.41; N, 18.89.

Di-[3-(3-benzyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalate

(7c): This compound was obtained as white needles (yield: 3.80 g, 53%); mp 312 °C; IR (KBr) (ν , cm^{-1}): 3179 (NH), 1743, 1709 (C=O), 1604, 1573 (C=N), 1237 (C-O), 825 (1,4-disubstituted benzenoid ring), 811 and 717 (1,3-disubstituted benzenoid ring), 760 and 701 (1,3-disubstituted benzenoid ring); 1H -NMR (DMSO- d_6 , δ ppm): 4.04 (s, 4H, 2CH₂), 7.16-8.36 (m, 22H, arH), 9.71 (s, 2H, 2N=CH), 12.00 (s, 2H, 2NH); UV λ_{max} (ϵ): 296 (2547), 247 (5050), 210 (4604) nm.

Di-[3-(3-p-methylbenzyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethin-phenyl] terephthalate (7d): This compound was obtained as white needles (yield: 3.36 g, 45%); mp 298 °C; IR (KBr) (ν , cm^{-1}): 3181 (NH), 1739, 1718 (C=O), 1598, 1588 (C=N), 1239 (C-O), 826 (1,4-disubstituted benzenoid ring), 787 and 685 (1,3-disubstituted benzenoid ring); 1H -NMR (DMSO- d_6 , δ ppm): 2.18 (s, 6H, 2CH₃), 3.98 (s, 4H, 2CH₂), 7.04 (d, 4H, arH, $J=7.7$ Hz), 7.17 (d, 4H, arH, $J=8.1$ Hz), 7.47-7.74 (m, 8H, arH), 8.14 (d, 1H, arH, $J=8.1$ Hz), 8.26 (d, 1H, arH, $J=8.7$ Hz), 8.37 (s, 2H, arH), 9.70 (s, 2H, 2N=CH), 11.98 (s, 2H, 2NH); UV λ_{max} (ϵ): 288 (20970), 248 (47575), 211 (46791) nm.

Di-[3-(3-p-chlorobenzyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethin-phenyl] terephthalate (7e): This compound was obtained as white needles (yield: 3.62 g, 46%); mp 307 °C; IR (KBr) (ν , cm^{-1}): 3172 (NH), 1741, 1716 (C=O), 1592, 1574 (C=N), 1235 (C-O), 824 (1,4-disubstituted benzenoid ring), 784 and 685 (1,3-disubstituted benzenoid ring); 1H -NMR (DMSO- d_6 , δ ppm): 4.08 (s, 4H, 2CH₂), 7.35 (s, 8H, arH), 7.49-7.53 (m, 2H, arH), 7.60-7.64 (m, 2H, arH), 7.73-7.76 (m, 4H, arH), 8.16 (d, 1H, arH, $J=8.2$ Hz), 8.28 (d, 1H, arH, $J=8.3$ Hz), 8.39 (s, 2H, arH), 9.74 (s, 2H, 2N=CH), 12.04 (s, 2H, 2NH); ^{13}C -NMR (DMSO- d_6 , δ ppm): 30.9 (2CH₂), ar-C: [120.7 (2C), 125.3, 126.6, 128.8 (4C), 130.2 (2C), 130.6 (2C), 130.9 (2C), 131.3 (4C), 131.9 (2C), 132.8, 133.9 (2C), 135.2 (2C), 135.7 (2C), 136.0, 146.4 (2C)], 151.4 (2triazole-C₃), 151.6 (2N=CH), 152.6 (2triazole-C₅), 164.3 (2C=O); UV λ_{max} (ϵ): 287 (6662), 246 (17462), 211 (16738) nm. *Anal.* Calcd. (%) for $C_{40}H_{28}Cl_2N_8O_6$: C, 61.00; H, 3.58; N, 14.23. Found; C, 61.02; H, 3.55; N, 14.26.

Di-[3-(3-phenyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalate

(7f): This compound was obtained as white needles (yield: 3.17 g, 46%); mp 301 °C; IR (KBr) (ν , cm^{-1}): 3170 (NH), 1737, 1712 (C=O), 1595, 1576 (C=N), 1238 (C-O), 822 (1,4-disubstituted benzenoid ring), 800 and 717 (1,3-disubstituted benzenoid ring), 762 and 680 (monosubstituted benzenoid ring); 1H -NMR (DMSO- d_6 , δ ppm): 7.51-7.55 (m, 6H, arH), 7.61-7.66 (m, 2H, arH), 7.73-7.80 (m, 4H, arH), 7.88-7.91 (m, 4H, arH), 8.14 (d, 2H, arH, $J=8.4$ Hz), 8.25 (d, 2H, arH, $J=8.4$ Hz), 8.34-8.35 (m, 2H, arH), 9.71 (s, 2H, 2N=CH), 12.34 (s, 2H, 2NH); ^{13}C -NMR (DMSO- d_6 , δ ppm): ar-C: [121.5 (2C), 125.6 (2C), 126.2, 127.0 (2C), 128.5 (3C), 129.0 (3C), 130.2 (2C), 130.6 (2C), 130.7 (2C), 130.8 (2C), 130.9 (2C), 132.7, 133.8, 135.5

(2C), 136.1, 145.1 (2C)], 151.4 (2triazole-C₃), 151.8 (2N=CH), 156.1 (2triazole-C₅), 164.4 (2C=O); UV λ_{max} (ϵ): 249 (29965), 211 (23965) nm. *Anal. Calcd.* (%) for C₃₈H₂₆N₈O₆: C, 66.08; H, 3.79; N, 16.22. Found; C, 66.07; H, 3.77; N, 16.21.

General method for the synthesis of compounds di-[3-(1-acetyl-3-alkyl/aryl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalate (8a-f)

The corresponding compound (**7**) (0.01 mol) was refluxed with acetic anhydride (20 mL) for 0.5 h. After addition of absolute ethanol (100 mL), the mixture was refluxed for 1 h more. Evaporation of the resulting solution at 40-45 °C in vacuo and several recrystallizations of the residue from EtOH gave pure compounds **8a-f** as colorless needles.

Di-[3-(1-acetyl-3-methyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethin-phenyl] terephthalate (8a): This compound was obtained as white needles (yield: 5.26 g, 81%); mp 276 °C; IR (KBr) (ν , cm⁻¹): 1731, 1720 (C=O), 1619, 1578 (C=N), 1250 (C-O), 835 (1,4-disubstituted benzenoid ring), 793 and 686 (1,3-disubstituted benzenoid ring); ¹H-NMR (DMSO-d₆, δ ppm): 2.38 (s, 6H, 2CH₃), 2.46 (s, 6H, 2COCH₃), 7.57-7.59 (m, 2H, arH), 7.65-7.69 (m, 2H, arH), 7.82-7.87 (m, 2H, arH), 7.91 (s, 2H, arH), 8.38 (s, 4H, arH), 9.68 (s, 2H, 2N=CH); UV λ_{max} (ϵ): 306 (1163), 246 (2008) nm. *Anal. Calcd.* (%) for C₃₂H₂₆N₈O₈: C, 59.08; H, 4.03; N, 17.22. Found; C, 59.06; H, 4.04; N, 17.22.

Di-[3-(1-acetyl-3-ethyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethin-phenyl] terephthalate (8b): This compound was obtained as white needles (yield: 6.03 g, 89%); mp 227 °C; IR (KBr) (ν , cm⁻¹): 1777, 1735 (C=O), 1614, 1578 (C=N), 1240 (C-O), 842 (1,4-disubstituted benzenoid ring), 770 and 684 (1,3-disubstituted benzenoid ring); ¹H-NMR (DMSO-d₆, δ ppm): 1.22 (t, 6H, 2CH₃), 2.48 (s, 6H, 2COCH₃), 2.75 (q, 4H, 2CH₂), 7.56-7.64 (m, 4H, arH), 7.76-7.90 (m, 4H, arH), 8.35 (m, 4H, arH), 9.64 (s, 2H, 2N=CH); UV λ_{max} (ϵ): 290 (9279), 251 (16678), 211 (13813) nm.

Di-[3-(1-acetyl-3-benzyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalate (8c): This compound was obtained as white needles (yield: 6.42 g, 80%); mp 236 °C; IR (KBr) (ν , cm⁻¹): 1782, 1760, 1740 (C=O), 1614, 1576 (C=N), 1245 (C-O), 843 (1,4-disubstituted benzenoid ring), 785 and 710 (1,3-disubstituted benzenoid ring), 764 and 691 (monosubstituted benzenoid ring); ¹H-NMR (DMSO-d₆, δ ppm): 2.54 (s, 6H, 2COCH₃), 4.17 (s, 4H, 2CH₂), 7.21-7.24 (m, 2H, arH), 7.30 (t, 4H, arH, *J*=7.6 Hz), 7.38 (d, 4H, arH, *J*=7.2 Hz), 7.56-7.57 (m, 2H, arH), 7.61-7.67 (m, 2H, arH), 7.77-7.80 (m, 4H, arH), 8.39-8.41 (m, 4H, arH), 9.63 (s, 2H, 2N=CH); ¹³C-NMR (DMSO-d₆, δ ppm): 24.0 (2COCH₃), 31.6 (2CH₂), ar-C: [121.1 (2C), 125.8 (2C), 127.4 (4C), 128.9 (4C), 129.5 (4C), 130.9 (4C), 133.9 (2C), 135.2 (3C), 135.3 (3C), 148.5 (2C)], 148.8 (2triazole-C₃), 151.4 (2N=CH), 154.4 (2triazole-C₅), 164.3 (2C=O), 166.60 (2COCH₃); UV λ_{max} (ϵ): 295 (578), 248 (1285), 210 (1550) nm. *Anal. Calcd.* (%) for C₄₄H₃₄N₈O₈: C, 65.83; H, 4.27; N, 13.96. Found; C, 65.83; H, 4.28; N, 13.93.

Di-[3-(1-acetyl-3-*p*-methylbenzyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azo-methinphenyl] terephthalate (8d): This compound was obtained as white needles (yield: 6.22 g, 75%); mp 298 °C; IR (KBr) (ν , cm⁻¹): 1768, 1734 (C=O), 1609, 1576 (C=N), 1250 (C-O), 800 (1,4-disubstituted benzenoid ring), 766 and 686 (1,3-disubstituted benzenoid ring); ¹H-NMR (DMSO-d₆, δ ppm): 2.09 (s, 6H, 2CH₃), 2.22 (s, 6H, 2COCH₃), 4.11 (s, 4H, 2CH₂), 7.09 (d, 4H, arH, *J*=7.9 Hz), 7.25 (d, 4H, arH, *J*=7.9 Hz), 7.56 (d, 2H, arH, *J*=8.7 Hz), 7.65 (t, 2H, arH, *J*=8.1 Hz), 7.79-7.81 (m, 4H, arH), 8.42 (s, 4H, arH), 9.63 (s, 2H, 2N=CH); UV λ_{max} (ϵ): 294 (23917), 250 (37583), 210 (50083) nm. *Anal. Calcd.* (%) for C₄₆H₃₈N₈O₈: C, 66.50; H, 4.61; N, 13.49. Found; C, 66.59; H, 4.42; N, 13.52.

Di-[3-(1-acetyl-3-*p*-chlorobenzyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azo-methinphenyl] terephthalate (8e): This compound was obtained as white needles (yield: 6.79 g, 78%); mp 239

°C; IR (KBr) (ν , cm^{-1}): 1787, 1760, 1740 (C=O), 1605, 1575 (C=N), 1259 (C-O), 799 (1,4-disubstituted benzenoid ring), 783 and 685 (1,3-disubstituted benzenoid ring); $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 2.48 (s, 6H, 2COCH₃), 4.16 (s, 4H, 2CH₂), 7.35-7.77 (m, 16H, arH), 8.38 (s, 4H, arH), 9.61 (s, 2H, 2N=CH); UV λ_{max} (ϵ): 249 (8843), 210 (9174) nm.

Di-[3-(1-acetyl-3-phenyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalate (8f): This compound was obtained as white needles (yield: 6.81 g, 88%); mp 301 °C; IR (KBr) (ν , cm^{-1}): 1750, 1739 (C=O), 1615, 1587 (C=N), 1230 (C-O), 839 (1,4-disubstituted benzenoid ring), 787 and 697 (1,3-disubstituted benzenoid ring), 774 and 687 (monosubstituted benzenoid ring); $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 2.57 (s, 6H, 2COCH₃), 7.59-8.35 (m, 22H, arH), 9.57 (s, 2H, 2N=CH); UV λ_{max} (ϵ): 247 (17602), 211 (14501) nm.

Results and Discussion

In this study, the structures of 6 new di-[3-(3-alkyl/aryl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalates (**4a-f**), 6 new di-[3-(1-acetyl-3-alkyl/aryl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalates (**5a-f**), 6 new di-[3-(3-alkyl/aryl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalates (**7a-f**), and 6 new di-[3-(1-acetyl-3-alkyl/aryl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] terephthalates (**8a-f**) were identified using elemental analyses and IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and UV spectral data, and the observed spectral values were seen to be compatible with literature values.^{11-16,25}

After the potentiometric titrations of compounds **4** and **7** with TBAH in non-aqueous solvents, the mV values from each titration were plotted against TBAH volumes used (mL) and the potentiometric titration curves were obtained for all the cases. From the titration curves, the HNP values and the corresponding $\text{p}K_a$ values were obtained. As an example, the potentiometric titration curves for 0.001 M solutions of di-[3-(3-methyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethinphenyl] isophthalate (**4a**) titrated with 0.05 N TBAH in isopropyl alcohol, *tert*-butyl alcohol, *N,N*-dimethylformamide, acetone, and dimethyl sulfoxide are presented in Figure 2.

The half-neutralization potential (HNP) values and the corresponding $\text{p}K_a$ values of compounds **4** and **7**, obtained from the potentiometric titrations with 0.05 M TBAH in isopropyl alcohol, *tert*-butyl alcohol, *N,N*-dimethylformamide, acetone, and dimethyl sulfoxide, are presented in Tables 1 and 2, respectively.

The *pH* of weak acids can be calculated using the following equation:

$$pH = \text{p}K_a + \log[A^-]/[HA]$$

where $pH = \text{p}K_a$ when $[A^-]$ is equal to $[HA]$ at the half-neutralization points. Therefore, the *pH* values at the half-neutralization points were taken as $\text{p}K_a$. When the dielectric permittivity of solvents is taken into consideration, the acidity order can be given as follows: dimethyl sulfoxide ($\epsilon = 47.2$) > *N,N*-dimethylformamide ($\epsilon = 37.0$) > acetone ($\epsilon = 20.6$) > isopropyl alcohol ($\epsilon = 19.4$) > *tert*-butyl alcohol ($\epsilon = 12.0$). As seen in Table 1, the acidity order for compounds **4b**, **4e** and **4f** is DMSO > DMF > isopropyl alcohol, for compound **4a** it is DMSO > DMF > isopropyl alcohol > *tert*-butyl alcohol > acetone, for compound **4c** it is DMSO > *tert*-butyl alcohol > DMF > acetone, while the ranking for compound **4d** is DMF > DMSO > isopropyl alcohol > acetone. Moreover, as seen in Table 1, for compounds **4b**, **4e**, and **4f** in acetone, for compounds **4b** and **4d-4f** in *tert*-butyl alcohol, and for compound **4c** in isopropyl alcohol, the

HNP values and the corresponding pK_a values were not obtained. All these compounds, except **4d**, show the strongest acidic properties in DMSO and compounds **4a**, **4c**, and **4d** show the weakest acidic properties in acetone.

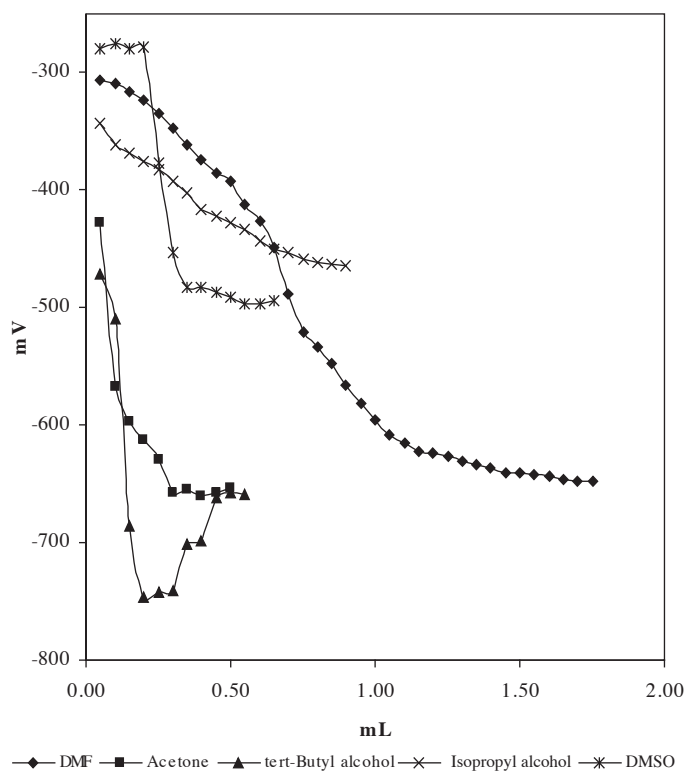


Figure 2. Potentiometric titration curves of 0.001 M solutions of compound **4a** titrated with 0.05 M TBAH in 5 non-aqueous solvents at 25 °C.

Table 1. The HNP and the corresponding pK_a values of compounds **4a-f** in isopropyl alcohol, *tert*-butyl alcohol, DMF, acetone, and dimethyl sulfoxide at 25 °C.

Compd. No.	Isopropyl alcohol		<i>tert</i> -Butyl alcohol		DMF		Acetone		DMSO	
	HNP	pK_a	HNP	pK_a	HNP	pK_a	HNP	pK_a	HNP	pK_a
4a	-371	14.58	-472	15.95	-354	14.24	-582	18.80	-276	12.71
4b	-329	13.41	-	-	-318	13.18	-	-	-173	10.38
4c	-	-	-299	13.08	-334	13.49	-365	14.43	-261	12.13
4d	-422	15.48	-	-	-270	12.28	-566	18.12	-300	12.87
4e	-406	15.29	-	-	-272	12.24	-	-	-249	11.86
4f	-385	14.86	-	-	-382	14.77	-	-	-292	13.10

Table 2. The HNP and the corresponding pK_a values of compounds **7a-f** in isopropyl alcohol, *tert*-butyl alcohol, DMF, acetone, and dimethyl sulfoxide at 25 °C.

Compd. c	Isopropyl alcohol		<i>tert</i> -Butyl alcohol		DMF		Acetone		DMSO	
	HNP	pK_a	HNP	pK_a	HNP	pK_a	HNP	pK_a	HNP	pK_a
7a	-	-	-	-	-265	12.05	-630	19.80	-233	11.44
7b	-	-	-	-	-256	11.73	-	-	-341	12.33
7c	-	-	-	-	-430	14.98	-689	-	-283	12.25
7d	-	-	-	-	-287	12.88	-	-	-	-
7e	-340	13.53	-	-	-302	13.24	-357	14.36	-320	13.61
7f	-	-	-376	14.90	-238	11.61	-645	-	-283	12.49

As seen in Table 2, in isopropyl alcohol only for compound **7e**, in *tert*-butyl alcohol only for compound **7f**, and in DMF for all the compounds **7a-f** the HNP values and the corresponding pK_a values were obtained. For compound **7d** in DMSO and for compounds **7b** and **7e** in acetone the HNP values and the corresponding pK_a values were not obtained. In addition, pK_a values bigger than 20.00 were not determined because this value is outside the range of the pH meter.

As is well known, the acidity of a compound depends on several factors. The 2 most important ones are the solvent effect and molecular structure.^{15,16,18-23} Tables 1 and 2 and Figure 2 show that the HNP values and corresponding pK_a values obtained from the potentiometric titrations depend on the non-aqueous solvents used and the substituents at C-3 in the 4,5-dihydro-1*H*-1,2,4-triazol-5-one ring.

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