Journal of the Korean Chemical Society
2012, *Vol. 56, No. 3*
Printed in the Republic of Korea
http://dx.doi.org/10.5012/jkcs.2012.56.3.348

Synthesis, Structure Investigation and Dyeing Assessment of Novel Bisazo Disperse Dyes Derived from 3-(2'-Hydroxyphenyl)-1-phenyl-2-pyrazolin-5-ones

M. A. Metwally*, S. Bondock, S. I. El-Desouky, and M. M. Abdou†
Department of Chemistry, Faculty of Science, Mansoura University, ET-35516 Mansoura, Egypt.
**E-mail: mamegs@mans.edu.eg*
†Scholarship of Academy of Scientific Research and Technology, ASRT, Egypt.

(Received February 14, 2012; Accepted May 7, 2012)

ABSTRACT. In an attempt to find a new class of bisazo disperse dyes with better dyeing properties, a series of novel bisazo dyestuffs based on 4-arylhydrazono-3-(2'-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-ones **3a-f** were prepared by diazocoupling of *p*-nitrophenyl diazonium chloride with 4-arylhydrazono-3-(2'-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-ones **2a-f**. Compounds **3a-f** were subsequently reacted with acetic anhydride in the presence of *p*-toluenesulfonic acid afford the corresponding O-acetyl derivatives **4a-f**. The latter products as well as spectral data indicated that compounds **3a-f** exist predominantly in the azo-hydrazone tautomeric form (**H**) as the *ZE*-configuration. Additionally, two series of the synthesized dyes **3a-f** and **4a-f** were applied as disperse dyes for dyeing polyester fabrics and their fastness properties were evaluated. Also the position of color in CIELAB coordinates (L*, a*, b*, H*, C*) was assessed.

Key words: Bisazo pyrazolin-5-ones, Azo-hydrazone tautomerism, Fastness properties, CIELAB coordinates

INTRODUCTION

It has been known for many years that polyester fibre are the most important synthetic fibre and reached the status of the highest volume of production among the other synthetic fibres. Disperse dyes are a major class of dyes used nowadays for dyeing polyester fibre owing to their brilliancy, wide range of hue, excellent fastness properties, in addition to the environmental and economic reasons.[1] A large fraction of such dyes are basically derivatives of pyrazolone, possessing the azo chromophore. They have attracted strong interest due to their widespread in a large number of azodisperses dyes,[2-4] as well as for their useful biological and pharmacological properties.[5-7] These compounds exist almost exclusively in the hydrazo tautomeric form both in solutions and in the crystalline state.[8-13]

In addition to, azophenols and their derivatives have aroused much interesting owing to their potential application in dyes chemistry. Due to their auxochromic nature, the resultant dyes have many advantages including bright hues and their useful for dyeing of almost all kind of fabrics, whether natural or synthetic. Another interesting feature of azophenols lies on its possibility to form an equilibrium mixture of two tautomeric form, azophenol or hydrazoquinone.[14-20]

Therefore, the aforesaid findings stimulated us to combine two of the above-mentioned azo dyes together in a single molecular framework, hoping to discover a new lead structure that would have a significant interesting tautomeric structures and dyeing characteristics, mainly strong ability of these dyes on fabrics. In the light of these applications, and in continuation of our recent work aiming at the synthesis and elucidation of the tautomeric structures of 4-arylhydrazono-3-(2-hydroxyphenyl)-2-pyrazolin-5-ones,[21,22] this paper is concerned with the synthesis and investigate the actual structure(s) of bisazo disperse dyes based on 3-(2-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-ones. In addition to synthesizing these proposed candidates, their spectroscopic properties and their application in dyeing polyester fabrics were studied.

EXPERIMENTAL SECTION

Materials and Instrumentation

All the chemicals used were of commercial grade. They were further purified by standard procedures prior to use.[23] 2,3,4-Chromantrione-3-arylhydrazones **1a-f** were prepared by the process reported in the literature.[24] The various 4-arylhydrazono-3-(2′-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-ones **2a-f** were prepared as previously we described.[21] Elemental analyses were performed at the Microanalytical Center, Cairo University, using CHNS-932 (LECO) Vario Elemental Analyzers and the results were within the accepted range (±0.40) of the calculated values. All melting points were measured on a Gallenkamp electrothermal melting point apparatus and were uncorrected. IR spectra were obtained using a Mattson 5000 FTIR spectrometer (ν, cm), using samples in KBr disks and only partial spectral data are listed. The Ultraviolet absorption spectra were recorded in the range 200-800 nm on shimadzul 700 spectraphotometer in dioxane using a concentration 0f 10^{-4} mol dm^{-3}. ^{1}H NMR spectra were measured on a Bruker WP300 (300 MHz) spectrometer (δ, ppm), using DMSO as a solvent and TMS as an internal standard. D_2O exchange was applied to confirm the assignment of the signals of OH, and NH protons. Mass spectra were recorded on a Finnigan MAT 212 instrument. All reactions were monitored by thin layer chromatography (TLC) performed on silica gel 60 F_{254} precoated aluminium sheets, visualized by a 254 nm UV lamp. Scoured and bleached polyester 100% (150, 130 g/m^2, 70/2 denier) was obtained from El-Shourbagy, Egypt. The fabric was further treated before dyeing with a solution containing 5 g/L nonionic detergent (Hostapal CV, Clariant-Egypt) and 2 g/L sodium carbonate at a liquor ratio 20,1 at 60 °C for 30 min, thoroughly washed in water and air dried at room temperature. The dispersing agent Setamol WS was supplied by BASF (Germany). The dyeing assessment, fastness tests, and color measurements were carried out in Laboratories and Research sector in El-Nasr Company for Spinning and Weaving, El-Mahalla El-Kubra, Egypt. The colorimetric measurements (L*, a*, b*, C*, H* and K/S) were carried out using a Gretag Macbeth CE 7000A spectrophotometer (D65 illumination, 10^0 observer). Fastness to washing was carried out using the automatic launder Rotadyer (sponsored by the British Standard Institute-Society of Dyers and Colourists), fastness to perspiration was assessed according to the test sponsored by the (BSS), fastness to rubbing was carried out according to the standard method of testing (BSS) using Crockmeter of Electric Hungarian FD-17 type, fastness to sublimation was carried out using the Electric Japanese Thermotester T-10 type and fastness to light was carried out using the "Weather-o-meter" (Atlas Electric Devices Co. USA), AATCC standard test method.

Synthesis and Spectroscopic Characterization

General procedure for the synthesis of 4-arylhydrazono-3-(5'-(4-nitrophenylazo)-2'-hydroxy phenyl)-1-phenyl-2-pyrazolin-5-ones (3a-f):

A well-stirred solution of *p*-nitroaniline (5 mmol) in conc. HCl (4 ml) and H_2O (2 ml) was heating until complete dissolution of the *p*-nitroaniline hydrochloride. The resulted solution was cooled at 0-5 °C and then diazotized with the solution of $NaNO_2$ (0.35 g, 5 mmol) in H_2O (2 ml). The cold diazonium solution was added dropwise over a period of 20 min to a well-stirred solution of 4-arylhydrazono-3-(2-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-ones **2a-f** (5 mmol) and sodium hydroxide (0.2 g, 5 mmol) in ethanol (20 ml). The resulting mixture was stirred at 0-5 °C for 60 min in ice bath. The precipitate solid was collected, washed with dilute ethanol and finally recrystallized from ethanol/DMF mixture to give the corresponding compounds **3a-f**.

4-Phenylhydrazono-3-(5'-(4-nitrophenylazo)-2'-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-one (3a).

Yield, 80%, mp.=240-242 °C, UV-Vis (λ_{max} in dioxane), 278, 362, 398, 436 nm. IR (KBr, ν_{max}/cm^{-1}), 3420 (OH), 3270 (NH), 3066, 3044 (CH, Ar.), 1656 (C=O, Pyrazol.), 1614 (<C=N), 1550 (C=C-NH-N=), 1520, 1367, 1330 (NO_2 and $C_{arom.}$-N), 1460 (-N=N-), 1272 (C-O), ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 7.01-8.22 (m, 17H, Ar-H), 10.22 (s, 1H, OH, D_2O exch.), 14.10 (s, 1H, NH, D_2O exch.). MS, *m/z* (%), 505 (M^+, 26), 487 (25), 399 (34), 356 (100), 340 (17), 242 (26), 223 (26), 158 (40), 120 (13), 105 (18), 99 (10), 84 (20), 77 (27). Anal. Calcd. for $C_{27}H_{19}N_7O_4$ (505.48), C, 64.15, H, 3.79, N, 19.40. Found, C, 64.31, H, 3.68, N, 19.48.

(4-Methylphenyl)hydrazono)-3-(5'-(4-nitrophenylazo)-2'-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-one (3b).

Yield, 76%, mp.=220-222 °C, UV-Vis (λ_{max} in dioxane), 276, 368, 415, 432 nm. IR (KBr, ν_{max}/cm^{-1}), 3438 (OH), 3270 (NH), 3070, 3050 (CH, Ar.), 2923 (CH, Aliph.), 1652 (C=O, Pyrazol.), 1623 (<C=N), 1589 (C=C-NH-N=), 1521, 1368, 1332 (NO_2 and $C_{arom.}$-N), 1468 (-N=N-), 1276 (C-O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 2.44 (s, 3H, CH_3), 7.05-8.34 (m, 16H, Ar-H), 10.30 (s, 1H, OH, D_2O exch.), 14.02 (s, 1H, NH, D_2O exch.). MS *m/z* (%), 519 (M^+, 36), 501 (26), 369 (100), 353 (19), 278 (16), 251 (12), 223 (19), 151 (23), 132 (33), 105 (15), 99 (15), 73 (21). Anal. Calcd. for $C_{28}H_{21}N_7O_4$ (519.51), C, 64.73, H, 4.07, N, 18.87. Found, C, 64.87, H, 4.18, N, 18.76.

(4-Methoxyphenyl)hydrazono)-3-(5'-(4-nitrophenylazo)-2'-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-one (3c).

Yield, 74%, mp.=190-192 °C, UV-Vis (λ_{max} in dioxane), 282, 368, 419, 434 nm. IR (KBr, ν_{max}/cm^{-1}), 3436 (OH), 3266 (NH), 3065, 3034 (CH, Ar.), 2911 (CH, Aliph.), 1658 (C=O, Pyrazol.), 1625 (<C=N), 1577 (C=C-NH-N=), 1522, 1366, 1327 (NO_2 and $C_{arom.}$-N), 1464(-N=N-), 1268 (C-O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 3.82 (s, 3H, OCH_3), 7.02-8.38 (m, 16H, Ar-H), 10.47 (s, 1H, OH, D_2O exch.), 14.26 (s, 1H, NH, D_2O exch.). MS *m/z* (%),

535 (M^+, 28), 534 (M^+-1, 21), 517 (26), 385 (22), 369 (41), 332 (100), 269 (9), 242 (31), 187 (36), 171 (13), 144 (35), 134 (14), 105 (34), 73 (22). Anal. Calcd. for $C_{28}H_{21}N_7O_5$ (535.51), C, 62.80, H, 3.95, N, 18.31. Found, C, 62.98, H, 3.88, N, 18.50.

(4-Chlorophenyl)hydrazono)-3-(5'-(4-nitrophenylazo)-2'-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-one (3d).

Yield, 86%, mp.=199-201 °C, UV-Vis (λ_{max} in dioxane), 284, 356, 418, 440 nm. IR (KBr, ν_{max}/cm^{-1}), 3426, (OH) 3261 (NH), 3066, 3043 (CH, Ar.), 1655 (C=O, Pyrazol.), 1627 (<C=N), 1540 (C=C-NH-N=), 1527, 1369, 1341 (NO$_2$ and C$_{arom.}$-N), 1469 (-N=N-), 1276 (C-O), 757 (C-Cl). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 7.13-8.49 (m, 16H, Ar-H), 10.41 (s, 1H, OH, D$_2$O exch.), 14.30 (s, 1H, NH, D$_2$O exch.). MS *m/z* (%), 541 (M^++2, 32), 340 (M^++1, 44), 522 (41), 399 (27), 389 (100), 374 (25), 356 (37), 279 (25), 242 (22), 158 (28), 141 (25), 106 (17), 84 (22), 73 (10). Anal. Calcd. for $C_{27}H_{18}ClN_7O_4$ (539.93), C, 60.06, H, 3.36, N, 18.16. Found, C, 60.28, H, 3.48, N, 18.33.

(4-Bromophenyl)hydrazono)-3-(5'-(4-nitrophenylazo)-2'-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-one (3e).

Yield, 78%, mp.=239-241 °C, UV-Vis (λ_{max} in dioxane), 286, 360, 422, 450 nm. IR (KBr, ν_{max}/cm^{-1}), 3447 (OH), 3255 (NH), 3065, 3020 (CH, Ar.), 1662 (C=O, Pyrazol.), 1626 (<C=N), 1550 (C=C-NH-N=), 1518, 1370, 1340 (NO$_2$ and C$_{arom.}$-N), 1472 (-N=N-), 1265(C-O), 565 (C-Br). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 7.22-8.43 (m, 16H, Ar-H), 10.27 (s, 1H, OH, D$_2$O exch.), 14.35 (s, 1H, N-H, D$_2$O exch.). MS *m/z* (%), 586 (M^++2, 39), 584 (M^+, 60), 441 (25), 435 (47), 417 (23), 370 (100), 356 (24), 341 (23), 279 (11), 235 (11), 183 (17), 144 (8), 84 (16), 73 (23). Anal. Calcd. for $C_{27}H_{18}BrN_7O_4$ (584.38), C, 55.49, H, 3.10, N, 16.78. Found, C, 55.77, H, 3.19, N, 16.95.

(4-Nitrophenyl)hydrazono)-3-(5'-(4-nitrophenylazo)-2'-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-one (3f).

Yield, 83%, mp.=246-248 °C, UV-Vis (λ_{max} in dioxane), 286, 359, 424, 465 nm. IR (KBr, ν_{max}/cm^{-1}), 3434 (OH), 3265 (NH), 3064, 3037 (CH, Ar.), 1660 (C=O, Pyrazol.), 1629 (<C=N), 1546 (C=C-NH-N=), 1500, 1380, 1324 (NO$_2$ and C$_{arom.}$-N), 1462 (-N=N-), 1250 (C-O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 7.11-8.51 (m, 16H, Ar-H), 10.37 (s, 1H, OH, D$_2$O exch.), 14.43 (s, 1H, NH, D$_2$O exch.). MS *m/z* (%), 550 (M^+, 30), 531 (34), 400 (100), 384 (37), 356 (28), 308 (26), 279 (22), 235 (25), 223 (15), 159 (27), 132 (13), 120 (17), 73 (14). Anal. Calcd. for $C_{27}H_{18}N_8O_6$ (550.48), C, 58.91, H, 3.30, N, 20.36. Found, C, 59.11, H, 3.42, N, 20.45.

General procedure for the synthesis of 4-arylhydrazono-3-(5'-(4-nitrophenylazo)-2'-acetoxyphenyl)-1-phenyl-2-pyrazolin-5-ones (4a-f):

A mixture of **3a-f** (5 mmol) and acetic anhydride (20 ml) in the presence of a catalytic amount of *p*-toluenesulfonic acid was stirred at 100 °C for 2-3.5 h. After removal of the solvent in vacuo, cold water was added to the residue. The resulting O-acetyl derivatives **4a-f** were filtered off and recrystallized from acetic acid.

Phenylhydrazono-3-(5'-(4-nitrophenylazo)-2'-acetoxyphenyl)-1-phenyl-2-pyrazolin-5-one (4a).

Yield, 73%, mp.=266-268 °C, UV-Vis (λ_{max} in dioxane), 274, 344, 398, 412 nm. IR (KBr, ν_{max}/cm^{-1}), 3279 (NH), 3066, 3030 (CH, Ar.), 1755 (C=O, ester), 1668 (C=O, Pyrazol.), 1623 (<C=N), 1546 (C=C-NH-N=), 1523, 1367, 1340 (NO$_2$ and C$_{arom.}$-N), 1465(-N=N-), 1274 (C-O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 3.86 (s, 3H, OCOCH$_3$), 7.01-8.04 (m, 17H, ArH), 13.89 (s, 1H, NH, D$_2$O exch.). MS, *m/z* (%), 547 (M^+, 29), 505 (20), 488 (41), 339 (24), 356 (100), 340 (13), 308 (26), 251 (35), 223 (39), 151 (23), 132 (33), 120 (9), 99 (15), 84 (12), 73 (13). Anal. Calcd. for $C_{29}H_{21}N_7O_5$ (547.52), C, 63.62, H, 3.87, N, 17.91. Found, C, 63.78, H, 4.09, N, 17.80.

(4-Methylphenyl)hydrazono)-3-(5'-(4-nitrophenylazo)-2'-acetoxyphenyl)-1-phenyl-2-pyrazolin-5-one (4b).

Yield, 74%, mp.=235-237 °C, UV-Vis (λ_{max} in dioxane), 276, 354, 402, 423 nm. IR (KBr, ν_{max}/cm^{-1}), 3285 (NH), 3068, 3022 (CH, Ar.), 2923 (CH, Aliph.), 1760 (C=O, ester), 1654 (C=O, Pyrazol.), 1627 (<C=N), 1546 (C=C-NH-N=), 1523, 1369, 1342 (NO$_2$ and C$_{arom.}$-N), 1469 (-N=N-), 1272 (C-O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 2.48 (s, 3H, CH$_3$), 3.86 (s, 3H, OCOCH$_3$), 7.21-8.34 (m, 16H, Ar-H), 14.41 (s, 1H, NH, D$_2$O exch.). MS *m/z* (%), 561 (M^+, 19), 519 (31), 501 (26), 411 (23), 399 (35), 369 (29), 353 (100), 292 (24), 235 (35), 223 (19), 158 (23), 145 (12), 120 (39), 99 (15), 84 (12). Anal. Calcd. for $C_{30}H_{23}N_7O_5$ (561.55), C, 64.17, H, 4.13, N, 17.46. Found, C, 64.30, H, 4.04, N, 17.29.

(4-Methoxyphenyl)hydrazono)-3-(5'-(4-nitrophenylazo)-2'-acetoxyphenyl)-1-phenyl-2-pyrazolin-5-one (4c).

Yield, 77%, mp.=214-217 °C, UV-Vis (λ_{max} in dioxane), 276, 364, 407, 430 nm. IR (KBr, ν_{max}/cm^{-1}), 3278 (NH), 3067, 3036 (CH, Ar.), 2913 (CH, Aliph.), 1766 (C=O, ester), 1658 (C=O, Pyrazol.), 1624 (<C=N), 1549 (C=C-NH-N=), 1520, 1366, 1343 (NO$_2$ and C$_{arom.}$-N), 1463 (-N=N-), 1272 (C-O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 3.34 (s, 3H, OCH$_3$), 3.94 (s, 3H, OCOCH$_3$), 7.15-8.33 (m, 16H, Ar-H), 14.49 (s, 1H, NH, D$_2$O exch.). MS *m/z* (%), 577 (M^+, 26), 535 (28), 517 (26), 427 (25),

385 (31), 369 (29), 332 (100), 234 (31), 187 (43), 159 (52), 136 (31), 98 (26), 84 (30). Anal. Calcd. for $C_{30}H_{23}N_7O_6$ (577.55), C, 62.39, H, 4.01, N, 16.98. Found, C, 62.20, H, 4.28, N, 17.09.

(4-Chlorophenyl)hydrazono)-3-(5'-(4-nitrophenylazo)-2'-acetoxyphenyl)-1-phenyl-2-pyrazolin-5-one (4d).

Yield, 67%, mp.=244-246 °C, UV-Vis (λ_{max} in dioxane), 280, 360, 410, 431 nm. IR (KBr, ν_{max}/cm^{-1}), 3283 (NH), 3070, 3040 (CH, Ar.), 1767 (C=O, ester), 1651 (C=O, Pyrazol.), 1622 (<C=N), 1548 (C=C-NH-N=), 1522, 1369, 1335 (NO_2 and $C_{arom.}$-N), 1471(-N=N-), 1275 (C-O), 765 (C-Cl). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 3.91 (s, 3H, $OCOCH_3$), 7.03-8.39 (m, 16H, Ar-H), 14.29 (s, 1H, NH, D_2O exch.). MS m/z (%), 582 (M^++1, 40), 541 (22), 522 (17), 389 (100), 374 (25), 356 (44), 279 (10), 235 (13), 159 (28), 119 (24), 106 (12), 99 (10), 77 (19). Anal. Calcd. for $C_{29}H_{20}ClN_7O_5$ (581.97), C, 59.85, H, 3.46, N, 16.85. Found, C, 60.12, H, 3.49, N, 16.98.

(4-Bromophenyl)hydrazono)-3-(5'-(4-nitrophenylazo)-2'-acetoxyphenyl)-1-phenyl-2-pyrazolin-5-one (4e).

Yield, 77%, mp.=255-257 °C, UV-Vis (λ_{max} in dioxane), 280, 362, 446 nm. IR (KBr, ν_{max}/cm^{-1}), 3283 (NH), 3078, 3048 (CH, Ar.), 1762 (C=O, ester), 1659 (C=O, Pyrazol.), 1626 (<C=N), 1552 (C=C-NH-N=), 1516, 1367, 1331 (NO_2 and $C_{arom.}$-N), 1469 (-N=N-), 1259 (C–O), 570 (C-Br). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 3.79 (s, 3H, $OCOCH_3$), 7.11-8.41 (m, 16H, Ar-H), 14.24 (s, 1H, N-H, D_2O exch.). MS m/z (%), 626 (M^+, 31), 584 (64), 565 (32), 434 (100), 417 (7), 371 (20), 356 (18), 279 (21), 234 (21), 183 (25), 159 (19), 120 (9), 73 (21). Anal. Calcd. for $C_{29}H_{20}BrN_7O_5$ (626.42), C, 55.60, H, 3.22, N, 15.65. Found, C, 55.87, H, 3.10, N, 15.80.

(4-Nitrophenyl)hydrazono)-3-(5'-(4-nitrophenylazo)-2'-acetoxyphenyl)-1-phenyl-2-pyrazolin-5-one (4f).

Yield, 75%, mp.=175-178 °C, UV-Vis (λ_{max} in dioxane), 285, 366, 415, 464 nm. IR (KBr, ν_{max}/cm^{-1}), 3268 (NH), 3102, 3073 (CH, Ar.), 1759 (C=O, ester), 1663 (C=O, Pyrazol.), 1619 (<C=N), 1548 (C=C-NH-N=), 1523, 1367, 1340 (NO_2 and $C_{arom.}$-N), 1468 (-N=N-), 1263 (C-O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm), 3.72 (s, 3H, $OCOCH_3$), 7.11-8.37 (m, 16H, Ar-H), 14.47 (s, 1H, NH, D_2O exch.). MS m/z (%), 592 (M^+, 22), 533 (35), 442 (17), 385 (17), 356 (18), 279 (29), 223 (100), 159 (24), 132 (9), 84 (14), 73 (24). Anal. Calcd. for $C_{29}H_{20}N_8O_7$ (592.52), C, 58.78, H, 3.40, N, 18.91. Found, C, 58.62, H, 3.51, N, 19.11.

Dyeing and Fastness Determinations

Preparation of dye dispersion:

The required amount of the dye (2% shade) was dissolved in 1 ml of acetone and then added dropwise with stirring to a solution of Setamol WS (sodium salt of a condensation product of naphthalene sulfonic acid and formaldehyde) as anionic dispersing agent of BASF. The dye was precipitated in a fine dispersion ready for use in dyeing after evaporation of the solvent by warming.

Dyeing of polyester fabrics:

The dye bath (1,20, good to dye liquor ratio) in a sealed stainless steel dye pots of 250 ml capacity in "Galvanin-Marino VI-Italy" dyeing machine. Additional dispersing agent (0.5-1.0 g/l) was added and the pH of the bath adjusted to 5.5 using glacial acetic acid. Dyeing carried out by raising the dye bath temperature from 20 to 130 °C at a rate of 3 °C/min and holding at this temperature for 60 min before rapidly cooling to 50 °C at 9.9 °C/min. The dyed fabrics were then rinsed with cold water, reduction-cleared using sodium hydroxide (2 g/l) and sodium hydrosulphite (1 g/l) and soaped with 2% nonionic detergent and ammonia (pH 8.5) at 50 °C for 30 min to improve washing fastness.

Color fastness tests:

The color fastness of dyeing was evaluated using the standard method[25] and given in *Table* 1. The fastness to light, sublimation and perspiration was assessed in accordance with AATCC-15 (1985). The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC-88 (1988) and the wash fastness test in accordance with IS, 765-1979.

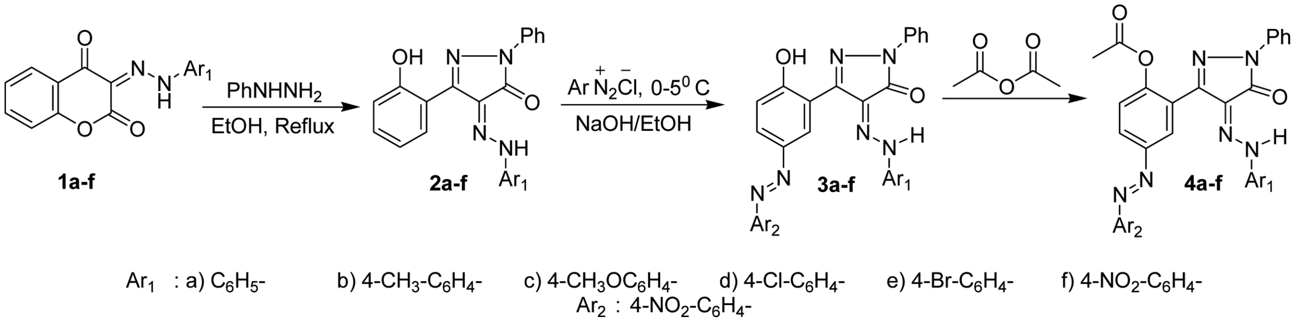
Color assessment:

The colorimetric parameters (*Table* 2) of the dyed polyester fabrics were determined on a reflectance spectrophotometer (GretagMacbeth CE 7000a), equipped with a D65/108 source and barium sulphate as standard blank, UV excluded, specular component included and three repeated measurements average settings.

RESULTS AND DISCUSSIONS

Synthesis and Tautomeric Structure

The synthetic approach to the target bisazo dyes is outlined in *Scheme* 1. The starting 4-arylhydrazono-3-(2-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-ones **2a-f** were prepared by refluxing phenylhydrazine with 2,3,4-chromantrione-3-arylhydrazones **1a-f** in ethanol as previously we described.[21] Coupling of **2a-f** with diazotized *p*-nitroaniline in an alkaline solution at 0-5 °C yielded the respec-



***Scheme* 1.** Synthesis of the studied compounds **3a-f** and **4a-f**.

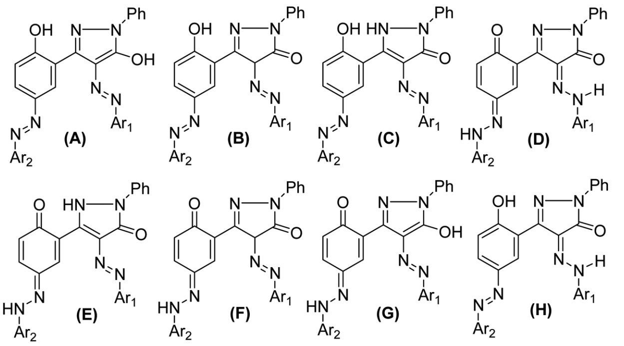


***Fig.* 1.** Possible tautomeric structures of 4-arylhydrazono-3-(5'-(4-nitrophenylazo)-2'-hydroxyl phenyl)-1-phenyl-2-pyrazolin-5-ones (**A**-**H**).

tive bis-arylazo derivatives **3a-f**. The latter products when reacted with acetic anhydride in the presence of *p*-toluenesulfonic acid gave the corresponding O-acetyl derivatives **4a-f**.

It is worthwhile to mention that bisazo dyes **3a-f** can display multiple tautomeric structures (**A**-**H**) (*Fig.* 1). The spectral features clearly reflect that such compounds have the structure (**H**).

The infrared spectral data of the compounds **3a-f** displayed a band at 1662-1652 cm^{-1} which is assigned to C=O stretching vibration[26] disregard of the tautomeric structure with no carbonyl group (**A**) structure from our consideration. The absence of tangible band associated with a conjugation of C=O with the C=N-NH at 1720 cm^{-1} [27] has also ruled out the existence of structures (**B**-**C**), which have incompletely conjugated chromophores, and leaves structure (**D**-**H**) as the possible tautomeric forms. In addition, the structures (**D**-**F**) were discarded on the basis of this compounds exhibit absorption bands between 3450-3440 cm^{-1} region are attributed to the hydroxyl OH group.[21,22] Further evidence that this compounds gave a deep color with ferric chloride that prove the existence of enolic hydroxyl group.[28] The prominent band occurs around 1550 cm^{-1}, on the basis of previous results,[29] reasonably be ascribed to the benzene ring C=C skeletal vibration associated with the -NH-N= linkage. In the region 1629-1614 cm^{-1}, the hydrazone $\nu_{C=N}$ stretching vibration is also expected.[30,31] The compounds investigated possess the hydrazono moiety, therefore, the stretching vibration of the C$_{arom.}$-N linkage show band between 1341-1324 cm^{-1} in their spectra[32] combined with observing a strong bands at 3270-3200 cm^{-1} characteristic to the hydrazone NH stretching vibration.[21,22] Also, the weak bands assignable to the stretching vibration of azo linkages in compounds **3a-f** can be observed at the frequency range of 1472-1460 cm^{-1} as reported in the correlation data for N=N bonds.[33] These results were compatible with a conclusion of such compounds have one of the two tautomeric forms (**G**), (**H**) and exclude the tautomeric forms (**A**-**F**).

Moreover, the structure (**G**) was discarded on the basis of the electronic absorption spectral data. Inspection of the foregoing data reveals that all investigated dyes showed in each case four absorption bands in the regions 276-286, 356-368, 398-434 and 431-465 nm. The first three absorption pattern were observed and these values are practically very close to those reported for the hydrazo chromophore of pyrazolin-5-one dyes[34,7] which also, is in agreement with that reported in our recent publications.[21,22] Absorption bands attributed to hydrazo-quinine between 475-510 nm are missing.[35] Thus, the observation of bands at 431-465 nm is indicative of the azophenol form of compounds.[20,36] It is evident, therefore, that these compounds **4a-f** does not exist in the tautomeric form (**G**) and it gave substantiate for the assignment of the tautomeric structure (**H**).

Corroborative evidence that compounds **3a-f** exist in the tautomeric form (**H**) comes from the ^{1}H NMR spectra since the conspicuous absence of a proton at C-4 signal at about 6.4 ppm[26] arising from the pyrazolinone possess the hydrazono moiety. The broad singlet peak at 10.22-10.47 ppm was attributed to the presence of the phenolic OH proton[21,22] while a signal that correspond to the pyrazoline N-H proton around 12.3 ppm[22] is absent. In addition, the highly deshielded singlet at 13.40-14.33 ppm was assigned to the presence of hydrazone-NH proton.[37-39] This down field position of N-H proton is in evidence of chelation with the carbonyl group.[21,22] On the other hand, the signals in the range 7.1-8.5 ppm are attributed to aromatic protons. These results were compatible with a conclusion of such compounds **4a-f** have the structure (**H**).

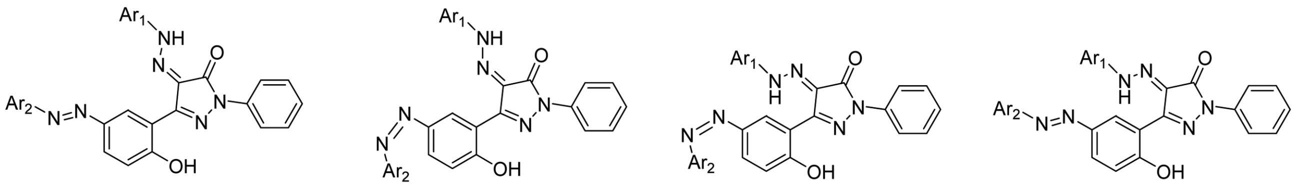
This assignment agrees with that we previously reported for structurally related compounds[21,22] and also this is rather confirmed from other investigations that were carried out to establish the tautomeric structures of arylazopyrazolone and arylazophenol using avariety of spectroscopic techniques. The spectral data generally led to the conclusion that the tautomeric equilibrium of the arylazopyrazolone dyes is in favour of hydrazo form[8-13] and the tautomeric equilibrium of arylazophenol dyes is in favour of azo form.[14-20] These suggest that these dyes are predominantly in azo-hydrazo form (**H**).

Next, conformity to the existence of tautomerism in the azo-hydrazo form (**H**), we carried out the acetylation of **3a-f**. Thus, thermal treatment of **3a-f** with acetic anhydride in the presence of *p*-toluenesulfonic acid afforded the O-acetyl derivatives **4a-f** (*Scheme* 1). Thus, ^{1}H NMR spectra of the esters **4a-f** revealed one proton, exchangeable with D_2O, confirming the presence of hydrazone-NH proton, while a signal characteristic for the phenolic OH proton is absent. Also, all of the esters **4a-f** obviously showed the presence of methyl group protons for each of them. This is coincident with the outputs of reading IR chart for compounds **4a-f**, which showed two absorption vibrational bands due to stretching of (C=O) at 1663-1654 and 1767-1755 cm^{-1} of both pyrazolone and ester carbonyls. The O-acetylation was assigned to take place at phenolic OH which is in agreement with the conspicuous absence of absorption bands characteristic for hydroxyl group between 3450-3440 cm^{-1} region. An additional proof of these proposed structure is found in the mass spectral fragmentation analysis. In the mass spectra of all the compounds, molecular ion peaks at the expected *m/z* values with relative intensities and their elemental analyses data are consistent with their assigned mono acetyl structure. Hence, these results arose the conclusion without any doubt that compounds **3a-f** exist in the tautomeric form (**H**).

It is noteworthy to point out that configurations of the double bonds of $C=N_{(hydrazo\ pyrazolone)}$ and $N=N_{(azophenol)}$ for the most stable tautomeric form (**H**) can lead to four possibilities, *ZE*, *ZZ*, *EE*, *EZ* isomers (*Fig*. 2). From these only the last two isomers are rejected for steric reasons. In agreement of this conclusion, the *Z*-configuration of hydrazone are expected to be stabilized by intramolecular hydrogen bonding between the C=O and hydrazo NH group. This also based on analog of the our recently reported structure of 4-arylhydrazono-3-(2'-hydroxyphenyl)-2-pyrazolin-5-ones, whose *Z*-isomer has been confirmed by spectroscopic data and supported by theoretical calculation.[21,22] Also, the preferential formation of transazophenol supports from the identity of the UV characteristics of them with those of *trans*-azobenzene (λ_{max}= 445).[40] This *trans* configuration can be evident from the diagnostic bands assignable to the stretching-vibration mode of N=N at 1472-1460 cm^{-1}.[41] The absence of tangible band associated with the bending mode at 927 cm^{-1} has also ruled out the existence of compounds in mixed conformers of *cis* and *trans*.[41] It is therefore realistic to conclude that the compounds **3a-f** exist in the tautomeric form (**H**) as the *ZE* configuration.

Dyeing and Fastness Properties

The development of disperse dyes "Dyes insoluble in water and applied from aqueous dispersion rather than from solution" was a revolutionary solution to the problem of coloration of synthetic fibers. The dyes were essentially insoluble in water and were prepared for application by being ground, in the presence of dispersing agents, to microscopically fine particles of the order of a few microns and, then, by pan drying the resultant suspension. The resulting readily dispersible solid could then dye the more hydrophobic acetate fiber by partitioning into the fiber from low dye bath concentrations. The synthesized disperse dyes under investigation **3a-f**, **4a-f** were applied



Z,E (cis-trans) Z,Z (cis-cis) E,Z (trans-cis) E,E (trans-trans)

***Fig*. 2.** Possibilities configuration for the compounds **3a-f** as they exist in the tautomeric form (**H**).

***Table* 1.** Fastness properties[a] of the synthesized dyes **3a-f**, **4a-f** on polyester fabrics

Compound no.	Washing	Perspiration		Rubbing		Sublimation fastness		Light (80 h)
		Acid	Alkali	Dry	Wet	180 °C	210 °C	
3a	4-5	4	4	4	4-5	4	3-4	6-7
3b	4-5	4	4	4	4-5	3-4	3	6-7
3c	4	3-4	4	3-4	3-4	4	4	6
3d	4	4	4	3	3-4	5	4-5	6
3e	4	4	4	4	4	5	4-5	7
3f	4	4	4	4	4	5	4-5	7
4a	4	4	4	3-4	3-4	4	3-4	6-7
4b	4	3-4	3-4	3-4	3-4	4	4	6
4c	4	3-4	3-4	4	4	4	3-4	6
4d	3-4	4	4-5	3	3-4	4	4	6-7
4e	3-4	3-4	3-4	3-4	4	4	3	6-7
4f	3-4	4	4	4	4	4-5	4	6-7

[a] = light fastness, 1-8 scale, washing, perspiration, rubbing and sublimation fastness, 1-5 scale.

to polyester fabric at 2% shade by high-temperature pressure technique (130 °C). The dyes on polyester fabrics were evaluated in terms of their fastness properties as shown in *Table* 1.

Fastness to Washing:

The dyed polyester fabrics have good fastness to washing according to the international Geometric Grey scale[42] and this may be attributed to inadequate diffusion of dye molecule into the fabrics.

Fastness to Perspiration (, acid and alkaline):

The majority of these dyes were found to have good perspiration fastness 3-4. Also, the acetylation of hydroxyl group reduced the fastness to perspiration properties.

Fastness to Rubbing:

The test is designed to determine the amount of color transferred from the surface of colored fabrics to another surface by rubbing. Most of the dyes have a moderate (3) to good (4) rubbing fastness and this may be attributed to inadequate diffusion of dye molecule into the fabrics.

Fastness to Sublimation:

Sublimation fastness properties of synthesized dyes expressed as color staining on the undyed polyester piece ranged from good to very good according to the international Geometric Grey Scale.[42] In most cases, the best sublimation fastness was obtained by unacetylated dyes.

Fastness to Light:

It is signicantly depended on nature of the substituents which change the electron density around hydrazo group. The high fastness to light may be attributed to electron accepting groups. This agrees with the notion that the azo compounds appended with electron-withdrawing substituents on the diazo components are less prone to photofading.[43] Generally, the prepared dyes showed satisfactory fastness to light ranging 6-7 according to the international Geometric Grey Scale.[42]

Color Assessment

The color parameters (*Table* 2) of the dyed polyester fabrics were measured using a spectrophotometer (GretaMacbeth Color Eye 7000A, USA) under illuminant D65, with a 10° standard observer. The assessment of color-dyed fabrics was made in terms of tristimulus colorimetry. The following CIELAB coordinates are measured, lightness (L^*), chroma (C^*), hue angle from 0° to 360° (h), (a^*) value represents the degree of redness (positive) and greenness (negative) and (b^*) represents the degree of yellowness (positive) and blueness (negative). The K/S value which has been employed as the dye uptake or color strength was calculated for each dyed specimen as well as for an undyed one at a maximum absorption wavelength of 360 nm from the reflectance values using the Kubelka-Munk equation[43] as follows,

$$K/S=(1-R)^2/2R$$

where K is the coefficient of absorption, S is the coefficient of scattering, R is the reflectance value of the fabric at peak wavelength. The parent dyestuff in each group is taken as the standard in the color difference calculation (ΔL^*, ΔC^*, and ΔH^*). The results were obtained using

***Table* 2.** Colour values of dyes **4a-f** on polyester fabrics (light source D65/10° observer)

Compound no.	K/S	L*	a*	b*	C*	H*	Δa*	Δb*	ΔC*	ΔL*	ΔH^*
3a	38.5	62.4	33.6	71.6	79.1	64.9	--	--	--	--	--
3b	39.9	65.1	29.4	75.8	81.4	68.8	-4.2	4.2	2.3	2.7	3.9
3c	40.5	63.1	38.6	77.7	86.7	63.6	5.0	6.1	7.6	0.7	-1.3
3d	40.3	71.6	19.8	68.4	71.2	73.8	-13.8	-3.2	-7.9	9.2	8.9
3e	39.8	64.9	29.2	71.9	77.6	67.8	-4.4	0.3	-1.5	2.5	2.9
3f	40.6	62.8	38.8	76.1	78.4	63.1	5.2	4.5	-8.8	0.4	-1.8
4a	39.8	73.2	21.6	81.6	74.0	75.1	-12.0	10.0	-4.9	10.8	10.2
4b	40.0	64.3	17.5	71.9	74.1	76.3	-16.1	0.3	-5.0	1.9	11.4
4c	40.8	66.5	24.9	75.1	79.1	71.6	-8.7	3.5	0.0	4.1	6.7
4d	40.5	77.2	15.3	75.9	77.1	78.6	-18.3	4.3	-1.4	14.8	13.7
4e	40.0	73.4	10.4	64.8	65.6	80.8	-23.2	-6.8	-13.5	11.0	15.9
4f	40.7	67.2	25.7	72.2	77.2	70.2	-7.9	0.6	-1.9	4.8	5.3

CIELAB techniques, and are given in *Table* 2, where ΔL* is the lightness difference, ΔC* is the chroma difference, and ΔH* is the hue difference. A negative sign of ΔL* indicates that the dyed fiber becomes darker than the standard, whereas a positive sign indicates that the dyed fiber becomes lighter than the standard. A negative sign of ΔC* indicates that the dyed fiber becomes duller than the standard, whereas a positive sign indicates that the dyed fiber becomes brighter than the standard. A negative sign of ΔH* indicates that the color shifted to a red color, while a positive sign indicates that the color shifted to yellowish. The results are shown in *Table* 2 tend to give the following conclusions,

I. K/S values in the dyes under investigation **3a-f**, **4a-f** vary from 38.5 to 40.8, which all members of this groups increases strength of the K/S value of the polyester fabric compared with that of the parent **3a**. Dyes **4a-f** which contain the acetate moiety are characterized by higher K/S values compared with their analogues **3a-f**, indicating that the introduction of acetate moiety in dyes **4a-f** increases the color strength on polyester fabric.

II. The color hues of the dyes under investigation on polyester fabric are shifted to the yellowish direction on the yellow-blue axis according to the positive values of b*.

III. The color hue of the most of the dyes on polyester fabric is shifted to the greenish direction on the red-green axis as indicated from the negative value of a*.

IV. In general, dyeings with the acetylated dyes **4a-f** were lighter and duller than the corresponding unacetylated dyes **3a-f** according to the color lightness values (L* and C*).

CONCLUSIONS

In this work, a series of novel bisazo disperse dyes having different substituted groups were synthesized. The influence of the dye structures on the spectroscopic and dyeing properties was investigated. The spectroscopic data of the compounds prepared and their acetylation reaction have provide a decisive evidence that such compounds exist predominantly in the azo-hydrazo structure (**H**) as the *Z*,*E*-configuration. The outstanding characteristics of the disperse dyes **3a-f** and **4a-f** on polyester fabrics exhibited very good to excellent light fastness properties with little variation in the moderate to good washing, perspiration, rubbing and sublimation fastness. Furthermore, it was also observed that the presence of an ester group have a little influence on visible absorption, fastness properties and color coordinates (L*, a*, b*, C*, H* and K/S).

Acknowledgments. The authors express their appreciation and gratitude to the authorities of the Laboratories and Research sector in El-Nasr Company for Spinning and Weaving, El-Mahalla El-Kubra, Egypt for dyeing assessment, fastness tests, and color measurements. Academy of Scientific Research and Technology, ASRT, Egypt, Grant, is gratefully acknowledged by Mr. Moaz M. Abdou.

REFERENCES

1. Annen, O.; Egli, R.; Hasler, R.; Henzi, B.; Jakob, H.; Matzinger, P. *Rev. Prog. Coloration* **1987**, *17*, 72.
2. Metwally, M. A.; Bondock; S.; El-Desouky; S. I.; Abdou; M. M. *Int. J. Modern Org. Chem.* **2012**, *1*, 19.
3. Karci, F.; Ertan, N. *Dyes Pigm.* **2002**, *55*, 99.
4. Ho, Y. W. *Dyes Pigm.* **2005**, *64*, 223.
5. Ozdemir, A.; Turan-Zitouni, G.; AsımKaplancıklı, Z.; Revial, G.; Demirci, F.; Iscan, G. *J Enzyme Inhib. Med. Chem.* **2010**, *25*, 565.
6. Kücükgüzel, S. G.; Rollas, S. *Farmaco* **2002**, *57*, 583.

7. Kücükgüzel, S. G.; Rollas, S.; Erdeniz, H.; Kiraz, M.; Cevdet Ekinci, A.; Vidin, A. *Eur. J. Med. Chem.* **2000**, *35*, 761.
8. Minkin, V. I.; Garnovskii, A. D.; Elguero, J.; Katritzky, A. R.; Denisko, O. V. *Adv. Heterocycl. Chem.* **2000**, *76*, 157.
9. Whitaker, A. *Acta crystallogr.* **1988**, *C44*, 1767.
10. Whitaker, A. *Acta crystallogr.* **1988**, *C44*, 1587.
11. Connor, J. A.; Kennedy, R. J.; Dawies, H. M.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Perkin Trans.* **1990**, *2*, 203.
12. Whitaker, A. J. Soc. *Dyers Colour* **1995**, *11*, 66.
13. Emeleus, L. C.; Cupertino, D. C.; Harris, S. G.; Owens, S.; Parsons, S.; Swart, R. W.; Tasker, P. A.; White, D. J. *J. Chem. Soc., Dalton Trans.* **2001**, *2*, 1239.
14. Sawicki, E. *J. Org. Chem.* **1957**, *22*, 915.
15. Sawicki, E. *J. Org. Chem.* **1957**, *22*, 1084.
16. Lycka, A.; Machacek, V. *Dyes Pigm.* **1986**, *7*, 171.
17. Ueno, K. *J. Am. Chem. Soc.* **1957**, *79*, 3205.
18. Burawoy, A.; Thompson, A. R. *J. Chem. Soc.* **1953**, 1443.
19. Hadzi, D. *J. Chem. Soc.* **1956**, 2143.
20. Ospenson, J. *Acta Chem. Scand.* **1951**, *5*, 491.
21. Metwally, M. A.; Bondock, S.; El-Desouky, S. I.; Abdou, M. M. *J. Korean Chem. Soc.* **2012**, *56*, 82.
22. Metwally, M. A.; Bondock, S.; El-Desouky, S. I.; Abdou, M. M. *Dyes Pigm.* 2012 (submitted).
23. Perrin, D. D.; Armarego, W. L. F.; Parris, D. R. *Purification of laboratory chemicals*, 2nd ed.; Pergamon: New York, 1980.
24. Shawali, A. S.; Harb, N. M. S.; Badahdah, K. O. *J. Heterocycl. Chem.* **1985**, *22*, 1397.
25. Anonymous. *Standard methods for the determination of the color fastness of textiles and leather*, 5th ed.; The Society of Dyers and Colorists: Bradford, England, 1990; p 619.
26. Yasuda, H.; Nidokawa, H. *J. Org. Chem.* **1966**, *31*, 1722.
27. Jones, R.; Ryan, A. J.; Sternhell, S.; Wright, S. E. *Tetrahedron* **1963**, *19*, 1497.
28. Geissman, T. A.; Armen, A. *J. Am. Chem. Soc.* **1955**, *77*, 1623.
29. Russell, P. E. *J. Am. Chem. Soc.* **1953**, *75*, 5315.
30. Randall, H. M.; Fuson, N.; Fowler, R. G.; Dangl, J. R. *Infrared determination of organic compounds*; D. Van Nostrand, Co., Inc.: New York, 1949; p 222.
31. Gagnon, P. E.; Boivin, J. L.; MacDonald, B. R.; Yaffe, L. *Can. J. Chem.* **1954**, *32*, 823.
32. Colthup, N. B. *J. Opt. Soc. Am. A.* **1950**, *40*, 397.
33. Bellamy, L. J. *Adv. Infrared group frequencies*; Methuen: London, 1968; p 52.
34. Yasuda, H. *Bull. Chem. Soc. Jap.* **1967**, *40*, 1239.
35. Oakes, J.; Gratton, P. *J. Chem. Soc., Perkin Trans.* **1998**, *2*, 1857.
36. Brode, W.; Herdle, L. *J. Org. Chem.* **1941**, *6*, 713.
37. Lestina, G. J.; Regan, T. H. *J. Org. Chem.* **1969**, *34*, 1685.
38. Yoder, C. H.; Barth, R. C.; Richter, W. M.; Snavely, F. A. *J. Org. Chem.* **1972**, *37*, 4121.
39. Snavely, F. A.; Yoder, C. H. *J. Org. Chem.* **1968**, *33*, 513.
40. Chakravorty, A.; Ktlia, K. C. *J. Org. Chem.* **1970**, *35*, 2231.
41. Bellamy, L. J. *The infrared spectra of complex molecules*; Chapman and Hall: London, 1975; p 303.
42. SDL. Atlas Ltd. P.O. Box 162, Crown Royal, Shawcross St., Stockport SK1 3JW.
43. Gordon, P. F.; Gregory, P. *Organic Chemistry in Color*; Springer-Verlag: Berlin, 1983; p 289.