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Tautomerism in 2-ketomethylquinolineazines

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HIGHLIGHTS

- Structure of a new series 2-ketomethylquinolineazines and identification of their tautomeric forms.
- Strength intramolecular hydrogen bonding.
- Different tautomers to be present in solutions.
- Tauatomerism.
- Azines.

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ABSTRACT

A series of new azines were prepared in three steps. Structures of all compounds have been elucidated using spectroscopic methods and elemental analysis. Our studies show that in chloroform solution generally two tautomeric forms are in equilibrium. In some cases, one tautomer was the dominant species.

1. Introduction

Azines are a class of compounds that undergo a wide variety of chemical processes and have interesting chemical properties. These compounds are also valuable intermediates for synthesis of heterocyclic compounds [1], show biological activities including antibacterial [2], antifungal [3] and antitumor [4], form complexes with transition metals [5], and are used as nonlinear optical materials [6] and in designing of liquid crystals [7].

2. Experimental

Melting points were obtained by a Stuart Scientific SMP2 apparatus and are uncorrected. Yields refer to the isolated products and all products were characterized by their physical and spectral data. IR spectra were recorded on IR-435 Shimadzu spectrophotometer. ^{1}H and ^{13}C NMR (500 and 125 MHz) spectra were recorded on a Bruker-Avance AQS 500 spectrometer in $CDCl_3$ and tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained on GC/MS/DS Varient-Sinngan spectrometer (EI mode at 70 eV). Elemental analysis was done on CHN-O-RAPID, Heraeus CHNS. UV–VIS spectra were recorded on Shimadzu UV-160 spectrophotometer. All 2-ketomethylquinoines were characterized by comparison of their spectroscopic data (IR, ^{1}H NMR) and melting points with those of reported in the literature [8].

2.1. General procedure for synthesis of symmetrical 2-ketomethylquinolineazine (**3a**)

2-Ketoiminomethylquinolines **1a–1b**, Scheme 2 were prepared by following Rousel [8c] literature method. **1a** was later used in preparation of symmetrical azines **3a**. 2-Ketoiminomethylquinoline (**1a**) (2.0 mmol) was dissolved in the minimum amount of ethanol and a drop of acetic acid and hydrazine monohydrate (1.0 mmol) was added. Content of the reaction vessel was stirred vigorously at 80 °C for 30 min. The reaction mixture was then cooled and the white solid formed separated by filtration. The crude product was purified by crystallization from ethanol.

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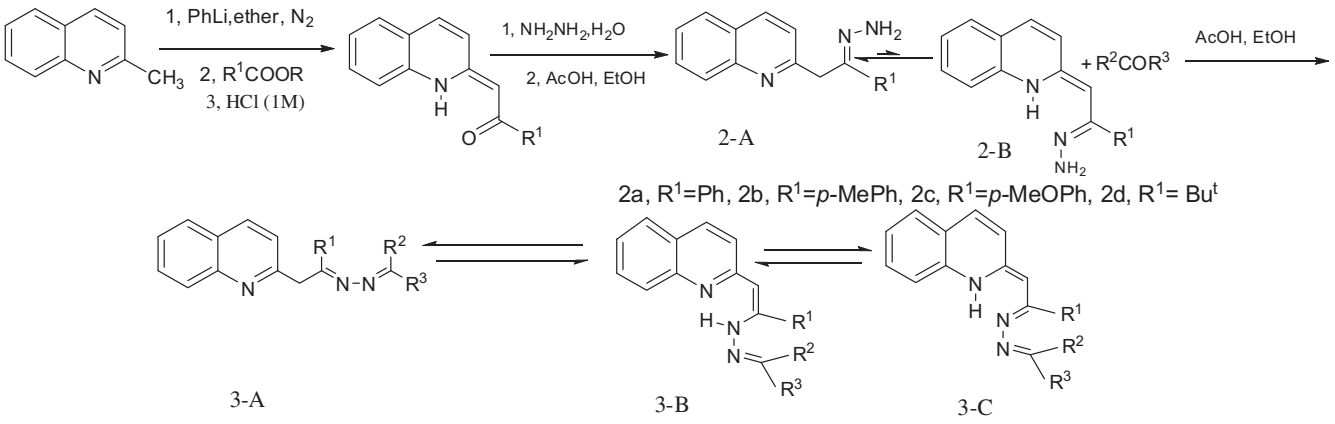


Scheme 1. Synthesis of 2-ketomethylquinolineazines.

*2.2. (Z)-3,3-Dimethyl-1-(quinolin-2(1H)-ylidene)butan-2-imine (**1a**)*

White needles; mp 100–102 °C; IR (KBr) ν: 3410, 1625, 1590, 1530 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.2 (s, 9H, CH_3), 5.2 (s, 1H, CH), 6.8–8.00 (m, 8H, C_9H_6N and 2NH).

*2.3. 1-Phenyl-2-(quinolin-2-yl)ethanimine (**1b**)*

White needles; mp 152–154 °C; IR (KBr) ν: 3340, 1615, 1585, 1530 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.8 (s, 1H, CH), 6.5–8.0 (m, 13H, C_9H_6N, C_9H_5 and 2NH), 6.5 (broad, 2H, 2NH).

*2.4. (1Z,2Z)-1,2-bis(3,3-Dimethyl-1-(quinolin-2-yl)butan-2-ylidene) hydrazine (**3a**)*

White needles; mp 174–176 °C; UV (nm) in choloroform; 317.0, 303.5, 278.5; IR (KBr) ν: 1615, 1590, 1570, 1555, 1500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.03 (s, 18H, CH_3), 4.27 (s, 4H, CH_2), 7.44–8.12(m, 12H, Ar—H). ^{13}C NMR (125 MHz, $CDCl_3$): 28.5 (CH_3), 38.2 (C), 39.6 (CH_2), 122.0, 126.1, 127.1, 127.8, 129.3, 129.6, 136.3, 148.3, 159.5, 165.5, 169.8 (Ar—C); MS (EI, 70 eV) *m/z* (%): 450 $[M]^+$, 393, 337, 225, 169, 143 (100%), 128, 57. Anal. Calcd. For $C_{30}H_{34}N_4$: C, 79.96; H, 7.60; N, 12.43. Found: C, 79.46; H, 7.41; N, 12.30.

2.5. General procedure for synthesis of 2-ketomethylquinolinehyd razones (2a–2d)

2-Ketomethylquinoline (1.0 mmol) was dissolved in the minimum amount of ethanol and a drop of acetic acid and hydrazine monohydrate (2.0 mmol) was added. The mixture was stirred vigorously at 80 °C for about 6 h. Progress of the reaction was followed by TLC (eluent:ethyl acetate/petroleum ether, 1:5). After completion of reaction the mixture was cooled and the solid formed separated by filtration. The crude product was purified by crystallization from ethanol.

*2.6. (Z)-2-(2-Hydrazono-2-phenylethyl)quinoline (**2a**)*

White needles; mp 121–123 °C; IR (KBr) ν: 3340, 3135, 1630, 1614, 1595 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.30 (s, 2H, CH_2), 6.5 (broad, 2H, NH_2). 7.0–8.5 (m, 11H, C_9H_6N, C_6H_5).

*2.7. (Z)-2-(2-Hydrazono-2-p-tolylethyl)quinoline (**2b**)*

White needles; mp 105–107 °C; IR (KBr) ν: 3360, 3130, 1645, 1600, 1590 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.3 (s, 3H, CH_3), 4.2 (s, 2H, CH_2), 6.5 (broad, 2H, NH_2), 7.0–8.2 (m, 10H, C_9H_6N, *p*-C_6H_4).

*2.8. (Z)-2-(2-Hydrazono-2-(4-methoxyphenyl)ethyl)quinoline (**2c**)*

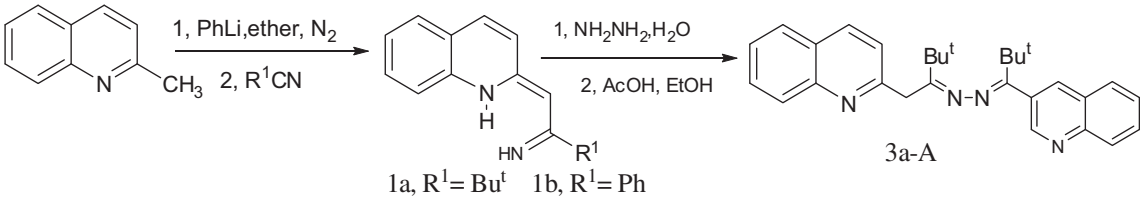
White needles; mp 152–154 °C; IR (KBr) ν: 3365, 3130, 1635, 1605, 1590 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.8 (s, 3H, OCH_3), 4.8 (s, 2H, CH_2), 6.5 (broad, 2H, NH_2), 6.5–8.5 (m, 10H, C_9H_6N, *p*-C_6H_4).

*2.9. (Z)-2-(2-Hydrazono-3,3-dimethylbutyl)quinoline (**2d**)*

White needles; mp 105–107 °C; IR (KBr) ν: 3320, 3205, 1640, 1620, 1595 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.1 (s, 9H, CH_3), 4.0 (s, 2H, CH_2), 6.2 (broad, 2H, NH_2), 7.0–8.2 (m, 6H, C_9H_6N).

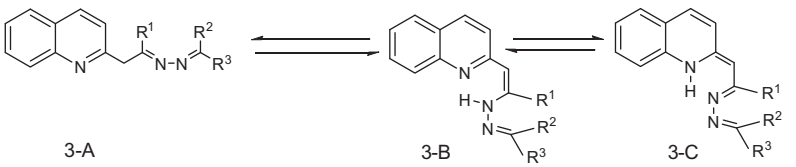
2.10. General procedure for synthesis of unsymmetrical 2-ketomethyl quinolineazines

2-Ketomethylquinolinehydrazone (2.0 mmol) was dissolved in the minimum amount of ethanol and a drop of acetic acid and aldehyde or ketone (2.0 mmol) was added. The mixture was stirred vigorously at 80 °C for the appropriate times (Table 1). Progress of the reaction was followed by TLC (eluent:ethyl acetate/petroleum ether, 1:5). After completion of reaction the mixture was cooled and the solid formed separated by filtration. The crude product was purified by crystallization from ethanol.



Scheme 2. Synthesis of symmetrical azine.

Table 1
The 2-ketomethylquinolineazines synthesized in this work.



3-A 3-B 3-C

Com.	R^1	R^2	R^3	mp (℃)	Reaction times (min)	Yield (%)
3a	*t*-Bu	*t*-Bu	CH_2(2-Q[a])	174–176	360	70
3b	Ph	Me	Ph	148–150	360	75
3c	*p*-MePh	Me	Ph	133–135	360	75
3d	Ph	H	Ph	127–129	360	75
3e	*P*-MePh	H	Ph	160–162	360	75
3f	Ph	H	*p*-NO_2Ph	186–188	30	90
3g	*p*-MePh	H	*p*-NO_2Ph	187–189	30	90
3h	*t*-Bu	H	*p*-NO_2Ph	163–165	30	90
3i	*p*-MePh	Me	*p*-BrPh	131–133	300	85
3j	Ph	Me	*p*-BrPh	160–162	300	85
3k	*t*-Bu	Me	*p*-BrPh	113–115	300	80
3l	Ph	H	*p*-ClPh	138–140	300	85
3m	*P*-MePh	H	*p*-ClPh	193–195	300	85
3n	Ph	H	*o*-NO_2Ph	201–203	300	90
3o	*p*-MePh	H	*o*-NO_2Ph	184–186	30	90
3p	*t*-Bu	H	*o*-NO_2Ph	155–157	30	90
3q	Ph	H	*m*-NO_2Ph	162–164	30	90
3r	*p*-MePh	H	*m*-NO_2Ph	167–169	30	90
3s	*t*-Bu	H	*m*-NO_2Ph	129–131	30	90

[a] Quinolinyl.

*2.11. 2-((Z)-2-Phenyl-2-((Z)-2-(1-phenyllidene)hydrazinyl)vinyl) quinoline (**3b**)*

White needles; mp 148–150 °C; UV (nm) in chloroform; 433, 300, 300; IR (KBr) ν: 3250, 1620, 1595, 1550, 1505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.64 (s, 3H, CH_3), 5.55 (s, 1H, CH), 7.16–7.92 (m, 16H, Ar—H), 13.94 (s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 14.3 (CH_3), 98.7 (CH), 123.1, 124.5, 125.2, 125.7, 125.9, 126.8, 126.9, 127.7, 127.8, 128.1, 128.4, 128.5, 128.5, 129.6, 129.7136.8, 138.9, 143.9, 147.1, 153.1158.3, 158.9 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 363 $[M]^+$, 348, 245, 230, 221, 169, 156, 143, 128, 118, 103, 91, 77 (100%), 57. Anal. Calcd. For $C_{25}H_{21}N_3$: C, 81.61; H, 5.82; N, 11.56. Found: C, 81.11; H, 5.84; N, 11.30.

*2.12. 2-((Z)-2-((Z)-2-(1-Phenylethylidene)hydrazniyl)-2-p-tolylvinyl) quinoline (**3c**)*

White needles; mp 133–135 °C; UV (nm) in chloroform; 437, 300; IR (KBr) ν: 3300, 1620, 1590, 1550, 1500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.29 (s, 1H, CH_3, tautomer B), 2.33(s, 2H, CH_3, tautomer A), 2.42 (s, 1H, CH_3, tautomer B), 2.64 (s, 2H, CH_3, tautomer A), 4.71 (s, 1.2H, CH_2), 5.55 (s, 0.4H, CH), 7.15–8.00 (m, 15H, Ar—H), 13.94 (broad, 0.4H, NH)7. ^{13}C NMR (125 MHz, $CDCl_3$): 14.0 (CH_3), 15.8 (CH_3), 21.5 (CH_3), 21.7 (CH_3), 38.9 (CH_2), 98.4 (CH), 121.2, 123.0, 125.9, 126.7, 126.8, 126.9, 127.4, 127.6, 128.0, 128.4, 129.2, 129.5, 129.7, 134.3, 138.4, 139.0, 140.1, 153.2, 158.5, 158.9, 159.0 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 377 $[M]^+$, 362, 244, 235, 169, 156, 143, 128, 104, 77, 44 (100%). Anal. Calcd. For $C_{26}H_{23}N_3$: C, 82.27; H, 6.14; N, 11.13. Found: C, 82.31; H, 6.12; N, 11.14.

*2.13. 2-((Z)-2((Z)-2-Benzylidenhydrazinyl)-2-phenylvinyl)quinoline (**3d**)*

White needles; mp 127–129 °C; UV (nm) in chloroform; 431, 303; IR (KBr) ν: 3200, 1622, 1590, 1560, 1540, 1500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.02 (s, 1.4H, CH_2), 5.55 (s, 0.2H, CH), 7.18–8.20 (m, 17H, Ar—H), 14.95 (s, 0.2H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 39.4 (CH_2), 97.0 (CH), 121.5, 126.4, 126.9, 127.9, 128.1, 128.3, 128.8, 128.9, 129.1, 129.2, 129.3, 129.9, 130.7, 131.3, 134.9, 137.1, 137.5, 148.3, 148.7, 160.7, 165.6 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 349 $[M]^+$, 245, 230, 221, 169, 156, 143 (100%), 129, 104, 91, 77, 51. Anal. Calcd. For $C_{24}H_{19}N_3$: C, 81.49; H, 5.48; N, 12.02. Found: C, 81.65; H, 5.48; N, 11.69.

*2.14. 2-((Z)-2((Z)-2-Benzylidenhydrazinyl)-2-p-tolylvinyl)quinoline (**3e**)*

White needles; mp 160–162 °C; UV (nm) in chloroform; 431, 303; IR (KBr) ν: 3200, 1622, 1590, 1540, 1500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 1.5H, CH_3), 2.48 (s, 1.5H, CH_3), 4.99 (s, 1.0H, CH_2), 5.55 (s, 0.5H, CH), 7.15–8.20 (m, 15H, Ar—H), 14.55 (s, 0.5H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 21.8 (CH_3), 21.9 (CH_3), 39.2 (CH_2), 97.8 (CH), 121.5, 122.2, 124.8, 126.9, 127.3, 127.9, 128.2, 128.8, 129.0, 129.6, 129.8, 129.9, 131.4, 135.6, 137.0, 140.9, 147.4, 148.4, 158.9, 160.4, 165.6 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 363 $[M]^+$, 285, 259, 245,169,156,143 (100%), 118, 104, 91, 77, 44. Anal. Calcd. For $C_{25}H_{21}N_3$: C, 82.61; H, 5.82; N, 1156. Found: C, 82.34; H, 5.82; N, 11.46.

*2.15. 2-((Z)-2((Z)-4-Nitrobenzylidene)hydrazinyl)-2-phenyvinyl) quinoline (**3f**)*

White needles; mp 186–188 °C; UV (nm) in chloroform; 449, 385, 303, 265.5; IR (KBr) ν: 3200, 1622, 1590, 1540, 1505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.92 (s, 0.3H, CH_2), 5.64 (s, 0.7H, CH), 7.22–8.20 (m, 15H, Ar—H), 14.76 (s, 0.7H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 39.0 (CH_2), 100.2 (CH), 123.3, 124.4, 125.9, 126.9, 127.4, 128.0, 128.2, 128.9, 129.3, 129.4, 129.7, 130.1, 136.2, 136.3, 137.3, 142.2, 147.2, 147.5, 158.5, 165.0 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 394 $[M]^+$, 245, 230, 169, 149, 143 (100%), 129, 104, 77, 57, 44. Anal. Calcd. For $C_{24}H_{18}N_4O_2$: C, 73.08; H, 4.16; N, 14.20. Found: C, 72.70; H, 4.62; N, 14.17.

*2.16. 2-((Z)-2((Z)-4-Nitrobenzylidene)hydrazinyl)-2-p-tolylyvinyl) quinoline (**3g**)*

White needles; mp 187–189 °C; UV (nm) in chloroform; 451, 386, 312, 300, 266; IR (KBr) ν: 3200, 1622, 1590, 1540, 1505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 0.75H, CH_3), 2.49 (s, 2.25H, CH_3), 4.92 (s, 0.4H, CH_2), 5.55 (s, 0.8H, CH), 7.20–8.25 (m, 14H, Ar—H), 14.78 (s, 0.8H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 19.9 (CH_3), 21.8 (CH_3), 39.4 (CH_2), 99.6 (CH), 121.2, 123.3, 124.4, 125.3, 126.9, 127.4, 128.0, 128.4, 128.9, 129.4, 129.6, 130.1, 133.4, 136.1, 137.2, 139.3, 142.3, 147.5, 152.4, 157.3, 158.5 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 408 $[M]^+$, 244, 149, 156, 143 (100%), 129, 118, 91. Anal. Calcd. For $C_{25}H_{20}N_4O_2$: C, 73.51; H, 4.94; N, 13.72. Found: C, 73.05; H, 4.98; N, 13.65.

*2.17. 2-((Z)-3,3-Dimethyl-2-((Z)-2-(4-nitrobenzylidene)hydrazinyl) but-1-enyl)quinoline (**3h**)*

White needles; mp 163–165 °C; UV (nm) in chloroform; 460, 382, 361, 310; IR (KBr) ν: 3200, 1625, 1595, 1520 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.31 (s, 6H, CH_3), 1.56 (s, 3H, CH_3), 4.36 (s, 1.4H, CH_2), 5.52 (s, 0.3H, CH), 7.20–8.35 (m, 10H, Ar—H), 15.18 (s, 0.3H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 28.2 (CH_3), 29.4 (CH_3), 38.1 (C) 39.0 (CH_2), 94.0 (CH), 120.1, 123.8, 124.3, 127.4, 128.5 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 374 $[M]^+$, 246, 225, 169, 158, 157, 156, 149, 143 (100%), 103, 76, 69, 57, 44. Anal. Calcd. For $C_{22}H_{22}N_4O_2$: C, 71.06; H, 5.83; N, 14.38. Found: C, 70.57; H, 5.92; N, 14.96.

*2.18. 2-((Z)-2((Z)-2-(1-Bromophenyl)ethylidene)hydrazinyl)-2-phenylvinyl)quinoline (**3i**)*

White needles; mp 131–133 °C; UV (nm) in chloroform; 434, 300; IR (KBr) ν: 3300, 1630, 1595, 1570, 1560 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.36 (s, 2H, CH_3), 2.65 (s, 1H, CH_3), 4.72 (s, 1.4H, CH_2), 5.63 (s, 0.3H, CH), 7.27–8.13 (m, 15H, Ar—H), 14.08 (broad, 0.3H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 14.3(CH_3), 15.7 (CH_3), 39.5 (CH_2), 99.4 (CH), 121.5, 126.4, 127.2, 127.6, 127.9, 128.0, 128.1, 128.7, 129.3, 129.9, 130.3, 131.8, 131.9, 136.9, 147.4, 148.4, 158.5, 159.6, 159.7 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 443 $[M]^+$, 441, 301, 299, 245, 230, 198, 196, 157, 156, 143 (100%), 103, 77, 51, 44. Anal. Calcd. For $C_{25}H_{20}N_3Br$: C, 67.88; H, 4.56; N, 9.5. Found: C, 67.46; H, 6.64; N, 9.43.

*2.19. 2-((Z)-2((Z)-2-(1-Bromophenyl)ethylidene)hydrazinyl)-2-p-tolylvinyl)quinoline (**3j**)*

White needles; mp 160–162 °C; UV (nm) in chloroform; 437, 300; IR (KBr) ν: 3300, 1625, 1590, 1540, 1500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 2H, CH_3), 2.38 (s, 1H, CH_3), 2.48 (s, 2H, CH_3), 2.59 (s, 1H, CH_3), 4.72 (s, 1.4H, CH_2), 5.62 (s, 0.3H, CH), 7.22–8.0 (m, 14H, Ar—H), 14.08 (broad, 0.3H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 14.9 (CH_3), 15.7 (CH_3), 20.0 (CH_3), 22.1 (CH_3), 39.0 (CH_2), 98.0 (CH), 121.48, 126.4, 127.2, 127.6, 127.9, 128.0, 128.1, 128.7, 129.3, 129.8, 130.3, 131.8, 131.9, 136.9, 147.4, 148.4, 158.5, 159.6, 159.7, 160.1, 167.5, 169.7 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 457 $[M]^+$, 455, 315, 313, 198, 196, 157, 156, 155, 143 (100%), 44. Anal. Calcd. For $C_{26}H_{22}N_3Br$: C, 68.43; H, 4.86; N, 9.21. Found: C, 68.49; H, 4.19; N, 9.20.

*2.20. 2-((Z)-2-((Z)-2-(1-(4-Bromophenyl)ethylidene)hydrazinyl)-3,3-dimethylbut-1-enyl)quinoline (**3k**)*

White needles; mp 113–115 °C; UV (nm) in chloroform; 442, 335, 323, 300; IR (KBr) ν: 3200, 1630, 1600, 1540 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.31 (s, 4H, CH_3), 1.61(s, 5H, CH_3), 2.19 (s, 1.3H, CH_3), 2.32(s, 1.7H, CH_3), 4.19 (s, 0.8H, CH_2), 5.52 (s, 0.6H, CH), 7.20–8.05 (m, 10H, Ar—H), 15.18 (s, 0.6H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 15.2 (CH_3), 15.3 (CH_3), 28.9 (CH_3), 30.1(CH_3), 36.7 (C), 38.6 (C), 39.7 (CH_2), 94.0 (CH), 120.1, 123.8, 124.3, 127.4, 128.5, 159.2, 165.8 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 374 $[M]^+$, 246, 225, 169, 149, 156, 143 (100%), 103, 76, 69, 57, 44. Anal. Calcd. For $C_{22}H_{22}N_4O_2$: C, 71.06; H, 5.83; N, 14.38. Found: C, 70.57; H, 5.92; N, 14.96.

*2.21. 2-((Z)-2-((E)-(4-Cholorobenzylidene)hydrazono)-2-phenylethyl) quinoline (**3l**)*

White needles; mp 138–140 °C; UV (nm) in chloroform; 311, 303; IR (KBr) ν: 1615, 1595, 1560, 1530, 1500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.99 (s, 2H, CH_2), 7.30–8.17 (m, 15H, Ar—H). ^{13}C NMR (125 MHz, $CDCl_3$): 39.4 (CH_2), 121.4, 126.4, 127.2, 127.9, 128.3, 128.9, 129.4, 129.5, 129.9, 130.1, 130.8, 133.4, 137.1, 137.4, 138.5, 158.6, 159.2, 165.8 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 385 $[M+2]^+$, 383 $[M]^+$, 245, 230, 169, 143 (100%), 104, 77, 51. Anal. Calcd. For $C_{24}H_{18}N_3Cl$: C, 75.01; H, 4.73; N, 10.95. Found: C, 74.96; H, 4.75; N, 10.92.

*2.22. 2-((Z)-2-((E)-(4-Cholorobenzylidene)hydrazono)-2-p-tolylethyl) quinoline (**3m**)*

White needles; mp 194–196 °C; UV (nm) in chloroform; 313, 300; IR (KBr) ν: 1622, 1585, 1570, 1550 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 4.93 (s, 2H, CH_2), 7.20–8.10 (m, 14H, Ar—H). ^{13}C NMR (125 MHz, $CDCl_3$): 21.8 (CH_3), 39.4 (CH_2), 121.4, 126.4, 127.2, 127.9, 128.3, 128.9, 129.4, 129.5, 129.9, 130.1, 130.8, 133.4, 137.1, 137.4, 138.5, 158.9, 159.2, 165.8 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 399 $[M+2]^+$, 397 $[M]^+$, 169, 143 (100%), 115, 69, 44. Anal. Calcd. For $C_{25}H_{20}N_3Cl$: C, 75.46; H, 5.07; N, 10.56. Found: C, 75.96; H, 4.95; N, 10.95.

*2.23. 2-((Z)-2-((Z)-2-(2-(4-Nitrobenzylidene)hydrazinyl)-2-phenylvi nyl)quinoline (**3n**)*

White needles; mp 201–203 °C; UV (nm) in chloroform; 440, 401, 303; IR (KBr) ν: 3300, 1622, 1590, 1570, 1540, 1510 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.90 (s, 0.14H, CH_2), 5.60 (s, 0.93H, CH), 7.21–8.70 (m, 15H, Ar—H), 14.84 (s, 0.93H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 39.0 (CH_2), 100.0 (CH), 123.1, 125.2, 125.5, 125.8, 127.6, 127.8, 128.1, 128.7, 129.1, 129.7, 130.3, 130.9, 133.4, 135,4, 136.1, 136.6, 147.2, 147.6, 152.4, 158.4 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 394 $[M]^+$, 348, 225, 169, 156, 143 (100%), 103, 46. Anal. Calcd. For $C_{24}H_{18}N_4O_2$: C, 73.08; H, 4.60; N, 14.10. Found: C, 73.32; H, 4.95; N, 13.58.

*2.24. 2-((Z)-2-((Z)-2-(4-Nitrobenzylidene)hydrazinyl)-2-p- tolylvinyl) quinoline (**3o**)*

White needles; mp 184–186 °C; UV (nm) in chloroform; 438, 303; IR (KBr) ν: 3300, 1625, 1590, 1570, 1540, 1510 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.37(s, 0.45H, CH_3), 2.48 (s, 2.55H, CH_3), 4.90 (s, 0.28H, CH_2), 5.60 (s, 0.86H, CH), 7.10–8.20 (m, 14H, Ar—H), 14.87 (s, 0.86H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 21.8 (CH_3), 39.0 (CH_2), 99.7 (CH), 123.1, 125.2, 125.4, 127.6, 127.8, 128.2, 128.6, 128.9, 129.6, 130.3, 133.4, 136.1, 136.8, 152.2, 158.6. (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 408 $[M]^+$, 362, 225, 169, 156, 143 (100%), 103, 46. Anal. Calcd. For $C_{24}H_{18}N_4O_2$: C, 73.51; H, 4.94; N, 13.72. Found: C, 72.91; H, 4.72; N, 14.17.

*2.25. 2-((Z)-3,3-Dimethyl-2-((Z)-2-(2-nitrobenzylidene)hydrazinyl) but-1-enyl)quinoline (**3p**)*

White needles; mp 155–157 °C; UV (nm) in chloroform; 450, 400, 312, 300; IR (KBr) ν: 3300, 1625, 1595, 1570, 1510 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.30 (s, 1.8H, CH_3), 1.56 (s, 7.2H, CH_3), 4.38 (s, 0.4H, CH_2), 5.50 (s, 0.8H, CH), 7.16–8.30 (m, 10H, Ar—H), 15.3(s, 0.8H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 28.7 (CH_3), 29.9 (CH_3), 36.5 (C) 38.9 (C), 39.5 (CH_2), 94.8 (CH), 121.3, 123.6, 124.8, 125.2, 125.5, 126.3, 127.4, 127.5, 127.7, 128.3, 130.2, 1314, 133.4, 133.8, 135.8, 147.5, 152.8, 158.6, 158.8, 159.7 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 374 $[M]^+$, 335, 285, 196, 169, 156, 143 (100%), 128, 91, 77, 51. Anal. Calcd. For $C_{22}H_{22}N_4O_2$: C, 70.57; H, 5.92; N, 14.96. Found: C, 70.17; H, 5.64; N, 14.49.

*2.26. 2-((Z)-2-((Z)-2-(3-Nitrobenzylidene)hydrazinyl)-2-phenylvinyl) quinoline (**3q**)*

White needles; mp 162–164 °C; UV (nm) in chloroform; 425, 300; IR (KBr) ν: 3300, 1622, 1580, 1560, 1540 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.93 (s, 0.26H, CH_2), 5.60 (s, 0.87H, CH), 7.20–8.32 (m, 15H, Ar—H), 14.70 (broad, 0.87H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 39.0 (CH_2), 99.5 (CH), 121.7, 123.1, 123.2, 125.3, 125.8, 127.4, 128.0, 128.2, 129.2, 129.7, 129.8, 130.1, 131.8, 136.1, 137.4, 158.5. (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 394 $[M]^+$, 245, 230, 169, 149, 143 (100%), 104, 77, 44. Anal. Calcd. For $C_{24}H_{18}N_4O_2$: C, 73.08; H, 4.60; N, 13.20. Found: C, 72.64; H, 4.66; N, 14.06.

*2.27. 2-((Z)-2-((Z)-2-(3-Nitrobenzylidene)hydrazinyl)-2-p-tolylylvinyl)quinoline (**3r**)*

White needles; mp 167–169 °C; UV (nm) in chloroform; 427, 303; IR (KBr) ν: 3250, 1622, 1580, 1560, 1540 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 1H, CH_3), 2.50 (s, 2H, CH_3), 4.96 (s, 0.7H, CH_2), 5.60 (s, 0.65H, CH), 7.20–8.35 (m, 14H, Ar—H), 14.72 (s, 0.65H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 21.8 (CH_3), 39.5 (CH_2), 99.0 (CH), 121.7, 123.1, 123.2, 125.2, 127.3, 128.9, 129.6, 130.1, 135.9, 137.4, 154.2, 158.4, 165.2 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 408 $[M]^+$, 259, 244, 169, 150, 149, 143 (100%), 128, 91, 76, 44. Anal. Calcd. For $C_{25}H_{20}N_4O_2$: C, 73.51; H, 4.94; N, 13.72. Found: C, 72.98; H, 5.02; N, 13.54.

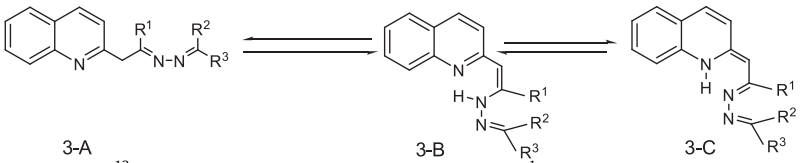
*2.28. 2-((Z)-3,3-Dimethyl-2-((Z)-2-(3-nitrobenzylidene)hydrazinyl) but-1-enyl)quinoline (**3s**)*

White needles; mp 129–131 °C; UV (nm) in chloroform; 430, 317, 281; IR (KBr) ν: 3300, 1630, 1600, 1580, 1570, 1550, 1515 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, 3H, CH_3), 1.57 (s, 6H, CH_3), 4.37 (s, 0.66H, CH_2), 5.47 (s, 0.67H, CH), 7.10–8.40 (m, 10H, Ar—H), 15.10 (broad, 0.67H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): 28.7 (CH_3), 29.9 (CH_3), 36.6 (C), 38.9 (C), 39.7 (CH_2), 94.2 (CH), 121.3, 121.5, 122.8, 123.9, 125.1, 126.3, 127.3, 127.8, 127.9, 129.3, 129.9, 131.5, 133.7, 133.8, 135.8, 136.6, 147.0, 154.8, 158.9, 160.0, 175.5 (Ar—C); MS (EI, 70 eV) *m*/*z* (%): 374 $[M]^+$, 226, 225, 169, 149, 143 (100%), 128, 57. Anal. Calcd. For $C_{22}H_{22}N_4O_2$: C, 70.57; H, 5.92; N, 14.97. Found: C, 70.03; H, 5.90; N, 14.97.

3. Results and discussion

New azines studied in the present paper have been synthesized in three steps. At first, a series of 2-ketomethylquinolines have been prepared using literature methods.[8] Tautomerism in this group of compounds have been well worked out by several investigators.[9,10] In the next step 2-ketomethylquinolines in reaction with hydrazine in ethanol solution and a drop of acetic acid as a catalyst were converted to 2-ketomethylquinolinehydrazones (**2a–2d**) in good to high yields (70–95%). Four of these intermediates (Scheme 1, R^1 = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, Bu^t) were isolated and their structures have been determined by spectroscopic

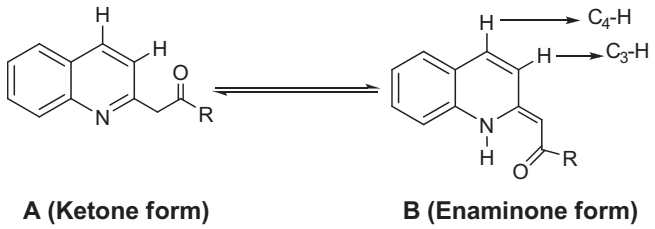
Table 2
Some ^1H and ^{13}C NMR, UV and IR, data of 2-ketomethylquinolineazines.



3-A 3-B 3-C

Comp.	^1H NMR ($CDCl_3$) (ppm)			^{13}C NMR ($CDCl_3$) (ppm)				IR (cm^{-1}, KBr disk)			UV (nm, in ethanol)	*A*:*B* ratio in $CDCl_3$
	C**H**	C**H**$_2$	N**H**	C**H**	CH_2	C=C	N=C	N—H[a]	C=C	C=N	λ_{max}	
3a	–	4.27	–	–	39.6	165.5	169.8	–	1590	1615	317	100:0
3b	5.55	–	13.94	98.7	–	158.3	158.9	3250	1595	1620	433	0:100
3c	5.55	4.71	13.94	98.4	38.9	158.9	159.0	3300	1590	1620	437	66:34
3d	5.55	5.02	14.95[a]	97.0	39.4	160.7	165.6	3300	1590	1622	431	79:21
3e	5.55	4.99	14.55	97.8	39.2	160.4	165.6	3200	1590	1622	449	50:50
3f	5.64	4.92	14.76	100.2	39.0	158.5	165.0	3200	1590	1622	449	35:65
3g	5.55	4.92	14.78	99.6	39.4	157.3	158.5	3200	1590	1622	451	20:80
3h	5.52	4.36	15.18	94.0	39.0	157.0	158.0	3200	1595	1625	460	67:33
3i	5.63	4.72	14.08	99.4	39.5	159.6	159.7	3300	1595	1615	434	63:37
3j	5.62	4.72	14.08	98.0	39.0	167.5	169.7	3300	1590	1625	437	72:28
3k	5.52	4.19	14.08	94.0	39.7	160.6	168.8	3300	1600	1630	442	40:60
3l	–	4.99	–	–	39.4	159.2	165.8	–	1595	1615	311	100:0
3m	–	4.93	–	–	39.4	158.9	165.8	–	1585	1622	313	100:0
3n	5.60	4.90	14.84[a]	100.0	–	158.4	–	3300	1590	1622	440	7:93
3o	5.60	4.90	14.87	99.7	–[b]	158.6	–[b]	3300	1590	1625	438	15:85
3p	5.50	4.38	15.33	94.8	38.9	158.8	159.7	3300	1595	1625	450	19:81
3q	5.60	4.93	14.70	99.5	39.0	158.5	–	3300	1580	1622	425	13:87
3r	5.60	4.90	14.84	99.0	39.5	162.0	165.2	3250	1580	1622	427	24:76
3s	5.47	4.37	15.10	94.2	39.7	160.0	175.5	3300	1600	1630	430	40:60

[a] Broad.
[b] Not appeared due to low concentration.



Scheme 3. Tautomeric forms for 2-ketomethylquinolines.

methods. Infrared spectra of these compounds (KBr discs) show strong absorption bands around 3360 and 3130 cm^{-1} for —NH_2 of primary amines. The compounds also show a strong absorption around 1645–1630 cm^{-1} for C=N vibrations.

The ^1H NMR data of these compounds (in chloroform solution) show a broad line at 6.2–6.5 ppm for the —NH_2 and another singlet (CH_2) in the aliphatic region around 4.0–4.8 ppm. Integrations of these signals confirm there are two protons present in each group. There was no signal around 14.0 ppm corresponding to possible enamine-imine form 2-B (Scheme 1). From these observations we conclude that the 2-ketomethylquinolinehydrazones exist exclusively in the imine form 2-A (Scheme 1).

In the third step 2-ketomethylquinolinehydrazones were treated with different aldehyde and ketone in ethanol solution and in the presence a drop of acetic acid (as a catalyst) to give unsymmetrical azines (Scheme 1). The reaction, completion time, yield and structure of the compounds are given in Table 1.

For comparison, a symmetrical azine was also prepared via a different route as shown in Scheme 2.

Following our previous work [11], we focused on the structure of a new series of 2-ketomethylquinolineazines, particular by focusing on identification of their tautomers.

UV, IR and NMR spectroscopy were used to determine the structure of the compounds. It was found that this group of compounds could be classified into three main categories, based on their tautomeric forms. Thus, in chloroform solution compounds **3a**, **3l** and **3m** are exclusively in the form 3-A. On the other hand, compound **3b** exist entirely in the form 3-B. Finally derivatives **3c**–**3k** and **3n**–**3s** were found to exist as mixtures of both forms (3-A⇆3-B). The concentration ratio of the two tautomers at equilibrium, *A*:*B* (in chloroform solutions) are reported in Table 2.

Typical *cis-s-cis* enaminone C=O and C=C vibrations (KBr disc) for 2-ketomethyquinolines at 1632 and 1585 cm^{-1} have been earlier reported [8].

The infrared data of 2-ketomethylquinolineazines reported in Table 2 show that in the solid state all the compounds were found to be exclusively in the 3-B or 3-C forms. Most of the entries in Table 2 (except **3a**, **3l** and **3m**) show a band around 1620 cm^{-1} for the C=N stretching vibration. Moreover, spectra of these compounds show a broad band around 3300 cm^{-1} for the N—H stretching

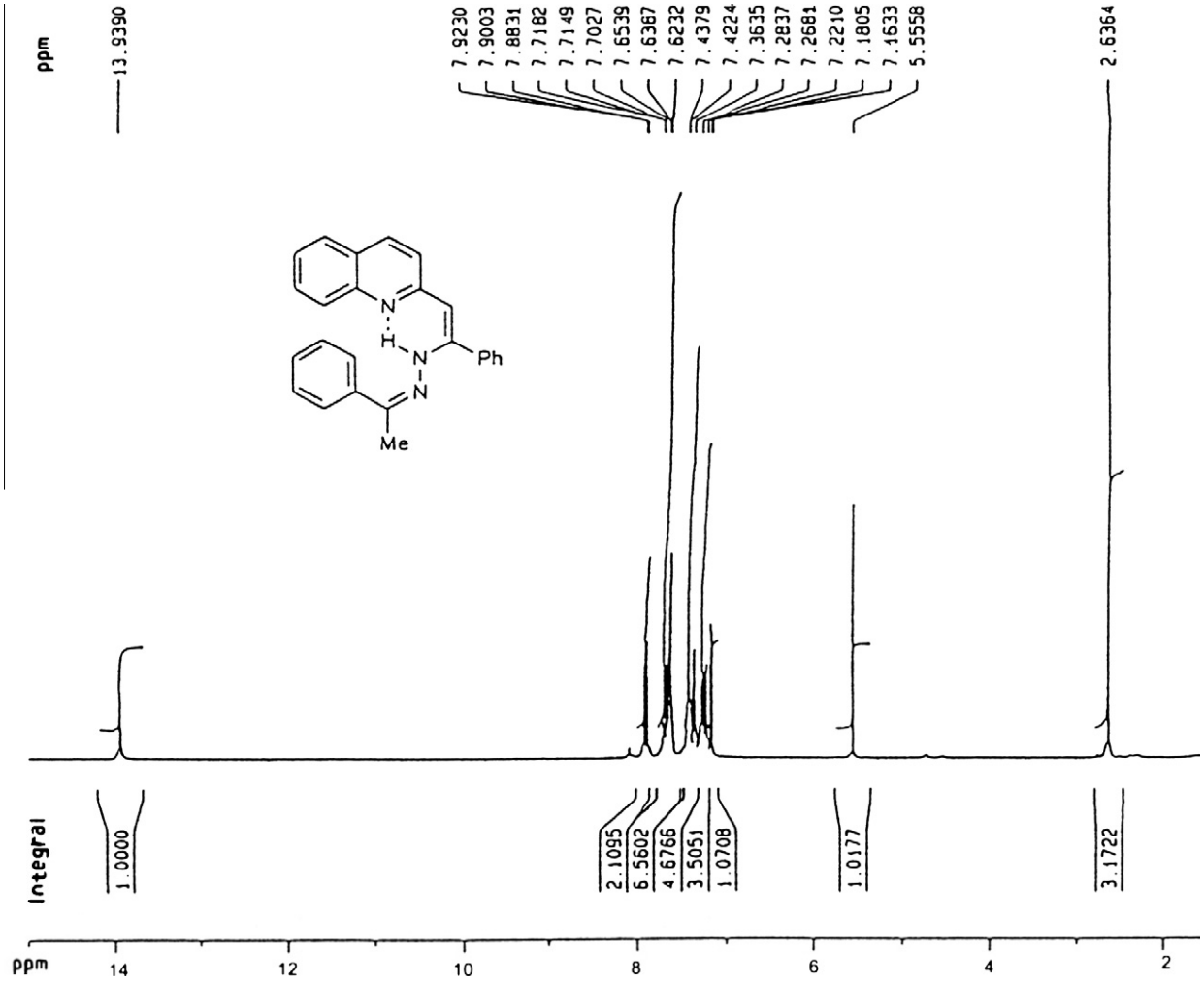


Fig. 1. ^1H NMR spectrum of compound **3b** in deuterochlorform solution.

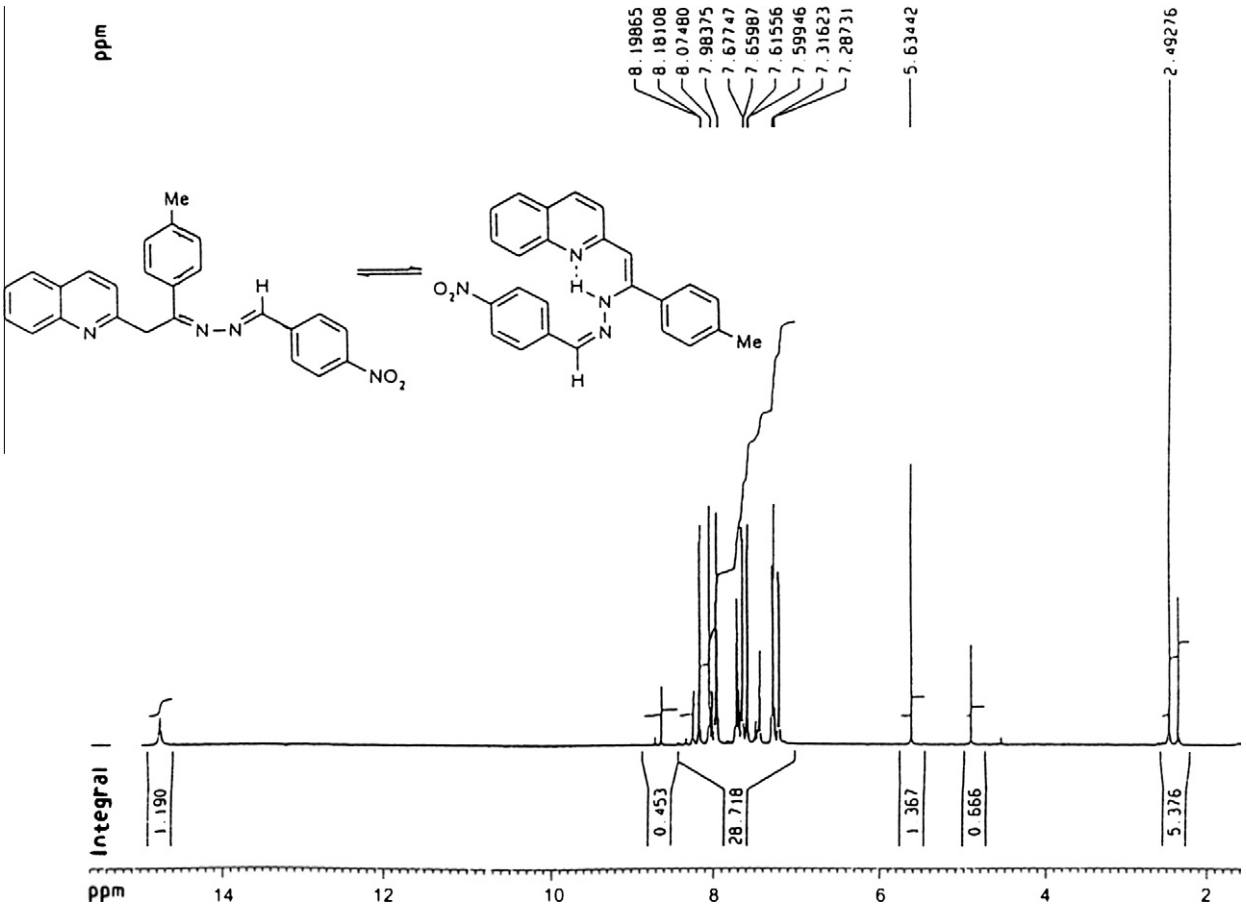


Fig. 2. ^{1}H NMR spectrum of compound **3g** in deuterochloroform solution.

mode. These data correspond to those of the similar azines have been earlier reported.[12] Position of the low field N—H signal in the ^{1}H NMR spectra is expected to be a measure of the strength of the intramolecular hydrogen bonding.

The IR spectra confirm that in the solid state, the compounds are exclusively in the conjugated forms 3-B or 3-C.

Typical absorption UV band λ_{max} (nm) in ethanol for 2-ketomethylquinolines (R = Ph) has been observed at 459 nm.[13] The UV spectral absorption data of the azines in chloroform solution are given in Table 2. These data show two types of absorption bands. For compounds **3a**, **3l** and **3m**, these absorption bands are located at 317, 311 and 313 nm, respectively (conjugation does not extend on the side and quinoline ring). Thus, only the form 3-A is present there. On the other hand, in the spectra of the other compounds studied, these absorption bands are observed around 425–460 nm which show that conjugation between the side chain and quinoline ring does take place, so they may be in the form 3-B or 3-C.

The ^{1}H NMR data of the azines studied are presented in Table 2. Typical ^{1}H NMR lines of the CH_2 and CH groups of the corresponding 2-ketomethylquinolines in chloroform solution have been reported at δ 4.04–4.75 ppm.[8] These ^{1}H NMR data of the azines are presented in Table 2. These ^{1}H NMR data for compounds **3a**, **3l** and **3m** in chloroform show a singlet at δ 4.27, 4.99 and 4.93 ppm, respectively. Integration of these signals was exactly proportional to two protons and there was no other signal for the vinylic proton and the N—H proton due to the formation of the second tautomeric forms 3-B or 3-C. There is a singlet corresponding to the vinylic proton at δ 5.55 in which this signal integrated to one proton only, the methylene protons is missing. Moreover, existence of the forms 3-B or 3-C is proved by the N—H signal at δ 13.94 which arises as a result of strong intramolecular hydrogen bonding between N—H proton and nitrogen in both forms. Tautomeric forms were also observed for the other **3c–3k** and **3n–3s** compounds. Tautomeric ratios were calculated for these compounds from the relative integrals of the signals of vinylic proton and methylene protons. These compounds also revealed broad downfield signals due to the N—H proton around δ 13.94–15.33 of the conjugated form 3-B or 3-C. It should be mentioned that the two doublets in the 6.7–7.9 and 7.6–8.1 ppm regions (C_3—H and C_4—H protons of the quinoline ring, respectively) exist exclusively in the enaminone form (B). The assignments of these doublets have already been reported by Mondelli and Merllini [9] (Scheme 3). However, for all azines which may have tautomeric forms (Scheme 2), these doublets did not appear. From these observations, we concluded that the compounds exist exclusively in the form 3-B. Obviously, substitution has effect on tautomeric ratio, but due to the limited number of samples we cannot draw a definite final conclusion. For comparison, ^{1}H NMR spectra of each category (**3b**, **3g** and **3l)** are presented in Figs. 1–3.

Some important ^{13}C NMR chemical shifts of the compounds studied are given in Table 2. These data show that there are signals around 38.8–39.7 and 94.0–100.0 ppm for the methylene and vinylic carbons, respectively. Low field signal at 158.9 ppm in the spectrum of compound **3b** which is found to be exclusively in the form B can be assigned to the quaternary carbon C=N. Moreover, the signal near 98.7 ppm can be attributed to the vinylic carbon atom. Since, no signal is detected around 38 ppm for the second tautomeric forms. Signals of the methylene carbons in the spectra of compounds **3a**, **3l** and **3m** were observed at 39.5 ppm. None of

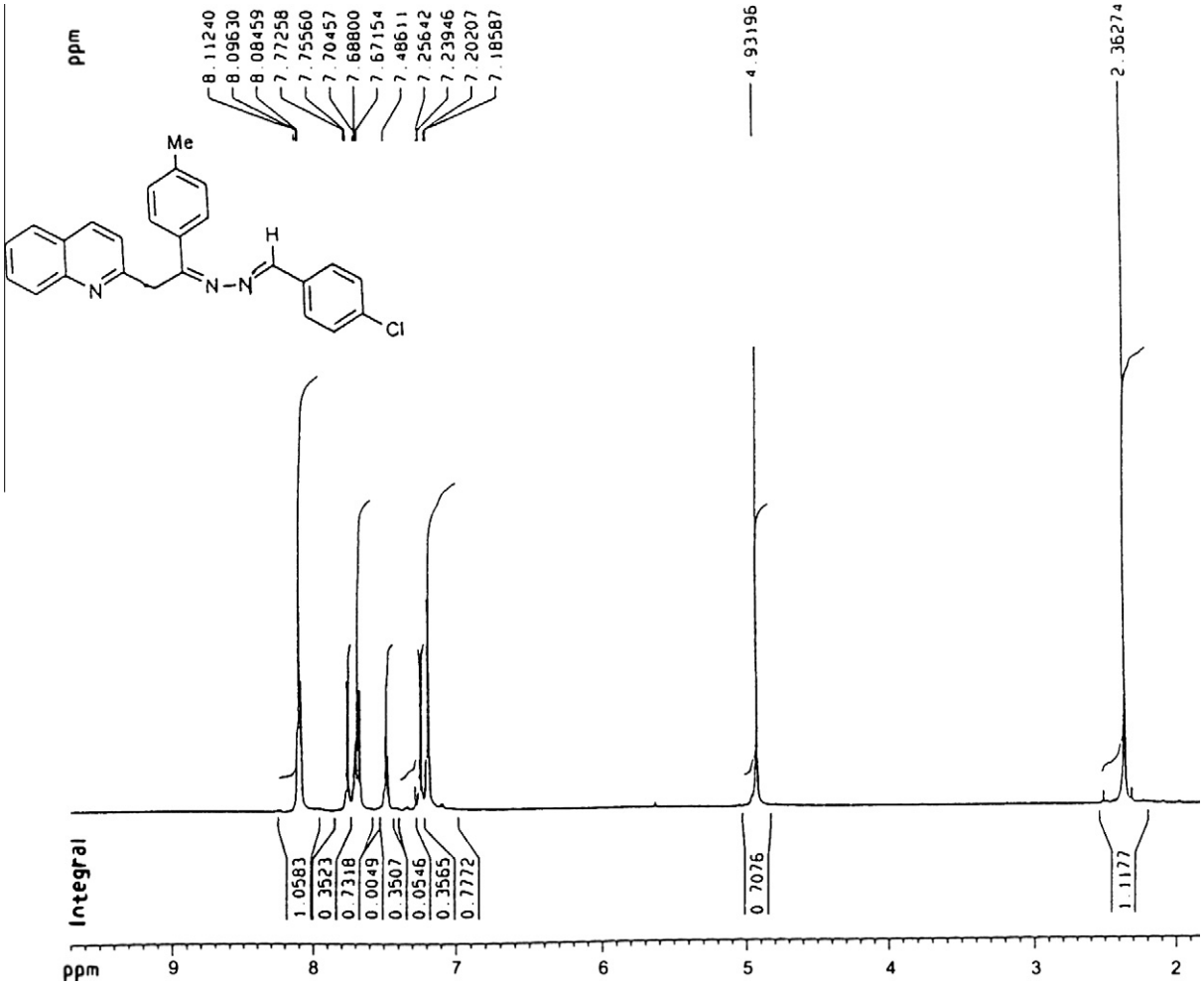


Fig. 3. ^{1}H NMR spectrum of compound **3l** in deuterochloroform solution.

the spectra for these compounds show the signal for the vinylic carbon around 98.5 ppm (the respective second tautomeric form is not present). Assignment of the above signals were confirmed by comparing the spectra with those of the DEPT spectra in which the signals are absent and the methylene signals are inverted. So, these observations show that the discussed compounds have only tautomeric form 3-A. On the other hand, the other (**3c–3k** and **3n–3s**) compounds exist as a mixture of tautomers which are proved by the presence of both methylene and vinylic signals observed around 39 and 99 ppm, respectively.

4. Conclusion

As it shown by IR, ^{1}H and ^{13}C NMR spectral data, tautomeric behavior of 2-ketomethylquinolineazines in chloroform solution depend on substitutions and in most of the samples studied two tautomeric forms are in equilibrium with each other, but in some cases one tautomer was dominate.

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