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SYNTHESIS AND STRUCTURE OF S-ALKENYL DERIVATIVES OF 8-QUINOLINETHIOL

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8-Vinyl-, styryl-, (1-propenyl)thioquinolines, 8-quinoline vinyl sulfoxide, and 8-quinoline vinyl sulfone have been synthesized. Their structures have been studied by molecular mechanics and quantum chemistry.

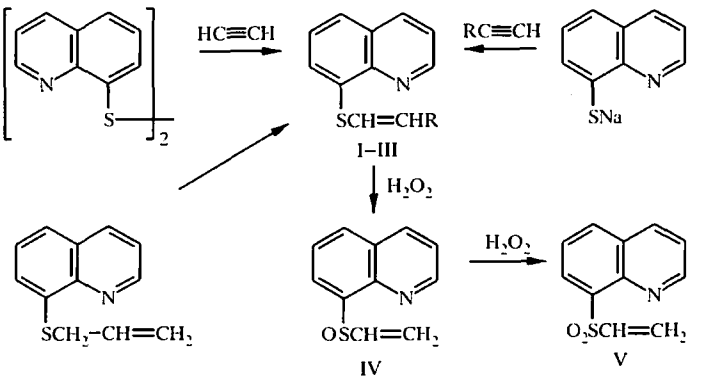
8-Vinylthioquinoline (I) was synthesized by vinylation of sodium or potassium 8-mercaptoquinolinate with acetylene in dioxane at 160-180°C in an autoclave [1]. In the present work sulfide I was obtained by reaction of 8,8-diquinolyl disulfide with acetylene in the presence of KOH in dioxane at 190-200°C. The possibility of synthesizing vinyl alkyl sulfides by reaction of dialkyl sulfides with acetylene has been shown previously [2].

We have obtained 8-styrylthioquinoline (II) in high yield (91%) by the reaction of sodium 8-mercaptoquinolinate with phenylacetylene in a superbasic medium (KOH + DMSO + H_2O) at 100°C. The reaction follows the rule of *trans*-nucleophilic addition of thiols to acetylenes [3] and proceeds with formation of the *cis* isomer exclusively. The reactions go with lower yields under analogous conditions in DMF and HMPTA and does not occur at all in dioxane. When the reaction temperature was raised to 180°C in dioxane sulfide II was formed. In the ^{1}H NMR spectrum of sulfide II (in $(CD_3)_2SO$ and $(CD_3)_2CO$, the protons of the vinylene groups are equivalent and form singlets at 6.79 and 6.93 ppm respectively. In $CDCl_3$ these protons are not equivalent and give a quartet centered at 6.79 ppm.

The *cis* and *trans* isomers of 8-(1-propenyl)thioquinoline IIIa,b were obtained by prototropic isomerization of 8-allylthioquinoline in DMSO in the presence of KOH at 100°C. According to the ^{1}H NMR data 60% of the *cis* isomer and 40% of the *trans* isomer were formed.

The IR spectra of sulfides I-III include bands of stretching vibratons of C–S bond in the 650 cm^{-1} region and deformation vibrations of the vinyl group in the 950 cm^{-1} region. The double bond stretching vibration bands are overlapped by the valence vibrations of the quinoline ring (a group of bands in the 1620-1480 cm^{-1} region).

8-Quinoline vinyl sulfoxide (IV) containing admixture of 8-quinoline vinyl sulfone (V) was formed by oxidation of sulfide I with equivalent amount of 30% hydrogen peroxide in acetone. On oxidation with excess of 60% H_2O_2 in acetone or acetyl hydroperoxide in diethyl ether a mixture of sulfone V and sulfoxide IV was formed. Sulfoxide IV, unlike the sulfone V, is readily soluble in diethyl ether which permits ready separation of the two.



I R = H, II R = Ph, III R = Me

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TABLE 1. Characteristics of the Synthesized Compounds I-V

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
		C	H	S		
I	$C_{11}H_9NS$	70.38 / 70.55	4.81 / 4.84	16.95 / 17.12	36	43
II	$C_{17}H_{13}NS$	77.28 / 77.24	5.16 / 5.03	12.24 / 12.31	120	91
III	$C_{12}H_{11}NS$	71.20 / 71.60	5.53 / 5.93	16.01 / 15.93	60	89
IV	$C_{11}H_9OS$	65.21 / 65.00	15.68 / 15.77	15.68 / 15.77	97	71
V	$C_{11}H_9NO_2S$	60.51 / 60.25	4.32 / 4.14	14.26 / 14.62	150	36

Oxidation of vinyl sulfide I with 30% hydrogen peroxide in acetic acid, a method widely used for the oxidation of sulfides, did not give sulfoxide IV and sulfone V. A mixture of compounds was produced from which 8,8-diquinolyl disulfide was isolated.

The direction of the oxidation reaction was confirmed by IR and ^{1}H NMR spectroscopy. A characteristic SO group band at 1058 cm^{-1} was observed in the IR spectrum of sulfoxide IV and SO_2 group absorbtion bands at 1135 and 1315 cm^{-1} appeared in the spectrum of sulfone V. Signals for the protons of the vinyl group were present in the ^{1}H NMR spectra of compounds IV and V but the chemical shifts were shifted to weak field in comparison with those of the starting compound I

Vinyl alkyl sulfides may exist in s-*cis*, s-*trans*, and *gauche* conformations [4, 5]. Theoretically 8-vinylthioquinoline may exist in the following conformations: two planar (A and B) and two nonplanar s-*trans* conformations (A1 and B1), two planar (C and D) and two nonplanar (C1 and D1) s-*cis* conformations. It is unlikely that sulfide I would exist in the *gauche* conformation because the sulfur atom lies in the plane of the quinoline ring. The conformational structure of compound I was studied by the PM3 quantum-chemical method and molecular mechanics (MM$^+$)(HyperChem program). The results from the both methods show that the most favourable conformations are planar s-*trans* (A and B) conformations. The nonplanar s-*cis* (C1 and D1) are better than the planar s-*cis* conformations. The energetic barriers between the conformations are not large. ^{1}H and ^{13}C NMR spectra show that sulfide I exists predominantly in the form A [6, 7].

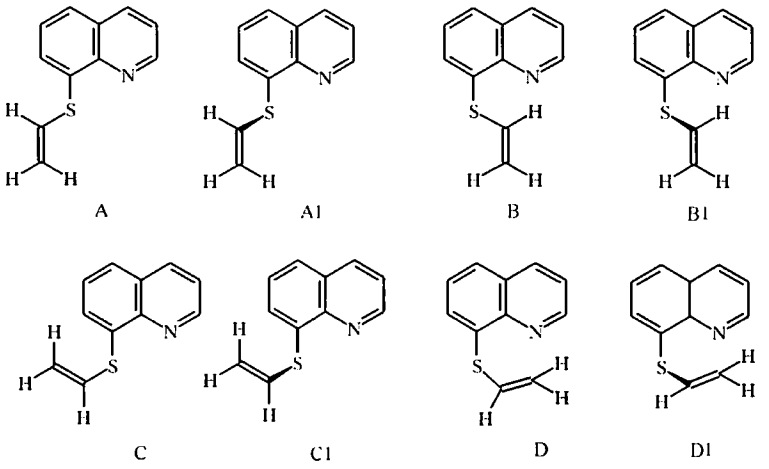

TABLE 2. Energetic Characteristics of Sulfide I (kcal/mol)

Form *	A	A1	B	B1	C	C1	D	D1
PM3*	-2453.48	—*[3]	-2453.28	-2452.85	-2452.41	-2452.63	-2450.01	-2453.27
MM**[2]	0.5611	—	1.1032	—	—	2.1666	5.9529	2.6352

* Bond energy.
*[2] Strain energy.
*[3] Transformation into the other conformation with optimization of the geometry (A1 → A, B1 → B, C → C1).

TABLE 3. Atomic Charges and ^{13}C Chemical Shifts (ppm) for 8-Vinylthioquinoline

Atom	N	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$
$\delta^{13}C$*	—	149.02	21.48	35.95	24.88	26.34
AM1	-0.140	0.044	-0.182	-0.081	-0.118	-0.113
PM3	-0.042	-0.053	-0.148	-0.056	-0.084	-0.086
CNDO/2	-0.156	0.101	-0.024	0.027	-0.006	0.010
PMX	-0.880	0.409	-0.066	0.088	-0.083	-0.033

$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	S	Cα	Cβ
28.48	36.84	44.73	27.99	—	29.33	20.17
-0.139	-0.179	0.020	-0.071	0.348	-0.336	-0.197
-0.117	-0.136	-0.022	-0.072	0.214	-0.279	-0.115
-0.011	0.038	0.090	0.011	-0.056	0.036	-0.059
-0.097	0.113	0.334	0.034	0.095	0.092	-0.280

* from [7].

In polyfunctional compounds the reactivity depends to a considerable extent on the electron density distribution. We have calculated the charges in sulfide I using the AM1, PM3, CNDO/2 and PMX methods. The ^{13}C NMR chemical shifts, which correlate with the charges on the carbon atoms [8], were used as a criterion for the correctness of the calculations.

We have found that the CNDO/2 and PMX methods gave the best correlation. The correlation coefficients were 0.948, 0.945, 0.555, and 0.4256 for CNDO/2, PMX, AM1 and PM3 respectively.

Thus the nucleophilic centers are predominantly the nitrogen sulfur atoms, and β-carbon atom of the vinyl group, while the electrophilic center is carbon atom $C_{(2)}$.

EXPERIMENTAL

^1H NMR spectra of the compounds II and III were obtained with a Tesla BS-497 apparatus (100 MHz) and those of the compounds I, IV, and V with a Tesla BS-497 apparatus (80 MHz) with TMS as internal standard. IR spectra of KBr disks were recorded on a Specord IR-75 spectrometer.

8-Vinylthioquinoline (I). 8,8-Diquinolyl disulfide (5.4 g, 0.017 mol), KOH (2 g, 0.03 mol), water (5 ml), and dioxane (50 ml) were placed into rotating steel autoclave and acetylene added at pressure of 15 atm. The autoclave was heated at 190-200°C for 1 h. After cooling, the water and dioxane were distilled off in vacuum and the residue was extracted with diethyl ether. Ether was distilled off and sulfide I crystallized from hexane, yield 2.5 g (43%). Mp. 36°C. ^1H NMR spectrum: 5.50 (1H, dd, HB, J_{AB} = 0.6, J_{AX} = 8.7 Hz); 5.67 (1H, dd, H_A); 6.70 (1H, dd, H_X); 6.98-7.40 (3H, m, 5-, 6-, 7-H); 7.3 (1H, dd, 3-H); 7.91 (1H, dd, 4-H); 8.79 ppm (1H, dd, 2-H).

8-Styrylthioquinoline (II). Sodium 8-mercaptoquinolinate dihydrate (2.19 g, 0.01 mol), phenylacetylene (1.02 g, 0.01 mol), DMSO (30 ml), and KOH (0.56 g, 0.02 mol) in water (5 ml) were placed in a flask and heated on a water bath for 5 h. After cooling water (300 ml) was added to the mixture and the precipitate was filtered off. Yield 2.37 g (91%); mp 120°C (propanol-2). ^{1}H NMR spectrum in $(CD_3)_2CO$: 6.93 (2H, s, HC=CH); 7.24-7.90 (9H, m, 3-, 5-, 6-, 7-H and C_6H_5); 8.36 (1H, dd, 4-H), 8.95 ppm (1H, dd, 2-H). In $(CD_3)_2SO$: 6.75 (2H, s, CH=CH); 7.0-7.8 (9H, m, 3-, 5-, 6-, 7-H and C_6H_5); 8.22 (1H, dd, 4-H); 8.75 ppm (1H, dd, 2-H). In $CDCl_3$: 6.79 (2H, q, J = 10.5 Hz, HC=CH); 7.2-7.9 (9H, m, 3-, 5-, 6-, 7-H and C_6H_5); 8.24 (1H, dd, 4-H); 8.99 ppm (1H, dd, 2-H).

8-(1-Propenyl)thioquinoline (III). A solution of 8-allylthioquinoline (0.40 g, 2 mmol) in DMSO (15 ml), and KOH (0.11 g, 2 mmol) in water (2 ml) were placed in a flask and heated at 100°C for 2 h. After cooling water (200 ml) was added to the mixture and the precipitate was filtered off. Yield 0.35 g (89%); mp 120°C (hexane). ^{1}H NMR spectrum ($(CD_3)_2CO$): 1.91 (3H, dd, J = 0.7 Hz, CH_3-*cis*); 1.94 (3H, dd, J = 0.7 Hz, CH_3-*trans*); 6.21-6.53 (2H, m, CH=CH); 7.78 (4H, m, 3-, 5-, 6-, 7-H); 8.30 (1H, m, 4-H); 8.88 ppm (1H, m, 2-H).

8-Quinolyl Vinyl Sulfoxide (IV). 30% H_2O_2 (2 ml) was added to solution of sulfide I (0.934 g, 0.005 mol) in acetone (20 ml) and the mixture was kept for 72 h. Water (100 ml) was then added, the precipitate was filtered off, dried, and recrystallized from hexane to give sulfoxide IV (0.71 g, 71%); mp. 97°C. ^{1}H NMR spectrum (CCl_4): 5.63 (1H, dd, $=CH_2$); 6.13 (1H, dd, $=CH_2$); 7.38 (1H, dd, CH=); 7.3-8.6 (4H, 3-, 5-, 6-, 7-H); 8.07 (1H, dd, 4-H); 8.85 ppm (1H, dd, 2-H).

8-Quinolyl Vinyl Sulfone (V). Acetyl hydroperoxide (2.5 g, 0.02 mol) was added dropwise to solution of sulfide I (1.87 g, 0.01 mol) in diethyl ether (10 ml) at 20°C and stirred for 2 h. The precipitate was filtered off and washed with ether. Yield 0.8 g (36%); mp 150°C (propanol-2). ^{1}H NMR spectrum ($CDCl_3$): 5.52 (1H, dd, $=CH_2$); 6.03 (1H, dd, $=CH_2$); 7.62 (1H, dd, CH=); 7.80-8.30 (4H, m, 3-, 5-, 6-, 7-H); 8.51 (1H, dd, 4-H); 9.09 (1H, dd, 2-H).

REFERENCES

1. D. G. Kim, G. G. Skvortsova, and Z. V. Stepanova, *Tez. Dokl. XIII Nauch. Sessii Khim. Tekhnol. Organ. Soed. Sery i Sernistykh Neftei*, Dushanbe (1974), p.127.
2. B. A.. Trofimov, N. K. Gusarova, A. S. Atavin, S. V. Amosova, A. V. Gusarov, N. I. Kazantseva, and G. A. Kalabin, *Zh. Org. Khim.*, **9**, 8 (1973).
3. W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, **78**, 2756 (1956).
4. I. Khargittai, *The Structural Chemistry of Sulfur Compounds* [in Russian], Nauka, Moscow (1986).
5. B. A Trofimov, *Heteroatomic Derivatives of Acetylene* [in Russian], Nauka, Moscow (1981).
6. A. V. Afonin, V. K. Voronov, B. V. Trzhtsinskaya, M. A. Andriyankov, L. V. Teterina, and Z. V. Stepanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 8, 1753 (1987).
7. A. V. Afonin, A. V. Vashchenko, V. K. Voronov, B. V. Trzhtsinskaya, N. D. Abramova, Z. V. Stepanova, and M. A. Andriyankov, *Zh. Org. Khim.*, **26**, 411 (1990).
8. G. Levy and G. Nelson, *Handbook on ^{13}C Nuclear Magnetic Resonance* [Russian translation], Mir, Moscow (1975).