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Note

Conformational Studies of Some Substituted Aryl Quinolyl Sulphones

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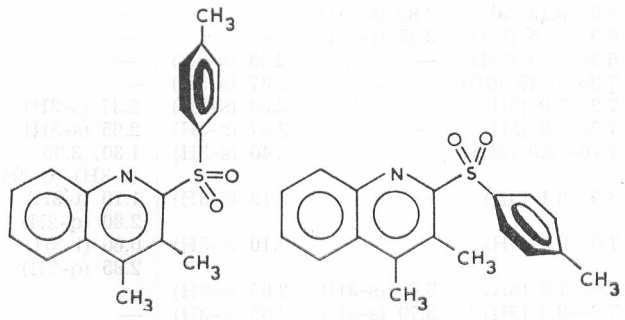
2-(4-methoxyphenylsulphonyl)-4-methylquinoline (*2*), 2-(4-methylphenylsulphonyl)-4-methylquinoline (*4*), 2-(4-methylphenylsulphonyl)-3,4-dimethylquinoline (*6*), 2-(4-methylphenylsulphonyl)-3-ethyl-4-methylquinoline (*8*) and 2-(4-methylphenylsulphonyl)-4-methyl-6-methoxyquinoline (*10*) have been synthesised by permanganate oxidation of the corresponding sulphides *1*, *3*, *5*, *7* and *9*[1,2,3]. This conversion was confirmed through elemental analyses and ir and NMR spectral data (c. f., Tables-I and II). Comparative NMR spectral studies have been done and the structures of *1* — *10* have been established (c. f., Table-II).

CONFORMATIONAL ANALYSIS THROUGH NMR STUDIES

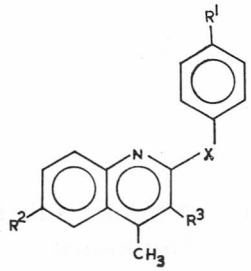
When *1*, *3*, *5*, *7* and *9* were converted to *2*, *4*, *6*, *8* and *10*, the signals for the protons of both methyl groups of the quinoline ring moved downfield to the same extent (δ 0.28). It appears that the phenyl is not overshadowing the methyl group attached to position 3 of the quinoline ring indicating thereby that the presence of a methyl group at position 3 results in restriction of rotation along the bond between sulphur and carbon 2 of the quinoline ring, which is also confirmed by the molecular model of *6*. Hence, *6* exists in the more stable conformation I in preference to II.



I II

On comparing the NMR spectrum of 7 with that of *8*, it was revealed that the signal for the methyl protons of the ethyl group moved upfield by δ 0.5.

TABLE I



Compound Number and Molecular formula	X	R^1	R^2	R^3	m. p. °C	Ir spectral values (nujol) in cm^{-1} λ_{max} Characteristic sulphonyl Bands
1 ($C_{17}H_{15}ONS$)	S	OCH_3	H	H	121	Missing
2 ($C_{17}H_{15}O_3NS$)	SO_2	OCH_3	H	H	148—49	1350, 1140
3 ($C_{17}H_{15}NS$)	S	CH_3	H	H	130	Missing
4 ($C_{17}H_{15}O_2NS$)	SO_2	CH_3	H	H	155	1350, 1145
5 ($C_{18}H_{17}NS$)	S	CH_3	H	CH_3	123	Missing
6 ($C_{18}H_{17}O_2NS$)	SO_2	CH_3	H	CH_3	182	1350, 1150
7 ($C_{19}H_{19}NS$)	S	CH_3	H	C_2H_5	93	Missing
8 ($C_{19}H_{19}O_2NS$)	SO_2	CH_3	H	C_2H_5	178	1350, 1145
9 ($C_{18}H_{17}ONS$)	S	CH_3	OCH_3	H	108	Missing
10 ($C_{18}H_{17}O_3NS$)	SO_2	CH_3	OCH_3	H	199	1360, 1140

Note: All the melting points are uncorrected. Microanalyses were done at C.D.R.I., Lucknow, (India). Ir spectra were recorded on Perkin Elmer Infracord.

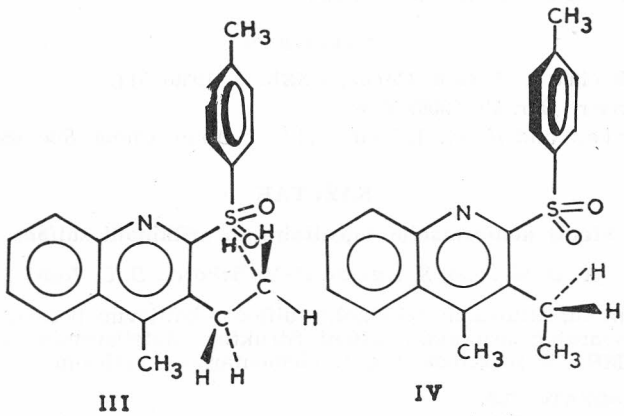
TABLE II

Compound No.	Solvent used	Aromatic protons	OCH_3	Alkyl protons of phenyl ring	Alkyl protons of quinoline ring Position 3	Alkyl protons of quinoline ring Position 4
1	$CDCl_3$	6.8—8.15 (9H)	3.85 (s-3H)	—	—	2.60 (s-3H)
2	$CDCl_3$	6.9—8.15 (9H)	3.85 (s-3H)	—	—	2.75 (s-3H)
3	$CDCl_3$	6.8—8.15 (9H)	—	2.45 (s-3H)	—	2.63 (s-3H)
4	$CDCl_3$	7.25—8.15 (9H)	—	2.37 (s-3H)	—	2.75 (s-3H)
5	$CDCl_3$	7.2—7.9 (8H)	—	2.50 (s-3H)	2.37 (s-3H)	2.57 (s-3H)
6	$CDCl_3$	7.3—8.0 (8H)	—	2.47 (s-3H)	2.65 (s-3H)	2.85 (s-3H)
7	$CDCl_3$	7.10—8.0 (8H)	—	2.40 (s-3H)	1.30; 3.05 (t-3H) (q-2H)	2.60 (s-3H)
	TFA[b]	6.9—8.1 (8H)	—	2.12 (s-3H)	1.10 (t-3H) 2.80 (q-2H)	2.37 (s-3H)
8	TFA	7.0—8.3 (8H)	—	2.10 (s-3H)	0.60 (t-3H) 2.85 (q-2H)	2.65 (s-3H)
9	TFA	6.9—7.6 (8H)	3.60 (s-3H)	2.05 (s-3H)	—	2.37 (s-3H)
10	TFA	7.2—8.2 (8H)	3.70 (s-3H)	2.05 (s-3H)	—	2.62 (s-3H)

[a] All the NMR spectra were recorded on Varian A-60 D Model. NMR spectral values are expressed in δ (p.p.m.)

[b] When the solvent $CDCl_3$ was replaced by TFA, the NMR signals of 7 showed an upfield shift by 0.25—0.30.

The molecular model of *8* indicates two conformational possibilities, III and IV. In conformation III, the CH_3 of the ethyl group is in proximity of the lone pairs of sulphonyl oxygen atoms. Their shielding effect explains the high field shift of the methyl protons. In this conformation, the methylene protons of the ethyl group are directed away from the sulphonyl group. As such, their signal would not move upfield. In fact, it has been found that this signal shows a downfield trend. This could be due to the electronic drift from the methylene group towards the heterocyclic ring caused by the sulphonyl group. This downfield shift is, however, not of the same order as that of the 3-methyl protons of *6*, because of the donor effect of CH_3 of the 3-ethyl group. The molecular model of conformation IV shows a pronounced steric hinderance between the CH_3 of the ethyl group and the CH_3 of position 4 of the quinoline ring. It would render conformation IV much less stable in comparison to III. This also indicates a restricted rotation along the C_2—CH_2 bond.



EXPERIMENTAL

All the melting points are uncorrected. Microanalyses were done at the Central Drug Research Institute, Lucknow (India). NMR and ir spectra were recorded on Varian A-60D model and Perkin-Elmer infracord respectively.

Synthesis of 2-(4-Methoxyphenylthio)-4-methylquinoline (1)

A mixture of 2-chloro-4-methylquinoline (0.05 mol) and 4-methoxythiophenol (0.5 mol) in methanol (30 ml) was allowed to stand at room temperature for 4 h and the solvent was distilled off. The residue, basified with dilute sodium hydroxide solution, was exhaustively extracted with ether. The ethereal extract was dried over anhydrous sodium sulphate and the solvent distilled off. The residue on repeated crystallisation from petroleum ether (40—60 °C) gave colourless shining prisms (m. p., 121 °C, 60—65%).

Anal. $C_{17}H_{15}ONS$ (281.31) calc'd: C 72.59; H 5.33; N 4.98%
found: C 72.18; H 5.22; N 5.03%

On similar lines, *3* (m. p., 130 °C; 50—55%) from 2-chloro-4-methylquinoline; *5* (m. p., 123 °C; 64.6%) from 2-chloro-3,4-dimethylquinoline[3]; *7* (m. p., 93 °C; 65.7%) from 2-chloro-3-ethyl-4-methylquinoline[3] and *9* (m. p., 108 °C; 65.2%) from 2-chloro-4-methyl-6-methoxyquinoline[3] were synthesised by reacting with 4-methylthiophenol.

Synthesis of 2-(4-Methoxyphenylsulphonyl)-4-methylquinoline (2)

To sulphide *1* (0.01 mol), dissolved in glacial acetic acid (30 ml), $KMnO_4$ solution (10%) was added with shaking, as rapidly as decolourisation occurred. Some excess $KMnO_4$ solution was added with shaking. Ethanol (5 ml) was then added and the reaction mixture was allowed to stand till the colour of $KMnO_4$ disappeared. The mixture was poured into ice-cold water and then filtered. The crude residue was extracted with hot acetone. The solvent was evaporated and the residue recrystallised from petroleum ether (40—60 °C), when colourless shining crystals (m. p., 148—9 °C; 70—75%) were obtained.

Anal. $C_{17}H_{15}O_3NS$ (313.31) calc'd: C 65.17; H 4.79; N 4.49%
found: C 65.47; H 5.01; N 4.16%

The sulphones, *4* m.p., 155 °C; 70.9%), *6* (m. p., 182 °C; 70.5%), *8* (m. p., 178 °C; 72.7%) and *10* (m. p., 199 °C; 73.2%) were synthesised on similar lines from sulphides *3*, *5*, *7* and *9*, respectively.

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SAŽETAK

Studij konformacije supstituiranih arilkinolil sulfona

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Oksidacijom supstituiranih arilkinolil sulfida s kalijevim permanganatom sintetizirani su odgovarajući arilkinolil sulfoni. Struktura sintetiziranih spojeva određena je s pomoću NMR i ir spektroskopije, te elementarnom analizom.

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